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Eighth EC Natural Analogue Working Group Meeting

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Edited by

H. von Maravic
European Commission
B-1049 Brussels

W. R. Alexander
NAGRA
Hardstrasse 73
CH-5430 Wettingen

Directorate-General for Research

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NAWG STEERING COMMITTEE STATEMENT

The 8th Natural Analogue Working Group (NAWG) meeting was held at the University Louis Pasteur in Strasbourg, France on 23 - 25 March 1999. The meeting was hosted by the Centre de Géochimie de la Surface (CNRS) and jointly organised and hosted by CNRS and the European Commission. The support and co-operation of the team of Dr François Gauthier-Lafaye is gratefully acknowledged.

1. Historical Context:

As was noted in the proceedings of the 4th NAWG workshop held in Pitlochry, Scotland, in 1990 (EUR 13014): "Carefully selected evidence of natural geological systems showing processes analogous to those operating in deep radwaste repositories, called 'natural analogues', are now viewed as the most convincing support to long-term performance assessment of geological radwaste disposal". Owing to the considerable upsurge of interest on this topic, and to its own R&D actions in this field, the European Commission (EC) took the initiative of establishing, in June 1985, a 'Natural Analogue Working Group' (NAWG) with a view to offering an international forum for:

a) discussion of natural analogue programmes, and
b) assessing their applicability as support to performance assessments

Since then, NAWG has held 7 plenary meetings (1985, EUR 10315; 1986, EUR 10671; 1988, EUR 11725; 1990, EUR 13014; 1992, EUR 15176; 1994, EUR 16761 and 1996, EUR 17851) and a major international symposium in 1987 in Brussels (EUR 11037).

The 8th plenary meeting at Strasbourg in 1999 provided, beside the traditional review of the status of various national natural analogue projects and programmes, the opportunity for the new members of the recently expanded NAWG to meet for the first time.

Originally, NAWG consisted of a "Core Group" of 8 members who were active in the natural analogue field. The main tenet of the group was to increase international awareness of the potential application of natural analogues to radioactive waste disposal via information exchange, presentations at international fora and by the organisation of a biannual NAWG workshop.

During the 6th NAWG workshop at Santa Fe, USA (EUR 16761), it was realised that the "…. sphere of NA studies is expanding beyond the restricted influence of the NAWG, so that direct distribution of information and expertise is no longer maintained by informal contact…." and it was therefore decided to expand the NAWG membership.

After the 7th NAWG workshop at Stein am Rhein, Switzerland (EUR 17815), the "Core Group" was disbanded and has since been re-constituted on a broader footing, which today includes a total of 21 members world-wide (see Table 1).

Due to a gradual evolution (and maturation) of natural analogue studies, the focus of NAWG has broadened, but one original pre-requisite remains, namely that each national representative is actively involved in analogue studies and will represent all domestic analogue programmes in their respective countries at future NAWG workshops, irrespective if more than one funding organisation is involved. NAWG is now headed by an elected Steering Committee (SC)[1] currently comprising a Chairman (Russell Alexander, NAGRA, CH) assisted by a vice-chairman (Jan Cramer, NRG, NL) and the scientific secretariat provided by the European Commission (Henning von Maravić, DG Research). The duty of the SC is to run NAWG, ensuring a regular distribution of analogue-related information within the group, ensuring a high profile for analogue studies in international scientific meetings and organising regular NAWG workshops and meetings. In addition, a NAWG web page was launched by the SC and it was intended that, with the support of the NAWG membership, this would aid wider distribution of natural analogue related information and help raise general awareness of the uses (and abuses) of natural analogues in the wider contexts of waste disposal, including the performance and safety of repositories and in public awareness.

2. Current Status:

Other than the traditional national programme reviews, the meeting focussed on 3 main areas:

- Natural Analogues in Performance Assessments
- Natural Analogues in Chemo-toxic Waste Disposal
- Natural Analogues in Communication

2.1 Natural Analogues in Performance Assessment

It has long been one of the stated aims of NAWG to promote the closer integration of NAs in PAs (see, for example, the proceedings of the 2nd NAWG meeting in 1986, EUR 10671 EN). There remains the general impression in the NA (and PA) community that not enough is being done to this end. This is despite a generally positive review of the application of NAs to PAs in the 6th NAWG workshop (McKinley and Alexander, 1994) and the recent publication of a whole raft of papers on the topic (e.g. Alexander and McKinley, 1999; Cramer and Smellie, 1994; Murphy, 2000; Smellie and Karlsson, 1996; Smellie et al. 1997, 2000).

Nevertheless, the mood of the NA community remains black and so it was felt useful to present at the Strasbourg workshop three, on-going major international NA projects that have integrated PA input in their work programmes from the outset. The results are arguably ambiguous.

[1] Chairman and vice-chairman are elected by the NAWG members for a 4-year period and the secretary is appointed by the EC. To help with the logistical arrangements in organising the biannual NAWG workshops, the NAWG representative of the host country will be elected to serve with the Steering Committee for one year spanning the workshop.

Although Grundfelt (these proceedings) rightly notes that the final evaluation of the PA applications of the Palmottu project awaits completion of the work, he could list a series PA support models which have been tested within the project.

Likewise Oversby (these proceedings) notes that, in the Oklo project, regular meetings between PA and NA workers have "... increased the understanding between the two groups of workers, but a great deal remains to be done before results from the Oklo project can be included quantitatively in PA analyses". Nevertheless, she then proceeds to note a range of areas where Oklo has so far provided qualitative data for PA.

Murphy et al. (these proceedings) is even more positive, stating "... studies at Peña Blanca have provided valuable NA information in recent PAs for ... Yucca Mountain ..." They go on to note that the NA programme and the repository programme both began at the same time (1987) and, perhaps crucially, that there are "... remarkable geologic, climatic, hydraulic and geochemical similarities between the environments at Peña Blanca and at Yucca Mountain". It is perhaps because of these clear connections in environments and programme evolution that a whole series of PAs for Yucca Mountain have cited the Peña Blanca study, even if the applications have been primarily qualitative, providing support for conceptual models and justification for the relevance of experimental studies.

Clearly then, even when considering only Palmottu, Oklo and Peña Blanca (but see also the other papers cited above), the qualitative application of NAs is now widespread in repository PAs (as it was argued in the review presented back at the 6th NAWG workshop in 1994). What remains more elusive is the quantitative application and here two factors mitigate against such usage.

First, as noted by Murphy et al. (these proceedings), although quantitative applications of data from Peña Blanca to Yucca Mountain have been attempted, their success has been limited by the "... approximations and uncertainties associated with understanding natural system evolution over long periods of time". Despite the fact that such approximations and uncertainties are also characteristic of PAs, this makes the quantitative use of NA data unappetising to the average PA modeller.

The implication is that we analogue workers should consider the form of the data provided to the performance assessors (although it should be noted that the provision of more precise data would not necessarily contribute to a reduction in the uncertainty of PA calculations).

This leads to the second factor against quantitative usage of NA data in PAs: even when perfectly good, quantitative NA data are available, performance assessors still tend towards simpler (and cleaner?) laboratory data (see, for example, the comments in Alexander et al., 1997). Arguably, this is more a reflection on performance assessors attitudes than the quality of natural analogue data but that would be to ignore the evidence clearly available 15 years after the founding of NAWG: namely that little or no quantitative data have been supplied by natural analogue studies to the performance assessments of radioactive waste repositories.

Despite this fact, the SC believes that analogues still play a decisive role in PA. Cramer (1996), for example, noted that, in the Canadian programme, despite the fact that the use of analogues has been predominantly qualitative, specific input has been significant with:

- feedback from analogue data to conceptual models of the disposal system
- feedback from analogues on the long-term relevance of short-term laboratory data
- the testing of assessment tools, such as thermodynamic databases
- the testing of the applicability of sub-models of an overall PA
- feedback from analogues to design concepts such as the effect of the thermal regime on the bentonite
- supporting reasoned arguments on the long-term performance of a repository by comparison with long-term natural processes
- provision of educational material

McKinley and Alexander (1996) came to the same conclusions from a study of a variety of natural analogue projects and national performance assessments although they noted that the use of analogues in PAs is often under-reported.

Alexander and McKinley (1999) went further with the specific example of the Swiss Kristallin-1 PA where they noted that natural analogues have been used to demonstrate the robustness of the engineered barrier system (EBS).

In the case of the steel canister longevity, for example, NAGRA assumed corrosion rates for reducing near-field conditions which are higher than corrosion rates measured on a suite of archaeological iron artefacts and iron meteorites from oxidising environments. The authors pointed out that the critical question for repository safety is whether:

"...the occurrence of processes which could short-circuit one or more of the multiple safety barriers be rigorously precluded? It was noted in the Kristallin-1 safety assessment that "...most phenomena that could be detrimental to safety are excluded or forced to low probability or consequence by the repository design and siting concept" (NAGRA 1994). This is aided by the use of relatively well understood materials within the EBS which are then further tested to assess their behaviour under repository specific conditions".

In most engineered systems, such as bridge construction, this testing would include a range of laboratory experiments backed up by expert judgement based on experience with the same or similar systems. But, as noted by Alexander et al. (1998), "...here repository design deviates from standard engineering practice in that no HLW (and only a few L/ILW) repositories yet exist and, when they do, testing their compliance to design limits will be somewhat difficult due to the time scales involved. This being the case, an additional level of testing has been developed within the radwaste industry, that of the natural analogue approach (see Chapman et al. 1984; Chapman & McKinley 1987, 1990; Miller et al., 1994)."

Despite the above affirmation, the authors go on to note that analogues are inherently ill defined and that certain processes are therefore better assessed under the well-constrained conditions of the laboratory. They go further to say that:

"Well designed, realistic *in situ* field tests can bridge the gap between the laboratory and natural analogues by offering repository relevant natural conditions with some of the constraints of the laboratory (and intermediate time-scales). In short, combining information from the three sources (long-term and realistic, if poorly defined, natural analogues, medium-term, better constrained, in situ field tests and short-term, less realistic but well defined laboratory studies) can provide greater confidence in the extrapolation of laboratory derived data to repository relevant timescales and conditions".

To conclude, the viewpoint that natural analogues have supplied little in the way of data to PAs seems unfounded, even if the main use has concentrated on qualitative rather than quantitative aspects. However, it is suggested that the way forward will be to combine the inherent strengths of natural analogues with those of laboratory studies and *in situ* field tests. As noted by Alexander et al. (1998):

"In short, combining information from the three sources (long-term and realistic, if poorly defined, natural analogues, medium-term, better constrained, *in situ* field experiments and short-term, less realistic but well defined laboratory studies) can provide greater confidence in the extrapolation of laboratory derived data to repository relevant time-scales and conditions."

Smellie et al. (2000) pointed out that integration of laboratory data with NA studies was already a feature of the Peña Blanca, Oklo and Palmottu studies. However, the fully integrated approach is now being applied for the first time to the question of the potential effects of hyperalkaline leachates (from a cementitious repository) on the repository host rock, where data from the Maqarin Natural Analogue Project will be combined with the results of laboratory column experiments and the Hyperalkaline Plume in Fractured Rock (HPF) experiment in the Grimsel Test Site, CH.

2.2 Natural Analogues in Chemo-toxic Waste Disposal

Interest in this area continues to grow with the realisation than the disposal of certain types of toxic waste also requires a long-sighted view. Little has been published to date but work is proceeding in Switzerland, for example, on comparing the stability of volcanic glasses with glass phases in fly ash. Interestingly, unlike in the case of vitrified radioactive waste (see comments in Miller et al., 2000), the chemistry of the volcanic and toxic waste glass is probably similar enough that the analogue data can be applied to the assessment of toxic waste glass durability (a report on this work is in preparation).

The toxic waste work is currently most advanced in France, with a programme that aims at testing the applicability of the NA approach to toxic waste disposal. Côme and Antoine (these proceedings) concluded that the NA approach has some advantage for:

- assessing the stability and durability of certain toxic waste streams
- the prediction of heavy metal release from stabilised waste
- definition of the regulatory framework for toxic waste disposal.

These encouraging results clearly show the potential for the NA approach in toxic waste disposal.

2.3 Natural Analogues in Communication:

The value and use of natural analogue studies in communicating various aspects of radioactive waste disposal concepts have slowly increased over the last decade (see comments in the proceedings of the 4th, 5th and 6th NAWG workshops).

However, the general feeling of the NAWG members (and the other workshop participants) is that natural analogues are still not used enough in this role. One point which was stressed at this workshop and more specifically in the presentation by Bill Miller is, that the complexity of natural systems and hence, by analogy, waste repositories, can only be communicated to the general public if the approach chosen is simple, illustrative and honest. Examples of analogue sites which would be suitable for public illustration purposes to explain and demonstrate aspects of important processes and time scales are, for example:

- the Swedish Kronan cannon, an archaeological analogue for copper corrosion;
- the Roman iron nails from Inchtutil in Scotland, an archaeological analogue for iron corrosion;
- the clay formation around the Cigar lake uranium occurrence, Canada and the Oklo reactor zone, Gabon, Africa as a near-field analogue to demonstrate the stability of bentonite buffer material under repository conditions;
- the preserved trunks of wood of the Dunarobba Forest, Italy, as an analogue for the confinement capacity of clay under defined physico-chemical conditions.

These four are but a few of the numerous examples currently available that could be better exploited immediately.

The availability of appropriate information in the form of brochures, newspapers and magazines, travelling exhibitions, videos, etc. are important to obtain greater perception and understanding by the general public for the sensitive issue of radioactive waste disposal in the geological environment. This information is made available by various waste management organisations, e.g. for:

* *brochures*: for example, AECL, ENRESA, NAGRA, SKB and the US-DOE have all produced colourful, glossy brochures for general consumption;

* *newspapers and magazines*: these have been used less frequently, but several good examples include the article about Cigar Lake, Canada in the *Neue Züricher Zeitung* (Wednesday, 9th October, 1992, No. 234), the microbiological article by J West and I McKinley in the New Scientist (1996) which cited much NA work and the series of articles in the Radwaste Magazine (January to September, 1995).

Of particular interest is the advertising campaign run by NIREX, UK a few years ago in several national newspapers and magazines. Here, the study of Roman cements from Hadrian's Wall in northern England was used as an illustration of cement longevity and this was related to NIREX's cementitious repository design.

* *travelling exhibitions*: a good example here is SKB's floating exhibition which includes examples from the natural analogue sites Cigar Lake and Oklo.

* *video films:* for example the video on "Traces of the future: Lessons learned from nature for waste disposal" as a result of a co-operative project of 7 Waste Management Organisations (AECL, ENRESA, NAGRA, ONDRAF, SKB, UK-NIREX and US-DOE) and the European Commission.

In this respect, NAWG could and should do more in the future by communicating the existing and new analogue information and data in an appropriate way to peer groups, politicians and especially to the non-technical community, the society which will finally decide whether the

disposal concept for radioactive waste will be implemented or not. Indeed, an example of such an approach has recently started in Japan (see Alexander et al., 2001, for details).

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Peter Airey	Australia	ANSTO
Pierre Manfroy	Belgium	ONDRAF/NIRAS
Henning von Maravić (Scientific secretariat)	Belgium	EC-Research
Jan Cramer (Vice-Chairman)	Norway	NGU
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C Hilvaci	Turkey	University of Izmir
Susan Duerden	U.K.	EA
William Murphy	U.S.A.	CNRWA-SWRI

Tab. 1: Members of the Natural Analogue Working Group (NAWG), Status January 2000

I NATURAL ANALOGUE OVERVIEW

Development of natural analogues in toxic waste disposal : a look to the future

B. Côme, ANTEA-BRGM Group (F)
P. Piantone, BRGM-Research Division (F)

ABSTRACT

In order to assess the durability of stabilized toxic wastes, a research programme was carried out by BRGM with funding of the RECORD Association, aimed at testing the applicability of the natural analogue approach. Technological and methodological achievements of this project are briefly outlined, and confirm that natural analogues should contribute to the optimized development of toxic waste stabilization processes.

1 – BACKGROUND AND SCOPE

French regulations state that "ultimate" toxic (mainly industrial) wastes must be stabilized before storage or re-use. In view of this, suitable processes have been developed, such as incorporation in hydraulic binders or asphalt, vitrification, etc.., in order to render wastes acceptable for storage or re-use (1). Acceptability is based on legal thresholds of pollutant elements measured by standard leaching tests (NX 31-210 or 211). However, these tests do not provide information about the long-term behaviour of the stabilized waste (possible degradation of the stabilizing matrix, neogenesis, increase in pollution levels etc). Considering the expected times scales for such processes to affect substances designed specifically to last hundreds (if not thousands) of years, only Nature can provide reasonably similar study cases ("analogues") to such wastes - cases, having evolved (or not) over the long term, and for which it is possible to reconstruct their evolutions.

The basic idea of the present research project was therefore to examine whether carefully chosen natural materials can provide sufficient analogies for some selected industrial wastes with a view to :

(i) assessing the durability and stability of these wastes under storage or re-use condition, and

(ii) acquiring indications concerning more appropriate solidification/stabilization processes.

The project was carried out, between 1993 and 1997, by BRGM under cost-shared contract with the RECORD Association (a network of industrial firms active in research about waste). It included three phases :

1) Orientation and preliminary analyses : for several existing candidate waste forms, potentially suitable natural analogues were screened and proposed for further examination;
2) Assessment of the long term stability of the screened waste forms by detailed examination of their natural counterparts ;
3) From the examination of existing natural phases showing trapping properties with respect to selected heavy metals, proposal of potentially suitable stabilization processes.

Before beginning the actual experimental work, an appropriate conceptual framework was developed for an analogical approach suitable for industrial toxic waste, based on the vast experience already acquired in radioactive waste disposal (2).

2 – WORK OVERVIEW AND MAIN RESULTS

2.1. - The orientation phase

Seven candidate waste were initially submitted to BRGM by RECORD, including several types of combustion ashes, used catalysts, metallurgic slags, one vitrified fly-ash (from domestic waste incineration), and one "metallic hydroxide sludge". These wastes were submitted to detailed laboratory characterization, including X –Ray and SEM examination, and quantitative analysis for major and trace elements. Eventually, the vitrified fly-ash was the one selected for further investigation (3).

2.2. - Assessment of the stability of the vitrified fly-ash

An hyperalkaline lava of the leucitic type was identified as promising analogue of the waste matrix (leaving aside the content in heavy metals, the major potential pollutants of concern), and sampled from a volcanic massif North of Rome (Italy); fresh and weathered material samples were collected with a view to comparative analysis of the lava and waste.
From a combination of laboratory testing (including flow-through column leaching tests on crushed materials), in-situ investigations and geochemical modelling, the durability of the vitrified fly-ash considered could be established, with the addition that potentially-formed alteration products would themselves lead to an efficient trapping of possibly released heavy metals from the waste form (4).
The modelling effort was amplified in a subsequent step of the programme, for simulating the degradation of vitrified products chosen to stabilize heavy metals ; this enabled to predict the reaction paths with water as a function of waste composition.

2.3.- Examination of natural mineral phases with a view to trapping heavy metals

A literature review was carried out about natural occurrences of heavy metal ore deposits, concentrating on eight candidate metals (Pb, Zn, Cd, Hg, Cu, Ni, Cr, As) identified as potential pollutants of concern for storage of industrial wastes. From this review, it appeared that some mineral phases do show efficient trapping properties for these heavy metals; their generation could therefore be favoured during the process of waste production and/or stabilization. Examples of these mineral phases are :

- sulfides for Hg;
- oxides and silicates for Cr and Zn;
- carbonates and phosphates for Pb, Zn, Cu, Cd;
- iron oxy-hydroxides for As;
- silicates for Ni.

In parallel to this review, available geochemical data were used to generate, via modelling, stability diagrams for the 8 candidate metals, thereby supporting the conclusions of the naturalistic approach. In the course of the work, limitations were identified in the presently available geochemical data, thus pointing to the desirability of improvements in this field.

3 – CONCLUSIONS ON THE POTENTIAL OF THE APPROACH

In general terms, this multi-disciplinary study has seen the testing and implementation of the natural analogue approach to industrial non-radioactive wastes in a preliminary, yet convincing, manner. Present conclusions are as follows :

3.1 - The potential of the analogical approach, rather than relying solely on the behaviour of a natural material analogous to stabilized waste, should rest on the behaviour of the constituent elements in their natural environment (geosphere and hydrosphere), considered either in groups or individually, whether forming mineral entities or not (5).

3.2 - The observation of natural processes, combined with appropriate geochemical modelling, was successful in identifying mineral phases suitable for the trapping of heavy metals, and in confirming the durability of presently proposed waste stabilization products.

3.3 - Potential releases in heavy metals from stabilized waste, in storage conditions, can now be better predicted using geochemical models, duly backed-up by naturalistic observations of analogous situations to be found in Nature.

3.4 - The natural analogue approach can be incorporated in the regulatory framework for waste storage, i. e. standards for waste acceptance testing, including their long-term behaviour.

3.5 - More extensive work of this type should mainly benefit from :
- the production of good thermodynamic data, for more reliable predictive modeling of waste behaviour, and
- the "validation" of modelling results through the examination of well-chosen occurrences of ore processing residues, ancient slag heaps, which could be termed "historical analogues" from anthropic origin.

In parallel to this research programme, the French Agency for waste management, ADEME, has been developing an "impact assessment" approach for waste storage facilities(6). This encompasses (a) the evaluation of performance of stabilized waste forms in terms of potential pollutant release under storage conditions, and (b) an assessment of "eco-compatible" pollutant fluxes which could be released from waste storages into the environment. Clearly, the natural analogue approach to waste form behaviour, as described above, is totally consistent with this ongoing line of action, and should therefore eventually contribute to the optimization of toxic waste stabilization processes.

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COMMUNICATION WITH NATURAL ANALOGUES

William Miller

QuantiSci Ltd., 47 Burton Street, Melton Mowbray,
Leicestershire, United Kingdom, LE13 1AF.

ABSTRACT

Natural analogues potentially can provide us with some of the most useful evidence in support of the safety of geological disposal of radioactive wastes. They can provide hard, quantitative information to include in performance assessments as well as soft, qualitative information to be used as illustrations in demonstrations of safety to non-technical audiences.

However, this potential does not appear to have been fully realised. Many performance assessments ignore analogue derived information and make no explicit recognition of analogues in their published documentation. On the illustrative side, analogues have sometimes been used only in a very half-hearted fashion or, worse still, have been used to present inadequate or incorrect information to the public.

In an attempt to rectify this situation, the analogue community needs to consider how best to communicate analogue studies and analogue-derived information to all interested parties. This paper sets out some suggestions for how natural analogue studies could be better represented and used in both technical and non-technical demonstrations of safety for a range of audiences.

INTRODUCTION

Every year, there are many papers on natural analogues presented at international meetings or published in journals or conference proceedings. Each of these papers represents a form of communication related to or about analogues. So, on this basis, it could be argued that the link between analogues and communication is working well, and is readily understood. However, to think this misses the point because there is no universal acceptance of the role or potential of analogues within national and international disposal programmes. Often, when we talk about natural analogues, we talk only to each other (preaching to the converted) and not to other members of the radwaste community, or to people on the outside, who would really benefit from proper communication about the role and potential of analogues.

There are two principal uses of natural analogue information: support for performance assessment (PA) and as illustrations to demonstrate repository safety to non-technical audiences. In both of these cases, appropriate communication is required to ensure that

the message we want to send to others is understood by the intended audience with clarity and without ambiguity. The role of communication in these two cases is discussed briefly in this paper.

COMMUNICATIONS WITHIN PERFORMANCE ASSESSMENT

The apparent lack of acceptance of natural analogues and analogue-derived information within the PA community is disheartening when the benefits that analogue studies can bring to geological disposal are so wide ranging and significant. Although these benefits have been widely discussed elsewhere (e.g. Miller et al., 1994 and Brandberg et al., 1993), it is worth restating them here. The support analogues can provide to PA can generally be considered within the following topics:

- natural analogues can help with the **development of conceptual models** because by investigating the processes that operate in natural systems, we learn much about the processes that are most significant for repository behaviour, and their couplings, and which must be represented in PA models;
- natural analogues can **provide quantitative data** to satisfy the parameter (data) requirements of the mathematical PA models – although very few quantitative data are actually provided by analogue studies (e.g. matrix diffusion depths, long term metal corrosion rates), the data that are available can be directly input to the models or else used to provide bounding limits and confidence in the alternative data acquired in the laboratory; and
- natural analogues can act as **test-beds for model validation** by providing sites with repository relevant physico-chemical conditions where the PA codes can be used in a realistic fashion in attempts to simulate actual measured conditions – so far this application has been limited to the testing of geochemical codes and databases but there is no reason why the methodology could not be extended to other types of codes if suitable test (analogue) sites can be identified.

Given these clear benefits, it is then surprising that the level of acceptance of analogues within the PA community has not been greater, at least with regards to their quantitative application. Unfortunately, it is very common to read in analogue publications (such as these NAWG proceedings) phrases such as:

"... failure of analogue studies to impact quantitatively on PA..." (Smellie et al., 1997)

"Less encouraging has been the very limited quantitative use of natural analogue data in PA modelling." (NAWG Core Group, 1996)

"Why do we not see more recognition of natural analogues in PA?" (McKinley, 1994).

It is worth considering why comments such as these appear so frequently in discussions of natural analogues. There are, of course, many reasons why this may be so. The first is that there have been some very poor analogue studies which were badly planned and unfocussed, and did little to improve our knowledge or confidence in geological disposal. As McKinley and Alexander (1996) put it: "To be quite blunt, it is probable that 50% of all reported natural analogue studies do not contribute to PA or any other aspects of waste management in any way whatsoever and hence are misnomers." Studies such as these deserve to be ignored.

But not all analogue studies are so bad: some are very well organised and really are focussed on PA requirements, so why might these not be given the recognition they deserve by the PA community? There is no simple answer to this, but one reason may be to do with a basic lack of understanding between the natural analoguers (who are often geologists and geochemists), the PA modellers (many of whom are mathematicians) and the experimentalists (who may have a 'pure' science background). Between these groups, there is generally no common technical background or even common language. Thus, when analogues are discussed, the significance of analogue results may not be apparent to a PA audience, and the actual message can be lost in a haze of background geological and geochemical detail. We have to remember that geological disposal is a multi-disciplinary task, and that often the audience for an analogue report or conference presentation will include physicists, chemists, modellers, material scientists etc., which means that the presentation must be made in such a way as to be accessible to all these people.

The point here is that better communication of analogue results and implications is required. Clearly, when an analogue study is completed, all aspects of the work need to be well documented. As a result, it is quite common for a large study to produce many reports that can take up metres of shelf space. Frequently, separate reports will be written on the geology of the site, another on hydrogeology, maybe one on the geochemical modelling and another on the colloids, and so on. All of this information is necessary to support the analogue study, but the information these reports contain is not strictly analogue information. What *is* analogue information, is the small nugget of information that can be taken from the study site, and transferred to the repository situation and applied to PA. For example, in one study, many months of field work may be undertaken and several reports could be written about groundwater chemistry and colloids; all of this will be documented but the real analogue information is the conclusion as to whether colloids could or could not transport radionuclides in this type of geological environment. This nugget of information needs to be extracted from all the background data, and presented simply and without ambiguity, to the modellers and experimentalists

in order for them to appreciate the implications of the analogue study. All too often this is not done, and the PA implications of analogue studies remain deeply buried in the background technical detail.

In essence, what is required from every analogue study is a separate PA implications report (or at least a separate chapter within a report) that presents a distillation of the project and spells out, in simple terms, what has been learnt from the study that is relevant to PA. Unfortunately, such reports are rare, possibly because the analoguers are unwilling to commit themselves to drawing such firm conclusions and implications from their work. One possible way forward would be for the organisations who pay for analogue work (disposers, licensors and other funding bodies) to insist that an implications document is written in addition to the supporting documents.

COMMUNICATIONS WITH A NON-RADWASTE AUDIENCE

In a democratic society whose public is actively concerned with environmental issues, it is not adequate to make demonstrations of safety only to the official licensing bodies for, without the 'approval' of both the licensors and the public, we are likely to fail in our attempt to site and build a repository. Recent events in a number of countries currently involved in siting activities prove this point.

It is thus necessary that demonstrations of safety are made to a number of 'stakeholder' groups, outside of the radwaste community. One of these groups is the public at large, but other groups can also be identified, such as government ministers and bureaucrats, academic peers and supporters of environmental pressure groups. What these groups have in common is that they generally are not familiar with the conceptual and technical aspects of geological disposal, even though they may have (in the case of academic peers) a high level of scientific training. For all of these interested groups, it is necessary to make demonstrations of safety that are appropriate to their level of understanding and concern.

In this regard, natural analogues can have an important role but one that has not, to date, been used to its full advantage. Natural analogues can be used as providers of illustrative and sometimes non-technical information to a broad range of audiences. The types of message that analogues can provide include:

- simple **illustrations of the overall disposal concept** although, when applying analogues to PA, we do not consider any analogue site to be a complete (global) analogue of a repository system, large ore bodies can be used in a simple illustrative manner to explain the broad concept of geological disposal (as has been done with the Cigar Lake site);

- demonstrations of the **similarity in materials, contaminants and radiation** between the repository and nature are important because we can demonstrate that essentially none of the components of a repository system are beyond our experience;
- recognition of the **important processes and events** that control the repository behaviour can be demonstrated from geological analogues - for example, never has an analogue site revealed any transport or retardation processes that has not previously been recorded or predicted and, hence, no such unique process should take place in the repository; and
- our understanding of the **relevant timescales** is an important message because the extended time periods of interest to disposal are generally beyond those usually considered by the public.

Unfortunately, despite all the positive messages that could be provided by analogues, there is an acute danger of either being condescending or overstating the case; usually both can arise because material is misrepresented or simply abused. The nuclear industry itself has not always represented natural analogues honestly, sometimes tending to oversimplify and overstate the facts. No doubt it may be argued that some simplification is necessary to make the scientific data readily digestible, but there is a fine line between necessary simplification and misrepresentation of the facts. The natural analogue that is most frequently oversimplified is Oklo, often to the point of being misleading. To the scientist, Oklo does not provide unequivocal proof that a repository will be safe; the situation at Oklo is simply too complex for that conclusion to be reached. Yet, Oklo is often presented in nuclear industry literature as 'proof'. An example of going too far is provided by the British Nuclear Forum (1991), who said:

"The Oklo reactors ran gently at the kilowatt-power level for millions of years. They never blew up. The radiation and waste from them did not deter surrounding life forms. Over immense timescales, the waste has barely moved away from the reactor site. As a result, scientists today are confident that waste in man-made stores and repositories is likely to move even less . . ."

Such statements challenge belief at all levels, apart from leaving themselves open to scientific ridicule if ever they have to be defended.

One the positive side, there are good examples of the use of natural analogues for public communications and we can cite the international 'Traces of the Future' video which was promoted by Nagra and co-funded by many national and international bodies, together with several brochures, leaflets and advertisements published by organisations such as SKB, Nagra, Nirex and ENRESA. However, good as these examples are, they clearly have

not been sufficient to quell public anxiety over geological disposal at home or abroad. It follows that there is a great need to develop better and more convincing communication materials. While it is hard to define exactly what form these materials should take or, indeed what the message should be they attempt to communicate, it is possible to draw up a few basic guidelines to follow, and these include:

- honesty is critical and must be the overall guiding principle;
- natural analogues alone should never be presented as 'proof' of repository safety and no analogue should ever be overinterpreted;
- any message should be presented as simply and as unambiguously as possible to avoid confusion;
- the messages should address the real concerns of the public (which might not be the same concerns as those held by people directly involved in radwaste disposal); and
- any analogue presentation should form part of a larger and coherent communications effort.

In choosing analogues to use in public communications we have a very wide choice and we can use all of nature and archaeology if it is relevant. Indeed, it may be possible to use systems and sites as illustrative analogues that might not be suitable for detailed quantitative studies to support PA; although it would probably always be better more persuasive to use the same site for both PA support and for public illustrations.

A further suggestion to choosing analogues for public communications would be to use sites or systems with which the public may have some familiarity or interest. In this regard, archaeological systems are particularly useful because the public may already have some context of time, material and environment with which to evaluate the message that is presented.

Communicating complex and contentious issues to the general public is fraught with difficulties and, hence, should not be undertaken lightly. This is, perhaps, one of the reasons that not more effort has been made in this regard. However, given that a disposal programme can be effectively halted by the public if they are fearful or misinformed, it is essential that this difficult task is faced.

Consequently, there needs to be a shift in emphasis towards the illustrative uses of natural analogues, so that they become an equal partner with the scientific investigations, rather than being seen as an aside to the main purpose of analogue studies.

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The role of the European Commission in the support of Natural Analogue studies

Henning von Maravić
European Commission, DG RTD, Brussels, B

Studies on natural migration systems including „**Natural Analogues**" have been supported by the European Commission in the past through the coordinated multidisciplinary project **MI**gration of **RA**dionuclides through the **GE**osphere (**MIRAGE**) from 1983 to 1994.

The ultimate goal of these studies was to (i) identify the migration and retardation processes (mainly geochemical) active in the geologic environment in order to assess the long-term behaviour of the natural system; (ii) test conceptual and numerical models developed on the basis of laboratory experiments and in-situ studies; (iii) provide qualitative and quantitative data/information applicable to repository performance assessment and (iv) improve the use of natural analogue studies in public perception.
The work comprised investigations at 15 different analogue sites in Europe (BE, ES, FR, IT, UK) and in Africa (Gabon) and focused on three main aspects: (1) diffusion and advection in sediments (including clay formations), (2) transport/retardation processes in fractured, crystalline rocks (including matrix diffusion) and (3) testing geochemical and transport models.

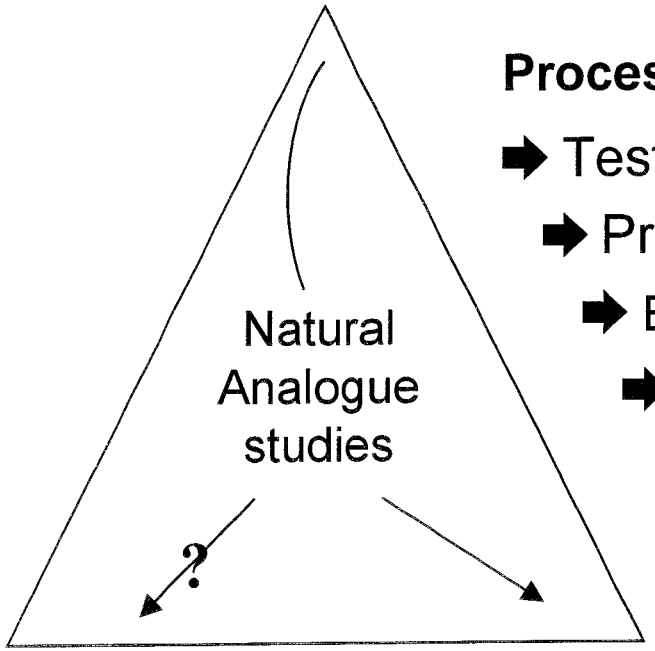
In response to the growing interest in natural analogue studies in the EU Member States and the formation of international co-operative analogue projects at that time, the Commission formed in June 1985 the international „Natural Analogue Working Group" (NAWG) in order to: (i) obtain recognition at international level in natural analogue activities; (ii) facilitate cross fertilisation of analogue information/data and new contacts between analogue workers and (iii) improve the relevance of analogue data to performance assessment. The group considered itself to be an alliance between natural analogue investigators (earth scientists, chemists, biologists, etc.), modellers and experts in performance (or safety) assessment. From the beginning the purpose of the group was to present and discuss the outcome of national and international analogue projects (natural and archaeological) and to evaluate their applicability as support for repository performance assessment.

Since then NAWG has organised 7 workshops (every two years) devoted to actual and important issues in analogue work (specific phenomena, near-field/far-field processes expected to occur within and around a repository), reviewed the achievements of international co-ordinated analogue projects (e.g. Pocos de Caldas, Brazil; Alligator Rivers, Australia) and addressed recommendations for areas where improvements were identified. For the first time, at the NAWG '96 workshop at Stein am Rhein (CH), the role of analogues in the application of the disposal of hazardous waste forms was discussed.

A review study of the MIRAGE project in 1994 [EUR 16489, 1995] and especially of the natural analogue studies concluded, that the methodological aspects of these studies, e.g. for site characterisation, represents a very positive progress. Although the understanding of the basic processes ruling natural elements/RN transport processes and their numerical representation has been improved their use in repository performance assessment is still in its infancy.

Based on the outcome of this review the present natural analogue studies (1995–1999) moved from more small-scale analogues, focused on a single process or single components of a repository system to large-scale multi-process analogues to understand better the complexity of the natural system through an interdisciplinary approach. Moreover, it has been recognised that there is a need to integrate repository performance assessment requirements from an early stage of the investigation on and to strengthen the illustrative part of the natural analogue studies in the confidence building process to the public. The use of natural analogue approach as a scientific methodology (tool) is given in Fig. 1.

Fig. 1: Use of the Natural Analogue approach as a scientific methodology



Process Understanding :

- ➡ Test laboratory and in situ based models
  - ➡ Provide input data
    - ➡ Establish initial physico-chemical boundary conditions
      - ➡ Reduce the effect of uncertainties in the spatial & temporal variability

Public Perception :

- ➡ Confidence building process
- ➡ Illustrate the use of NA
- ➡ Long-term safety of a disposal system

Performance Assessment :

- ➡ Confidence in PA model testing including UA/SA
- ➡ Transfer of quantitative analogue data to “robust” PA models

II PRESENTATION OF NATIONAL NA PROJECTS/PROGRAMMES

Ruprechtov Natural Analogue Study: Behaviour of U and Th in Argillaceous sediments. Pilot phase (Czech Republic)
V Harlová and A Laciok, NRI (CZ)

Projects BARA, MATRIX and ARCHEO: The ENRESA programme in natural analogues
P Hernan, J Astudillo and A Cortes, ENRESA (E)

The role of the Tsukiyoshi Fault as a control on nuclide migration in the Tono uranium deposit, Central Japan
K Tsubota, H Yoshida, K Huma, K Amano, JNC (JAP); A E Milodowski and R Metcalfe, BGS (UK)

German natural analogue research activities
W Steininger, FZK-PTE (D)

Present status of the Swedish natural analogue programme
J A T Smellie, Conterra AB (S) and F Karlsson, SKB (S)

The natural analogue study at the Steenkampskraal Monazite Mine, South Africa
N V Jarvis, AECSA (SA); D Read, Enterpris (UK); T Willliams, NHM (UK); M Knoper, RAU (SA) and M A Andreoli, SRC-UW (SA)

Use of natural analogues in the U.S. High-Level Nuclear Waste Programme
A M Simmons, LBNL (USA); P R Dixon, LANL (USA) and R A Levich, US-DOE (USA)

The Boom clay formation as a natural analogue for the geological disposal of radioactive waste
D Delleuze, M de Craen, G Volckaert, A Sneyers and M Put, SCK.CEN (B)

Solid Radioactive Waste Disposal in England and Wales: The use and application of natural and anthropogenic analogue studies
S L Duerden, R A Yearsley, EA (UK); J L Knight, Nirex (UK) and P Humphreys, BNFL (UK)

Ruprechtov Natural Analogue Study: Behaviour of U and Th in Argillaceous Sediments. Pilot phase (Czech Republic)

Havlová V, Laciok A (Nuclear Research Institute Řež plc, Czech Republic)

Abstract

The pilot phase of the Ruprechtov Natural Analogue Project (1996 - 1998) proved suitability of the site (W Bohemia, Czech Republic), where U accumulation in Tertiary argillaceous sediments can be found, for studying materials and processes relevant to the long-term barrier performance of bentonite. In the pilot phase basic geological, geochemical and hydrogeological parameters of argillaceous sediment environment, i.e. sediment, ground water and pore fluid features, were determined and evaluated.

1. Introduction

Long-lived and high level radioactive wastes (HLW) are generally supposed to be disposed in deep geological formations. Underground repositories are based on multi-barrier concept consisting of a system of engineered and geological barriers. Argillaceous materials can be involved in both near field and far field of the repository as

- buffer/backfill material (bentonite clay)
- cover of deep host geological formation, considered for radioactive waste disposal.

The main tool in the process of demonstrating the efficiency of the multi-barrier system to isolate radionuclides for sufficiently long period is performance assessment (PA). This procedure is based on modelling of relevant processed using reliable data from both laboratory and in-situ experiments. The question raised is whether the results from small-scale, short-term experiments can be successfully extrapolated to relevant time and scale of deep underground repository performance.

Natural analogues can provide such valuable information for reasoning into safety, reliability and acceptance of underground repositories for wide public.

Geochemical processes controlling radionuclide migration in argillaceous materials, including retention and mobilisation processes, are of interest of both Czech Republic and Germany. The Czech Republic considers using bentonite as buffer/backfill material. In Germany, argillaceous materials form part of cover of salt domes, considered for deep geological disposal of HLW. On the basis of this consideration, cooperation between Nuclear Research Institute Řež and GRS Braunschweig was established in 1995. All the activities in the Project pilot phase (1996 – 1998) were performed in close bilateral co-operation.

2. Goals and objectives of the Project Pilot Phase

The main goal of activities performed in the pilot phase of the Ruprechtov Natural Analogue Study (NAS) Project (1996 – 1998) was to achieve basic information and evaluate suitability of the Ruprechtov site (Western Bohemia, Czech Republic) for studying materials and processes analogous to those that bentonite/clay material can undergo and be involved in during deep radioactive waste repository performance.

3. Pilot stage of the NAS Project

3.1 Geological setting

The Ruprechtov NAS site is situated in a Tertiary basin in the west part of the Czech Republic (see Fig. 1). The main geological units found at the site are Quaternary sediments (soils), Tertiary volcanodendritic layers that underwent argilitisation and were transformed into clays, followed with kaolin layers, resulting from intensive weathering of underlying granite (Carlsbad granite).

Characteristic feature of the site is sediment heterogeneity in a small scale. Unevenly distributed U accumulation occurs in Eocene - Miocene clays in the depth of 10 - 40 m (within so-called volcanodetritic layers).

3.2 Site characterisation

In 1996-1997 three pilot boreholes (NA1-NA3) were drilled at the site within 15m. distance. The purpose was namely to obtain basic information about sedimentary system, i.e. to identify U accumulation within argillaceous sediments and to gain data about sediment composition, groundwater and pore fluid geochemistry and site hydrogeology.

U accumulation was identified using field activity measurements of the core. U-bearing layer was identified in all boreholes in the depth of approx. 33 - 38.5 m. In one borehole (NA1) there was also found one shallower horizon (the depth of approx. 12 - 14 m). This fact, all together with lithological description of the cores, confirmed expected heterogeneity of the sediment system in a small scale.

Sequences of the core with increased radioactivity were sampled and taken for further detailed laboratory analysis.

Groundwater from the boreholes was also sampled, both mixed samples (from the whole sedimentary sequence) and samples from U accumulation layer.

Basic hydraulic tests were performed at NA3 borehole in order to determine sedimentary environment hydraulic parameters, i.e. hydraulic conductivity K and transmissivity T.

All the activities were performed as a joint effort of NRI Řež and GRS Braunschweig.

3.3 Analysis

Following laboratory analysis were performed:

- detailed gamma spectrometry measurement of core samples
- determination of sediment mineralogical composition
- determination of major and trace elements in the sediment (Na, K, Ca, Mg, Si, Mn, Fe_{tot}, Al, F, Cl, Br, S, P, C_{tot}, TOC, As, Cu, Zn, V, Sb, Sn, REE)
- determination of U and Th content
- isotopic composition of sediment samples
- sequential extraction of U forms in the sediment, using methodology proposed in the frame of the Cigar Lake Natural Analogue Project [1, 2]
- determination of material retention properties (cation exchange capacity CEC, specific surface area, particle size analysis)
- test of possibility to use SHRIMP, i.e. sensitive high resolution ion microprobe technology (ANSTO, Australia), to identify character of mineral surfaces [3]
- pore water extraction from solid samples, using high pressure squeezing technique, and chemical analysis of pore fluids [3]
- ground water chemical analyses (Na, K, Ca, Mg, Si, O_2, Mn, Fe_{tot}, HCO_3, F, Cl, Br, SO_4, NO_3, PO_4, Al, U, Th, C_{tot})

3.4 Results

Field activities on the site and detailed laboratory analysis brought the overall description of the sedimentary system. The results and their interpretation allowed evaluating the possibility to study processes relevant to the long-term barrier performance of bentonite material at the site.

The deeper U horizon (33 – 38 m) passed through all of the three boreholes. On the other hand, the shallow layer (12 – 14 m) was located just in the NA1 borehole. The borehole profiles are presented on Fig. 2. Site-characteristic feature is heterogeneity in a small scale, i.e. differences in occurrence and thickness of lithological layers (alternation of clayey, sandy, organic rich material), in thickness of U-bearing sequences, in U content etc.

Main sediment forming minerals are quartz, kaolinite, montmorillonite, pyrite, anatase/rutile, gypsum, siderite. Uranium minerals, however rare, were also identified - ningyoit (U phosphate) and Ti bearing leucoxene (product of Ti mineral weathering).

Predominant U form seems to be non-crystalline one (inter-granular amorphous matter, identified during the first test measurement using SHRIMP technique) [3].

The U concentration within sediment sequence showed that the element content varied although the three boreholes were drilled within the distance of 15 m. The maximum values found were compiled in Tab. 1.

Tab. 1: Maximum U concentration in the boreholes NA1 - NA3 ($mg.kg^{-1}$ = ppm)

Borehole	Depth (m)	U concentration ($mg.kg^{-1}$)
NA1	12.4	139
NA1	35.5	**234**
NA2	34.9	111
NA3	36.3	191
NA3	38.1	212

Uranium accumulation is connected with increased content of organic matter, however not in all cases. Neither straightforward correlation could be made with pyrite. There could be found some trends within one U bearing layer (see trends on Fig. 3) where in some cases U accumulation is connected with increased organic matter (on Fig. 3 represented with total organic carbon, TOC, content). Sequential extraction of U forms showed similar results: the most frequent U-forms in the sediment are U bound on organic matter, on amorphous Fe oxyhydroxides and onto residual minerals.

The pyrite and organic matter presence in the sediment proves reducing conditions within uranium accumulation layers. Those two phases play most probably the role of agents causing/buffering reducing conditions.

After sediment contact with oxidising conditions, i.e. when non-protected sediments samples was left under atmospheric conditions, sediments became altered. Extracting pore water under aerobic conditions following changes can be, for example, observed: it was found that sulphate concentration in pore fluid increased (oxidation of S(-II) in pyrite) and consequently pH decreased. Increased acidity then caused leaching of mineral phases and release of U from the sediment into pore water. U concentration in pore fluid increased from 836 $\mu g.l^{-1}$ (anaerobic conditions) up to 34 000 $\mu g.l^{-1}$ (under oxidising conditions; measured in the sample with U content approx. 212 $mg.kg^{-1}$) [3].

Studying U decay chain isotope ratios (i.e. $^{234}U/^{238}U$, $^{230}Th/^{234}U$, $^{226}Ra/^{234}U$), disequilibria in U decay chain were observed (see Fig. 4). The value of ratio $^{230}Th/^{234}U < 1$ was caused by higher mobility of U in comparison with Th during weathering processes and transport [4]. Further, depletion of samples in ^{226}Ra was most probably caused by changes in redox conditions during U deposition. ^{226}Ra in oxidising groundwater is usually bound as sulphate. When Eh conditions changed, S(+VI) was reduced to S(-II), bound in pyrite and other sulphides, and consequently Ra was released from the system [5].

Hydraulic tests, followed by determination of hydraulic conductivity K on the basis of particle size analysis [3, 6], brought K values for the Tertiary volcanodendritic layers in the range of $K = 10^{-6} - 10^{-7}$ $m.s^{-1}$. Values for granite aquifer (upper part of underlying crystalline rocks) varied in the range of $K = 10^{-3} - 10^{-7}$ $m.s^{-1}$. On the south part of the site there is an evidence for a zone with increased permeability with NW-SE direction.

Groundwater of Ca-HCO_3 type with variable amount of sulphate was reducing at U-bearing horizons. U content did not increase above the value of 25 $\mu g.l^{-1}$. Connection with deep

circulation water of underlying granite horizon, presumably more mineralised and with increased temperature, was not proved.

Pore-water, extracted from the sediment using squeezing technique, lacked HCO_3 and was of Ca-Mg-SO_4 type. High U content in pore fluid (34 $mg.kg^{-1}$ of U) was measured for aerobic conditions, anaerobic conditions did not cause such a U release (0.8 $mg.kg^{-1}$).

4. Future plans

The pilot phase showed that the site was suitable for natural analogue studies considering potential mobility of critical radionuclides through argillaceous material under representative long-term conditions. Following processes could be studied at the site:

- behaviour of U and Th (i.e. distribution in the sediment, mobilisation and transport processes) in argillaceous sediments
- evolution of ground water and pore water chemistry in argillaceous sediments
- influence of redox changes on U and Th transport

The continuation of the activities is prepared in collaboration with other European organisations as a project to be submitted to the 5th EURATOM Framework Programme. The project addresses migration behaviour of natural U-decay chain isotopes in diverse argillaceous sediments, in different geological, geochemical and physical environments, ranging from plastic clays to shales.

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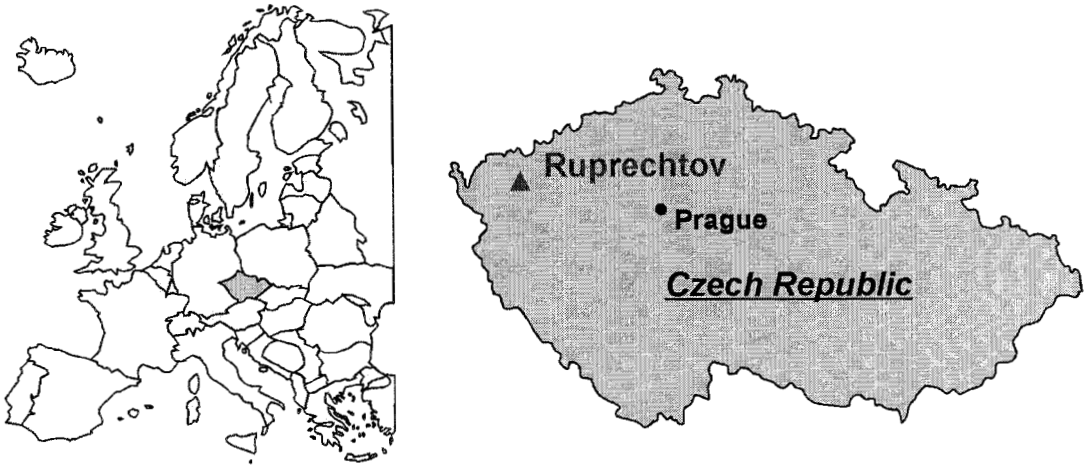
Fig. 1: Localisation of the Ruprechtov site (W Bohemia, Czech Republic)

Fig. 2: Borehole lithological profile (simplified)

Fig. 3: U content (here represented with ^{226}Ra activity) along the NA1 - NA3 cores in correlation with organic matter content (TOC). Considered trends are shown.

Fig. 4: Isotopic composition of selected sediment samples.

Fig. 1: Localisation of the Ruprechtov site (W Bohemia, Czech Republic)



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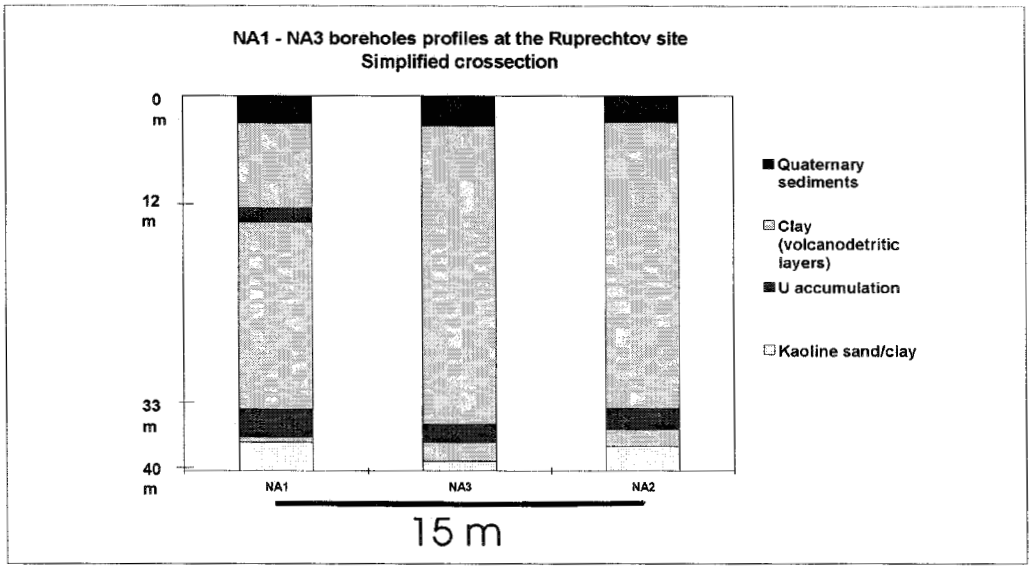


Fig. 3: U content (here represented with ^{226}Ra activity) along the NA1 - NA3 cores in correlation with organic matter content (TOC). Considered trends are shown.

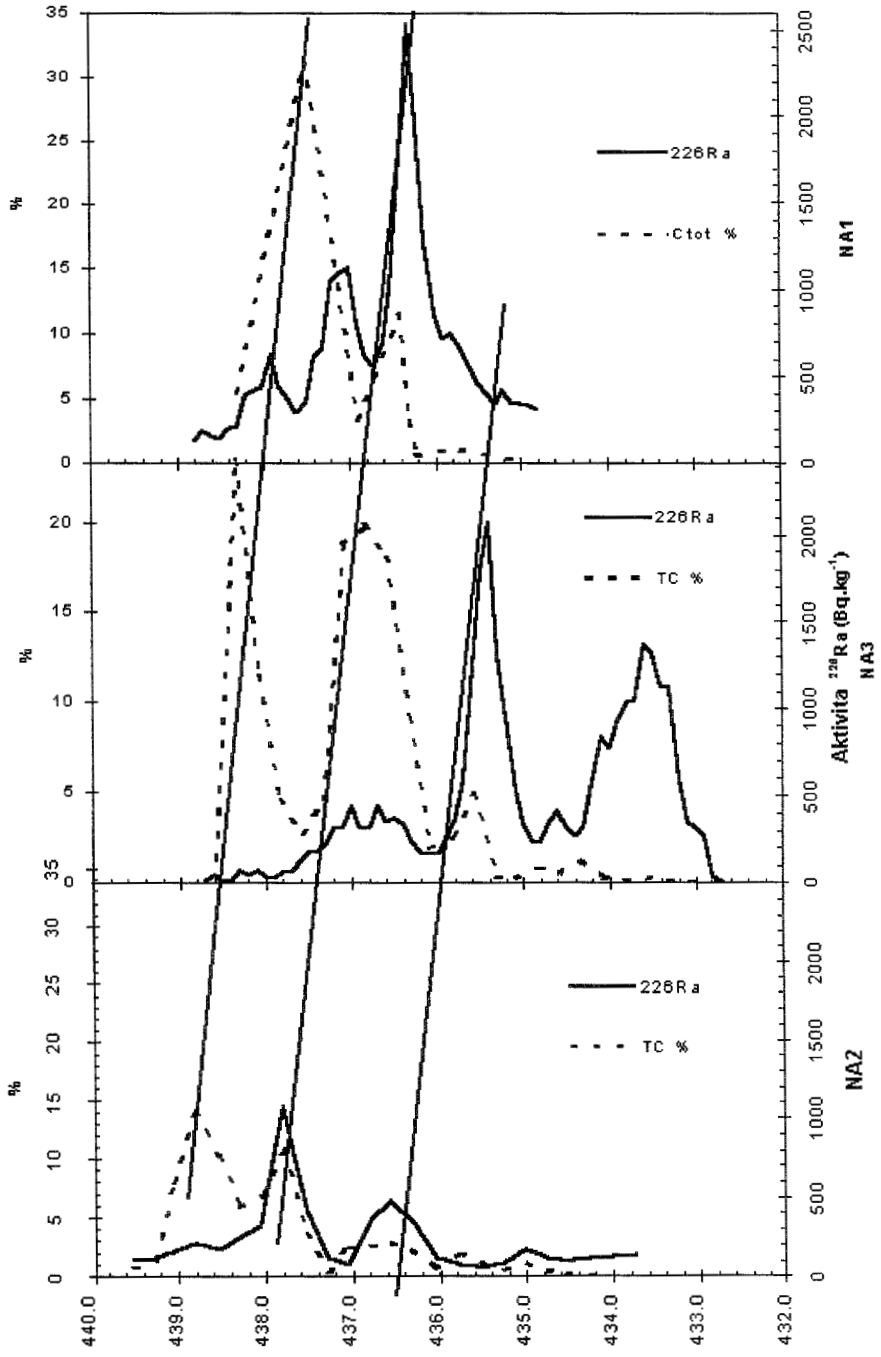
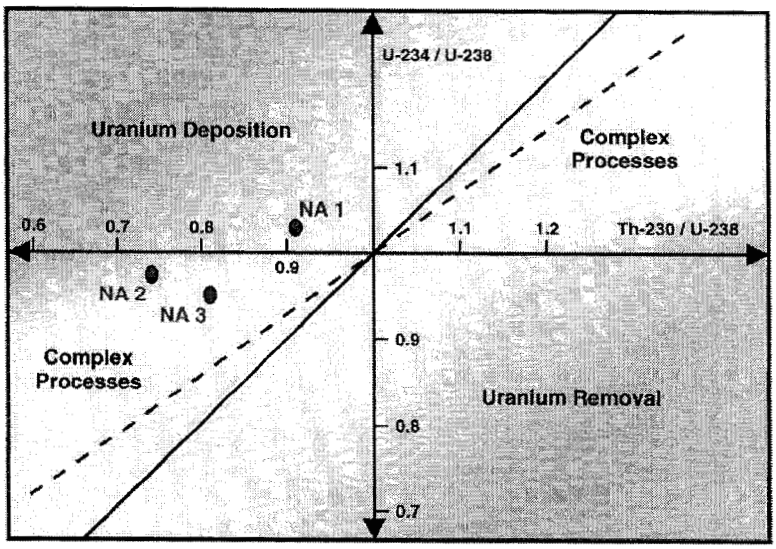


Fig. 4: Isotopic composition of selected sediment samples.



Projects BARRA, MATRIX and ARCHEO:

The ENRESA Programme in Natural Analogues

P Hernán, J Astudillo and A Cortés

ENRESA

Introduction

The three Natural Analogue Projects described here currently constitute the ENRESA Programme on Natural Analogues. These Projects were selected among a series of sites, being the main criteria for selection, the coverage of the Deep Geological Disposal concept, in those parts less extensively treated in previous Natural Analogues studies, both at domestic and international scales. Previous ENRESA studies on Natural Analogues were basically concentrated in the El Berrocal Project; migration radionuclides in a far field fractured media. Two of the current studies are representative of the near field; BARRA, analogue of the long-term behaviour of the clay engineered barrier material and ARCHEO, based on archaeological metallic specimens and addressed to the study of corrosion, the third one, MATRIX is representative of the geosphere in meta-sedimentary rocks.

MATRIX PROJECT

1. Objectives

The study of the uranium ore deposit of Mina Fe (Salamanca, Spain) as a Natural Analogue of radionuclide migration has a twofold objective:

- To study conceptual and numerical models for the stability of the spent fuel matrix with varying redox conditions.
- To study the migration processes; dispersion, and retention of radionuclides.

The most important processes to be considered are oxidative dissolution of uranium (IV) minerals, sorption mechanisms onto iron (III) oxy-hydroxides and clay minerals, and matrix diffusion.

2. Geology of the site

The "Mina Fe" deposit is hosted by the schist-graywacke complex (SGC), which is of Upper Proterozoic to Lower Cambrian age and consists mainly of a metamorphosed sequence (in part turbiditic) of carbonaceous pelitic and fine-grained sandstones. The carbonaceous slates, (about 40% of the stratigraphic sequence), have significant uranium contents (from 30 to 200 ppm), indicating that these rocks could be the source for uranium during a re-concentration process.

Hercynian faults and fracture zones which were reactivated during the Alpine orogeny, were critical for the formation of uranium deposits, providing not only flow-channels for mineralising fluids but also sites for mineral deposition. The Natural Analogue study selected

one of the U-mineralised fractures (Falla Boa), as the main site for the project. The Boa fault has a dip between 75°NW and 40°NW and a variable but maximum thickness of 0.5 m.

3. The ore mineralogy

The dominant primary minerals are carbonates (calcite, dolomite, and ankerite), adularia, pitchblende, coffinite, pyrite, and marcasite with minor amounts of galena, sphalerite, chalcopyrite, and quartz, and traces of fluorite and hematite. The wall rock adjacent to the mineralization presents a narrow chloritization halo (up to 5 cm wide).

Supergene alteration resulted in the formation of several secondary uranium minerals such as gummite, ianthinite, uranotile, autunite, phosphuranylite, kasolite, renardite, sabugalite, johannite, zippeite, and uranopilite.

4. Analogies and PA- addresses expected outcomes

The analogies of the Boa fault zone to a hypothetical spent fuel repository can be summarised as follows:

- Spent fuel analogue: The uranium ore located in the Boa fault.
- Spent fuel oxidation analogue: Uranium-bearing minerals with different uranium redox states (pure U(IV), mixed U(IV)/U(VI), and pure secondary U(VI) minerals).
- Analogue of canister corrosion products: Presence of iron (III) oxy-hydroxides as gangue minerals associated to the uranium ore.
- Clay barrier analogue: A clay matrix corresponding to the fault zone locally surrounds the uranium ore.

The study of the behaviour of this natural system should contribute to the understanding of some geochemical processes and their validation through numerical models. The most outstanding processes are the co-precipitation and sorption of radionuclides with Fe(III) oxy-hydroxides, diffusion, sorption and cationic exchange processes related to clay minerals. These clay minerals can affect the migration of radionuclides through the clay barrier, and the far field. A final but not less important issue is the oxidation of U(IV) minerals.

5. Site characterisation studies in the frame of the current natural analogue project.

This characterisation has been based in the detailed study of a quarry front after restoration and also in the study of core samples coming from the drilling of 4 short boreholes (total meters drilled 212). At present, only the results provided by the studies in the quarry front are available, those coming from borehole cores, are currently undertaken as it is also the case for the hydrotesting and water sampling activities on site.

All these works will provide a complete set of data enabling to initiate the studies focused to achieve the objectives of the project. The available data obtained up to now refer mainly to four activities: structural study of the quarry front and boreholes, radiometric measurements, solid geochemistry and mineralogy and preliminary geochemical modelling.

One of the conclusions provided by **the structural study** indicates that the northern block has a higher fracture density than the one at the south of the fault. This is coherent with the radiometric studies showing that the northern block is poorly mineralised whereas in the southern block the amount of uranium is higher.

In **lithologic and mineralogical terms** three zones have been distinguished:

- Oxidised zone: clay minerals + Fe(III) oxy-hydroxides + quartz.
- Transition zone: clay minerals + Fe(III) oxy-hydroxides + pyrite + carbonates + quartz + gypsum.
- Reduced zone: clay minerals + pyrite + carbonates + chlorite + quartz.

Geochemical modelling: A preliminary geochemical model has been performed following the conceptual model for the supergene alteration. Considering that the primary ore is composed of pitchblende, pyrite, carbonates, chlorite and clay minerals and their interaction with infiltrating oxidising meteoric waters. The geochemical model was performed as a reaction-path using the PHREEQC geochemical code simulating the interaction of the primary ore with infiltrating oxidising meteoric waters.

The modelled results are in agreement with the observed mineralogical data. The pH evolution shows the consumption of atmospheric oxygen as meteoric water infiltrates and reacts with the rock, whereas pH is lower in the oxidised zone due to the lack of carbonates to buffer the pH. The uranium concentration in the water is higher in the oxidised Eh due to the fact that meteoric water is initially undersaturated with respect to all uranium minerals becoming progressively saturated after reacting with the rock.

6. Further work

The remaining work to be carried out during the current phase I of the project (up to the end of 1999) consists of the following actions. Continuation of the geochemical and mineralogical studies from borehole and quarry front samples, characterisation of the hydrodynamic behaviour of the system using borehole data, hydrogeochemical sampling in boreholes and selection of samples for detailed experiments on migration and water-rock interaction. These last studies will be the basis of the Phase II (2000-2003) activities in which the following issues will be covered: Sorption measurements on clay minerals and Fe(III) oxy-hydroxides, uranium series disequilibrium, matrix diffusion, laboratory experiments modelling, modelling of oxidative ore dissolution, sorption, and matrix diffusion processes, reactive transport modelling, predictive geochemical behaviour at depth. It is quite likely to undertake additional deep borehole drilling, for a final model testing and "validation".

BARRA PROJECT

1. Introduction

ENRESA has been studying the bentonite deposits in the Cabo de Gata (Almería, Spain) area with three main objectives:

1) As a supply source of the candidate buffer material for their repository concept.
2) To provide homogeneous material for the construction of the *in situ* FEBEX experiment at Grimsel test site.
3) A Natural Analogue of the bentonite engineered barrier bentonites. This project is known under the name of BARRA. The specific aim of the project is to study, and determine the effects on the buffer, of several processes that have been identified in some of the bentonite outcrops of Cabo de Gata, as well as building up the models enabling to quantify such processes and their related effects.

The performance of clay barrier functions can be significantly affected by the effects of extreme variations in water chemistry (salinity increase, continuous inflow of oxidising waters) and/or physical gradients (increased temperature due to heat generation from the canister, induced pressure by the waste canisters on the buffer). From the preliminary investigations at the Almería deposit, there are indications of the occurrence of these events and associated processes and, consequently, the BARRA project is focusing its efforts on the study of these phenomena.

2. Objectives

The objective of the BARRA project is to qualify and quantify the observed effects of pressure and thermal loading and oxic and saline intrusions in several bentonite outcrops of Cabo de Gata.

Some of these processes will necessarily occur in the near field of a repository (such as the thermal gradient due to the heat diffusion from the spent fuel), whereas others are likely to occur during the operating stage of the repository. The study of selected bentonite outcrops, where the processes listed above have been shown to have occurred during long time periods, is of primary importance as it is possible to observe the chemical and mineralogical changes that these processes have produced in the bentonite. The main changes expected are: illitisation, accessory mineral dissolution, cementation, cation exchange, Pore-water replacement, variations in swelling pressure capacity, changes in hydraulic and mechanical properties.

The occurrence and extent of the chemical processes involved (illitisation, accessory mineral dissolution, cementation, and cation exchange) will be quantitatively assessed by geochemical modelling.

3. The geology of Cabo de Gata and the origin of bentonites

The volcanic rocks from Cabo de Gata belong to a calc-alkaline series, mainly represented by basaltic andesites, andesites, dacites, and rhyolites. Up to three different events that started with explosive phases produced the formation of pyroclastic rocks and large calderas (sometimes over 5 km in diameter), followed by the extrusion of lava flows and subvolcanic dome intrusions. The alteration of pyroclastic rocks (tuffs) resulted in the formation of the bentonites, whose outcrops are widespread in the Cabo de Gata area.

The alteration processes were due to two different types of hydrothermal fluids that affected the pyroclastic rocks most intensely. Acid-sulphate hydrothermal fluids produced alterations typically related to epithermal deposits, such as that in the Rodalquilar gold mineralisation, whereas near neutral fluids, more widespread than the former, produced the bentonite formation by interaction with pyroclastic rocks.

4. Selected bentonite outcrops

There are more than 30 bentonite deposits in Cabo de Gata, among them a few have been selected as they are of particular interest, having been affected for long periods of time by some of the processes to be considered in the performance assessment.
Temperature increase: Cala del Tomate, Morrón de Mateo, Curva de Felipe.
Pressure effect produced by canister Loading: Pozo Usero
Intrusion of oxidising waters: El Corralete, CalaRajá

High saline effects: Cortijo de Archidona, El Corralete and Saqan José, Pozo Usero (intrusion of Ca and Mg rich waters).
Interface effects: Cala del Tomate, Pozo Usero

5. Temperature increase

Some of the bentonitic deposits are crosscut by sub-volcanic domes and other intrusions that injected in pre-existing bentonites. These intrusions produced a weak metamorphic aureole due to the high temperature of intrusion, even though these intrusions get cool very quickly (tens of years).

Among the outcrops intruded by this type of subvolcanic rocks, two have been selected for further study. Morrón de Mateo and Cala del Tomate, both outcrops are located in Los Frailes zone.

In **Morrón de Mateo** a suite of lava domes composed of massive amphibole-biotite dacites intruded the bentonite deposit. The temperature values obtained by the dome are in the range of 770 to 886°C, with a mean value of 820°C. As the intrusion took place in successive pulses, the thermal front could have been acting for some tens of years.

The results show neither clear trend in the mineralogical composition, nor in ^{18}O isotopic contents of the samples taken in a profile from the intrusion. Several hypotheses could explain why there is no change in the mineralogical and isotopic composition of these samples. A more detailed study is anyhow needed in order to evaluate any possible changes in the bentonite. In spite of this lack of gradients, pore water analysis of samples taken in the vicinity of the contact show accumulation of K, NO_3 and HCO_3, together with Cl, SO_4, Na, Ca and Mg, migration indicating movement of fluids.

In the **Cala del Tomate** area, a pyroxene andesite dome, 10.5-11 Ma in age intruded the bentonite deposit. The thermal effect is more evident than in the case of Morrón de Mateo. The intrusion temperature in this case has been calculated by extrapolation from other pyroxene andesite domes, which are equivalent to that of the Cala del Tomate area, giving a temperature range between 930 and 1020°C. In principle it is unlikely for the duration of the effect to have exceeded a few tens of years.

In this case, the effect of the thermal metamorphism on the bentonite is very obvious even at the outcrop; the bentonite near the contact presents a brownish tint, up to more than one metre from the contact, which is a clear intrusive one.

From the mineralogical data of the sampled profiles it is possible to observe that quartz, cristobalite, and illite contents increase closer to the contact, whereas the smectite content in the <20 μm fraction increases with the increasing distance from the contact.

The effect of the thermal gradient is also evident from the oxygen isotopic composition, the $\delta^{18}O$ increases with the distance from the contact with the volcanic rock. Nevertheless it is still necessary to obtain reliable data on the temperature reached by the bentonite

6. Pressure effect and Ca/Mg interaction

The bentonites at the Pozo Usero locality are covered by a thick reef limestone unit, deposited during the Upper Miocene. The reef structure has remained essentially constant with minimal erosion effects. As this limestone unit has a variable thickness, the underlying bentonite

could have suffered a variable loading effect so providing chemical and mineralogical changes due to the limestone. In addition, Ca and Mg rich groundwaters will have permeated down through the limestone and interacted with the bentonite inducing some chemical and mineralogical changes.

In the Pozo Usero bentonite deposit, the reef limestones that overlay the bentonite might provide useful hydraulic and mechanical properties data relating the canister loading effect. Already available data indicate some mineralogical changes, namely the smectite crystallinity decreases when the load pressure increases. Further, more detailed studies are envisaged.

This location does not provide an ideal "canister sinking" analogue, as the load has existed over a broad region, rather than as a point load. Consequently, there is no obvious "settlement" to be measured. However, some useful data on variations of hydraulic conductivity or mechanical properties at different load ratios might be determined. Although it is not currently clear whether these potential variations could be related to the behaviour of highly compacted bentonite.

7. Oxidising water intrusion

Some of the altered tuffs in Cabo de Gata are covered by a palaeosoil, as in the case of El Corralete and Cala Rajá. The interaction of meteoric waters (rainwater) with these palaeosoils could produce an oxidising front, penetrating the bentonites. Thus, the chemical and mineralogical changes produced by such an oxidant front could be studied. It is still pending to locate a proper bentonitic material where this effect had certainly taken place.

8. High saline water

The main process considered here is related to saline pore water often found to be present in the bentonite. This issue has an additional importance, due to the fact that salinity is not homogeneously distributed in the area, while Serrata de Nijar exhibits a very high salinity other area show moderate saline contents. It has been observed a certain correlation between high salinity and presence of smectitie-illite interlayering, being the smectite content, clearly higher when lower salinities are observed. In theory the presence of high saline fronts could provoke the appearance of the "interlayer" being this issue an important objective of the project.

The study of the effects of high saline pore waters in bentonite is a key factor in the repository design of ENRESA, as it can lead to important changes in the bentonite properties (illitisation and cementation) as well as the formation of saline fronts that can affect canister integrity. The work is ongoing and little information is available.

9. Further work

Sufficient data has now been gathered to indicate that the Cabo de Gata region offers a number of potentially valuable bentonite analogue study sites. Further multidisciplinary work is required to develop these studies.

In particular, several additional types of investigations are needed to interpret both the available and extend them: Thermal and radiation modelling, detailed SEM characterisation of pore structures, hydraulic and mechanical property determinations, extensive conceptual and geochemical modelling of the processes expected.

The kind of activities to be developed will include further detailed sampling, with the possibility of local short core drilling. The studies to be performed will generically cover the following techniques for all the activities: clay mineralogical analyses. XRD and TEM + EDAX, chemical analyses for the solid phases, optical and electro-microscopy, isotopic studies and chemistry of the pore waters.

Specifically addressed to some activities, the following studies are envisaged: Sampling zoom on discontinuities (thermal and pressure effects, looking for specific alterations and surface precipitation minerals), complementary laboratory studies specifically designed for study of thermal effect, oxidative alteration, alteration effects of high saline solutions, and micro-textural studies in oriented samples (pressure effect). There exists the possibility of studying of marine core drillings, from pre-existing ocean platform studies, thus providing samples with a long time in contact with marine waters for study of saline front effects.

ARCHEO PROJECT

The studies carried on metallic specimens in several archaeologic sites will provide valuable information in understanding their evolution versus time. These studies will allow establishing analogies between the metallic materials selected to build up the disposal canister and the metallic pieces behaviour found in a natural environment.

An exhaustive analysis of these pieces (buried during thousand of years, 2.000-7.000 y) will provide accurately data about metallic materials behaviour. Data from laboratory tests does not suffice, because it is developed in a short time period and the geochemistry of the environment has not been taken into account.

Up to now, ENRESA has carried out projects to study the corrosion processes and corrosion products in laboratory tests. These laboratory experiments have reproduced artificial environments (saline atmosphere in a chamber), and have been carried out in a short time period (3-5 y).

Results from these tests have provided data on corrosion rates, main corrosion products generated, and also on some properties as elasticity, plasticity, toughness, and so on.

The main results, coming so far from the ARCHEO Project, indicate:

Chemical assimilation of external elements. All the studied specimens show that the external oxide layer is contaminated by inorganic substances. These contaminants are found incorporated to the FeO.

Selective corrosion. The presence of two or more phases of different composition into a heterogeneous metallic sample allows establishing an electron flux between different oxidation potentials.

Secondary oxides formation. The corrosion of the original material leads to the generation of pores and cracks. In these structures, secondary oxides are generated. The role of these oxides is to seal those defects created by the original oxide generation.

The role of the Tsukiyoshi Fault as a control on nuclide migration in the Tono uranium deposit, central Japan

K. Tsubota[1], H. Yoshida[1], K. Hama[1], K. Amano[1], A.E. Milodowski[2] and R. Metcalfe[1]

1: JNC, Tono Geoscience Center, 959-31, Jorinji, Toki, Gifu, Japan
2: Mineralogy and Petrology Group, British Geological Survey, Keyworth, Nottingham, U.K.

Abstract

To date, relatively little use has been made of natural analogue studies to build an understanding of long-term processes that will control the hydraulic behaviour of faults around a High Level Radioactive Waste (HLW) disposal system. Typically, Performance Assessment (PA) for such systems assumes that the properties of faults are temporally invariant. Often, it is also assumed that the properties of any particular fault will be spatially invariant. In most cases, PA incorporates conceptual models for faults that are based largely upon investigations of normal faults. These PA models may be inappropriate for geologically recent reverse faults in a convergent plate margin setting, such as that of Japan. For all these reasons, the Japan Nuclear Cycle Development Institute (JNC) is conducting a natural analogue study of a reverse fault, the Tsukiyoshi Fault, which cuts the Tono uranium deposit of central Japan. The initial results of this investigation are presented in this paper. These results suggest that a description of the fault as a single planar fracture is inaccurate. Instead, it is more appropriate to describe the fault as a relatively complex zone of fracturing, extending for several metres around a central zone of fault rocks and fault gouge, up to several tens of centimetres wide. Furthermore, there has been a complex history of fluid movement through the fault zone. There is also evidence that the hydraulic properties of the hanging wall and footwall are different and may have varied over time. However, uranium-series isotopic data suggest that uranium has been retained in the fault's gouge for at least one million years. It is postulated that water/rock interactions have created suitable chemical conditions in the fault gouge to immobilise the uranium even though past fluid movement has occurred through the fault zone.

Introduction

Performance Assessments (PA) for potential deep geological repositories for High Level Radioactive Waste (HLW) must take into account the influence of faults on mass transport through the geosphere. It is necessary to ensure that the conceptual and numerical models underpinning PA incorporate appropriate representations of faults, based upon a sound understanding of the relevant mass transport processes and flow pathways. However, typically, PA assumes that faults have temporally invariant properties. It is often also assumed that these properties are spatially invariant in any particular fault. It is important to test these assumptions, particularly in active tectonic settings where relatively recent faults are widespread. In particular, it is desirable to evaluate whether such faults behave in the same way as the faults that occur in relatively stable tectonic settings, that have been considered by most PA to date.

In Japan, any future underground disposal of HLW will take place close to a convergent plate margin. Thus, it is likely that a PA for any future HLW repository in Japan will need to consider mass transport through geologically recent reverse faults. However, there is relatively little information upon which to base representations of the long-term behaviour of such faults in the PA. This deficiency arises because globally, most research related to HLW disposal has focussed upon stable tectonic shield settings and/or extensional sedimentary basin settings.

To help fill this gap in knowledge, the Japan Nuclear Cycle Development Institute (JNC) is conducting research on a reverse fault, the Tsukiyoshi Fault. This fault cuts a uranium deposit at the natural analogue site of Tono Mine, in Gifu Prefecture, central Honshu, Japan (Figure 1). Here, we outline the general approach to the investigations of this fault and present the initial findings.

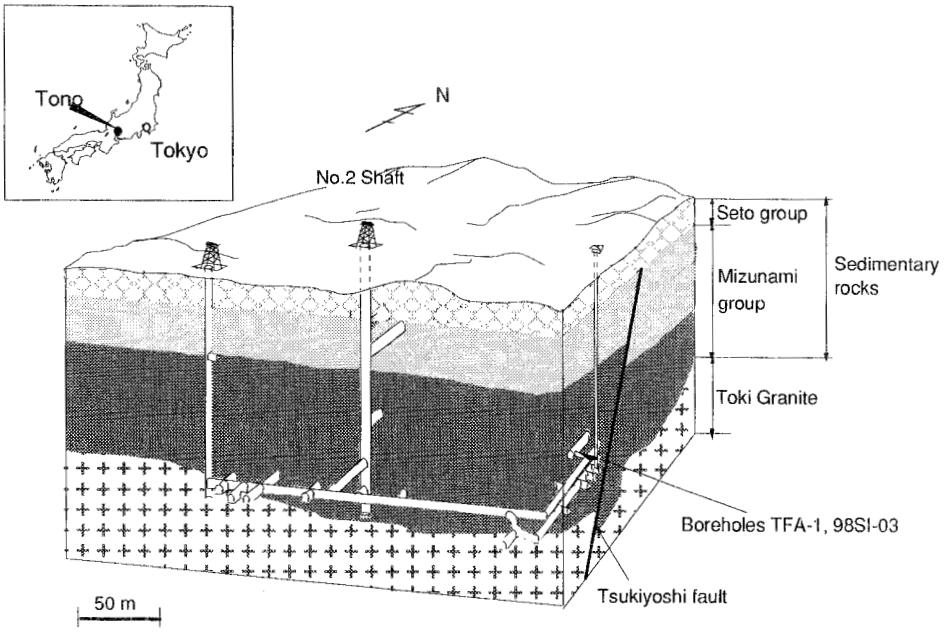


Figure 1 Geology and in-situ experimental area at Tono

Geological Setting

In central Japan, a series of small Neogene to Quaternary basins are developed on pre-Tertiary granitic basement rocks. The Tono Mine is located almost entirely within Miocene to Pleistocene sedimentary rocks that fill one of these basins (Figure 1). These sedimentary rocks were deposited between 20 Ma and 0.7 Ma and the lowermost strata lie directly on the eroded surface of the late Cretaceous Toki Granite (Yusa et al. 1993). The deepest of the sedimentary rocks contain the Tono uranium deposit, which was formed approximately 10 million years ago (Ochiai et al., 1989; Kobayashi, 1989). The uranium mineralisation lies immediately above the unconformity, in a zone that is 2–5 m thick, with an area of several hundred meters wide and 2-3 km long.

In the vicinity of the mine, the Tsukiyoshi Fault has an approximately east-west orientation, a southerly dip of between 60° and 70°, and a reverse displacement of about 30 m. The fault displaces the Toki Granite and overlying Miocene strata of the Mizunami Group (deposited between 20 Ma and 15 Ma; Itoigawa, 1974), including the Tono uranium deposit.

However, the fault does not displace the Pliocene to Pleistocene Seto Group, which overlies the Mizunami Group unconformably (Figure 1). Previous investigations have identified the fault as a dominantly planar feature, which usually contains a green clay gouge of variable width, but which is up to around 20 cm wide.

From bottom to top, the Mizunami Group consists of three formations: the Toki Formation (divided into the Lower Toki Formation and the Upper Toki Formation), the Akeyo Formation and the Oidawara Formation. The Toki Formation is considered to consist mainly of fresh water lacustrine deposits (Yusa et al., 1993), although fluvial sediments may also be present (Yoshida et al. 1994). In contrast, the Akeyo Formation is considered to represent brackish to shallow marine sedimentation, while the overlying Oidawara Formation is thought to be a deeper water marine deposit (Yusa et al., 1993).

Methods

The Tsukiyoshi Fault was examined in exposures in the walls of Tono mine and in two horizontal, parallel, fully-cored boreholes, 98SI-03 and TFA-1, that were drilled from a mine gallery (Figure 1). These boreholes were drilled 0.5 m apart, for distances of 18 m and 30 m respectively. They intersected the fault at a distance of 14.6 m from the gallery wall. The core from Borehole 98SI-03 was logged systematically and then sampled for more detailed petrographic analysis. In addition, the fault clay of the Tsukiyoshi Fault was sampled from accessible exposures in the mine galleries. A single sample was also taken from near the base of Borehole TFA-1.

It was particularly challenging to collect and prepare poorly consolidated samples of fault rocks and gouge, for microscopic investigations. Such samples were collected from both the core and the exposures in the mine walls, by means of 'Kubiena' tins (Figure 2). These tins are aluminium boxes with sharpened edges and lids on opposite sides. The boxes were pushed into the soft clay-rich fault rocks and rock material was then scraped from around each box until it was freed from the core or mine wall. The boxes were then capped and sealed.

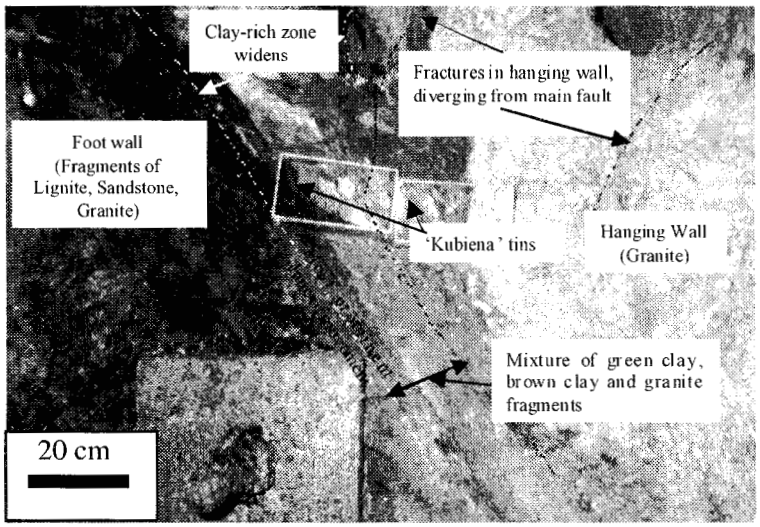


Figure 2 A Photograph illustrating an exposure of the Tsukiyoshi Fault in the walls of an adit in the Tono mine.

The samples were air-dried and then vacuum-impregnated with epoxy-resin to stabilise the friable materials during sectioning. A blue dye was added to the epoxy-resin to highlight the porosity during optical microscope observation. Sections were cut and polished under paraffin in order to preserve any water-soluble minerals (e.g. gypsum or anhydrite) that might be present. Those sections to be examined using backscattered scanning electron microscopy (BSEM) were coated under vacuum with a thin film of approximately 25 nm thick, to provide them with an electrically-conductive surface.

The sections were examined initially by optical microscopy. They were then investigated in more detail by back-scattered scanning electron microscopy (BSEM), to provide high-resolution mineralogical and spatial information on mineral relationships and rock microfabric. Simultaneously, semi-quantitative microchemical information was obtained by energy-dispersive X-ray microanalysis (EDXA). BSEM-EDXA and SEM analyses were performed using a variable pressure digital scanning electron microscope (SEM). Semi-quantitative EDXA analysis during the SEM investigations aided mineral identification. SEM-EDXA analyses were largely performed under high-vacuum mode (i.e. $<10^{-4}$ torr). However, some samples were examined by low vacuum/variable pressure SEM (i.e. chamber vacuum of approximately 3×10^{-2} torr) to overcome problems with high sample moisture content and sample outgassing (due to high smectite contents).

The bulk and clay mineralogy of samples of fault gouge, fault rock and representive samples of different sandstone, siltstone and mudstone lithologies were determined by X-ray diffraction (XRD).

Pore fluids were extracted from samples of the fault gouge by means of a squeezing procedure. These fluids were analysed for a range of major, minor and trace elements by inductively coupled plasma mass spectroscopy (ICPMS) and ion chromatography (IC).

As part of the regional hydrogeological studies, the impact of the Tsukiyoshi fault on groundwater flow in the Tertiary sediments has also been studied. During the construction of Number 2 Shaft (Figure 1) the resulting drawdown effect on the piezometric head in the surrounding rock mass was studied, by observing groundwater levels and hydraulic heads in 14 nearby boreholes (Koide et al., 1996).

Initial Observations and Discussion

An exposure of the fault in the mine tunnel is illustrated in Figure 2. This figure shows the complex zone of clay gouge and brecciation associated with the fault and some major associated fractures in the hanging wall. The width of the fault zone varies markedly, even over distances parallel to the fault, of a few tens of centimetres.

The main features of the mineral paragenesis in the zone of fracturing associated with the Tsukiyoshi Fault are summarised in Table 1 and a simplified log of the core from Borehole 98SI-03 is presented in Figure 3. This figure shows the relationship between the frequency of fracturing in the core and the prominent plane of movement, identified as the 'Tsukiyoshi Fault'

in previous studies. It can be seen that the frequency of fracturing becomes greater as this prominent fracture plane is approached. A damaged zone that is at least 7 m wide occurs around this fracture plane.

Table 1 Fracturing and diagenetic history

Stage of Mineralisation	Characteristics
Sediment Deposition	Deposition of immature organic-rich sediments containing abundant granite-derived clasts and volvanic-derived material
Early Diagenesis (i)	· Precipitation of authigenic KAOLINITE (Hanging wall ONLY - higher level) · Kaolinite "books" form in open porosity · interlayer replacement and exfoliation of detrital micas · Precipitation of authigenic PYRITE ➡ framboidal in matrix
Early Diagenesis (ii)	· Replacement of volcanic detritus and glass by SMECTITE + ZEOLITE (Clinoptilolite) · Secondary TiO2 (?anatase) alteration product of Ti-Fe oxides and ferromagnesian minerals
Compaction	· Deformation of micas · PYRITE + CALCITE associated with mica deformation bands · Alteration of micas to SMECTITE · Deformation of plastic SMECTITE-replaced clasts · Loss of matrix porosity
Reverse Faulting	Formation of CLAY GOUGE and CRUSH BRECCIA
Normal Faulting	Deformation of clay beds - formation of clay smears
Calcite veining	· CROSS FIBRE CALCITE VEINING - Cross-cutting fault gouge and crush bbreccias ➡ Overpressuring - crack-seal growth · DIALATIONAL CALCITE VEINING ➡ Hanging wall only
Late fracture dilation	· Dilation of slickensided fractures (locally cross-cut calcite veins) · Late stage SMECTITE + CALCITE in open fractures ➡ 'Fresh water'1 CALCITE morphology

Chlorite and smectite occur in the fault gouge, while calcite veining occurs in both the gouge and in fractures within the damaged zone. The rocks surrounding the fault gouge are rich in smectite, K-feldspar and quartz fragments. Some albite fragments are found in a smectite matrix. Detailed textural features of one sample of fault gouge in the core from Borehole 98SI-03, are illustrated in Figure 4. This figure shows that smectite in the fault gouge has evidently been deformed during movements of the fault, indicating more than one phase of movement. A further important feature of this illustration is the occurrence of small calcite crystallites that compose the majority of the calcite 'vein' cutting this sample. Isolated calcite spherulites can be seen in the deformed smectite. These crystallites evidently nucleated within the smectite matrix and post-date smectite deformation.

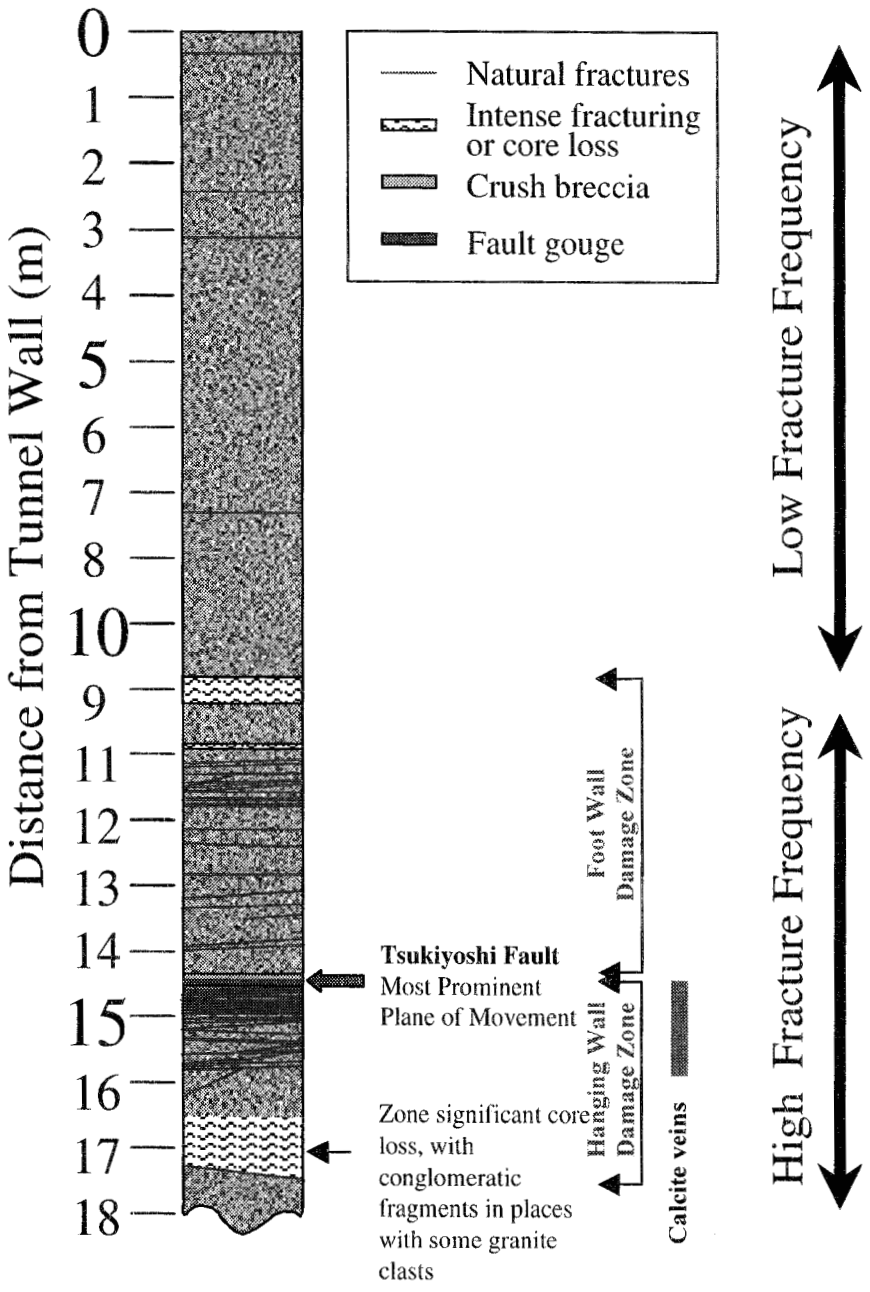


Figure 3 A simplified geological log illustrating visual observations made on the core from Borehole 98SI-03.

Fine-grained calcite was also found to coat the surfaces of fine fractures within the fracture-damaged zone around the Tsukiyoshi Fault in borehole 98SI-03. This calcite appears to be paragenetically late and where there has been sufficient pore space for euhedral crystal growth, it typically forms fine equant crystals. Some vein calcite also shows a cross-fibre texture, as illustrated in Figure 4. The relationship of this calcite to the euhedral, equant calcite is unclear, but the cross-fibres are indicative of its formation by a 'crack-seal' mechanism (Barker, 1990). The calcite from the Tsukiyoshi Fault zone appears either to be manganese- and iron-free or else to be only very weakly ferromanganoan.

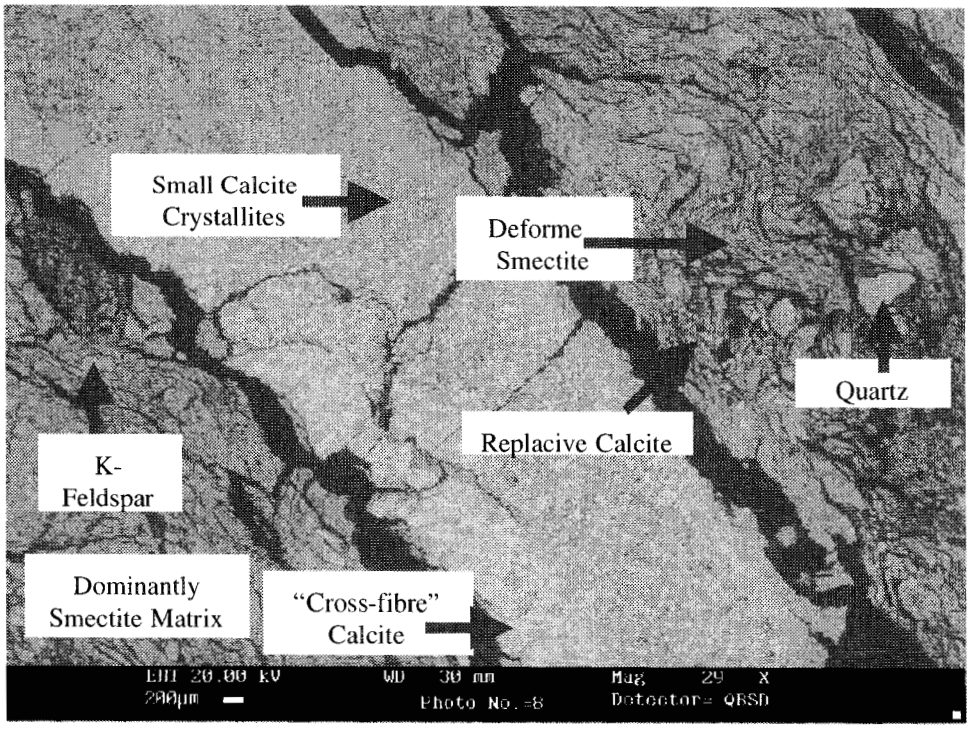


Figure 4. Scanning Electron Micrograph showing evidence for temporal variations inthe characteristics of the Tsukiyoshi Fault.

The observations show that the Tsukiyoshi Fault is not simply a two-dimensional planar feature, but instead is a three-dimensional zone with characteristics that vary from place to place (c.f. Figure 2 and 3). The hydraulic data for the present groundwater system suggest that this zone presently restricts groundwater flow across it. Notably, boreholes on opposite sides of the fault showed differing hydraulic responses during the sinking of the Number 2 shaft (Figure 5).

However, there has clearly been some flow of meteoric water through the sedimentary rock sequence in the recent geological past. No component of residual marine water has been found in the Tono area, even though sedimentological and palaeontological data indicate that such water was once present here. Instead, previous investigations of stable oxygen and hydrogen isotopes have demonstrated that all the groundwaters sampled in the Tono area had a meteoric origin (Mizutani et al., 1992). Radioacarbon data suggest that the groundwaters in the base the Mizunami Group were recharged earliest, at approximately 15000 years before the present (Mizutani et al. 1992). Thus, any older waters that were present have been flushed from the sedimentary rocks of the Tono area.

The available data are consistent with the Tsukiyoshi Fault playing a role in such flushing. In studies of other deep groundwater systems, the calcite crystal morphology has been shown to correlate closely with groundwater composition (Milodowski et al., 1998). Crystals with c-axis flattened and equant crystal forms have been found to coexist with fresh groundwaters, whereas forms with elongated c-axes occur with saline groundwater (Milodowski et al., 1998). If this relationship holds generally, then the presence of relatively late, equant calcite crystals within the fracture zone associated with the Tsukiyoshi Fault, may also indicate the passage of fresh groundwater through this fault zone in the past. This hypothesis is supported by the chemistry of

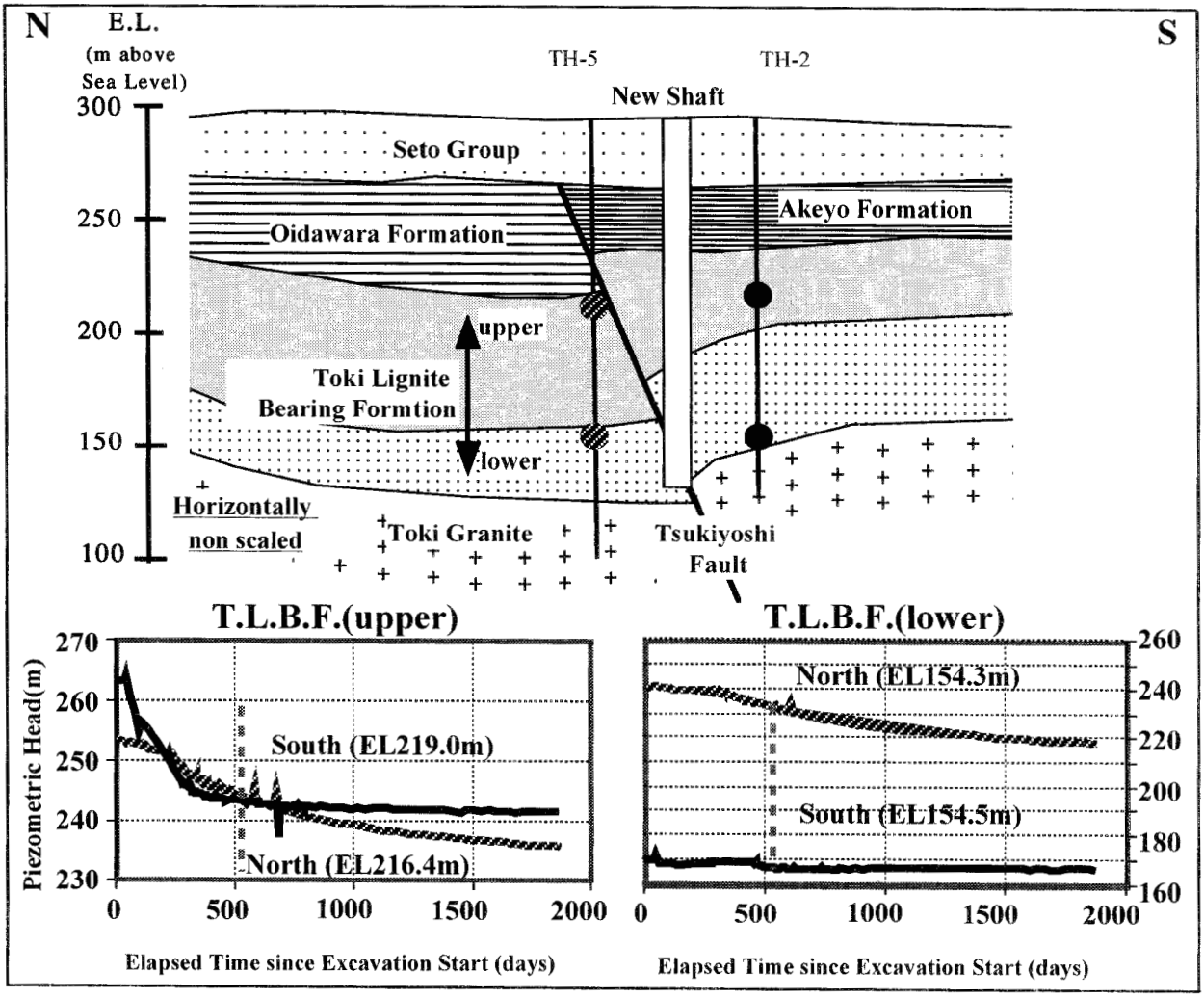


Figure 5 Variations in piezometric head versus time, during the sinking of Number 2 Shaft, for two points in each of two boreholes, TH-5 and TH-2. The former borehole is located to the north of the Tsukiyoshi Fault, whereas the latter is located to the south of this fault. For a given depth, different head variations versus time were observed in each borehole.

the calcite. The very low to zero concentrations of Fe and Mn in the calcite imply that the water from which it precipitated had low concentrations of Fe(II) and Mn(II). Possibly, these low concentrations could have resulted from the water being very fresh and/or being too oxidising for Mn2+ and Fe2+ to exist in solution. In either case, an implication is that the fault may have conducted meteoric waters. However, while it can be stated that such circulation occurred relatively recently in the history of the fault and clearly post-dates any fault movement, it has yet to be established whether or not this circulation is on-going. If such circulation does occur at present, it is not necessarily inconsistent with the hydraulic evidence for the fault acting as a barrier; the fault may be hydraulically anisotropic, allowing flow along it, but not across it. Certainly, the petrographic and mineralogical observations made in the present study are consistent with different parts of the fault zone behaving in different ways. For example, dilational calcite veining occurs only in the hanging wall, implying that fluid circulation occurred here, but not elsewhere.

The porewater extracted from the fault gouge in core from Borehole TFA-1 is fresh and is broadly similar in composition to flowing groundwaters extracted from other parts of the sedimentary sequence.
This finding is also consistent with the possibility that the fault zone has conducted fresh water. However, the timing of such water flow and the relationship between the pore water and the present groundwater circulation is unclear.

The hydraulic characteristics of the Tsukiyoshi Fault at the location of the core examined have clearly changed over time. For example, within relativley small areas of the fault, some calcite formed by a crack-seal mechanism, whereas other calcite filled open porosity. The small veins of calcite and the evidence for parts of the rock matrix being replaced by calcite are evidence that mass transport occurred in the fault gouge which is now a barrier to groundwater movement. However, the extent to which such mass transport occurred in the past is presently unknown. The most recent movement of the fault had a normal sense, although the normal displacement was smaller than the earlier reverse displacement. The mineralogical evidence for the circulation of fresh-waters post-dates this last movement and may reflect a change in the hydraulic properties of the fault zone caused by the changing sense of displacement.

In spite of this evidence for groundwater movement in and around the Tsukiyoshi Fault Zone, there is no evidence for significant movement of uranium since the formation of the Tono ore deposit around 10 million years ago (Yusa et al. 1993). Uranium-series isotopes imply that uranium has been almost immobile in the gouge of the Tsukiyoshi Fault for at least the last million years (Shinjo et al. 1997). A possible explanation for this is that water/rock interactions have buffered the chemistry of the waters in such a way as to prevent uranium being dissolved significantly in circulating waters. It has been suggested by Iwatsuki et al. (1995), that reactions involving organic matter in the Toki Lignite Formation have effectively caused reducing conditions to be maintained (Shikazono and Utada, 1997)

Conclusions

The present study has demonstrated that the Tsukiyoshi Fault is not simply a single planar fracture. Instead,, it is associated with a zone of fracturing that is up to at least 7 m in width. There has clearly been a complex history of fluid movement through this fault zone. Some evidence suggests that the hanging wall and foot wall of the fault zone had differing hydraulic properties for at least part of the history of the fault zone. The mineralogical data suggest that some of these hydraulic properties may have changed over time. There has been mass transport along the fault zone, but this has caused insignificant mobilisation of uranium.

On-going research aims to characterising further the spatial variations in the characteristics of the fault and the temporal variations in its hydraulic properties. The goal is to evaluate the degree to which spatial and temporal variations in properties are significant over scales of space and time that are relevant to PA.

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German Natural Analogue Research Activities

Walter Steininger
Forschungszentrum Karlsruhe GmbH
Projektträger des BMWi und BMBF für Entsorgung
Postfach 3640, D-76021 Karlsruhe, Germany

Abstract

The Research Concept on Underground Disposal of BMWi (Ministry for Economy and Technology) and BMBF (Ministry for Education and Science) is the general basis for generic, non-site specific R&D dealing with the disposal of toxic wastes in deep geological formations.
Although a specific programme addressing natural analogues does not exist in Germany, several topics of research implicitly are dealing with this subject. Several German research institutions are working in this field mostly in co-operation with international partners.
A brief overview of the German R&D-Concept will be given and the NA-Studies will be described in some detail.

1. Introduction

The Research Concept on Underground Disposal /PTE 98/ deals with the disposal of toxic wastes (i.e. radioactive as well as non radioactive) in deep geological formations. According to the Atomic Energy Act, radioactive waste is defined as radioactive material which cannot be reused and, therefore has to be disposed of in an orderly manner. Deep geological disposal is obligatory for all sorts of radioactive waste in Germany. The rationale of the Research Concept is in line with the goals of the government programmes on energy and environmental research. The funding of R&D on underground disposal of toxic waste is a precautionary measure, restricting itself thereby to applied, but not site-specific, basic research. The R&D results are to help protect humans and the environment against hazards that could originate from disposal facilities. The results are at the disposal of authorities, reviewers, and operators of underground repositories. They can be used by private industry and public authorities for planning, reviewing, licensing, and operating purposes.
Although R&D-activities are mainly concentrated on rock salt as host rock formation for a repository, the study of alternative host rock formations such as granite or clay are also an important issue. The goal of these activities is to increase knowledge and to take part in the international dialogue.

The R&D-goals of the Research Concept are as follows:

A Further development of repository concepts with emphasis on their safety
B Improvement of tools to evaluate long-term safety
C Further development of nuclear material safeguards and adaptation to the needs of direct disposal

Natural analogue related issues are addressed only within the item "Improvement of tools to evaluate long-term safety" (marked by italics) which comprises the topics

B1 Scenarios
B2 Behaviour of the host rock formation
B3 Chemical and physical effects in the near field
B4 Behaviour of geotechnical barriers
B5 Behaviour of geological barriers
B6 Development of models and codes for safety analysis
B7 Model validation

Based upon the recommendation of the German Expert Group "Natürliche Analoga" (Ste 96) German NA-projects were started in 1995. Nowadays the conviction prevails that, despite their limitations natural analogues can provide valuable information to performance assessment, and the use of natural analogues is well established within the German radwaste management community.

2. Natural Analogue Activities

Four German research institutions work on NA-Studies: i) GRS- Gesellschaft für Anlagen- und Reaktorsicherheit, FB Endlagersicherheitsforschung, ii) TU Clausthal, Institute for Mineralogy and Mineral Resources, iii) FU Berlin, Institute for Anorganic and Analytical Chemistry, and iv) Forschungszentrum Karlsruhe, Institut für Nukleare Entsorgungstechnik.
Each institution has close scientific co-operation with different national and international partners. Some projects are still running, some are finished more or less lately. A summary of the projects is given below.

2.1 Activities at GRS

GRS presently is involved in two natural analogue related projects. The first one entitled "Scientific Basis for the Proof of long-term Safety of Repositories " addresses general R&D-aspects concerning safety analysis with regard to German requirements and uses among other things the output of NA-studies. The activities within this project aim at providing knowledge to improve and to develop further the instruments, i.e. models, codes, necessary for long-term safety assessment. The outcome of national and international R&D-projects are to be evaluated and utilized to refine and update these tools. Moreover, international developments in fields like scenario development, methodologies, model validation, acquiring actualized data and models are essential tasks. Within this project natural analogue projects are accompanied with regard to questions relevant to performance assessment requirements. In the frame of this

project GRS-activities concerning the co-operation with international partners, particularly for NA from Australia, Japan, Czech Republic, France, are co-ordinated and managed. Membership held in several international committees gives hereby valuable input.

The second project dealing with natural analogues concerns "U-Th-Migration in Tertiary Sediments" and comprises both experimental and theoretical work on specific sites. This project is presently in its second phase. It was initiated against the background that clay materials play an important role in the near field and for the far field of repositories: Bentonite is used as backfill and buffer material, and argillaceous sediments are often found in caprocks of geological formations. Exactly in such sedimentary formations geochemical processes can occur which control radionuclide retention and mobilisation.
The project pilot phase was finished in 1998 (Bre 97, 98, Nos 98). After having performed a comprehensive literature research, the information on U-deposits in Europe and Germany was compiled in a database. It was the basis for the decision to focus the investigations on the Ruprechtov-Site (Czech Republic) and to perform some exploratory investigations of a German site. In this project phase first sampling campaigns and preliminary investigations comprising site characterisation and lab experiments as well as planning the main project were performed. A close co-operation with scientists from NRI (Czech Republic) was started during this project phase (Lac 99, this Conference).
The main project was started in late 1998. Main objectives are to determine in situ sorption parameters of tertiary/quaternary sediments (proof of the barrier function of clay material for selected radionuclides, aspects of long time scales), and to apply geochemical codes to get a better understanding of the processes at the sites. Moreover, of interest is to test the transferability to German requirements and to get input or provide output to other NA-projects (Oklo, ASARR). The outcome of this project is to increase the understanding of geochemical processes and parameters, to modify or, if necessary, develop experimental and theoretical methodologies, to test models and data used in PA and input for use in other projects.
The work is mainly concentrated on investigations of the Ruprechtov-site. By experimental investigations hydraulic and geochemical parameters are to be determined, groundwater and porewater are to be analysed, and sediment samples will investigated and characterised by several analytical methods. Theoretical activities concentrate at evaluating experimental data, geochemical modelling, and a summary of the results to characterise the site concerning the U-Th interaction processes of the sediment-groundwater system. An essential task is to check the relevance of the results with regard to performance assessment (comparison of models and test of transferability).
A joint project with partners from Belgium, Spain, Switzerland, and the UK subjected to study the U-Th-Migration in different argillaceous sediments is in the planning phase and will be proposed to EC for funding.

The project „Investigation of Old Backfill as an Analogue for Convergence and Compaction of Backfilled Drifts during Long Times" was started in 1996 and was planned as a pilot phase. This project was finished in 1998 (Bre 99). Creep closure and compaction of crushed salt backfill have a strong influence on dose (Sto 92). Parameter values for the used constitutive models are still only available from laboratory or in-situ experiments. Therefore, data from old backfill might be useful to get information about the long-term behaviour influenced by several relevant parameters in order to improve or validate the basic models with regard to their ability to predict backfill behaviour over decades.
The objectives of the project were to define the requirements to be fulfilled by potential suitable objects: rock salt, age of backfill (older than 10 y), material state (dry, porosity below 40 %) . Design calculations showed that only backfill at depths between 800 and 1000 m would be suitable for detailed investigations. Four suitable objects in German potash and rock

salt mines were found. During this project phase a few samples were taken for preliminary lab investigations. A first survey showed that humidity plays an important role on the compaction and that compaction was caused by the weight of the backfill material. No creep closure induced compacted backfill was observed. In a future project more detailed investigations are to be performed accompanied by model calculations.

2.2 TU Clausthal, Institute for Mineralogy and Mineral Resources

The project "Genesis, Mobilisation and Migration of Fluid Components in Rock Salt as a Natural Analogue for Mineral Reactions and Mass Transport in Underground Disposal Repositories" was finished at the end of 1998. In was carried out in co-operation with national and international (France, UK, US) research partners. Its overall objectives were to evaluate the isolation potential of an evaporite body, to improve instruments to interpret the genesis of fluid components, to investigate gaseous components in order to get information on transport and solution processes, and to determine if the system was open or closed.

The project comprised three tasks. The first task was to perform isotope analyses of strontium, sulphur, and lithium, the second one to study REE and transition metals in evaporites, the third one to analyse gases in fluid inclusions by Raman Spectroscopy.
Lithium can be detected by the developed method, but a genetic classification of the data is not possible because of missing basic geological data. The observed low values of isotopic sulphur may be explained by a synsedimentary transformation of the sulphide from algae mats of the sea basin. The strontium concentrations observed in the investigated saline solutions can presently not be explained by a static evaporation of sea water.
In the frame of the second task a method to analyse saline solutions and evaporite minerals regarding their REE and transition metal content was developed. The REE-content is too low to be detected by ICP-MS. However, transition metals are measurable in saline solutions as well as in evaporite minerals. Concerning the interpretation of the measured manganese and zinc values, the preliminary conclusion might be drawn that they originate from a mixture of residual solutions of sea-water and formation waters.
The investigations of gases in fluid inclusions was performed by improved and refined experiment set-ups. Even though a grouping of the measured inclusions is possible, a stratigraphic classification is not possible and discrete inclusion gave no hint to their origin within the salt dome. In some groups of inclusions higher hydrocarbons and hydrogen were detected. A preliminary interpretation is that hydrogen might have been generated by radiolytic decomposition of hydrocarbons, esp. methane. It seems that hydrogen was present since the generation of the inclusions. This finding is of some relevance for performance assessment with regard to gas generation and transport (Sie 97, 98, Ell 98, Pro 98).

The project "U-Th-Isotope Distribution as a Natural Analogue for Actinide Migration in Granitic Rock" was started in October 97. The work is carried out in the frame of the Swedish-German cooperation treaty concerning the research activities in the HRL Äspö.
The main objective of the project is to investigate the space and time dependent mobility of U and Th in granitic rocks of the Grimsel and Äspö sites in order to qualify and characterise the geologic barrier with regard to its behaviour against actinide mobility. Because tracer experiments with actinides are difficult to perform it is quite convenient to study the homologues U and Th. Because U-isotopes are incorporated in calcite minerals from natural solutions, studying the decay can provide information concerning the chemical environment of the carbonates coexisting with natural underground solutions. The work aims at selecting and characterising carbonates with regard to the U and Th content, investigating the isotope system in

fresh carbonates (located in fractures, disturbed zones, and on grain boundaries) with regard to the secular equilibrium, interpreting their mobility with regard to the hydraulic system and the time dependence, as well as interpretation and modelling to predict actinide mobility. As far as possible the methods developed are to be transferred to other silicates. The Äspö granite samples which contain mainly calcite were analysed with respect to the U-Th-isotope ratio and showed different activity ratios. This means different ages of calcite-fluid reactions and leads to the preliminary interpretation, that the secular equilibrium was disturbed during the past 60000 to 400000 years. The investigations will continue till 2000.

2.3 Activities at FU Berlin, Institute for Inorganic and Analytical Chemistry

The project "Immobilisation and Retardation of Radionuclides by Hydroxylapatite" was finished in December 1998. The basic idea underlying the project was to find an additive to crushed salt backfill to improve the retardation capability against radionuclides. Choosing hydroxylapatite (HAP) as a candidate material was based, among other things, upon the knowledge, that natural minerals contain U in different oxidation states, and HAP could fulfil the requirements to an additive. The goal was to investigate the properties of HAP with regard to mineralogical, geological and chemical aspects, to provide data for geochemical modelling and finally to evaluate this material. Experiments were conducted to determine the solubility products of U-phosphates in water and brines and in presence of iron (container material), and to study the interaction of theses components concerning the immobilisation capacity of HAP. The experiments were accompanied by geochemical modelling. (Gau 97, Gau 99). The main results are as follows:
At oxidising conditions hydrogen-uranylphosphates, tri-uranylphosphates, saleéite, and autunite were formed, the last one most stable if HAP was present. At reducing conditions the mineral ningyoit was found. Both autunite and ningyoit are found in nature (USA, Japan). Moreover it was observed, that the chemical reactions between U and HAP are not disturbed, the solubility of new formed minerals was not increased, and the solubility of U-minerals in sodium chloride and magnesium chloride brines was lower than in pure water.
It can be concluded that HAP has promising features to act as additive material for backfill.

2.4 Activities at the Institut für Nukleare Entsorgungstechnik (INE), Research Centre Karlsruhe

INE´s R&D objectives focus on the development of experimental and theoretical methods for the proof of long-term safety of radioactive waste repositories in deep geological formations (rock salt and hard rock) based upon geochemical approaches. Natural analogue related work at INE shall provide information for validating data and models and is concentrated at natural analogue studies for the near field of a repository for vitrified HLW in rock salt.

The investigations of basaltic dykes (a natural analogue for the corrosion of glass) in the Werra-Fulda salt deposit (Hesse, Thuringia) are finished.(Ste 97, 99). As a result of volcanic activity the intrusions occurred about 15 Mio. y ago. Detailed sampling and isotope measurements (K-Ar and Sr) were performed. It could be shown that radiogenic argon from surrounding rock salt was transported by hydrothermal solutions and was incorporated into secondary silicates. It was concluded that for millions of years no gas exchange, i.e. no diffusion, occurred with the environment. The central part of the dykes was not influenced by solutions therefore the argon content was not changed. This led to the conclusion that the post-intrusive

alterations are a good analogy to changes of vitrified glass which may occur after brine inflow into a repository. Furthermore, this may be interpreted as an indication for the retardation capability of glass for radiogenic gas- even after local corrosion - and is essential for long-term safety. Sr-Isotope measurements indicate an intake of Sr from salt and post intrusive reactions between the basalt and saline solutions. REE investigations showed a pattern which is typical for light-REE enriched alcali basalts. Moreover it was found that REE fractions come from secondary apatite which is interesting, because it is known from weathering profiles that light-REE enrichment is typical for secondary formed apatites. Furthermore, it can be concluded from the investigations that the system lost no REE during apatite formation. Only a redistribution of REE occurred by corrosion. In summary the isotope measurements and EDS-analyses showed the mobilisation, fraction and subsequent fixation of REE, i.e. the REE precipitated. This is an important result and relevant for safety analysis.

The second project deals with the investigation of corrosion processes of natural basaltic glasses and will be finished in 1999. Icelandic basaltic hyaloclastites coming from several locations (Hengill, Husafell,and Vatnajökull) were sampled. They were generated after eruption of sub-glacial lava and are of ages of several thousand to 3.1 M years.
It was found that beside stable phases, metastable phases are present which were unaltered over geological times. Moreover, large amounts of glassy fragments exist in natural glasses which also are expected in waste form glass, and furthermore, secondary phases have influence on permeability and pathways for fluids. The corrosion of 3.1 My old glassy fragments by water led to the formation of zeolithes. The pore spaces are nearly filled with analcimes and zeolithes, which led to a solid body with reduced porosity. With regard to safety aspects this observation is of importance because this fillings may have a retarding effect on dissolved glass components. Further observations showed, that glass dissolution slows down with the formation of a hydrated seam, and it seems that only clay minerals act as a sink for U, Thorium, a nd REE. Mineral associates found in natural glasses are found both in experiments and by modelling. Even though there is a correspondence between results from laboratory experiments, modelling and results from natural samples, the latter also show results which cannot be found by modelling and lab experiments (i.e. hydrated glass, Fe-rich silicates). Essential for safety analysis are the conclusions that an exact time scale for glass dissolution is of minor interest - because of locally delayed reactions - and that a compact body is formed by totally corroded glass.

3. Summary

Topics addressing natural analogue issues are integrated within the German Research Concept on Underground Disposal.
Since 1995 several projects dealing with natural analogues are carried out in German research institutions mostly in co-operation with international partners. A promising joint international project is dealing with the investigation of the U-Th-migration behaviour in argillaceous materials.
The results produced and the knowledge gained so far by the projects gave a valuable input to safety analyses.

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Present Status of the Swedish Natural Analogue Programme

J A T Smellie
Conterra, Sweden

F Karlsson
SKB, Sweden

1. Introduction

The present Swedish natural analogue programme covers a wide range of interests both internationally and domestically. International collaboration and participation is being maintained at Maqarin (Jordan), Palmottu (Finland), Hyrkkölä (Finland) and Oklo (Gabon), with more limited input within Sweden where focused studies on cement analogues are being addressed. Where possible (e.g. Palmottu and Oklo), field studies are being supported by laboratory and *in situ* experiments to try and achieve more quantitative and meaningful data for performance assessment use.

2. International natural analogue participation

2.1. Maqarin, Jordan

Sweden has a general interest in the overall geological, hydrogeological and hydrogeochemical character of the site, since this forms the basis for site conceptualism and successful modelling of the high pH water/rock interactions. More specifically, small-scale studies have focused on two areas: a) clay stability, and b) microbial activity.

Clay stability

In a cementitious repository environment, the Swedish concept uses bentonite as a packing material between the cement silos (and other cement structures) and the bedrock. It is therefore important to predict the changes in properties of the bentonite (and therefore its efficiency to retard radionuclide transport) when coming into contact with high pH fluids over a reasonably long period of time (several hundreds to a thousand years).

Nature of study: Comparative study of clay-rich samples from locations in contact with high and normal pH groundwaters
Analogue: Bentonite stability in a high pH cementitious environment

Microbial activity

In general little is known about microbial behaviour in high pH waters.

Nature of study: Studies of microbe abundance and tolerance in different high pH groundwater locations. Characterise the microbial populations by employing new DNA techniques.

Analogue: Organic material in low- to intermediate-level wastes can be decomposed by bacteria. This could generate, for example, methane,which needs to be released without compromising the stability of the engineered barrier system. Contrastingly, microbes could be of value, for example by decomposing potential complex-forming organic products in the repository.

2.2. Palmottu, Finland

Sweden has had a major input in characterising the hydrogeology and hydrogeochemistry of the Palmottu site, together with detailed mineralogical studies of fracture zones. Participation in laboratory studies to further understand sorption/precipitation processes and uraninite stability has also been a focal point.

Hydrology and hydrogeochemistry

Nature of study: Conceptualisation of the groundwater flow system and its interaction with the bedrock.

Analogue: Far-field transport of radionuclides in a fractured crystalline bedrock similar to that considered for repository construction in Sweden.

Mineralogy and geochemistry

Nature of study: Detailed *in situ* studies regarding the up-take of radionuclides/trace elements on fracture mineral fillings and the adjacent unaltered host-rock. This data will be integrated with laboratory determinations of radionuclide Kd's using the same rock/fracture materials.

Analogue: Far-field *in situ* sorption/retardation of radionuclides/trace elements.

2.3. Oklo, Gabon

Initially, Swedish interests were focused on conceptualising the far-field groundwater flow systems of the Bangombé site by the successful coupling of hydrogeology and hydrogeochemistry. Currently, there has been a shift in emphasis to near-field (reactor) studies, although there is continued interest in further quantification of the groundwater flow systems, with particular interest in the hydrogeochemistry and the presence and role of colloids and microbes in radionuclide transportation.

Hydrology and hydrogeochemistry

Nature of study: Conceptualisation of the groundwater flow system at Bangombé as a basis for radionuclide (and trace element) mass transport modelling.

Analogue: Far-field transport of radionuclides.

Colloids and microbes

Nature of study: Further characterisation of colloid material and microbe populations from the Bangombé site (oxic and anoxic conditions).

Analogue: Influence of colloids and microbes on radionuclide (and other trace elements) transportation in the near- and far-field environments.

Mineralogy and geochemistry

Nature of Study 1: Emphasis at Bangombé on the interaction between the reactor zones and overlying clay-rich horizons where radionuclide diffusion has occurred, or is occurring, under ambient conditions.

Analogue: Near-field migration/retardation of radionuclides, REEs and other trace elements through clay.

Nature of Study 2: Characterisation of the weathering fronts which are actively penetrating downwards into the sediments overlying the Bangombé reactor zone

Analogue: Propagating redox fronts through clay under ambient conditions and their influence on migration/retardation of radionuclides, REEs and other trace elements.

Detailed mineralogy and geochronology of the natural fission reactor zones

Nature of study: Detailed mineralogy and paragenesis of the Bangombé and some of the Oklo/Okelobondo reactor zones.
Based on SIMS analyses, the ages and processes of ore reactor zone formation are being determined, based on galena, apatite and native Pb; the behaviour of fission products Tc (via ^{99}Ru) and Mo are also being quantified. Spent nuclear fuel and the Oklo reactor zones show close similarities, i.e. both contain metal inclusions of Ru, Rh, Pd, Mo and Tc. As Mo is more easily oxidised and removed from the metal phase, it should be possible to use Mo to place bounds on the behaviour of Tc, one of the critical actinides in safety performance assessment.

Analogue: Spent nuclear fuel stability.

2.4. Copper analogue at Hyrkkölä, Finland

Naturally-occurring native copper, in association with copper sulphides and oxides, occurs in open, water-conducting fracture zones in bedrock similar to that planned for a Swedish repository.

Swedish participation in the project has included a specific study to determine whether the identified Cu-bearing phases (including native copper), are presently in contact with the groundwater system. Because the present groundwater system is oxidising, this study represents a worst-case scenario since reducing conditions are expected to prevail at repository depths.

Nature of study: Application of U-decay series measurements to fracture fillings, including Cu-bearing phases, to establish active contact with present-day groundwaters.

Analogue: Copper canister stability under repository conditions

3. Miscellaneous analogue studies in Sweden

3.1. Cement analogues

Compared to bedrock, cement is an unstable material that will change its properties with time. The structural changes and the speed of reaction are dependent on the interaction with water. These studies address the concepts behind cement evolution and degradation based on theory and using analogue studies of several old cement constructions dating from the turn of the century to the 1970s. The main objective is to examine well-documented cement-based structures to establish, by analogy, the long-term reliability of repository construction materials such as portland cement, mortars and concrete.

Case histories

Several varieties of concrete-bearing structures in long-term contact with water have been examined; some dry environments for comparison have also been included. These varieties include:

- water tank, built in 1906 and consisting of steel with an inner lining of mortar 10-20 mm thick, has been continuously filled with drinking water of stable composition for 90 years. The tank was demolished in 1994, the steel showing no evidence of rusting.
- hydroelectric power dams constructed in 1930, and in 1941/45.
- inspection tunnel and discharge chamber to a hydroelectric power station.
- old water mill dam constructed in 1900.
- concrete floor of a school constructed in 1896 (dry environment).
- a series of water filtration concrete basins constructed at different times from 1913 to 1974, with an interval of 10-15 years between each construction. Samples have been taken above and below the filter sand level for analysis.

The Natural Analogue Study at the Steenkampskraal Monazite Mine, South Africa

NV Jarvis[1], D Read[2], T Williams[3], M Knoper[4] and MAG Andreoli[1,5].

[1]Atomic Energy Corporation South Africa Ltd, PO Box 582, Pretoria 0001, South Africa.
[2]Enterpris, University of Reading, Whiteknights, Reading RG6 6BX, UK.
[3]Natural History Museum, Cromwell Rd, London SW7 5BD, UK.
[4]Rand Afrikaans University, PO Box 524, Auckland Park 2006, South Africa.
[5]Schonland Research Centre, University of the Witwatersrand, PO Wits 2050, South Africa.

Introduction

The Steenkampskraal monazite mine is being studied as a natural analogue for the Vaalputs National Nuclear Waste Facility which lies about 100km to the north in a similar geology. Steenkampskraal is among the richest monazite ores in the world comprising up to 45% REE, 8.8% Th and 600ppm U. Mining has not occurred since the early sixties.

Vaalputs which currently serves as a low and intermediate level waste disposal facility, is being assessed as a potential high level waste disposal site. Steenkampskraal provides an excellent analogue site for Vaalputs and has been studied as such by the Atomic Energy Corporation of South Africa [1]. Preliminary studies on the actinide and REE concentrations in groundwater [2,3] gave very high values for these elements. Colloid mediated mobilisation of these elements was therefore suspected. The implications of this aspect of the study attracted collaboration and some funding from the UK.

Over the last few years the following studies have been performed:

- Characterisation of source term - monazite degradation [4].
- Preliminary study of colloids in groundwaters [5].

Geological Description of Steenkampskraal

Steenkampskraal, located in southwestern Namaqualand, South Africa, is well known for a distinctive monazite ore vein situated within crystalline Mesoproterozoic granitic gneisses. Good exposures of the monazite vein on the surface and in underground mine tunnels has led to considerable interest in the monazite vein as a natural analogue of a high-level radioactive waste repository, thereby presenting an unique opportunity to study monazite degradation and chemical dispersal of actinides by surface and groundwater movement. Geological mapping of Steenkampskraal at a scale of 1:2500 indicates that the granitic gneisses hosting the monazite vein comprise two fundamental rock types: megacrystic gneiss and leucogneiss. Mineralogically the megacrystic gneiss is characterized by microperthite + quartz + plagioclase + biotite +

garnet; microperthite megacrysts (up to 1 cm) in the megacrystic gneiss are surrounded by a matrix of feldspar + quartz + biotite. Garnet porphyroblasts (0.4-1.5 cm) are commonly concentrated in quartz-feldspar segregations that occur as outcrop scale sheets, veins, and lenses within the megacrystic gneiss. The leucogneiss contains microperthite + quartz + plagioclase + garnet but with little or no biotite. Unconformably overlying the granitic gneisses are Neoproterozoic-Cambrian Nama quartzite and shale.

The monazite vein is exposed for about 200 m on the surface as an E-W striking, 0.2-4 m wide band associated with an intrusive suite comprising dykes of granodiorite, granite, and quartz syenite, and also minor leucotonalite, leuconorite, leucodiorite, quartz-bearing anorthosite, charnockite, enderbite, and monzonite. Underground exposures and exploratory boreholes indicate that the monazite vein dips 40-60° S with a known downdip extension of approximately 350 m below the surface. The granitic gneisses hosting the monazite vein represent a fractured-rock aquifer, and the monazite vein is located within a narrow E-W zone of closely spaced subvertical fractures. In contrast to the subvertical fracture cleavage, the Mesoproterozoic subhorizontal gneissic foliation is a pervasive, early structural fabric with low permeability. Significant groundwater flow along the gneissic foliation is therefore considered unlikely.

A "continuum" approach to characterise the hydrogeologic characteristics of the granitic gneisses and monazite vein suggests that the Steenkampskraal fractured-rock aquifer is likely anisotropic and heterogeneous, and that Darcy's law will not accurately describe hydraulic conductivity as in porous media. Therefore, groundwater flow is likely to be confined to the highly permeable subvertical fracture cleavage as supported by field observations of staining along fractures on surface and underground exposures of the granitic gneisses. Along this fracture system that is strongly developed in the immediate vicinity of the monazite vein, fast and turbulent groundwater flow typical of fractured-rock media is expected.

Monazite-Bearing Rocks – Petrography

Type 1: phosphatic ore. The typical ore of the mine, with up to 80% of phosphate minerals (monazite>apatite); the remainder 20% consists of sufides>oxides>zircon. Monazite grains are generally fresh and stable but incipient alteration may be locally present. Alteration is strongest in samples that are sheared or collected in the open pit. The monazite grains frequently present brownish rims caused by iron oxide staining, whereas altered, cloudy patches are less common. Hydrothermal (?) allanite may be occasionally present along fractures.

Type 2: oxide-rich ore. Magnetite-hercynite-ilmenite ironstone with disseminated grains of monazite and zircon. This type of ore occurs as rare bands within the phosphatic rock. Monazite grains are generally stable.

Type 3: quartzo-feldspathic ore. A monazite-rich tonalite. Chlorite, zoisite and allanite extensively replace plagioclase, biotite and monazite. The monazite grains are

frequently found in various stages of alteration that are most developed at the contact between the ore and its leucotonalite host.

Type 4: siliceous ore. Glassy, smoky quartz rock with disseminated small crystals of monazite, apatite, sulphides and zircon. Monazite tends to be stable.

Monazite Alteration: Geochemistry and Mineralogy

The following alterations are noted on inspection of photomicrographs and elemental maps [6].

Cryptic alteration: No visible alteration: monazite grains remain optically pristine in thin section. Electron-microprobe analyses reveal large variations in U, Th content, and heavy REE depletion.

Partial alteration: Monazite grains appear cloudy and in all cases very depleted in Th and U, but less depleted in Gd and heavier REE.

Complete alteration: Micro-crystalline phases, often inter-grown with each other, consisting of Th-silicates-oxides, and Y/Th-phosphates, rich in the heavy REE. These include an almost pure Y-phosphate (xenotime or churchite), with low Th and U contents, but an extreme HREE enrichment.

Implications for Radioactive Waste Disposal

The following is a list of implications for waste disposal arising from this study. Th is used as an analogue for Pu(IV) and theREE for Am(III).

- Synthetic phosphate matrices have been proposed for waste immobilisation due to refractory nature of monazite and successful laboratory leaching experiments [7].
- Results from this study indicate that monazite can be altered and U, Th and REE can be mobilised from the matrix. This should be taken into account for phosphate waste forms.
- REE can be mobilised and fractionated even at temperatures around 200-350°C [8,9].
- Th, though regarded as less mobile, is released on alteration of monazite, tending to concentrate in secondary micro-crystalline phases. This may have implications for Pu(IV) as evidence exists for rapid Th-silicate migration in colloidal form [10].
- U appears to be readily removed from Steenkampskraal monazite. Although re-concentrated in some alteration products, notably Y-Th phosphates, it is likely that substantial U has been lost from the system as is evidenced in the high levels of U in the groundwaters [2,3].

Groundwater chemistry

During June 1997, the Atomic Energy Corporation of South Africa led a joint field trip to Steenkampskraal to sample existing boreholes. The sampling and analyses were performed by scientists from AEA Technology. Five boreholes were found to have enough water to allow purging followed by sampling to collect colloid concentrates. The procedure produced an ultrafiltrate, a colloid concentrate and unfiltered water. pH, temperature and conductivity were measured *in situ*. Unfortunately, little is known about local hydrology at the mine site making it impossible to say with certainty that the boreholes sampled are connected with the orebody. Consequently interpretation of the results [5] obtained is problematic at this stage, as the waters do not reflect what is expected from the study on monazite degradation. *One important result was that neither actinides nor REE were significantly associated with colloids*. A more definitive study whereby boreholes are sunk into fractures connected to the ore is planned.

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Use of Natural Analogues in the U.S. High-Level Nuclear Waste Program

Ardyth M. Simmons, Lawrence Berkeley National Laboratory; Paul R. Dixon, Los Alamos National Laboratory; and Robert A. Levich, U.S. Department of Energy

Introduction

Few of the analogue sites studied previously in the international arena have been directly applicable to Yucca Mountain, due to its unique setting in unsaturated, fractured, welded ash flow tuff. Yucca Mountain is located in semi-arid, block-faulted terrain about 100 km northwest of Las Vegas, Nevada. In this area, precipitation and infiltration are low (an average of 170 mm/yr precipitation and 4.9 mm/yr infiltration; U.S. DOE, 1998) and ground waters are oxidizing. Furthermore, potential repository design thermal loads may sustain rock temperatures of >100°C for hundreds of years, although lower thermal loading options are being considered. Therefore, the U.S. has begun a program to investigate analogue sites where processes similar to those expected to take place under these specific repository conditions have occurred in the past or are now taking place.

The U.S. Department of Energy has identified four repository system attributes upon which it will build a safety case for the Yucca Mountain license application: 1) limited water contacting waste packages; 2) long waste package lifetimes; 3) slow rate of radionuclide release; and 4) concentration reduction of radionuclides during transport. Field and laboratory experiments are too limited in duration and scope to provide the needed level of confidence that these attributes will be met for 10,000 years or more.

Natural analogues will play a role in the license application for Yucca Mountain in several ways. Analogues will be used to understand the bounds of processes over long time periods and to test and "validate" process models. Data from radionuclide transport analogues may be used directly to bound distribution coefficients of the radionuclide between mineral and aqueous phases (i.e. K_d), plume dispersion, and other total system performance assessment parameters. Analogues will also serve an important function in illustrating technical concepts related to waste isolation to the public.

Components of the 1999-2000 natural analogue program include the following: 1) preparation of a Synthesis Report on Natural Analogues that summarizes past work in the international community and at various U.S. and other sites, and recommends use of applicable information in performance assessment and design; 2) a focused field and modeling study at Peña Blanca, Mexico as an analogue to radionuclide transport in unsaturated ash flow tuffs; and 3) testing Yucca Mountain flow and transport models using data from anthropogenic analogue sites in the U.S. and Russia to gain a better understanding of plume dispersion, colloidal transport of Pu, and fracture/matrix interactions.

Analogues to Radionuclide Transport

At the Nopal I uranium deposit at Peña Blanca, Mexico, transport of uranium has been almost entirely along major fractures (on the order of ½ cm aperture) with minor transport along microfractures, and almost no matrix diffusion (Murphy, 1992). The matrix consists primarily of quartz and feldspar, which has largely altered to kaolinite. The presence and abundance of uraninite, uranophane, and uranium-silicate minerals, as well as its young age and absence of lead, make the Nopal I deposit an attractive analogue to spent fuel alteration.

Anthropogenic sites with contaminant plumes provide an opportunity to study plume migration over a period of decades as well as radionuclide transport and retardation mechanisms. Although the anthropogenic sites have a much shorter history than natural analogues, their initial conditions are better known and some have been closely monitored. Data from plumes at Hanford, Washington are used to learn about dispersion in saturated alluvium, the media through which radionuclides would reach the environment at Yucca Mountain. Data from other plumes at the Idaho National Engineering and Environmental Laboratory (INEEL) are applied to build understanding of retardation of ^{237}Np, ^{236}U, ^{129}I, and ^{99}Tc. Beasley et al. (1998) demonstrated that ^{237}Np, ^{236}U, and ^{129}I were retarded, whereas ^{99}Tc was not retarded in the Snake River Plain aquifer with distance from the Idaho Chemical Processing Plant at

INEEL. Data from contaminant plumes in Russia and the Ukraine may be used to augment understanding of radionuclide retardation and plume dispersion.

Plutonium was measured in groundwater at the Nevada Test Site (NTS) ER-20-5 wells at a maximum level of 0.63 pCi/L (Kersting et al., 1999). The ratio of $^{240}Pu/^{239}Pu$ indicates that the Pu originated at the nuclear test BENHAM, a distance of 1.3 km from the wells. BENHAM was detonated in 1968 at a depth of 1,402 m below the water table. Therefore, the minimum distance for Pu migration at the NTS has been 1.3 km in 28 years. The Pu detected was associated with colloidal material consisting mainly of clays, zeolites, and silica (Kersting et al., 1999). It is not likely that the Pu was transported by prompt injection or that its soluble fraction migrated along fast flow paths. Colloidal transport is a possible mechanism for Pu migration, since colloidal transport of radionuclides was observed at the CHESHIRE site. However, stability arguments limit the amount of colloids in suspension that are able to migrate. Because colloidal transport is a viable mechanism for Pu migration, it should be incorporated into modeling of transport in the saturated zone and into performance assessment calculations for radionuclide releases at Yucca Mountain.

Geothermal Analogues

Many of the same processes that are expected to take place under repository conditions, such as evaporation, boiling, condensation, single- and two-phase fluid flow, mineral alteration, and permeability changes, to name a few, are processes that occur in geothermal fields. Data and analyses that have been observed, measured, and simulated for more than two decades in the geothermal industry yield important information about expected thermohydrologic conditions at Yucca Mountain and about perturbations generated by thermally induced geochemical and mechanical changes in the rock mass. At the Wairakai, New Zealand geothermal field, rock matrix and ground water chemistries are similar to those at Yucca Mountain. Wairakai data have been used to test geochemical modeling codes and databases in order to match observed chemical reactions and rates in geothermal fields with mineral assemblages and rates of reaction predicted by the codes.

Geothermal plants have used various cement formulations to construct silencers, cooling towers, and drain channels in production fields. These materials have been in contact with hot water and steam ranging in chemistry. Furthermore, microbially-induced degradation has accelerated the breakdown of concrete at Wairakai. Although cement compositions used at Yucca Mountain for engineered barrier support may differ from those used at geothermal plants, the rate of degradation under aggressively harsh conditions provides conservative estimates of concrete stability at the potential repository.

Applications

Natural analogues will play a role in the license application for Yucca Mountain in several ways. Analogues will serve an important function in illustrating technical concepts related to waste isolation to the public. Analogues will also be used to understand the bounds of processes over long time periods and to test process models. Data from radionuclide transport analogues may be used directly to bound K_ds, plume dispersion, and other total system performance assessment parameters. Furthermore, natural analogue data can sometimes be used directly in total performance assessment models, as shown by Murphy and Codell (in press, 1999). From calculation of the maximum average oxidation rate of U at Peña Blanca, they determined a maximum possible release rate of U, which they then scaled to 63,000 metric tons of U (the amount of spent fuel to be disposed in a potential Yucca Mountain repository). The authors constructed complementary cumulative distribution functions (CCDFs) for peak doses to a receptor population located 20 km from a proposed repository site over periods of 10,000 and 50,000 years after repository closure. The CCDFs demonstrated an improved performance (lower total dosages) by using both spent fuel dissolution data and natural analogue data from Peña Blanca, as compared to using base case PA data.

Summary

In the future, the U.S. will continue natural analogue studies into the performance confirmation period as models are refined and updated. Natural analogue information will be incorporated into process model reports that directly feed performance assessment. The Natural Analogue Synthesis Report, to be completed in the fall of 1999, will be used to identify gaps in understanding or areas of high uncertainty where natural analogues may contribute to increased understanding and confidence. By using the Synthesis Report as a

guide for future direction, DOE will evaluate whether to continue current natural analogue investigations or whether to explore new areas. One area that DOE would like to investigate is evidence of retention or migration of ^{99}Tc, ^{237}Np, ^{239}Pu, and other radionuclides along fractures in Oklo cores. The complexity of coupled thermal-hydrologic-mechanical-chemical processes and limitations to studying them through laboratory and field experiments also suggests that coupled process natural analogues may provide useful insights into these processes and may receive increased attention in coming years.

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The Boom Clay Formation as a Natural Analogue for the Geological Disposal of Radioactive Waste.

Delleuze D., De Craen M., Volckaert G., Sneyers A., Put M.
Belgian Nuclear Research Centre (SCK•CEN), Waste and Disposal, Mol (Belgium)

ABSTRACT

The Boom Clay is studied as potential host rock for the deep disposal of radioactive waste. To fill the lack between information on radionuclide behaviour from the short term laboratory or *in situ* experiments and the long term need for performance assessment, SCK•CEN studies the Boom Clay (Rupelian) as natural analogue since 1996. The natural analogue study on Boom Clay focuses on the behaviour of REE, U, Th and their natural isotopes in the clay considered as chemical analogues to critical radionuclides.

XRD mineralogical analyses and XRF, ICP-MS, INAA chemical analyses were performed on solid samples from the Mol-1 drilling core in the Boom Clay. The uranium content varies from 3 to 7 ppm in the solid fraction. The thorium content varies from 8 to 15 ppm. Multivariate statistical analyses allow to divide the Boom Clay in three groups according to their influence on the chemical analogue behaviour: (1) quartz, muscovite and feldspars have a trace element dilution effect; (2) clay minerals, such as chlorite, illite, smectite and intersratified illite-smectite, sorb thorium, caesium and LREE's; (3) carbonates, pyrite and organic matter concentrate HREE's and redox sensitive elements such as U, Cu and Ni.

Radiochemical analyses (α- and γ-spectrometry methods) were performed on the same samples. Most of the daughter/parent activity ratios measured in bulk Boom Clay samples are equal to unity within the 2σ standard deviation uncertainties. One important exception is observed in the Double Band which is a silty layer in the Boom Clay, and therefore, expected to be a potential zone of higher permeability and pore water mobility. In this layer, the $^{230}Th/^{234}U$ and $^{226}Ra/^{230}Th$ activity ratios are significantly different from unity, indicating that radionuclide mobility/immobility has been occurred. Furthermore, radionuclide mobility in the surrounding aquifers is suggested by the daughter/parent activity ratios which are different from unity within the 2σ standard deviation uncertainties.

Apart of the Double Band, the current distribution of the chemical analogues (U, Th and REE) is completely explained by their behaviour during deposition and early diagenetic processes. No recent geochemical process seems to have influenced their distribution.

Future work concerns the improvement of the squeezing technique to extract pore water and the study of uranium and thorium distribution in various fractions obtained by mineralogical separations and chemical sequential leaching.

INTRODUCTION

The Belgian Nuclear Research Centre (SCK•CEN) studies the Boom Clay as potential host rock for the geological deep disposal of radioactive waste. To fill the gap between information on the radionuclide behaviour obtained from the short term laboratory or *in situ* experiments and the long term need for performance assessment, chemical analogues behaviour is studied in the Boom Clay. This natural analogue study has started in 1996.

In this study, natural occurring REE, U, Th and their isotopes are considered as chemical analogues to critical radionuclides. Their behaviour in the clay is studied within a geological time scale. The main advantage of this study is the direct link between the natural analogue site and the potential geological repository that guarantees the representativity of the data from this natural analogue study. The main disadvantage is the low concentration of chemical analogues in the Boom Clay (3 to 7 ppm U and 8 to 15 ppm Th).

APPROACH

Specific objectives of the natural analogue study are (fig. 1):

- to study the concentration and distribution of natural rare earth elements, uranium, thorium and their isotopes in the Boom Clay;
- to study the geochemical control of the trace element distribution in both solid fraction and pore water;
- to study the mobility of uranium and thorium isotopes;
- to model the processes involved in U-Th mobilisation.

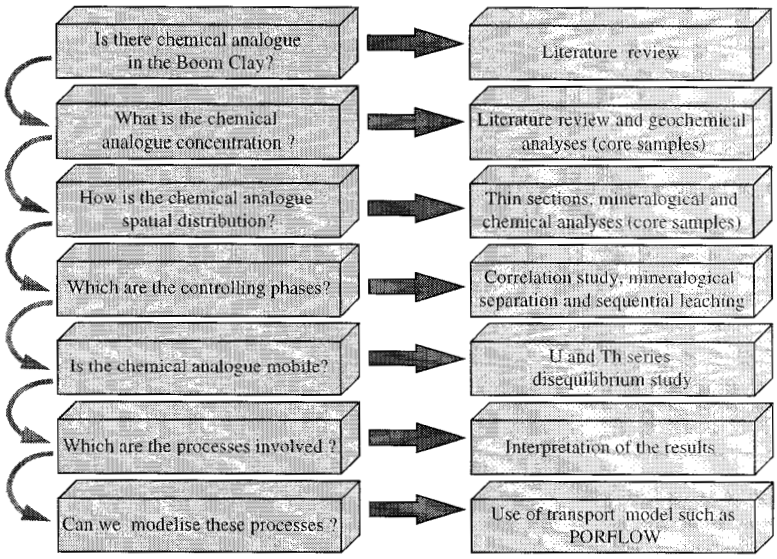

***Fig.1* : Different steps of the study**

In general, the Boom Clay (Rupelian, 30-35 My) can be considered as a homogeneous clay deposit. However, variations in grain size, organic matter and carbonate content, giving the Boom Clay a typical layered appearance, point to a heterogeneous composition on a smaller scale (Vandenberghe, 1978, Vandenberghe & Van Echelpoel, 1987).

For this study, samples were selected from the Mol-1 borehole, which was drilled in April 1997 at the SCK•CEN domain (Mol, Belgium, Fig. 2). The first set of samples was taken to get an idea of the 'average' geochemical composition of the Boom Clay. For the selection of the second set of samples, a particular interval was sampled more in detail because of its higher uranium concentration and the presence of the 'Double Band'.

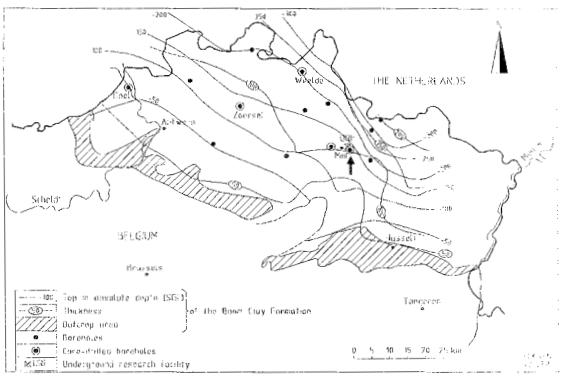

***Fig. 2*: Outcrop area of the Boom Clay and localisation of the Mol-1 borehole.**

Chemical (XRF, ICP-MS and INAA), mineralogical (XRD) and radiochemical (I- and K-spectrometry methods) analyses are performed on each sample. The pore water is currently extracted from each sample by the squeezing technique and will be analysed by ICP-MS. For the radiochemical study, naturally occurring isotopes of U (^{238}U, ^{234}U), Th (^{232}Th, ^{230}Th, ^{228}Th) and Ra (^{228}Ra, ^{226}Ra) are measured.

CURRENT STATUS: RESULTS AND DISCUSSION

In general, variations in major and trace element concentration in the Boom Clay are small (Fig. 3) suggesting that the mineralogical composition of the Boom Clay is more or less constant. Only at the bottom and the top of the clay deposit, a higher SiO_2 concentration and lower Al_2O_3 and LOI concentrations has been recognised. These geochemical variations relate to variations in the mineralogical composition of the deposit: towards the bottom and the top, the deposit is siltier, contains more quartz and less clay minerals and organic matter. These variations are also reflected in the trace element distribution.
Apart from the bottom and top of the deposit, the variations in REE are small, except for Eu and Ce for which significant variations can been recognised. These variations are often associated with the variation in U concentration, and relate to changing Eh-pH conditions during deposition as indicated by the high concentration in redox sensitive elements such as organic matter, Cu, and Ni.

From the geochemical results, multivariate statistical analyses (correlation and principal component analyses) allow to define in the Boom Clay three mineralogical groups according to their influence on the chemical analogue behaviour:

- quartz, muscovite and feldspars, which have a trace element dilution effect;
- clay minerals, such as chlorite, illite, smectite and intersratified illite-smectite, which sorb Th, Cs and LREE's;
- carbonates, pyrite and organic matter, which concentrate HREE's and redox sensitive elements such as U, Cu and Ni.

The daughter/parent activity ratios are generally equal to unity within the 2σ standard deviation uncertainties, indicating that the Boom Clay has remained relatively stable, at least within the last 1 M year. Only at the bottom and the top, daughter/parent activity ratios suggest that groundwater in the aquifers over- and underlying the Boom Clay have redistributed or removed some of the original uranium (De Craen *et al.*, 1999).

At the base of the Putte Member, a zone with higher uranium content (up to 13 ppm) has been observed (Fig. 4). The U anomaly seems to be primary in origin and relates to different Eh-pH conditions during deposition of the clay. The higher U concentration is not the result of recent U precipitation as indicated by the equilibrium of daughter/parent activity ratios.
Just above, the 'Double Band' is present which consists of two silty layers and which is expected to be a potential zone of higher pore water mobility. In the Double Band, radiochemical analyses have shown that the ^{230}Th/^{234}U and ^{226}Ra/^{230}Th activity ratios are significantly different from unity, indicating that radionuclide mobility/immobility has been occurred within this layer (De Craen *et al.*, 1998).

PRELIMINARY CONCLUSIONS AND IMPLICATIONS FOR PERFORMANCE ASSESSMENT

Apart from the Double Band, the geochemical distribution of the chemical analogues (U, Th and REE) in the Boom Clay is completely explained by their behaviour during deposition and early diagenetic processes. No more recent geochemical process seems to have influenced their distribution. Their distribution is completely described by the variation of three geochemical groups: the quartz group, the clay group, and the last group composed of carbonates, phosphates and organic matter. These observations point to the high geochemical

stability of chemical analogues in the Boom Clay for low concentrations, favourable to its selection for the long term geological of radioactive waste.

PERSPECTIVES

Future work concerns both the improvement of the squeezing technique and the interpretation of pore water compositional and radiochemical data. The study of the interstitial pore water will allow to give upper limit to Kd values, used in performance assessment calculations, and to test models used in performance assessment studies such as PHREEQE (Parkhust et al. 1980) for the geochemistry and PORFLOW for transport simulation.

ACKNOWLEDGEMENT

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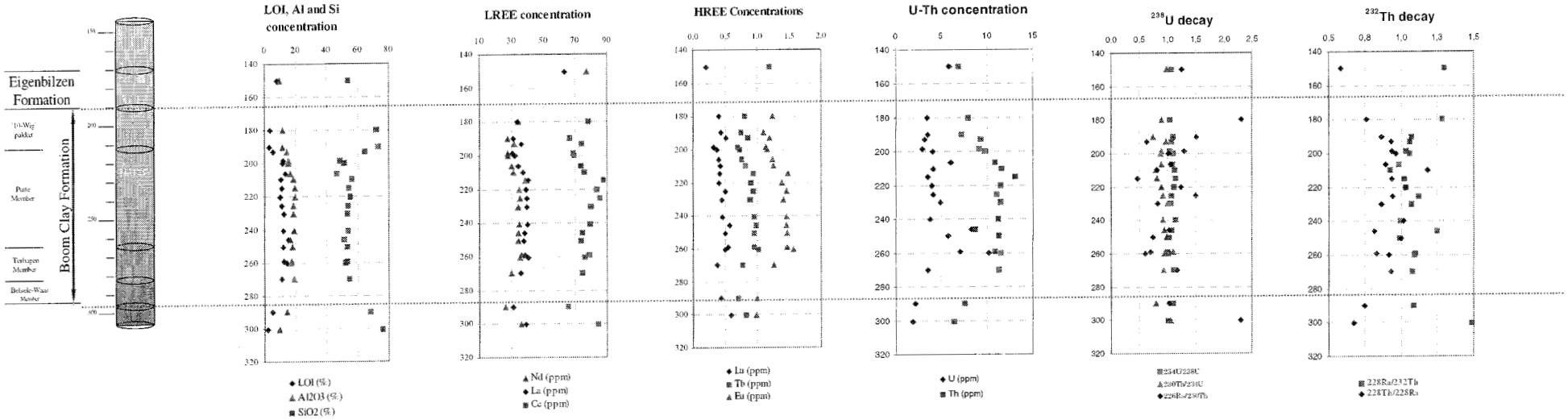

***Fig. 3**: Geochemistry profiles of the Mol-1 drilling core in the Boom Clay*

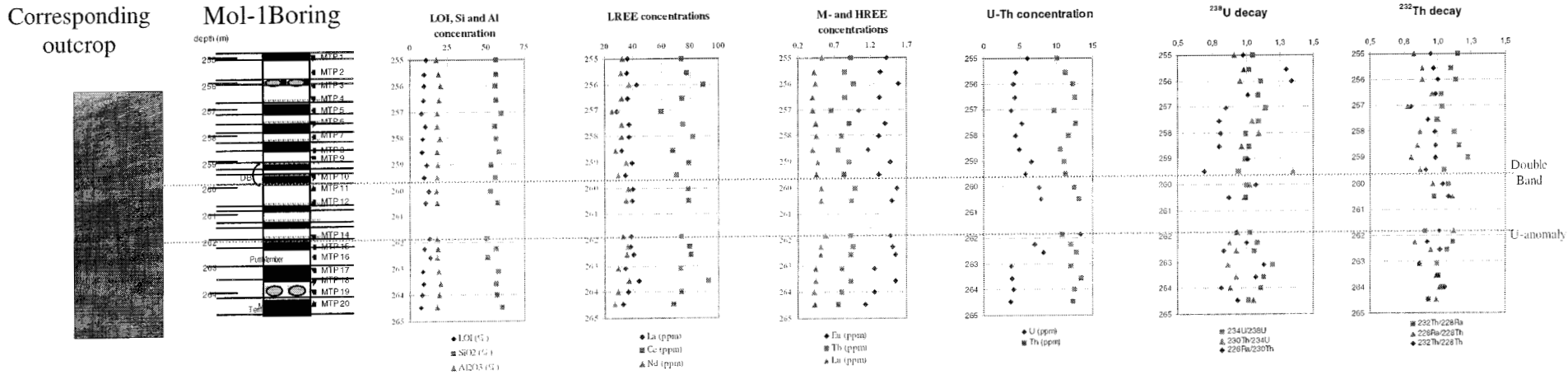

***Fig. 4**: Geochemistry profiles of the Mol-1 drilling core in the Boom Clay: specific zone.*

Solid Radioactive Waste Disposal in England and Wales: The use and application of natural and anthropogenic analogue studies

S.L.Duerden &
R.A. Yearsley, Environment Agency of England and Wales, Steel House, Tothill Street, London, SW1H 9NF

J. L. Knight
United Kingdom NIREX Limited, Curie Avenue, Harwell, Oxon.OX11 0RH

P. Humphreys,
British Nuclear Fuels Limited, Rutherford House, Risley, Warrington, Cheshire WA3 6AS

1. INTRODUCTION

1.1 Regulation

In the United Kingdom, disposal of solid radioactive waste requires an authorisation under the Radioactive Substances Act 1993 (RSA93). The Environment Agency is responsible for granting such authorisations in England and Wales. In Scotland and Northern Ireland responsibility rests with the Scottish Environment Protection Agency (SEPA) and the Department of the Environment for Northern Ireland, respectively. These agencies have jointly issued a document "Disposal Facilities on Land for Low and Intermediate Level Radioactive Waste Disposal: Guidance on Requirements for Authorisation" (the GRA [1]). The guidance in "the GRA" focuses on issues of regulation under RSA 93 in respect of the disposal of low and intermediate-level radioactive waste to specialised facilities on land, taking into account government policy as expressed in the White Paper of July 1995 [2].

Any application for authorisation of disposal of radioactive waste to specialised facilities on land will be considered by the Environment Agency and take into account the guidance contained in "the GRA". For new developments, the limits and conditions of authorisations will be based on the principles and requirements set out in "the GRA". The GRA states that the Agency will also use "the GRA" in reviewing the authorisations for future disposals to existing specialised land disposal facilities, applying the general principles it contains.

1.2 Classification of radioactive waste

In the United Kingdom solid radioactive waste is broadly categorised as:

1.2.1 **Very Low Level Wastes (VLLW).** Radioactive waste that can be safely disposed of with normal refuse, under the terms of authorisations under the Radioactive Substances Act 1993. VLLW includes typically arisings from medical and research activities on non-nuclear premises involving small quantities of specific radioisotopes.

1.2.2 **Low Level Wastes (LLW).** Wastes containing radioactive materials not exceeding 4GBq/t alpha emitting radionuclides or 12 GBq/t beta/gamma emitting radionuclides, but more radioactive than VLLW. Low level waste arises principally from operational activities and decommissioning operations at larger nuclear sites. Such waste consists largely of lightly contaminated protective clothing, redundant equipment and scrap metal arising from operations in radioactive facilities.

1.2.3 **Intermediate Level Waste (ILW).** Waste with radioactivity levels exceeding the upper limits of LLW but of a lower activity and heat output than high level waste. ILW can contain long-lived radionuclides such as plutonium. ILW is currently stored on nuclear sites as there is no suitable disposal route available for such wastes.

1.2.4 **High Level Waste (HLW).** Waste in which the temperature may rise significantly as a result of radioactive decay (also known as Heat Generating Waste). HLW is the concentrated waste from the primary stages of plants designed to reprocess irradiated nuclear fuel.

1.3 The current position on solid radioactive waste disposal in England & Wales.

The UK government is currently reviewing its policy for management of radioactive waste. A review is being undertaken by a House of Lords Select Committee on Science & Technology. This commenced in January 1998 and is due to report late March 1999.

Intermediate and high-level radioactive wastes are currently stored on nuclear sites awaiting decisions on final disposal strategy. Most of the HLW is stored in vitrified form at BNFLs Sellafield site, and work is in progress to define a research strategy which might lead to disposal [3].

The Drigg near-surface disposal facility, operated by British Nuclear Fuels, is authorised by the Environment Agency, under RSA93, to accept solid LLW from nuclear sites and non-nuclear premises for disposal. The Certificate of Authorisation is subject to periodic review by the Environment Agency. Such a review is proposed to be undertaken in 1999 and will include a requirement to produce a post-closure safety case for the Drigg site.

VLLW has a very low radioactivity content and disposal can be authorised to landfill sites or to certain incinerators.

1.4 Use of natural and anthropogenic analogues.

The value of natural or anthropogenic analogues in providing qualitative and quantitative information to help build confidence in the understanding and modelling of processes relevant to performance of radioactive waste disposal facilities is becoming increasingly recognised. Indeed, this has been an area of interest in the House of Lords enquiry into the management of nuclear waste, relevant extracts are provided in Appendix 1. Natural and anthropogenic analogues are used to provide a means of identifying and understanding possible features, events or processes that may be significant with respect to safety of a disposal facility and to build confidence in the models, codes and parameters used to assess disposal facility performance. Natural and anthropogenic analogues may also serve as useful demonstrations of features, events or processes occurring in situations, which are more readily understood or recognised by non-technical audiences.

The Environment Agency has been involved in a number of natural analogue studies, through collaboration with the European Commission and other international contacts. Some of this work is ongoing (e.g. the "CARESS", "PROGRESS" and "Fault Zone Heterogeneity" projects). The Environment Agency participated in Phase III of the Maqarin study, which is due to report soon, and has recently completed a study of the role of colloids in actinide migration at the Steenkampskraal site in South Africa, in collaboration with the Atomic Energy Corporation of South Africa [4]. The Environment Agency intends to keep under review the potential for the use and application of natural and anthropogenic analogue studies in developing any future research programme, pending the outcome of the current government review and any future radioactive waste management strategy.

In addition, UK NIREX Ltd and British Nuclear Fuels Ltd maintain their own programmes on natural and anthropogenic analogue studies. These are summarised in the following sections.

2. NIREX'S VIEW OF THE ROLE OF NATURAL ANALOGUES.

Natural analogue studies in the radioactive waste community have focused on materials and processes likely to be found within the repository near-field. The definition proposed by Come & Chapman [5] would limit their use to such situations. However, natural analogues defined in this way represent only a small subset of all naturally occurring materials and processes that may influence the performance assessment of a repository and for which naturally occurring analogues exist [6]. In the geosciences, reasoning by analogy is ubiquitous and enshrined in the Principle of Uniformitarianism. Well characterised situations are used as blueprints for understanding and predicting the development of similar situations in space and time and appear in widely used concepts such as, 'facies', 'type', 'model', 'precedence' in sedimentology, ore petrogenesis, geophysics and rock mechanics respectively. NIREX has recognised that naturally occurring analogue data of this type, as well as relevant anthropogenic analogues (industrial and archaeological) should not be ignored. They provide a means of identifying the range of possible features, events, or processes (FEPs) that may impact on a repository in the future [7, 8]. For this reason the NIREX use of analogues may appear more wide-ranging and perhaps less explicit than has been the case historically in other programmes.

2.1 Geospshere Transport and Retardation

The flux and concentrations of naturally occurring uranium series elements in appropriate geological conditions and climate regimes may provide a benchmark against which to compare expected repository-derived concentrations and fluxes. NIREX is currently co-funding a project along with Mitsubishi Materials, SKI, SSI, and GRS to collate relevant natural information.

NIREX has sought evidence of diffusive transport of natural uranium series radioelements into the rock matrix adjacent to hydraulically active fractures. Initially this was based around the uranium orebody at

El Berrocal [9] but more recently attention was switched to the Sellafield area. The combination of very low natural uranium concentrations in the Sellafield rocks, the fact that 80-93% of the uranium is associated with 'residual' mineral phases, unlikely to be involved in water-rock interactions, and the natural heterogeneity in uranium distributions led to results that were difficult to interpret unambiguously. The work did however indicate the importance of Mn-oxyhydroxide phases as sinks for natural U and Ra and a laboratory programme has been initiated to investigate this further.

A number of natural analogue studies have included assessments of the total numbers of colloids and the partitioning of U, Th between colloids, solution and suspended particles. These have shown that while the population of colloids is normally low, the nature, number and ability to partition radionuclides is site-specific [6]. Building on experience gained from the El Berrocal project, NIREX determined natural U, Th partitioning on colloids from Sellafield groundwaters as an analogue of possible repository derived radionuclides. Colloid numbers were found to be ~$8x10^{10}$ colloids dm-3 (~0.5 mg dm-3) with 0.1% U and up to 2.2% Th associated with the colloid phase. These values are similar to those reported from El Berrocal [10] and other natural analogues in which inorganic colloids dominate.

It is generally accepted from precedence that faults and their associated damage zones may have hydrogeological and transport properties different from their host rocks. Further these properties may evolve over time in response to water-rock interactions and stress perturbations caused by seismic and glacial loading transients. NIREX and the Environment Agency have collaborated in funding an EC project on Fault Zone Heterogeneity that has reviewed the geometry and hydrogeological properties of faults in a wide range of rock types. These analogues have then been used to paramaterise discrete fracture network models to explore the role of the fault core, surrounding damage zones, and relay zones on the magnitude and direction of groundwater flow. Models have also been developed to indicate the transient effects of seismic and aseismic stress changes in fault zones on groundwater flow [11].

The role of biodegradation of wastes by micro-organisms in the NIREX repository concept has been studied in detail. The existence of micro-organisms capable of utilising isosaccharinic acid has been shown from studies of industrial analogue sites associated with paper pulping and bacteria have been found in the high pH lakes of the African Rift Valley and at Maqarin in Jordan [12]. Together, the analogue data show that micro-organisms may be expected to be able to survive high pH repository conditions although active metabolism may be restricted to lower pH microniches. Recently academic, oil-industry and radwaste research has shown that indigenous micro-organisms are likely to be far more common in the geosphere than previously believed. Against this background NIREX has commissioned a review of the literature on deep microbiology as analogues of the types, origins and numbers of micro-organisms that may be found in the geosphere around a deep repository. The extent to which they could interact with the groundwater plume to alter its chemistry or modify permeability pathways is also being considered. The work is currently ongoing.

2.2 Cement Phases & High pH water-rock interactions

The area around Maqarin, Jordan, includes a number of locations where high pH groundwaters are migrating through fractured marls and valley-floor colluvium. It provides a natural analogue of a wide range of processes likely to be found within and around a cementitious repository in fractured rock. Since 1990 three phases of an international collaborative natural analogue study have been completed. NIREX has been involved since the start and the Environment Agency joined the third phase in 1993. A fourth phase is under consideration. This would focus on gaining a better understanding of the age and developmental history of the high pH plume and its effect on the host rock.

2.3 Engineering aspects

NIREX commissioned a precedence study of the long-term stability of underground caverns in 'hard rocks' as a function of size, depth, and support characteristics as analogues for the feasibility of constructing the NIREX deep repository concept [13]. Subsequently, a further preliminary precedence study has been undertaken of caverns constructed in mudrocks and evaporites.

2.4 Gas Migration

As part of the EC collaborative PROGRESS project NIREX commissioned a review of the literature on the migration of natural gas (methane), with a view to understanding qualitatively which mechanisms are most important for gas migration. Subsequently, NIREX has funded a study to review published data on the near-surface dispersion of a wider range of gases, including releases above underground gas storage caverns as analogues for the dispersion of repository-derived gases in the near-surface. This work is ongoing.

2.5 Future climate states and transients

Variations in climate are determined by the response of the climate system to internal and external forcing factors, such as, for example, atmospheric CO_2 content and variations in the Earth's orbital characteristics respectively. It is widely recognised that climatic variability is the ultimate driver for many of the transient processes that affect radionuclide transport in the geosphere and biosphere. Therefore, a good understanding of the climatic processes leading to such variability, and the ability to model them, is required for analogues of future conditions considered by non-steady state performance assessments.

Every two years NIREX has commissioned a review of literature and modelling in the field of climate research. Models that incorporate the effect of varying solar insolation by reproducing the Earth's precession, obliquity and eccentricity can be tested against climatic proxy data, such as the oxygen isotope compositions of foraminifera and the climatic record derived from ice cores. The historical record of climatic variability derived from models that are tested and validated against field evidence can be considered as an analogue for the future, albeit with an evolving set of input parameters.

Palaeoclimatic reconstructions have made use of differences in the distribution of beetle species. The beetle populations at present-day sites are influenced by climatic conditions. Thus, the correlation of the distribution of species to spatially varying climatic conditions at the present-day has been found to be representative (i.e. analogous) to the record of the colonisation and migration patterns of beetles observed at a single site in response to changing climate.

NIREX sponsored work has led to the development and validation of a downscaling methodology for sectorised results from the University of Louvain-la-Neuve sectorised global circulation models to information on a regional scale. Various downscaling methodologies were initially considered, including a rule-based approach in which analogue stations were chosen at different locations in the northern hemisphere to represent different climatic settings at the present time. These analogue stations are considered representative of the climate conditions likely at a single western European site under an evolving climate.

NIREX have considered the importance of present day glacial processes as analogues for the system responses likely to be operative within, adjacent to, and beneath, future glaciers in the British Isles. The characteristics of the groundwater system in the vicinity of a glacier can be considered by studying the present-day hydrochemical and hydraulic variability at various locations in relation to an ice sheet. The resulting information is potentially analogous to similar settings at a future time for locations elsewhere. Work has been proposed that will ultimately lead to coupled models simulating the interaction of mechanical, hydrochemical and groundwater flow processes. The programme of work should include field data for calibration and validation of models.

2.6 Geosphere to biosphere transfer

A site in west Cumbria (Robertgate) was chosen to study in detail the interaction between groundwater and near surface hydrology. The area is one of general discharge to a small stream and springs. The site was instrumented, boreholes were drilled and refurbished and numerous geophysical surveys run. Data was collected for approximately 18 months.

The information is being analysed with the intention to derive an improved understanding of the processes by which regional groundwater reaches the ground surface. This includes a generic understanding that should be applicable at a range of sites. As such, Robertgate can be considered to be an analogue for certain other localities that might be considered as suitable for repository investigations.

3. THE USE OF ANALOGUE STUDIES TO SUPPORT DRIGG POST CLOSURE SAFETY CASES

3.1 Introduction

BNFL owns and operates Britain's principal solid Low Level Radioactive Waste (LLW) disposal site at Drigg in Cumbria, north west England, six kilometres to the south east of the Sellafield site. Drigg has been receiving waste since 1959 with approximately 900,000 m^3 of waste disposed of to date. Drigg is a near surface disposal facility excavated into a sequence of glacial deposits overlying a sandstone aquifer. Historically untreated waste was loose tipped into shallow trenches cut into the local geological strata, with a natural, low permeability layer forming the trench base. Current operations involve the disposal of a containerised, compacted and grouted waste form to a concrete lined vault.

This vault (Vault 8) which was commissioned in 1988, has a nominal capacity of 180,000 m^3, and an estimated fill date of around 2005. Future vaults will extend the operational lifetime of the Drigg site into the middle of the next century.

The Drigg technical programme (DTP) is a collection of interrelated programmes that exist to support current and future post-closure safety cases (PCSC) for the Drigg site. Analogue studies have been used in a number of ways within the DTP to generate information to support and build confidence in Drigg PCSCs. Although some work on natural analogues has taken place to generate fundamental understanding of radionuclide behaviour [14], the majority of analogue work has concentrated on the use of anthropogenic analogues to provide insight into the performance of engineered barriers and to build confidence in the codes used to generate the post closure risk assessment component of the safety case. These uses of analogues are discussed in greater detail below.

3.2 Engineering Analogues

It is expected that operational disposals at Drigg will continue until at least the middle of the next century. This operational phase would be followed by a further period of management (≈100yrs) of the site. During this time the site would be maintained and appropriate facilities and environmental pathways monitored. Also during this period operational facilities would be progressively decommissioned and long-term site closure features constructed. Once this period is over, subject to a final assessment, the site would be closed as a disposal site, then being subject only to some form of institutional management such as planning controls and potentially being available for other uses.

It is currently expected that specific engineering features will be provided during the post-operational management phase in order to augment the natural barriers provided by the site geology. These features would take into account both the trenches and the vaults and will be designed as an integrated system potentially composed of the following components:

- a multi-layer cap that includes vegetative cover, both human and animal/plant intrusion barriers and a number of infiltration barriers;
- a cut-off barrier surrounding the disposal area which will limit groundwater intrusion and lateral migration of leachate; and,
- an enhanced engineered drainage system within the disposal area to capture any ingress of water and to conduct any resulting leachate out of the site via a preferred pathway.

The overall aim of such a system is to minimise water ingress into the wastes, and manage leachates and discharges. At the same time the system incorporates a number of features which are designed to minimise inadvertent human intrusion into the wastes and to allow gas release.

The DTP includes an engineering evaluation studies programme to develop and evaluate appropriate closure measures and assess their potential modes of failure [15, 16]. One source of information regarding the long-term performance of these engineering features is the investigation of archaeological analogues and analogues have been sought for all components of the potential site closure system. The DTP has addressed the issue of archaeological analogues though the use of desk studies rather than field investigations. This has been possible due to the large body of archaeological source material freely available. The attraction of these analogues is obvious, since they provide an insight into the performance of materials and structures over thousands of years. They have to be treated with caution however, since it is only possible to investigate those structures that have survived. It has to be borne in mind that a large number of similar structures may have ceased to exist in the time between their construction and the present. In view of this it is clear that these analogues can both provide supporting evidence for the longevity of engineering structures and insight into their potential failure mechanisms. A few examples of archaeological analogues identified by the DTP are outlined below with reference to the barrier system they represent.

The potential capping system for Drigg has a number of components, such as a vegetated cover, biotic intrusion barrier and infiltration barrier, with no single analogue being relevant to them all. However, analogues for individual components can be found, for example the vegetated soil cover. This is important since it protects the other cap components from exposure to the elements. One excellent analogue for the longevity of vegetated earth mounds is Silbury Hill in Wiltshire, UK. This Neolithic (3200-1800 BC) turf mound and surrounding shallow ditch, is the largest structure of its kind in Europe. It stands 40m high with a diameter of 160m at the base and 30m at its flat top. Its importance as an analogue comes from the fact that it appears to have lost very little of its original volume through weathering throughout its lifetime, and no surface sliding appears to have taken place. Silbury hill provides evidence that domed, vegetated caps can survive for up to 5000 years, however other

structures in the UK have not survived as well. Investigation into the erosion of these other archaeological monuments (Table 1) provides an insight into the likely erosion mechanisms the Drigg system may have to withstand. Not surprisingly these mechanisms (Table 1) fall in to three categories; natural erosion due to rivers etc, erosion promoted by animal activity and erosion promoted by human activity.

Another potential component of the Drigg capping system is a layer of ceramic tiles, which, through virtue of the fact that they contain a warning message, may act as a barrier to human intrusion [17]. For this barrier to function the tiles need to survive intact for a significant length of time. There is a significant amount of evidence for the survival of pottery in the archaeological record but perhaps the most convincing evidence comes from the Moenjodaro site in Pakistan. The site, which contains materials from 3000 BC to 1800 BC, demonstrates good survival of fired pottery found both at the surface and buried at the site. The value of the site as an analogue for the survival of man made artefacts is due to the severity of the environmental conditions found at the site (Table 2). Estimates for the survival of modern materials at the Moenjodaro site suggest that concrete would survive 5-10 years, brick 20 –30 years and steel 10 to 20 years. The value from the Drigg perspective being that if fired pottery can survive at the Moenjodaro site for >3000 years then it is likely to survive the more benign conditions found at Drigg. This evidence would also support the potential longevity of ceramic pipe drains if they were to be used in the Drigg post closure designs.

Two examples have been given here of archaeological analogues which can provide an insight into the performance and failure of engineering features of near-surface radioactive waste disposal sites. This is not an exhaustive list, and other examples include:

- support for the long-term performance of compacted soil cut-off barriers drawn from experience with embankment dams which have been performing for over 100 years without failure;
- the interceptor drains in some dam designs as analogues for cut-off drains which intercept infiltration;
- filter designs and drainage blankets in embankment dams as analogues for horizontal drainage systems; and,
- the migration of soil into the construction materials of Bronze age cairn barrows is analogous to the failure of the biotic intrusion barrier of the proposed cap that is formed by a layer of cobbles.

3.3 Model Testing

The use of analogues to assist in model testing is a central aspect of the realism testing component of BNFL's model testing protocol [18, 19]. This protocol has been developed to provide a rigid framework within which the development and testing of complex software tools can take place. The aim of realism testing is to ensure that the codes are sufficiently detailed, both conceptually and numerically, to adequately represent the situations modelled.

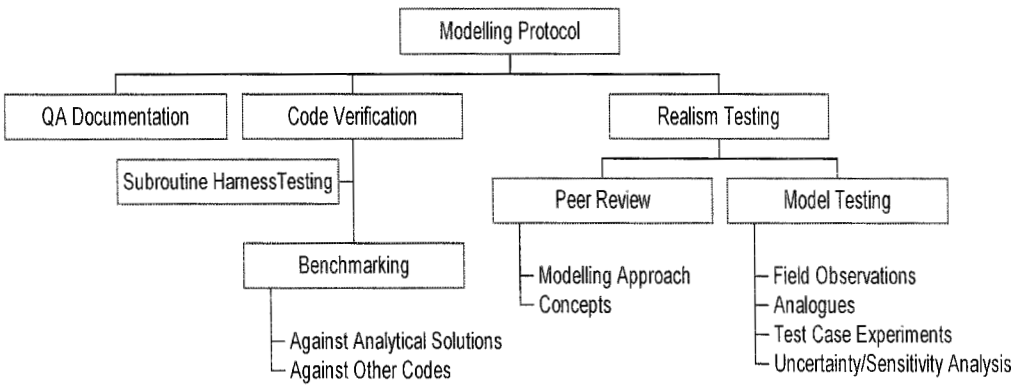

Figure 1. Model Testing Protocol

Work on analogue studies has mainly concentrated on anthropogenic analogues. These analogues have proved to be more useful for model testing because there is a better fit with the processes of interest, they are more dynamic both spatially and temporally and the data set quality is generally better. In recent years effort has concentrated on modelling the Savannah River F-Area [20] in collaboration with

scientists from the Westinghouse Savannah River Company. This work involved the comparison of the BNFL code GRM and the U.S. code BLT-EC and site data.

For 33 years, low-activity liquid wastes from the chemical separation areas at the U.S. Department of Energy's Savannah River Site (SRS) were disposed of in unlined seepage basins. Groundwater at this waste site exhibits lowered pH values and elevated levels of metals, radionuclides, and nitrate. This site has been monitored extensively, and so provides an excellent opportunity to test reactive transport codes in a well-defined field system with large geochemical gradients.

The extensive field and laboratory support programme allowed the modelling of uranium transport over a range of increasingly complex contaminant sorption approaches. These include:

1. single best fit Kd values derived from laboratory and in-situ measurements;
2. empirical fit of non-linear pH-dependent sorption behaviour from field and laboratory data; and,
3. surface complexation model fitting parameters derived from laboratory data of uranium sorption to site background soils and simple mineral oxide surfaces.

The results of the modelling simulations for each code (GRM and BLT-EC) and the various sorption models were compared to field monitoring data. The groundwater flow field used as input to the codes was based on previous groundwater modelling efforts [21, 22]. The results of this study gave good agreement with the BNFL in house code GRM (Figure 2). The results of the study indicated that uranium transport is dominated by low levels of uranium sorption, coupled with large transverse dispersion and relatively fast advection down-gradient to the contaminant boundary conditions. This means that increasing the complexity of the uranium sorption models and adding additional geochemical complexity did not have a significant impact on the simulated results.

Other analogues have been taken from the literature and include the nitrate reduction case described by Postma et al. [23]. This test case is based on an aquifer contaminated with nitrate emanating from agricultural areas. A sharp redox boundary is seen in the aquifer where oxygen and nitrate are reduced through pyrite oxidation. This analogue allows GRM's ability to model microbial oxidation of reduced minerals to be tested with satisfactory results (Figure 3).

3.4 Closing Comments

The use of analogue studies to support the Drigg post closure safety case has concentrated on the use of anthropogenic analogues to provide insight into the long term performance of engineering structures and to provide examples against which codes can be tested. Current work on analogues is focussing on their use for code testing and new analogues are being actively sought.

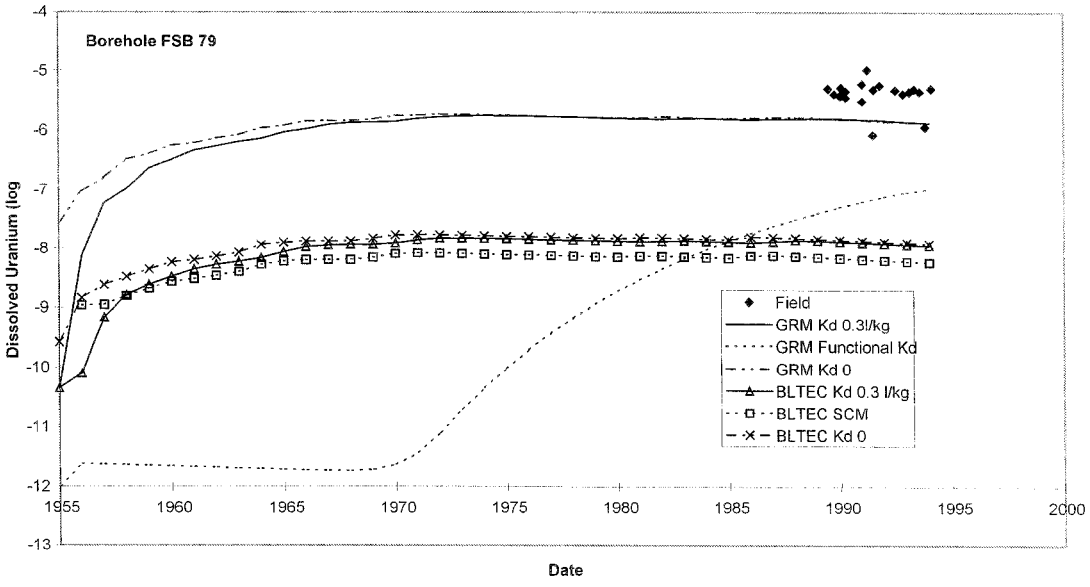

Figure 2. Comparison between GRM, BLT-EC, and data from the Savannah River F-Area

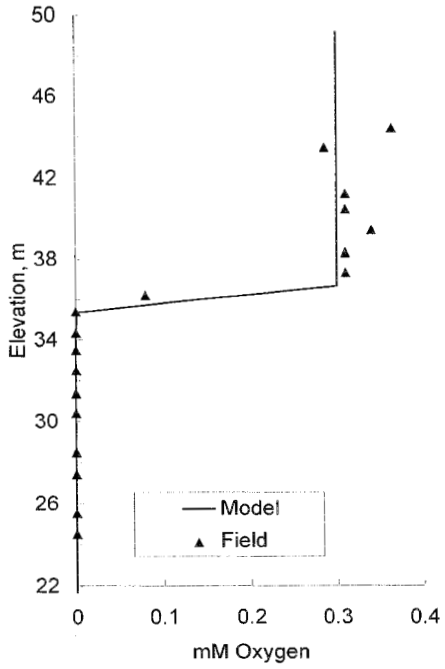

Figure 3. The Oxygen Profile within a Nitrate Contaminated Aquifer [10].

Name	Type of Monument	Nature of Erosion
New Wier	Roman Buried Site	River bank erosion and landslip.
Dinedor Camp	Iron Age earthwork	Scaring at picnic site.
Herfordshire Beacon	Iron Age earthwork and Medieval Motte	natural erosion scar on 35° slope.
Bryn Amwig Castle	Medieval Motte	Deep scaring to masonary on 35° slope.
Hobbs Moat	Post Medieval Moat	Surface loss due to motorcycles and BMX on a 30° slope.
Addinston fort	Iron Age embankments	Deep scaring from sheep and rabbits.
Corn Du and Pen-y-fan	Bronze age cairns	Surface loss through visitors feet.
Owain Glyndwr's Mount	Medieval Earth work	Animal poaching and burrowing, tree root exposure an moisture reduction.
Maes Celyn	Motte and Bailey	Surface erosion
Castella Heinif	Iron age fort	Surface erosion
Offa's and Wat's Dyke	Early Medieval bank and dyke	Damage resulting from: cultivation (38%), trees and scrub (5%), erosion and burrowing (7%), water courses (1%), roads/tracks/railways (10%), development (10%) (undamaged 29%)

Table 1. Examples of Erosion of Archaeological Monuments in the UK

General Details	
Location	200 miles north of Karachi, Pakistan
Age of Materials	3000BC to 1800 BC
Climate over last 1000 years	
Winter	Nights down to freezing days up to 25°C
Summer	Nights down to 25°C days up to 55°C
Water	Maximum rainfall 400mm during monsoon
	Dew during winter
	snow once every 3 years
Humidity	30 to 60%
Ground Conditions	
Water table	Fluctuates between 1 to 3m below surface in summer, 3 to 5m below surface in winter.
Surface temperature	+70°C mid summer to –5°C in winter
Soil moisture	Below surface layer soil has a moisture content in the 12-25% range.
Animal Infestation	Significant ants, termites and rodents
Vegetation	Generally bare surface with sparse cover.
Material Durability (Buried)	
Good survival	Soft-fired brick and pottery, hard/oven fired brick and pottery, ivory, snail shells, limestone, chert, semiprecious stones, gold, soil.
Moderate survival	Bone
Poor survival	Copper
No survival [1]	wood, leather
Material Durability (Surface)	
Good survival	Hard/oven fired brick and pottery, slag, chert.
Moderate & poor survival	All other materials

[1] It is reasonable to assume that these materials were present at the site during occupation

Table 2. Environmental Conditions and Estimated Material Durability from the Moenjodaro site in Pakistan

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Appendix 1

Extracts from Evidence to the House of Lords Select Committee on Science and Technology, The Management of Nuclear Waste.

Question 7: Has enough been learnt from the experience of natural analogues to determine the optimum design and geological conditions for a nuclear waste facility?

"Studies of natural analogues have a useful role to play... Natural analogue studies can provide useful information to aid decisions on selection of suitable geological conditions for a nuclear waste facility... they can provide information on hydrogeological and geochemical processes operating over timescales relevant to an assessment of repository performance... studies can be used to illustrate the role of natural processes in the movement of radionuclides in ground water, and provide information relevant to the needs of performance assessment studies." Extract from the Environment Agency's evidence to the House of Lords Select Committee on Science and Technology, January 1998.

"While recognising that natural analogues cannot possibly provide the whole safety case for a repository, the Government considers it desirable that as much as possible should be learnt from them,.." Extract from DETR's evidence to the House of Lords Select Committee on Science and Technology, January 1998.

"... natural analogue studies provide invaluable calibration data for performance assessment modelling. It is probable that as yet undiscovered (or unrecognised) natural analogues will provide further understanding of the performance of different repository designs/settings.... The RWMAC believes that natural analogue studies have generated a great deal of critical data and knowledge to date and recognises the probability that further studies of this kind would be worthwhile. Involvement of UK scientists in future international collaborations should be continued and encouraged." Extract from RWMAC's evidence to the House of Lords Select Committee on Science and Technology, January 1998.

"Full advantage has been taken of knowledge from natural analogues to help build confidence in the understanding, and models, of processes that determine the performance of a repository..... Continuing work on natural analogues will play a useful role in relation to our understanding of the long-term behaviour of a repository system..." Extract from UK NIREX Ltd's evidence to the House of Lords Select Committee on Science and Technology, January 1998.

III INTERNATIONAL NATURAL ANALOGUE PROJECTS

III.1. Cement-Analogue Project

The Maqarin Natural Analogue Project (1989 - 1998)
W R Alexander, NAGRA (CH) and J A T Smellie, Conterra AB (S)

The Maqarin Natural Analogue Project (1989-1998)

W R Alexander
Nagra, Switzerland (russell@nagra.ch)

J A T Smellie
Conterra AB, Sweden (john.smellie@conterra.se)

Abstract

The Maqarin Natural Analogue Project site (in NW Jordan) appears to be unique in that the hyperalkaline groundwaters in the area are the product of low temperature leaching of an assemblage of natural cement minerals produced as a result of high temperature/low pressure metamorphism of marls (i.e. clay biomicrites) and limestones. Investigations provide a consistent picture explaining the origin of the hyperalkaline waters, the persistence of some of the hyperalkaline springs/seepages, and the sequence of alteration occurring when such waters react with various rock-types. Additionally, the studies have produced good quality measurements of the concentration (and general speciation) of some repository-relevant elements in high pH groundwaters, along with microbial and colloidal populations.

The Maqarin natural analogue site therefore provides a rare oportunity to examine the mechanisms of processes associated with cementitious repositories for radioactive and chemotoxic wastes, particularly when cement pore fluids will be dominated by the dissolution of portlandite and calcium silicate hydrate gel phases.

1. Introduction

The Maqarin Natural Analogue Project was initiated in 1989 with Phase I, continuing with Phase II in 1991 and Phase III in 1993 (see Alexander, 1992, Linklater, 1998, Smellie, 1998, and references therein). The Maqarin site appears to be unique in that the hyperalkaline groundwaters in the area are the product of leaching of an assemblage of natural cement minerals produced as a result of high temperature/low pressure metamorphism of marls (i.e. clay biomicrites) and limestones (see Fig. 1). In Jordan as a whole, at least three different hyperalkaline groundwaters have been identified and they appear to represent, by analogy, three different stages in the theoretical evolution of a cementitious repository for the disposal of low- to intermediate-level wastes. The three stages are:

1: early, active, high pH Na/KOH leachates (Western Springs, Maqarin; see Fig. 2)
2: intermediate, active, lower pH $Ca(OH)_2$ buffered leachates (Eastern Springs, Maqarin; Adit A-6, Railway Cutting and Waterfall Road Cutting in Fig 2)
3: late, inactive (fossil), lower pH silica dominated leachates (Daba region in central Jordan).

Whilst Phase I and Phase II were very much site-specific and process-oriented (e.g. studies of the source term and its interaction with the host rock; testing the applicability of available thermodynamic data to hyperalkaline conditions; predicting the extent of high pH water/rock

interaction using coupled models etc.), Phase III provided a more regional perspective to the geological and hydrogeochemical evolution of the entire cementitious system.

2. Recent geological evolution of the Maqarin Site

The Maqarin area (Fig. 2) comprises Cretaceous-Tertiary carbonate rocks overlain by Quaternary basalts, soils and alluvium. The E-W trending Yarmouk River Valley is a relatively recent geomorphological feature, having eroded through some 400 m of the Irbid Plateau exposing the Bituminous Marl Formation which is overlain by the Chalky Limestone Formation, in turn capped by basaltic lava flows. There is no direct evidence that the Yarmouk Valley is structurally controlled by tectonic events associated with the Jordan Rift Valley system.

Regionally, the exposed strata show very little deformation and are almost horizontal to gently dipping; flexures with very small curvatures are also evident. Locally, at Adot A-6, the Bituminous Marl Formation has been slightly uplifted by a N-S trending anticline which plunges to the NE. Detailed structural mapping on a local scale underlines the heterogeneity of the system, in part explained by gravity tectonics (i.e. slumping) facilitated by the steep hillslope angles (~ 45°). Localised slump features bordering the Yarmouk River Valley are widely observed in the Eastern Spring area.

Less is known from the Western Springs locality where talus and colluvium cover most of the hillslopes. There is, however, some indication of a N-S trending fault system and the possibility of localised shear and rotation between such faults. Gravity slumping features on the scale present at the Eastern Springs locality are not readily observed, but evidence exists of valley bulging on the floor of Wadi Sijin and the presence of a landslide on the western valley side of the wadi.

The mechanisms which have activated spontaneous combustion in the Bituminous Marl Formation to produce the metamorphosed "cement zones", and subsequently the formation of the hyperalkaline groundwaters in the area, are still uncertain. Whilst earthquake shock is not seen as a likely mechanism for creating fissures and joints directly in the rock, it may be a significant factor in triggering landslides and causing abrupt rupturing of superficial strata followed by erosional downloading. If this has contributed to the process of combustion in the Eastern Springs area, then, from geomorphological considerations, a probable date of ignition is around 600 ka, and certainly not later than 150 ka. More hypothetically, a second, later phase of triggered landslides, might also be considered to explain the geomorphological features observed in the Western Springs area. Speculatively, such an event might have occurred in the last 100 ka (Late Quaternary), or even as recently as the last 10 ka (Holocene). These two phases of landslip activity indicate that the Eastern Spring system is geologically older than the Western Springs system.

In addition to the possibility of these two major landslip events, reactivation on a smaller scale may be expected to be recurrent, triggered rapidly by heavy rainfall and more gradually over longer timescales by continued lateral erosion of the Yarmouk River. This may account for the periodic sealing and reactivation of hyperalkaline groundwater conducting fracture pathways indicated from mineralogical studies and field observations.

3. Groundwater flow and hydrogeochemical evolution of the Maqarin Site

In northern Jordan, regional hydrostratigraphic units dominate with flow generally from the central plateau westwards to the Jordan River Valley and northwest to the Yarmouk River Valley, with a component from southern Syria flowing southwest towards the Yarmouk Valley. On the local scale (see Fig 3), three main groundwater bodies can be recognised in the Eastern Springs area flowing northwards to the Yarmouk River Valley:

1: Deep confined aquifer water from the Amman Formation (B_2); some of these waters may move upwards along discontinuities in the overlying Bituminous Marls where there is an artesian head.
2: Infiltration of meteoric water through the Chalky Limestone Formation in the plateau lying east of Maqarin, penetrating the Bituminous Marl Formation (B_4/B_5 units) down to the contact (B_3) between the metamorphosed "cement zones" and unmetamorphosed clay biomicrites. The groundwaters follow this interface eventually discharging as seeps and springs along the Yarmouk Valley sides. This is the main groundwater source and their passage through the cement zones gives rise to the hyperalkaline varieties.
3: Water infiltrates directly into the Chalky Limestone Formation above Adit A-6, down into the Bituminous Marl and the cement zone, possibly mixing with type (2), or locally discharging along the roof and walls of the adit. If the main hyperalkaline source is in the vicinity of Adit A-6, the maximum extent of the hyperalkaline plume downflow to the river 400-500 m.

In the Western Springs area the groundwater flow is also northwards towards the Yarmouk River Valley. The waters totally originate from rapid vertical recharge into the Chalky Marl Formation at the plateau south of the Western Spring location, facilitated by widespread open karst features. These groundwaters are eventually channelled through the Bituminous Marl Formation and the cement zone, to discharge through a thick colluvium sequence along the Yarmouk Valley at an elevation of 1-4 m above the river bed. Reaction with the cement zone has also produced the hyperalkaline groundwaters at this locality, and the extent of the hyperalkaline plume downflow to the river is somewhat less than at the Eastern Springs.

Hydrogeochemical and isotope studies largely support the hydrogeological conceptualisation of the major groundwater flow pathways. The recharge groundwaters are meteoric and local in origin, of normal pH and dilute bicarbonate in type, contain measureable tritium and are the probable precursors to the high pH groundwaters. No significant mixing of groundwaters from the underlying confined Amman Formation aquifer is indicated. Interaction of the normal pH groundwaters with the cement zones in the Bituminous Marl Formation has produced two chemically distinct high pH groundwaters; Eastern Spring Ca-OH type and the Western Spring Ca-K-Na-OH-SO_4 type. Both types are believed to be older than at least 40 years (tritium-free), although minor amounts of tritium (~4 TU) in some samples may indicate slightly younger ages if mixing with recent recharge waters is excluded. The absence of thermonuclear ^{36}Cl is also consistent with recharge prior to 1950.

Hydrogeochemical modelling suggests that the observed differences in groundwater composition between the Eastern and Western Springs localities can be attributed to different stages of water/rock interaction evolution. There is no convincing evidence that the high Na, K and SO_4 concentrations at the Western Springs locality are due to initial differences in the composition of the cement zone, variable infiltration conditions, or anthropogenic contamination. A possible scenario is that the Eastern Springs area groundwater circulation has occurred over a much longer timespan and readily soluble mineral phases are already

completely dissolved. This supports the analogue that the Western Springs groundwaters represent the first pore volume discharging from the cement zone, and that the Eastern Springs groundwaters represent late, more evolved, discharge. The scenario is consistent with the field observations which suggest that the Eastern Springs system is geologically older than the Western Springs system (Smellie, 1998).

4. Conceptual model of plume evolution

To model the evolution of a hyperalkaline plume, in a cementitious repository setting, it is assumed that that the initial leachates are pushed from the cement in a piston effect, due to the flow of groundwater into the cement further upstream in the repository. At the cement/host rock interface (the proximal part of the plume; see Fig. 4), the hyperalkaline leachates have not yet reacted with the host rock and so have a high pH and high concentrations of Na, K and Ca, reflecting the cement porewater chemistry. As the plume reacts with the host (aluminosilicate-bearing) rock, the pH falls, as do the Na, K and Ca concentrations in the groundwater, while the concentrations of Al and Si rise fractionally. Beyond the distal edge of the plume, in the, as yet, undisturbed host rock, the groundwater pH is near neutral, the Na, K and Ca concentrations are low, while the concentrations of both Al and Si are high. This pattern has consequences for the secondary mineralogy: C-S-H phases will be found in the fractures (through which the plume has migrated) in the proximal part of the plume, reflecting the fact that the leachate has not yet reacted with the host rock and is equilibrated with the C-S-H phases which make up the cement. As the leachate moves downstream and interacts with the aluminosilicates in the host rock (and the host rock groundwater and porewater), the Al concentration increases, precipitating C-A-S-H phases. At the distal edge of the plume, the leachate has reacted with an even larger volume of host rock (and the host rock groundwater and porewater) and eventually precipitates zeolites as the Al and Si concentration in the groundwater becomes high enough and the pH low enough.

If it is assumed that the plume continues to migrate, then the zeolite zone produced by the distal part of the plume will later be over-run by the middle of the plume, inducing some re-dissolution of the zeolite phases and replacement by C-A-S-H phases. This mixed zeolite/C-A-S-H zone will be then over-run by the proximal part of the plume, inducing further re-dissolution of the zeolite/C-A-S-H phases and replacement by C-S-H phases. These complex mixtures have been observed repeatedly at Maqarin (Alexander, 1992, Linklater, 1998).

5. Mineralogical and geochemical evolution within the plume

The fracture mineralisation and alteration of the clay biomicrite/limestone due to interaction with hyperalkaline groundwaters has been examined in detail at the Eastern Springs and Western Springs localities. Several successive stages of fracture mineralisation have been observed, reflecting both the evolution of the cement leachates and changes in rock-water interactions. The system is highly complex; in reality, the sequence of secondary mineralisation may be reversed, repeated or parts may be missing entirely in areas, depending on the specific evolution of the cement zone and the reactivation of previously sealed fractures. In addition, individual fractures may seal at any point in the sequence and, unless reactivated tectonically, remain sealed.

5.1. Western Springs location

The data currently available are limited to the examination of large boulders and clasts of basalt and limestone/clay biomicrite (including chert), embedded in Quaternary colluvium deposits which characterise the Yarmouk River Valley sides above the river bed. The hyperalkaline groundwaters preferentially flow through, and along the base of the colluvium deposits, before discharging as seepages and small flows into the Yarmouk River. As a general conclusion, quartz, chert, K-feldspar, glass and plagioclase are the most reactive phases with the hyperalkaline groundwaters, dolomite is moderately reactive, augite, hypersthene (orthopyroxene) and olivine are weakly reactive, and apatite and Ti-Fe oxides appear to be largely unreactive. Similar reactivity is observed in the sand-silt matrix that characterises the colluvium.

Although the reported results refer to a porous media (namely the colluvium), nevertheless it is still possible to produce a paragenetic mineral sequence. Mineral paragenesis of the secondary alteration phases indicates the following sequence: 1) a carbonate stage, 2) a very hydrous Ca-K-Na-Al 'zeolite-type' stage, 3) a CSH gel stage with a variable Ca:Si ratio covering the range CSH(I) to CSH(II) (i.e. suolinite-afwillite), 4) a more Si-rich CSH gel (i.e. okenite-type), and 5) a low Ca-Si ratio CSH phase (i.e. truscottite-type). The latest stage of alteration is the filling of remaining pore spaces and blanketing of the CSH and CASH phases by calcite or aragonite. Stages 3, 4 and 5 repeat in places, indicating pulses in the hyperalkaline plume flow.

5.2. Eastern Springs location

As the groundwater flow at the Eastern Springs location is fracture/joint controlled, most alteration processes and mineral paragenesis are confined to these features. Most wallrock alteration takes place within 0.5 to 4 mm of the fracture. Within this zone, the fine-grained matrix calcite, kaolinite, silica, traces of illite, albite and organic matter are dissolved and pyrite, trace sulphides and glaucony are oxidised. The wallrock porosity is significantly enhanced for up to 1 mm from the fracture and the original wallrock mineralogy tends to have been totally replaced by fine-grained secondary phases.

The fracture mineralisation is highly complex and the hyperalkaline groundwaters appear to have exploited existing calcite veins in the clay biomicrite/limestone, utilising partings, which opened up between the calcite vein-fill and the wallrock. The exposed surfaces have been mineralised initially by needles of aragonite. The remaining fissure has been infilled by a complex mixture of gypsum, ettringite-thaumasite, amorphous C-S-H gel (or C-A-S-H gel) and very hydrous, fibrous to gel-like zeolites and gypsum. Textural evidence, such as the existence of complex zonations within the mineralised fractures that contain different minerals in different textural settings, and the sharp boundaries between the zones, indicate that the fractures were repeatedly re-opened (presumably by tectonic movements) and re-sealed by fracture minerals. Based on this field evidence, it is suggested that each phase of mineralisation (and possibly also of cement leaching) is preceded by tectonic reactivation of the fractures, which in turn are efficiently sealed by secondary phases precipitating from groundwaters percolating through the open fractures. It is worth noting that each reactivation event only affected a fraction of all fractures present in the rocks, such that the exact sequence of mineralisation phases differs from fracture to fracture.

The alteration pattern, closest to the 'source' and best observed deep in Adit A-6, reveals the following mineral paragenesis: 1) aragonite stage, 2) ettringite -thaumasite stage, 3) C-S-H stage, and 4) zeolite stage. Further downflow along the hyperalkaline plume (e.g. nearer the mouth of Adit A-6 and at the Railway Cutting), at least eleven paragenetic episodes of mineralisation have been identified. The temporal alteration can be summarised as: 1) Initiation Stage (carbonate - portlandite - brucite/hydrotalcite), 2) Ettringite-Thaumasite Stage, and 3) C-S-H Stage.

5.3. Summary and conclusions

The spatial and temporal evolution of the secondary phases observed at Maqarin have been placed in the framework of the conceptual model for a hyperalkaline plume discussed above. The data from the Western Springs colluvium present a snapshot of the likely temporal evolution of a plume in any flow system where the central part of the plume may over-run the distal edge which may then be over-run by the proximal portion, with each new section of the plume replacing wholly, or in part, the previous mineral assemblage. Thus, the observations from the Western Springs have proved immensely useful in suppporting the validity of the conceptual model but, as the data are only of relevance to a highly advective system (e.g. in a highly porous rock or in a fractured rock in a tectonically highly active region), care is required if the observations are to be extrapolated to a repository site.

The Eastern Springs may be seen to represent a snapshot of the likely spatial evolution of a plume in any flow system with the observed mineralogical changes with distance from the cement source in close agreement with the conceptual model. Although the Eastern Springs data initially proved extremely difficult to interpret, the overall pattern at the Eastern Springs is now seen to differ little from that at the Western Springs; but the fact that the system seals and re-opens in a complex sequence makes interpretation difficult. However, what is clear at Maqarin is that the fractures seal; in a tectonically quiet area the fractures would presumably remain sealed, but at Maqarin they are constantly re-activated, so producing the complex paragenetic patterns observed.

A literature compilation of thermodynamic data of zeolites has been carried out because of the potential of zeolites to sorb and retard certain radionuclides of importance to the long-term performance assessment of a cementitious repository. The zeolites observed at Maqarin are not in thermodynamic equilibrium with the current hyperalkaline groundwaters; the concentrations of major aqueous species are probably controlled by equilibrium with portlandite and an ettringite-thaumasite solid solution. The formation of zeolites at the Eastern and Western Springs localities is intimately linked with pore fluid composition (pH, activities of aluminium and silica) and probably reflects alteration in the very early stages of sealing (see Fig 3).

6. Rock matrix diffusion studies

A detailed study of the extent of rock matrix diffusion was carried out on four profiles taken perpendicular to water-conducting fractures from Adit A-6 (Linklater, 1998). Each profile was analysed for a suite of elements and natural decay series radionuclides along with porosity variations and the results are highly ambiguous. Significant variations in the unaltered clay biomicrite signature has made it impossible to detect any potential perturbations due to hyperalkaline water/rock matrix interaction (i.e. the background noise is too great). In only one case is there some suggestion of a clear signal: the $^{226}Ra/^{238}U$ ratios in

two of the profiles suggest relatively young rock/water interaction at up to 4-7cm depth. However, these depths should be treated cautiously considering that all four samples are heavily influenced by microfracture networks extending several centimetres into the rock, and by pre-existing lithological variations (bedding etc.).

It is intended to collect additional samples from a less tectonically disturbed site (Waterfall Cutting, to the east of the Eastern Springs) for further matrix diffusion studies in the hope of obtaining an unambiguous picture of the effects of the hyperalkaline leachates on the host rock.

7. Age of the hyperalkaline flow systems

Some vein minerals (and associated fracture wallrock) from sealed fractures in Adit A-6 have been analysed for natural decay series radionuclides and dates can be very tentatively assigned to the hyperalkaline groundwater alteration. A diagenetic calcite vein was dated by the ^{230}Th ingrowth method at between 500 ka and 2 Ma, providing a maximum age for the metamorphism that produced the cement zone mineral assemblage. This can be compared with the geomorphological assessment of uplift and erosion in the Yarmouk Valley area which suggests a probable date of ignition at around 600 ka, and certainly not younger than 150 ka. Analyses of samples of tobermorite vein filling and jennite-ettringite vein filling produced ages of 90 ka and 80 ka respectively. A reported ^{14}C age of less than 650 a for recarbonated cement zone material from Adit A-6 does not necessarily contradict the ^{230}Th ingrowth ages, rather it confirms the scenario of repeated re-activation of fractures (due to gravitational tectonics) with consequent mutli-phase fracture infill.

Indeed, the persistence of secondary fracture materials of differing ages suggests that, once sealed, the secondary fracture-filling mineralogy in the hyperalkaline disturbed zone can remain stable for safety assessment relevant timescales - with the implication that radionuclides associated with these secondary phases also can be isolated from the evolving groundwaters. No data exist for the porous media flow Western Springs system although the petrological data cited above suggests that the system has remained open throughout its lifetime, implying that any age calculated must be a reflection of a complex multi-phase reaction.

8. Microbes, organics and colloids

8.1. Microbes

Microbiological studies have clearly shown the presence of populations (~10^5 microbes mL^{-1}) of heterotrophs and sulphate reducing bacteria (SRB) in the groundwaters and, at least an order of magnitude more bacteria on the fracture faces. Gene sequencing work on microbial material from Maqarin carried out during Phase III have shown that the total number of bacteria are within the range of other subterranean sites and that there is a diverse microbial population present. Some *in situ* evidence was found of attached biofilms on fracture faces in contact with hyperalkaline water, and also signs of growth in some cultures (albeit at a maximum pH of ~11).

Unfortunately, many of the bacteria present in the groundwaters still remain unidentified because of the difficulty of maintaining appropriate conditions (especially pH) in the laboratory in which to cultivate enough cells to enumerate and classify.

8.2. Organics

Studies have shown that the high DOC content in the groundwater from the Western Springs locality can hardly be explained by dissolution of organic matter from the Bituminous Marl by percolating high pH groundwaters. Solution experiments show that only a minor part of the organics could dissolve in the water; in addition, aromatics are found in the DOC whereas organic material is predominantly non-aromatic in the marls. Organic matter does not appear therefore to play any major role in the geochemistry of the trace elements studied. Furthermore, *in situ* groundwater speciation analyses suggest that organic complexation is insignificant in these hyperalkaline groundwaters.

8.3. Colloids

In the case of a cementitious repository, degradation of the cement may provide a significant source of colloids at both the near-field/far-field interface and at the margins of the hyperalkaline plume (which may extend downstream of the repository). Evidence from the Maqarin groundwaters suggests that the numbers of colloids generated in the cement zone will be low. This is supported by the very low amounts of colloids measured from the Adit A-6 (10^7 colloids mL^{-1}). It has been also demonstrated that no uranium (or other trace elements) is associated with the colloidal material characterised. However, as a note of caution, sampling for colloids was conducted under oxidising conditions, not representative of the reducing conditions expected around a repository.

9. Clay/leachate interaction

Studies of smectite stability under hyperalkaline conditions have been hindered by the small amounts of clay (~5 wt/%) present in the host Bituminous Marl. Nevertheless, studies of altered clay biomicrite samples from Maqarin (e.g. near the entrance of Adit A-6) showed the presence of smectite alteration products, namely volkonskite (chrome smectite). However, the smectite seems to be an exogenic precipitate within hyperalkaline-altered chalks and hydrated marbles, rather than an *in situ* reaction product of primary clay-rich lithologies. In general, more field studies are necessary to better assess the availability of clay-rich zones.

10. Model, code and database testing

10.1. Thermodynamic Databases (TDB)

Two tests of a suite of geochemical databases have been carried out within the project to date. All the TDBs were limited in the representation of the controlling solid phases. Most of the predicted solubility controlling solids were non-representative of the natural system, being pure end-members whereas the actual mineralogical data indicated the involvement of trace elements in solid solutions or as trace incorporations with C-S-H gels, for example. Nevertheless, the TDBs generally produced conservative estimates of trace element solubility, as is required in a repository performance assessment.

10.2. Geochemical codes

A limited test of geochemical codes was conducted during the early stages of the Maqarin study with the aim of comparing code predictions in the relatively high ionic strength (up to

0.1M) hyperalkaline waters. Two codes, MINEQL/PSI and PHREEQE were examined (using similar thermodynamic databases) and the results indicated that, for the Maqarin groundwaters and model cement waters (ionic strength 0.2M), the differences in activity coefficient calculations carried out by the codes were usually one order of magnitude smaller than the uncertainties in the equilibrium constants contained in the databases (and so the resulting speciation calculations and predicted solubilities were almost identical).

10.3. Coupled (geochemistry-transport) code testing

To date, only two tests have been carried out; in both instances, a comparison was carried out between an equilibrium approach (CHEQMATE) and a kinetic approach (MARQUISS). Note, both tests were carried out prior to all site and mineralogical data being available; this would probably warrant an alternative approach in hindsight.

Two modelling scenarios were identified, for the Eastern and Western Springs localities respectively:

Eastern Springs:

1) Diffusion perpendicular to the fracture into the marl; the aim of the modelling was to predict the type and scale of mineralogical changes.

2) Advection along the fracture with diffusion into the rock matrix; the aim here was to predict the changes in the water composition in the fracture.

Western Springs:

1) Diffusion of hyperalkaline water into individual clasts in the Western Springs colluvium; the aim here was to predict the nature (width, secondary mineral distribution etc.) of the reaction rims around/in the clasts (looked at basalt, chert and clay biomicrite).

2) Diffusion/advection of hyperalkaline water through the colluvium; the aim here was to predict the position and nature of reaction fronts.

The most significant result of the tests show that the codes' predictions are relatively insensitive to the lithological, hydrogeological and hydrochemical differencies between the sites, with the predicted sequence of mineral reactions being very similar in all cases and, in gross terms, in agreement with the observed mineralogy.

Initially, CHEQMATE predicted fracture sealing with ettringite within five years while MARQUISS predicted fracture sealing around 0.6m from the cement source, also with ettringite. CHEQMATE also predicted the observed calcite 'front' within the clay biomicrite matrix but it has not been possible to check the predictions for other secondary phases in the matrix due to the complexity of the fracture re-activations. Later calculations showed reasonable agreement between the predicted reaction rims on the clasts in the colluvium and observations, although the thickness of the rims was significantly over-predicted.

10.4. Microbiology code testing

For modelling purposes, the Maqarin site was divided into three zones, A (upstream of the cement zone), B (cement zone) and C (downstream of the cement zone). The code predicted

that, in zones A and B, the limit on maximum microbial growth could be defined by the phosphorous availability whereas in zone C, growth is limited by the amount of energy available (i.e. carbon). The results for zones A and C are surprising in that the groundwaters from all three zones are saturated with respect to apatite, a common accessory mineral in the rock. It may be that the phosphorous in apatite is not easily accessible or that the microbes can only use phosphorous from an organic source.

The MGSE code properly predicted that zones A and C contained the higher populations (it was presumed that the lower population in B was due to loss of energy and nutrient sources during the combustion event) but, for all three zones, the predicted populations were three to five orders of magnitude greater than were observed, suggesting that further code development may be necessary and that more appropriate data are still required from the site (e.g. better definition of the *in situ* carbon source, better hydrogeological data etc.).

11. Performance assessment considerations

The Maqarin site now provides a consistent picture explaining the origin of the hyperalkaline waters, the persistence of some of the hyperalkaline springs/seepages, and the sequence of alteration occurring when such waters react with various rock-types. Additionally, the studies have produced good quality measurements of the concentration (and general speciation) of some relevant elements in high pH groundwaters, along with microbial and colloidal populations).

The Maqarin natural analogue site is therefore a unique location to be able to examine the mechanisms of processes associated with cementitious repositories, particularly when cement pore fluids will be dominated by the dissolution of portlandite and calcium silicate hydrate gel phases. Evidence from Maqarin shows that:

- the conceptual model for the evolution of a hyperalkaline plume in a host rock is largely consistent with observations at the site,
- hyperakaline pore fluid conditions generated by minerals analogous to those envisaged for cements are long-lived (in excess of tens of thousands of years),
- predictive models of the solubility of elements of interest to radioactive waste disposal provide conservative estimates of solubility (i.e. solubilities are overestimated),
- the amounts of colloidal material generated at the cement/host-rock interface zone probably will be low,
- sequences of minerals predicted by thermodynamic and coupled modelling are similar to those observed in hyperalkaline alteration zones at Maqarin,
- due to ambigious data, it is not yet possible to say if the rock matrix will be accessible to diffusion of aqueous species even during the phase of on-going wallrock alteration,
- small aperture fractures will be self-healing, larger aperature possibly so,
- tectonic effects upon fracture sealing and the site hydrology need to be considered on a repository site-specific basis.

12. Demonstration and validation

One of the strengths of the Maqarin natural analogue site has been the possibility of studying directly, at repository scale, the *in situ* impact of perturbations on the original retardation qualities of the host Bituminous Marl Formation. Furthermore, these site studies have been closely coupled with ongoing laboratory and *in situ* (i.e. rock laboratory) experiments, which

will eventually provide greater confidence in the transferability of data and also test the limits of applicability of such data to performance assessment models of hyperalkaline systems.

13. Acknowledgements

The authors would like to acknowledge all their colleagues in the Maqarin Natural Analogue Study Group for their work over the last 10 years which forms the basis of this publication. The financial support during this time has come from Nagra and Nirex (Phases I, II and III), SKB (Phases II and III) and Ontario Hydro (Phase I), who are gratefully acknowledged. Finally, the authors would like to thanks Nagra and SKB for funding the production of this short overview.

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15. Further Reading

The material cited above, while open, has a somewhat restricted circulation. Interested readers may also find further information on the project in:

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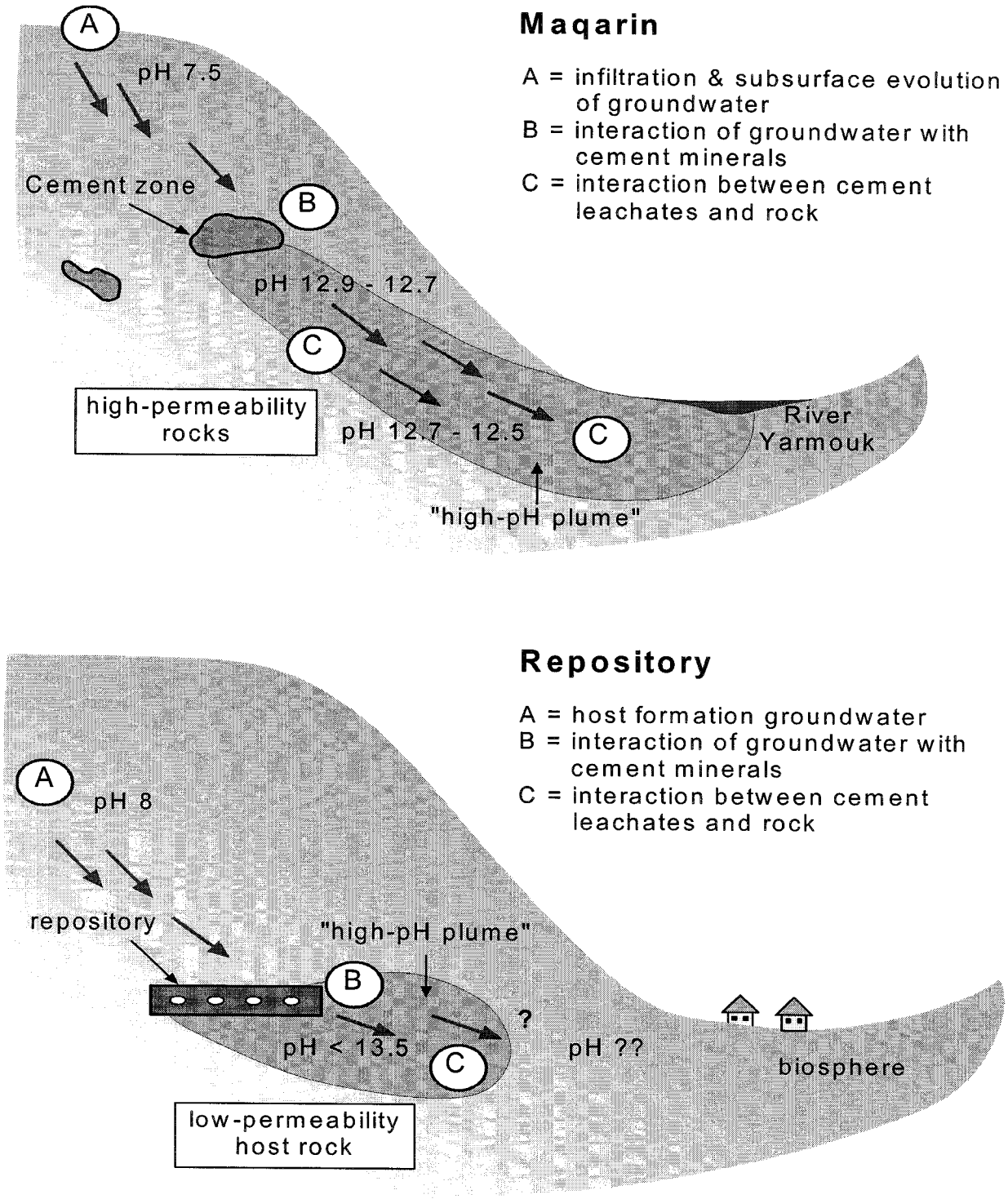

Figure 1: The basis of the analogy (From Alexander and Mazurek, 1996)

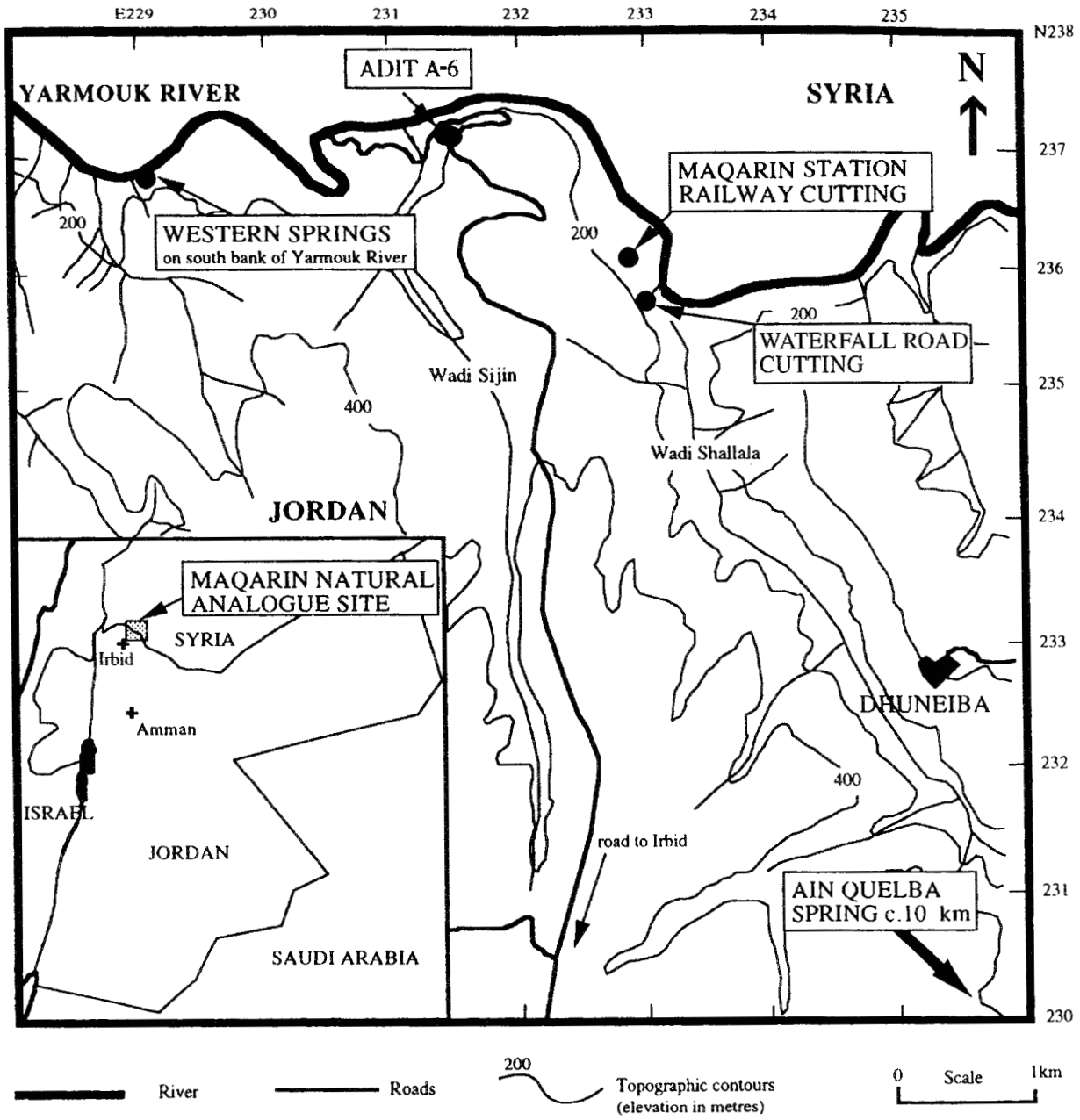

Figure 2: Map of Jordan and the Maqarin Site (from Smellie, 1998)

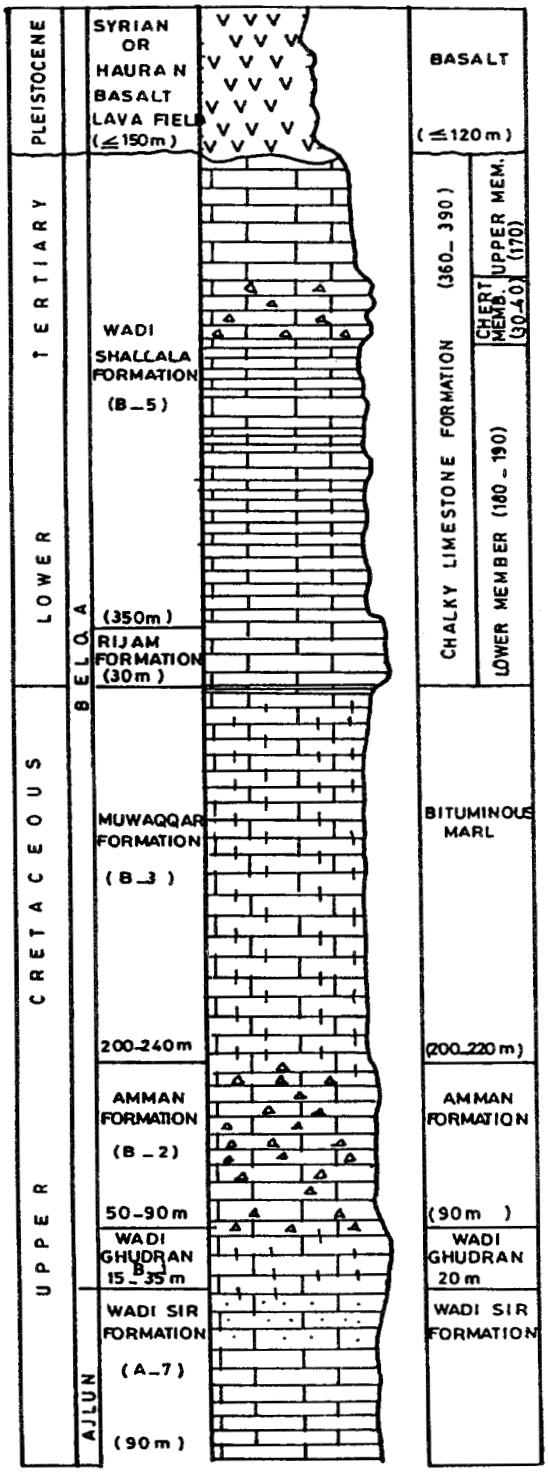

Figure 3: Regional lithostratigraphic correlation chart (from Khoury et al., 1998)

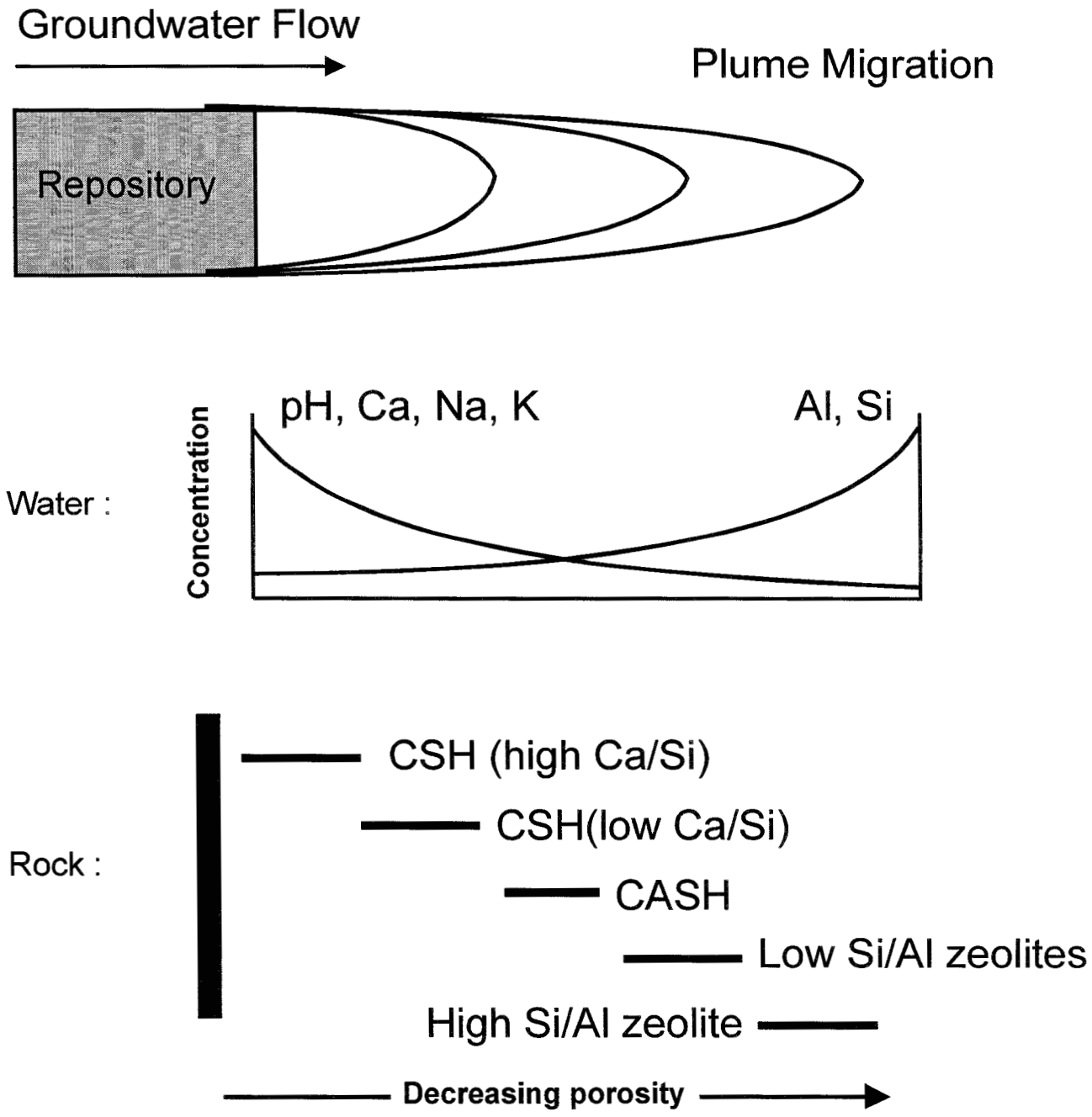

Figure 4: Conceptual model of the hyperalkaline plume evolution (after Savage, 1999)

III.2. Clay-Thermal Analogue Project

Thermal effect of clay barrier materials: Stress-related effects
R Pellegrini, ISMES (I); S Lombardi, UR (I); C Rochelle, BGS (UK); J Y Boisson, IPSN (F) and J C Parneix, ERM (F)

Mineralogical and chemical changes due to volcanic intrusion into clay Formations
A Bouchet, ERM (F); J Y Boisson, IPSN (F); S J Kemp, BGS (UK); J C Parneix, ERM (F); R Pellegrini, ISMES (I) and C Rochelle, BGS (UK)

THERMAL EFFECTS OF CLAY BARRIER MATERIALS: STRESS RELATED EFFECTS

R Pellegrini (1); S Lombardi (2); C Rochelle (3); J Y Boisson (4); J C Parneix (5)

I.S.M.E.S. S.p.A.;via Pastrengo 9, 24068 Seriate (BG) Italy
University of Rome, Dipartimento di Scienze della Terra Piazzale A. Moro , Roma, Italy
B.G.S. Kingsley, Dunham Centre, Keyworth, Nottingham, NG12 5GG, United Kingdom
I.P.S.N., BP 6, 92265 Fontenay aux Roses, France
E.R.M. Espace 10-République 2, Rue Albin Haller,86000 Poitiers, France

Introduction

This paper focuses on the analysis of stress – related effects in some geological structures selected as potential natural analogues for the evaluation of long term hydro-thermo-mechanical effects on deep clay formations subjected to heat. Thermo-mechanical effects in clay rocks are the subject of many laboratory investigations (e.g., Baldi *et al.*; 1993; Del Olmo *et al.*, 1996) as well as of medium to full scale heating tests (e.g., Pellegrini and Trentesaux, 1998; De Bruyn and Labat, 1998). Such tests showed important pore water overpressures generated by the differential expansion of clay and pore water as well as consolidation due to their dissipation under the form of water flow, which is accompanied by irreversible straining in the clay. Natural analogues are seen as a good opportunity to understand how far the observed short-term effects are stable in time and to possibly identify additional long-term running effects, such as the stability of the physico-chemical environment, typically, dehydration shrinkage effects (Hokmark, 1995).

Results were achieved in a research partly funded under contract FI4W-CT95-0014 of the European Commission (Pellegrini *et al*, 1999).

Analogue sites

Three examples of emplacement of intrusive rocks into clay formations were studied: one is located on the Isle of Skye (UK), one at the Col du Perthus (Hérault, France), and one at Orciatico (Tuscany, Italy). Two of these structures are basaltic dykes emplaced in Jurassic mudstones (Skye) and Toarcian shales (Col du Perthus) respectively; the one at Orciatico is a laccolith still largely concealed in Pliocenic clays.

The dyke at Col du Perthus is 1.1m wide. No exact age is available for the dyke, but it is probably linked to a system of dykes in the Lodève area dated to 1.7 to 2 Ma ago. The igneous body within this analogue was emplaced at the greatest depth into a very stiff, carbonate-rich, highly overconsolidated mudstone. The main analogue sites investigated in the Isle of Skye occur on the shoreline and in small coastal gorges cut by streams. Investigations concentrated in Lùb Score, where a dyke 2.0m wide was studied, emplaced in a Jurassic mudstone (Kemp *et al.*, 1998). The Orciatico analogue site is 0.5 km^2 wide, still partially concealed within the host pliocenic marine mudstone, in the form of a sill-laccolith body fed by a narrow NW-SE trending dyke (Fig. 1a,b). The emplacement of this selagite intrusive body was probably controlled by the NNW-SSE trending faults related to the post-tectonic extensional regime of the Val d'Era graben. Dating of this unit yields an emplacement age of 4.1 Ma (Borsi S. *et al.*, 1967).

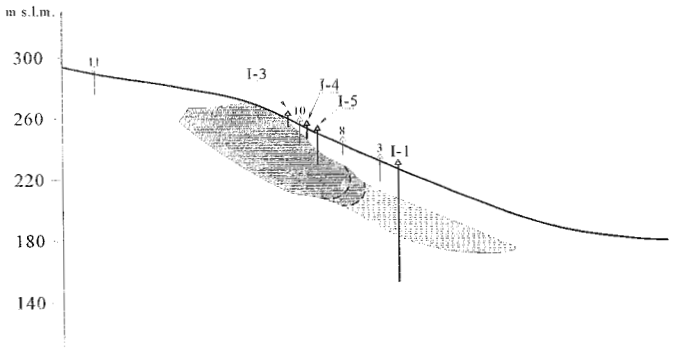

Figure 1a: Orciatico. Alignment D-D'. Location of drillings. Darker the final shape of the laccolith as resulting from geophysical surveys respect to the previous interpretation (lighter).

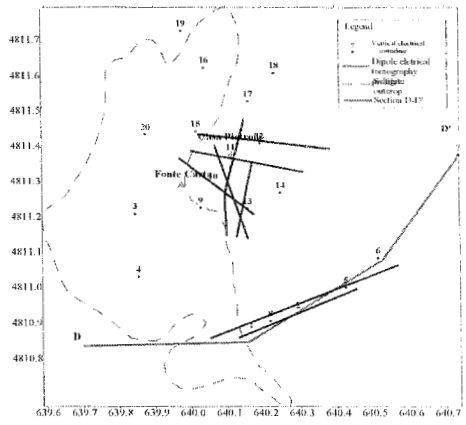

Figure 1b: Location of DET profiles and electrical soundings. The dashed line represents the plan view of the laccolith. (Di Filippo et al., 1998)

Observations related to strength and stiffness change in the host clay approaching the magmatic intrusion were made at all sites; detailed study of stress – related effects were concentrated at Orciatico. Several boreholes were in fact drilled in different zones to evaluate the alteration sequence and the degree of alteration of the clay, with a view to relating them to the heat released (Fig. 1a)

Hydro-mechanical effects

Stress-related observations of all candidate analogue structures investigated have shown that the host mudstones become stiffer and more compact as the intrusive rock is approached. The amount of thermal alteration (be it a change in texture, mineralogy, or physico-chemical properties) is related primarily to the dimensions of the intrusive body and to the extent of the surrounding host mudstone. Other effects that may have contributed include the presence of water and the related possibility of vapour production during heating (most likely at Orciatico due to the comparatively shallow emplacement conditions, i.e. -100m).

Various length scales of cracks have been observed on the exposed surfaces of the analogues at Col du Perthus and Skye. A proportion of these cracks may be related to cooling-induced shrinkage and textural changes in the clay, with some now filled with minerals that have precipitated from circulating fluids (e.g. calcite).

At Orciatico, gas permeability investigations (mainly CO_2 Rn, and He) suggest the presence of relatively major emplacement-induced fractures at the laccolith/clay boundary, together with other fractures in the altered clays themselves (Fig.2a, b).

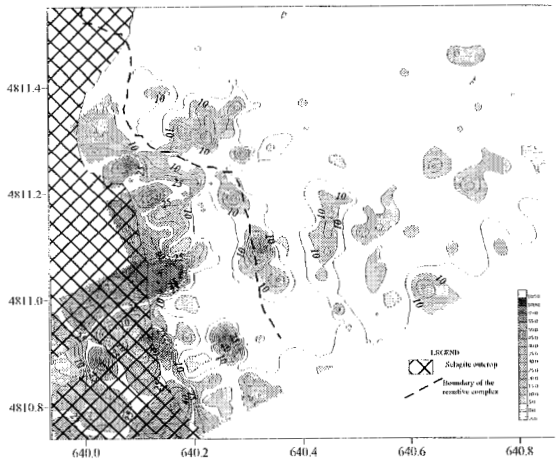

Figure 2a Radon (Bq/L) distribution in soil-gas. It is possible to note the presence of anomalous values (>25 Bq/L) in correspondence of the boundary of the resistive complex supposed on geoelectrical results. All over the north-eastern sector, in non metamorphosed clays, radon values are very similar to background values reported in literature (10-15 Bq/L).

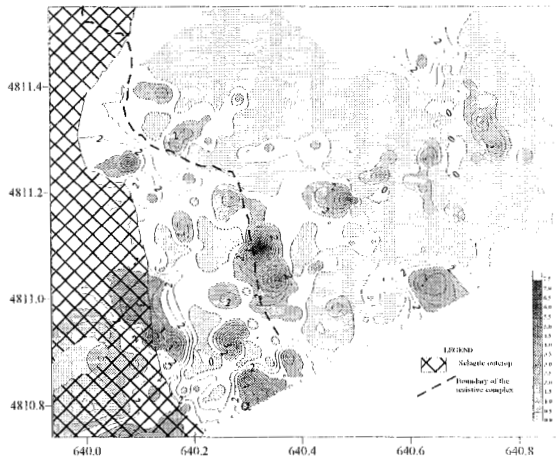

Figure2b Carbon dioxide (%, v/v) distribution in soil-gas. Highest values (>2 %,v/v) are mainly concentrated at the selagite-clay contact

Examination of borehole material from Orciatico shows the contact to be formed from severely altered clays (thermantites) and magmatic rock. The intrusive rock itself appears to be fractured (as a result of shrinkage due to cooling).

This may act as a preferential path for fluid flow. The presence of major fractures in the upper portion of the clay bed, acting as a preferential path for water flow, seems consistent with salinity distribution inferred from chemical analyses of pore water, Reeder *et al.*, 1998. In fact, studies of the porewater chemistry from the Orciatico analogue site (a relatively 'young' analogue) have shown that the original saline porewater, present when the intrusion was emplaced, is no longer present. Indeed, this appears to have been replaced by fresh water to a depth of at least 50 m, and possibly over 100 m.

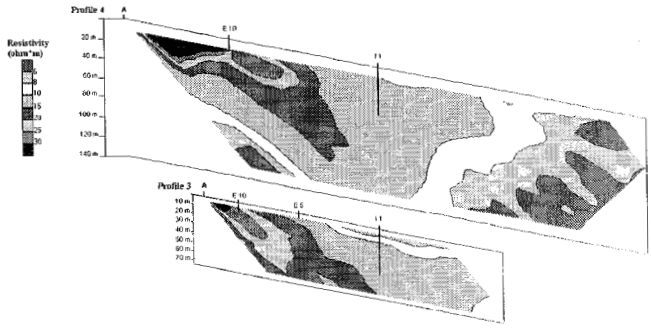

Figure 3 DET profiles 3 and 4: Resistivity decrease from intrusion to every direction.

Results from resistivity studies (Di Filippo *et al.*, 1998) suggest the possibility of a 'lens' of fresh porewater close to the Orciatico intrusion which becomes progressively more saline with distance (both lateral and vertical) from the intrusion (Fig. 3). This region of fresh porewater might define a modern day hydrogeologically-active zone. It may be possible that freshwater ingress into the clay has been aided by some intrusion-induced process (e.g. thermal cracking of the surrounding mudstones), and that the present-day hydrogeology reflects thermally-altered mudstones.

Thermomechanical response

Physical and mechanical properties of the mudstone were measured at Orciatico from the present day ground surface to the contact with the intrusive rock. Short–term laboratory tests to assess the thermo-mechanical effects of heating-cooling cycles on overconsolidated clays have shown that maximum overconsolidation stress of the clay rock is a good measure of its stress history, and the void ratio of the associated strain history (Del Olmo *et al.*, 1996).

Maximum palaeotemperature increases at the three sites have been reconstructed by the illite cristallinity and vitrinite reflectance methods (Kemp and Murphy, 1998, Baily, 1998). Also the disappearance of kaolinite has been used as an indicator of the past heating event.

Mechanical tests were generally limited to the portion of mudrock that did not undergo severe textural changes, and most probably represents the so-called 'thermal analogue' zone. As a consequence, borehole I-3 (Fig. 1a) material was not used (being predominantly intrusive rock), and neither was the 'contact' mudrock from boreholes I-4 and I-5. While for most of the clay samples, the carbonate content is constant (13%), changes are observed in the maximum pre-consolidation stress, void ratio and permeability (Fig. 6a,b,c,d).

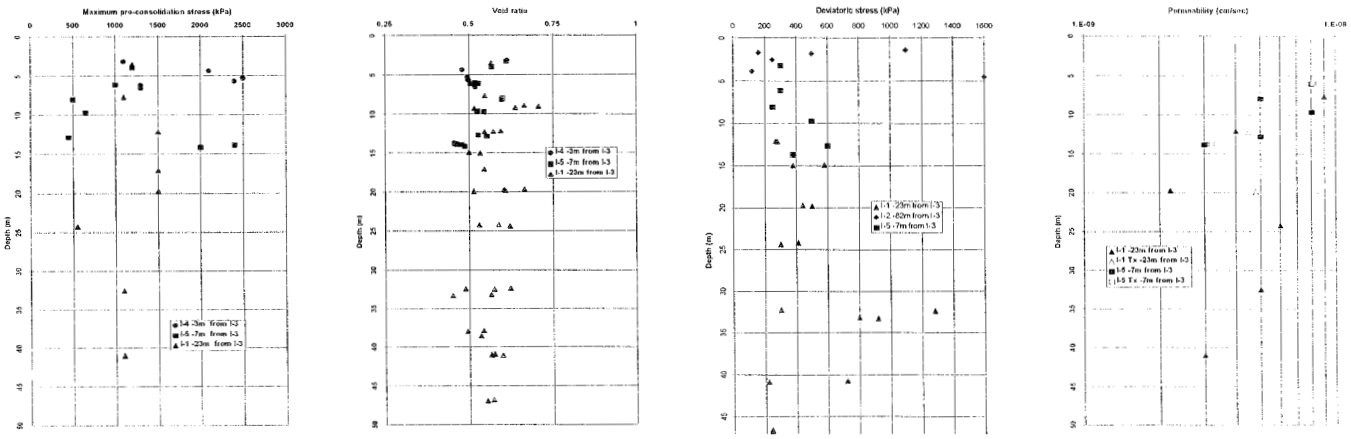

Figure 6a,b,c,d Maximum pre-consolidation stress (a); void ratio (b), devitoric stress (c), and permeability change versus depth along boreholes I-1; I-5 and I-4.

The maximum pre-compression stress ($\sigma'_v{}^{max}$) has been derived from the results of the oedometer tests. In borehole I-1, $\sigma'_v{}^{max}$ has a visible peak, reaching values of 1.7 MPa in the depth range 12–19 m. A local trend of decreasing void ratio may be observed in the depth range of increased $\sigma'_v{}^{max}$, which might be a signature of a past thermal consolidation event. This hypothesis does not contradict the observed absence of important mineralogical alterations, so long as the heating was mild. In borehole I-4, a similar peak, with higher values, located at 4-6 m depth might reveal a stronger thermal consolidation effect. Below this depth, changes in the clay texture and mineralogy should be considered in the interpretation of the observed sudden decrease of past pre-consolidation stress. An important amount of smectite in the contact zone may characterise the mechanically weaker rock observed. Borehole I-5 displays a pre-consolidation stress trend opposite to that of I-4. The observed gradient of $\sigma'_v{}^{max}$ is the opposite to that expected on the basis of short-term thermo-mechanical laboratory tests. The above observations would still be consistent with the appearance of smectite, this being possibly a stronger effect than the thermal consolidation one.

No effects of silica precipitation have been reported or observed at the Orciatico site. Permeability changes reflect void ratio changes. However, values stay approximately twice those of the unaffected clay, suggesting that this might be considered an effect of natural inhomogeneity within the clay formation.

Physico-mechanical changes in light of mineralogy and temperatures changes

The trends observed in geo-mechanical properties (such as the apparent maximum vertical pre-stress and related properties) were linked with information and data available on the mineralogy and palaeo-temperatures. Taking advantage of the topographic proximity of Borehole I-4 with 10 (Fig. 1a), and of the similarity of their geognostic profiles, trends of the above properties could be compared with quantitative mineralogic profiles already available for 10. For 10 it was possible also to retrieve a palaeo-temperature profile from previous data (Benvegnù F. *et al.*, 1988), which is in agreement with bounds established by investigations of ERM (Pellegrini *et al*, 1999, Bouchet *et al.*, 1999.).

A temperature of approximately 130°C is suggested for the interface between thermantite and clay. At 3.80 m from the contact with the intrusive rock, the temperature is estimated to be 400°C. The temperature distribution is quite uniform within a zone less than 7 m from the present surface, and reaches about 50°C at the present surface. Figure 7 shows that severe changes in mineralogy, temperatures above 100°C and changes in geomechanical properties, all tend to occur at the same location.

Comparing σ_v^{max} for the reference clay (evaluated as 1050 kPa) and those of I-4, it may be concluded that: three specimens have a higher σ_v^{max} (2100-2500 kPa) at a presumed temperature range of 80÷70 °C in non-morphosised clay. It is proposed that these specimens acquired their enhanced apparent preconsolidation stress through a heating–cooling cycle. Two specimens have a lower σ_v^{max} than that in the previous zone (1300 kPa) at a presumed temperature range of 100÷80 °C in the morphosised clay. This occurs where the rate of change of clay minerals is highest. It is important to note that the values of plasticity index, water content and void ratio, in this batch are all indistinctly different from those for the previous batch. It is proposed that these specimen acquired their apparent preconsolidation stress through a heating–cooling cycle, followed by re-smectitisation. Presence of smectite is notorious for weakness of clay soils, but it cannot at this stage be decided whether the material weakness should be attributed to it, or to the «scaly» nature of the clay, which may have been caused by hydrofracturing due to the hot fluid.

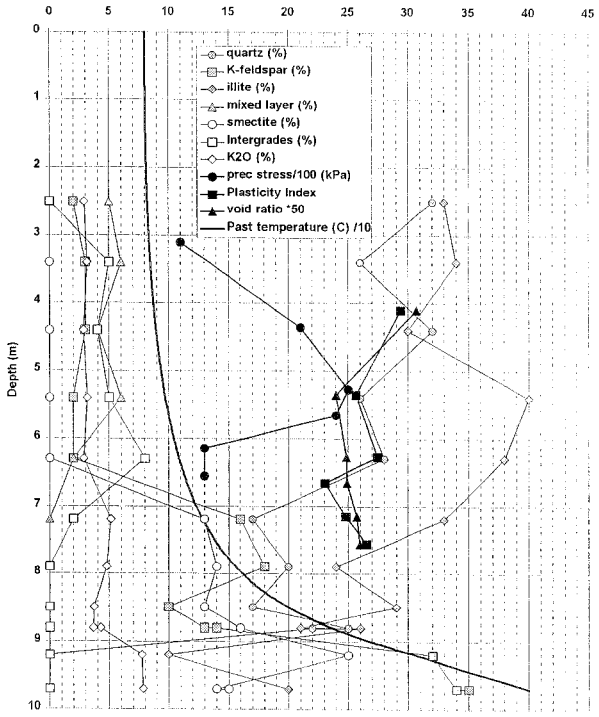

Figure 7: Changes of clay minerals (ENEA, 1983), palaeotemperature and geomechanical properties along borehole I-4. The scaling factor applied to incorporate all the data in a single graph is given in the legend

Short–term thermo-mechanical predictions and long–term results

Data obtained from HITEP thermo-mechanical tests have been processed to calibrate the thermo-mechanical short-term constitutive model by Hueckel and Borsetto, 1990 based on a critical state plasticity.

Maximum past temperatures have been reconstructed from the observed maximum pre-consolidation stresses, making use of this calibration. The *in situ* stress at the moment of intrusion has been assumed to coincide with the lowest value of σ_v^{max} encountered in the whole population of thermally affected specimens (450 kPa). This is consistent with the theory of plasticity of chemical or thermal softening processes. During this, σ_v^{max} decreases throughout the process causing the softening to be stopped, which must be then equal to the constant value of stress acting on the clay. This assumption leads to an overconsolidation ratio at the moment of intrusion of 2.33.

When clay was subjected to heating due to the magmatic intrusion, σ_v^{max} started to drop from the value of 1050 kPa. When σ_v^{max} reaches the value of the in situ stress, and the thermo-plastic process starts, the predicted temperature increase is equal to ΔT = 25. °C. All subsequent heating up to an undetermined maximum local temperature is thermo-plastic for which σ_v^{max} remains constant. However, all subsequent cooling is associated with an entirely elastic expansion of the yield domain, increasing σ_v^{max}. To reach σ_v^{max} = 2500 kPa the temperature should have grown; if the final ambient temperature was 20 °C, to the maximum heating temperature of 83 °C. The specimens of morphosised clay appear to have undergone a very similar cycle to the one just discussed. However, they were also subjected to chemical process, as smectite formation, which brought their σ_v^{max} to a much lower level (1330 kPa). Using a chemo-plasticity model (Hueckel T., 1997) such process may be modelled in a very similar way as the thermal effect.

As for borehole I-1, in the zone under investigation from 12.1-19.74 m depth, by applying the same procedure as above, the maximum absolute temperature was estimated to be near 50 °C.

Conclusions

Physico-mechanical changes, evaluated in light of mineralogy and temperatures changes, showed a decrease in the maximum pre-consolidation stress is observed to correspond with major mineralogical and textural changes (characterised by the appearance of smectite and disappearance of illite). The clay becomes very stiff and compact, but potentially weaker and more plastic upon failure. At the contact with the intrusive rock, its texture is similar to that of a

brick. The cooler parts of the analogues (temperatures <100 °C, very mild mineralogic changes) are characterised by increased overconsolidation, leading to potentially more brittle behaviour upon local failure, but also to increased strength before such a failure mechanism is displayed.

Temperatures predicted by the short-term thermomechanical model (Borsetto and Hueckel, 1990) are in reasonable agreement with measured palaeotemperature data, indicating the mechanical stability of the clay in the thermally-altered (though not severely metamorphosed) zone.

In conclusion, certain findings of this study suggest that a MAT of approximately 100 °C in the near-field is a reasonable value to avoid uncontrolled modifications of the host clay barriers. As a consequence, short–term thermomechanical effects can be used to explain the longer-term effects. However, slight modifications to mudstone permeability can not be ruled out even under such limiting conditions.

At higher temperatures, effects are more pronounced. Several have been observed which can stimulate conceptual modelling of long–term overheating. However, they are dependent on the heating rate and on the heating flux actually available, which needs to be quantified further.

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Mineralogical and chemical changes due to volcanic intrusion into clay formations

A Bouchet[1], J-Y Boisson[2], S J Kemp[3], J-C Parneix[1], R Pellegrini[4], C Rochelle[3]

[1]*E.R.M. Espace 10- République 2, Rue Albin Haller, 86000 Poitiers, France*
[2]*I.P.S.N, BP 6, 92265 Fontenay-aux-Roses, France*
[3]*B.G.S, Kingsley Dunham Centre, Keyworth, Nottingham, United Kingdom, NG12 5GG*
[4]*I.S.M.E.S, via Pastrengo, 9, 24068 Seriate (BG), Italy*

Introduction

Natural analogue investigations of thermal effects on clays are important when considering possible conditions within a deep underground repository for heat-emitting radioactive wastes, where clays might be used as either host rock or buffer/backfill. The thermal effects on clays have been based previously on diagenetic studies, with literature data usually describing the transformation of smectites or interstratified illite/smectite (I/S) towards more illitic minerals. The present study (EC/CEA contract FI4W-CT95-0014) involves a variety of different clay rocks intruded by volcanic intrusions, and attempts to identify reaction processes common to all sites. It also aims to compare new observations from thermal analogues with information from typical diagenetic studies.

Analogue sites

Studies have been undertaken of three analogue sites [Pliocene clays, Orciatico, Tuscany, Italy; Toarcian shales, Col du Perthus, north east of Lodève area, Hérault, France; and Jurassic mudstones, Lùb Score, Isle of Skye, Scotland]. The Isle of Skye site consists of Jurassic clays (up to 10 cm thick) and limestones, cut by a Tertiary basaltic intrusion (2 m wide). The Col du Perthus site consists of Toarcian indurated claystones cross-cut by a 1.1 m wide, relatively young basaltic dyke (possibly 1.7 to 2 Ma in age: Gillot, 1974). At Orciatico, the intrusive system (Pliocene selagite sill/laccolith, about 4.1 Ma in age) covers approximately 0.5 km^2 in a Pliocenic clay formation. On Skye and at Col du Perthus, surface outcrops were sampled, whereas the samples from Orciatico come mainly from five boreholes.

Mineralogical and geochemical studies show important changes (contact metamorphism assemblage with mainly diopside and feldspar) close to the flanks of the intrusion (a few centimetres for the Col du Perthus and Skye sites), with more minor changes extending up to distances similar to the width of the intrusion. At Orciatico, a transformed clay rock (named 'thermantite', and at least 1 m thick in places) is developed at the contact with the intrusion.

Methods

Investigation of thermally-induced clay mineral transformations required a specific approach, and Figure 1 shows the methods employed for this task. A first set of methods concerned analyses of the bulk rock, and included: quantitative chemical analyses of major elements, cation exchange capacity (C.E.C.) and carbonate content measurements. Illite crystallinity and vitrinite reflectance were also performed on the samples. A second set of methods were aimed at acquiring point data on mineralogy and chemistry, and included: petrographic observations of thin sections from indurated material using optical microscopy and scanning electron microscopy (SEM) to investigate a few sites previously selected with the optical microscope. X-ray diffraction (XRD) analyses have also been undertaken. Acquisition of X-ray diffraction patterns on both randomly oriented powders and on oriented-samples (air-dried state, and after ethylene glycol solvation) was done to identify precisely the various clay minerals. The oriented-sample diffraction patterns were then 'decomposed' with

DECOMPXR, a decomposition programme conceived by B Lanson (1992, 1997), and designed to deal with clay minerals that have peaks with a very variable full width at half maximum intensity (from 0.1° 2□ to several ° 2□).

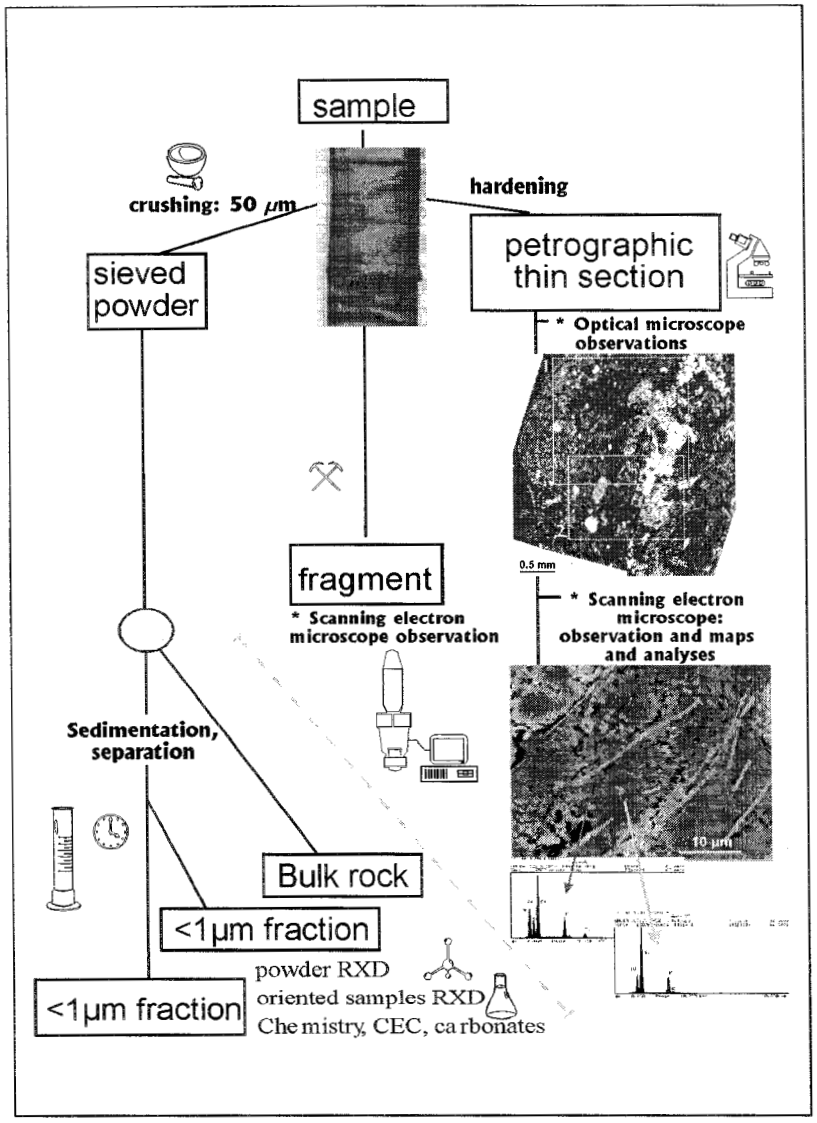


Figure 1. Methods used for the study of clay samples.

Analytical results

The main results are shown on Figures 2 (XRD patterns) and 3 (evolution of some mineralogical and physico-chimical characteristics of the samples).

Isle of Skye site

Eighteen samples were analysed from both sides of the Lùb Score dyke so as to verify the influence of the geometry of the studied geological structure. Based upon the mineralogical composition of the rock, the original basaltic intrusion temperature was estimated to be about 1200/1250 °C using the basalt crystallisation diagram (Weill et al., 1980).

From the smectite-bearing nature of the original Skye clay (randomly interstratified illite/smectite: R=0 I/S), the main trends (Figure 2) as a result of heating are: an increase in the quantity of newly-formed swelling clay minerals ("smectite") and a decrease in the

quantity of kaolinite in the vicinity of the intrusion. It appears that the quantity of phyllosilicates of the mica group (mica ± illite ± I/S >90% of illite) was modified to a lesser degree. In these samples, significant quantities of newly crystallised feldspars were also observed. Near the intrusion, the (060) peaks of clay minerals clearly show the presence of a mixture of two smectites: one is dioctahedral (aluminous) and the other is trioctahedral (ferro-magnesian; newly crystallised smectite of the saponite group). Removal of pyrite and calcite from samples adjacent to the intrusion may reflect the ingress of modern oxidising groundwaters.

The smectite content in the host mudstone remained almost unchanged at distances of 3 meters or more from the intrusion, but increased continuously in close proximity to the intrusion. Additional parameters (surface area and C.E.C. measurements) exhibit similar trends (Figure 3), with the C.E.C. being higher to the NE side of the dyke than to the SW. The abundance of MgO and Fe_2O_3 both increase close to the contact.

By using a combination of illite crystallinity, mineral stability and vitrinite reflectance, the thermal history of the mudstone was determined based upon a background palaeotemperature of about 50 °C; the intrusion caused: >300 °C within ~0.25-~0.5 m of the dyke, >200 °C within 1-3 m of the dyke, and >100 °C within ~ 6+ m of the dyke.

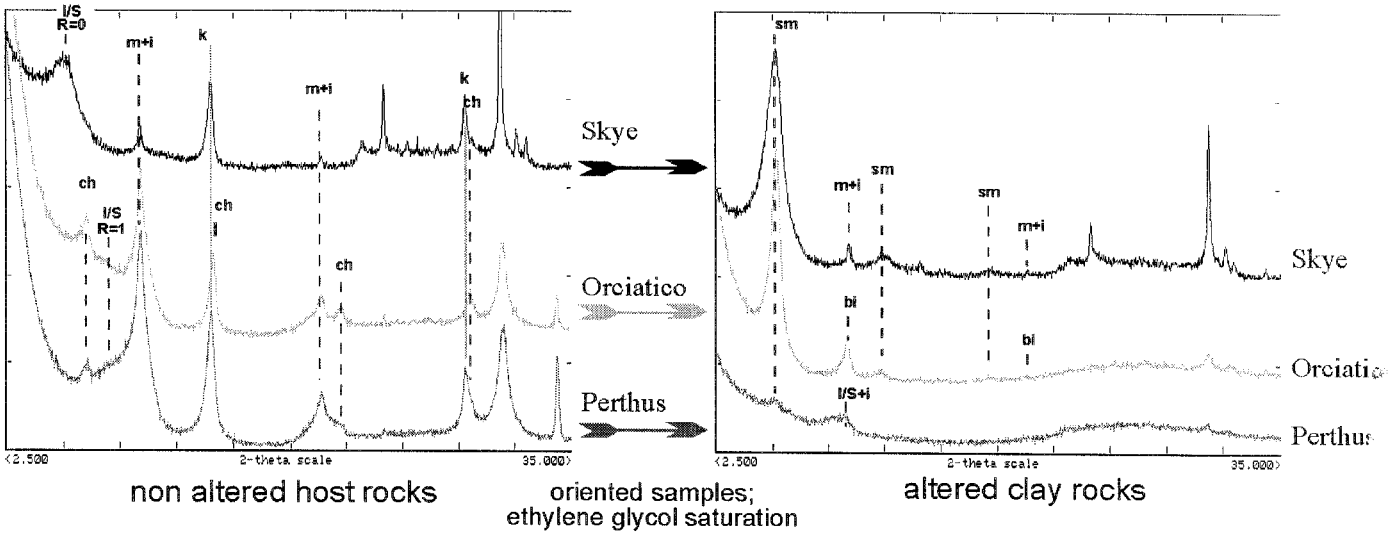
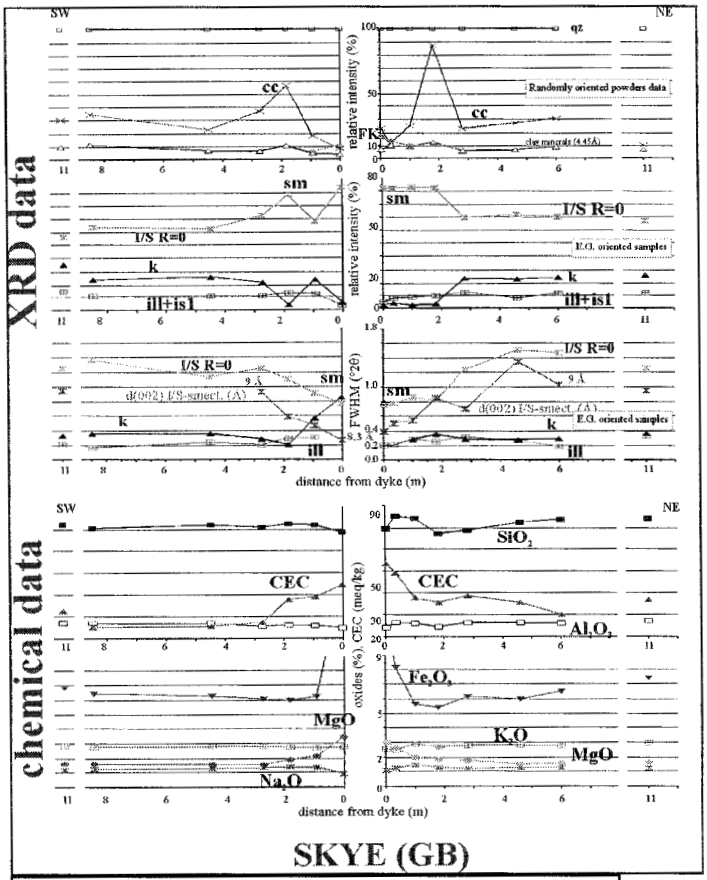


Figure 2. XRD patterns (glycol-saturated oriented samples) of the non-altered clay host rocks (left) and of the altered (heated) host rocks for the three analogue sites studied. Minerals: ch: chlorite; m+i: micas (detrital origin) and illite [±illite-rich I/S minerals]; k: kaolinite; I/S R=0: random I/S minerals; I/S R=1: ordered I/S minerals; sm: smectite.

Col du Perthus

The host mudstone at this site is an indurated argillaceous rock with carbonate content of approx. 10%, and very low water content (3 to 5%). Mineralogical investigation of two profiles around the basaltic intrusion (approximately 1.10m width) revealed the following trends:

- disappearance of kaolinite, quartz and calcite;
- at some of the sites, formation of diopside ± plagioclase (albite) ± calcium silicate [?] at the contact with the basaltic intrusion (limited to the first centimetres);
- evolution of the illite/smectite mixed-layer minerals (I/S R=1) towards more micaceous compositions;
- formation of a swelling clay mineral ("smectite" of saponite type) in the vicinity of the basaltic intrusion.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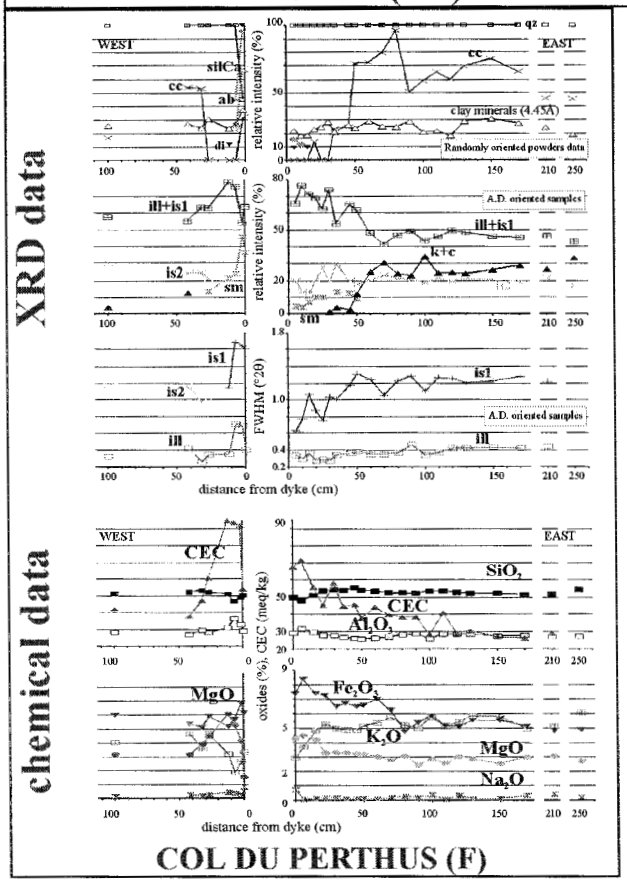
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COL DU PERTHUS (F)

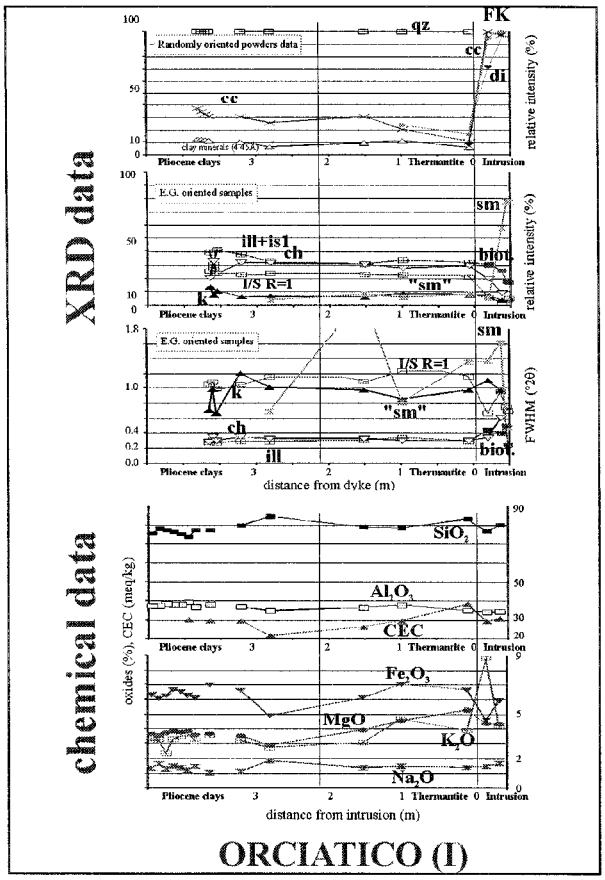

Figure 3. Evolution of XRD patterns and of chemical data in the three sites as a function of the distance from the intrusion. For Skye and Col du Perthus, data of both sides of the dyke are given; for Orciatico, the data are a compilation of information from boreholes I1 (unaltered Pliocene clays) and I5. Abbreviations: ch: chlorite; ill: illite; I/S R=0: random I/S minerals; I/S R=1, IS1, IS2: ordered I/S minerals; sm: smectite; k: kaolinite; c: chlorite; cc: calcite; qz: quartz; di: diopside; FK: K-feldspars; d(002)I/S-smect(Å): position (Å) of the 002 peak of smectite and of I/S R=0; AD: air dried; EG: ethylene-glycol; FWHM: full width at half maximum intensity (XRD peaks); C.E.C.: cation exchange capacity.

It is noteworthy that the limited increase in the C.E.C. was a more sensitive indicator of proximity to the intrusion than was the detection of smectite (saponite) by X-ray diffraction methods. The changes in C.E.C. were also mirrored by increases in iron and magnesium contents. This limited increase in the C.E.C. was also related to the disappearance (more or less complete) of kaolinite and chlorite, which have a very limited exchange capacity.

On the east side of Col du Perthus dyke, maximum measured temperatures are in a range 200-250 °C based on vitrinite reflectance measurements (Baily, 1998a), but only about 140 °C based on an Illite cristallinity method (Kemp and Murphy, 1998). On the western side, a temperature of about 350-400 °C was given by Correia and Maury (1975). Considering a temperature of 1200 °C for the original liquid basalt, a width of 1.20 m for the dyke and a thermal diffusivity of 0.0023 m²/h, the maximum temperature probably reached in the sediment, calculated with Pytte's model (1982), is about 600 °C. A time period of one month is sufficient for this maximum temperature to be reached. After one year, the temperature in the nearest 200cm of sediment is predicted to be around 120 °C.

All these methods cannot give a precise temperature for the alteration effects, but a range of temperature and time where mineralogical changes take place can be proposed, with mineralogical transformations affecting clays up to 100 cm away from the dyke and taking place at temperatures between 100 and 250 °C. The time duration of transformations is probably very short (in the order of a few years).

The petrographic study of the intruded clays (Figure 4a) show the presence of fractures (of various degrees of fill) in the first few centimetres adjacent to the contact with the intrusion. These cracks are less abundant as the distance from the intrusion (and hence drop in temperature) increases. It was also observed that both sides of the wall rock were not transformed with the same intensity. Correia and Maury (1975) described the host mudstone on the west side the dyke: at macroscopic scale, the intruded clay was bleached over several few centimetres (cornean with albite and diopside), and this phenomenon was not so intense

on the east side of the dyke. It is suspected that heat distribution was not symmetrical on either side of the dyke.

The above highlights a limitation of a purely mineralogical approach, and indicates the importance of taking other processes into account, such as the potential circulation of hot fluids (Best, 1982). Considering the geometry of the analogue, it appears that the relative orientation of the dyke relative to the host rock are significant, the curved shape of the basaltic dyke creating a dissymmetry. On the east side, the wall rock allowed release of fluids (and hence heat and possibly elements), whereas on the west side this was restricted, possibly because of the presence of the dyke itself which acted as an obstacle to this release. This implies that the wall rock had a minimum of permeability, in which case the release of heat and fluids will limit the transformations while facilitating the transport of elements (Best, 1982).

Orciatico

The aim of the study of samples from Orciatico was to characterise the mineralogical evolution of a Pliocenic clay formation intruded by a small laccolith. Although locally termed 'selagite', based upon its mineralogy this intrusive rock appears to be a lamprophyre of "minette" type (Velde, 1967; Peccerillo et al., 1998), and is generally formed under high water pressures. The observation of calcite in the outer part of the rock appears to indicate that chemical exchanges occurred between intruded and intrusive rock. A highly metamorphosed clay rock (locally termed 'thermantite') constitutes an aureole around the intrusion.

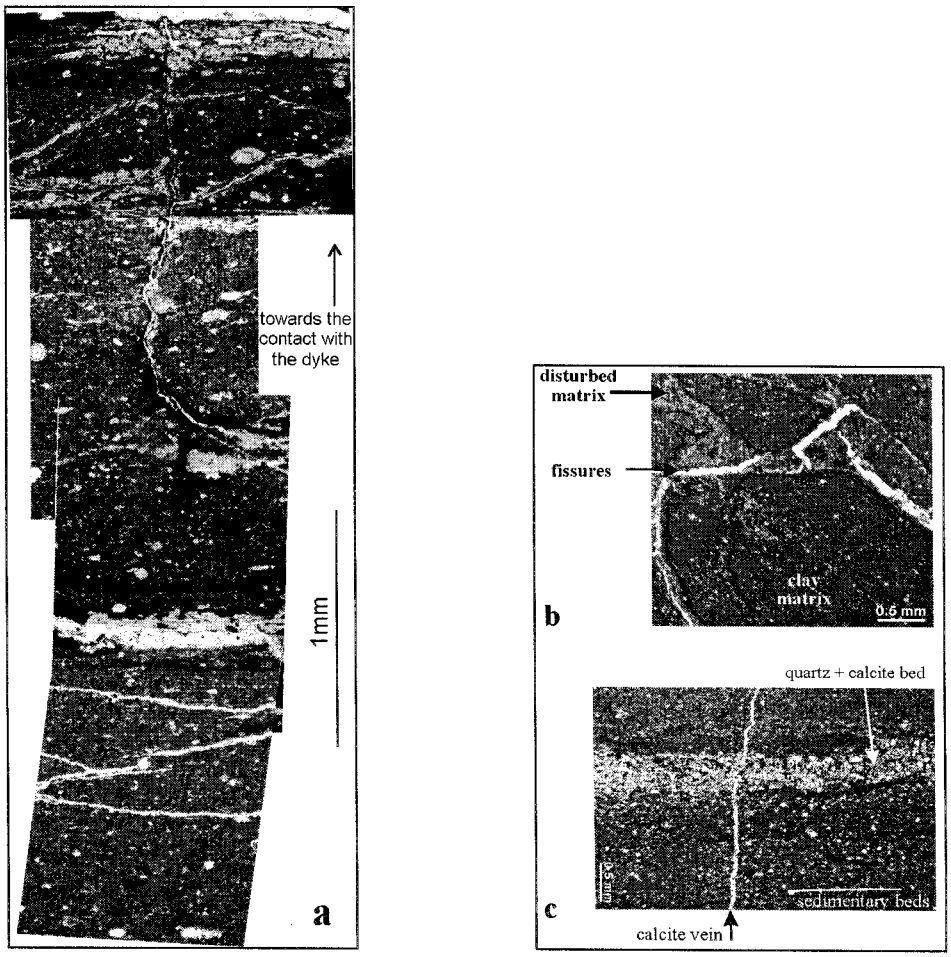

Figure 4. Photomicrograph showing the structure of the intruded clays. a: Col du Perthus: heterogeneous aspect of the Toarcian clay towards the contact with

the intrusion.. b: Orciatico: structure of the unaltered Pliocene clays. c: Orciatico: structure of the thermantite.

In unaltered Pliocene host rocks, minerals identified from randomly oriented powder XRD patterns include quartz, calcite, feldspars (plagioclases), and possibly pyrite and/or hematite, dolomite and/or ankerite. The following clay minerals were also identified by X-ray diffraction, on oriented sample diffraction patterns for the Pliocene argillites representative of the regional background (from borehole I1): ordered mixed-layer illite/smectite (I/S R=1) with more than 90 % of illite (XRD peaks of this mineral are superimposed to that of illite stricto sensu and of detrital micas also present in the rock), ordered mixed-layer illite/smectite (I/S R=1) with ~ 70% of illite, chlorite and kaolinite.

The primary mineralogy shows several effects due to heating by the intrusion: kaolinite disappears near to the intrusion, and chlorite is replaced by mixed layered chlorite/smectite. In the thermantite, the R=1 I/S minerals and illite are totally replaced, while biotite crystallises. A trioctahedral smectite (saponite) and a dioctahedral smectite (beidellite or montmorillonite) also coexist in the thermantite. Of the non-clay minerals, small quantities of diopside and K-feldspars are present in the host mudstone near the intrusion.

Analysis of overall chemical compositions shows that in the thermantite, the amounts of potassium increase strongly, this element being more abundant in the volcanic rock than in the Pliocenic formation (Figure 3); MgO and Fe_2O_3 also increase in the same zone. Thermally-induced changes in the distribution of the other chemical elements are less strongly evident. Nevertheless, illitisation does not take place, even with the presence of I/S minerals potentially available for such a transformation. The reason could be probably the control of potassium by biotite or K-feldspar, or perhaps of the relatively short duration of the heating which did not allow the reaction to continue to completeness.

In the thermantite, the newly formed smectite is trioctahedral (magnesian and/or ferrous), but a dioctahedral smectite is also present. The mica observed in the thermantite is biotite, which can be easily distinguished from dioctahedral micas (illite, muscovite, etc) because the relative intensity of its (002) peak (5 Å) which is much lower than would be the (002) peak of a dioctahedral mica (Figure 2).

Vitrinite reflectance data give background paleotemperatures in the range of 50-85 °C, but close to the contact with the intrusion these rise to >200 °C in the thermantite at the bottom of borehole I5 (Baily, 1988b).

The structure of the unaltered clay rocks is characterised by the presence of many fissures (possibly shrinkage cracks) sometimes filled with what appears to be reworked from the Pliocene mudstones (Figure 4b). The width of fissures is between 10 - 50µm, while the reworked zones can be 500µm wide. In the thermantite, the main sedimentary structures of the wall rock are preserved. Calcite seems to fill pre-existing fissures that cross cut the stratigraphy, and indicate the existence of late-stage circulation of carbonated fluids. A calcite-rich fringe, discontinuous and of variable thickness, underlines the contact between the thermantite and the intrusive rock.

Discussion and conclusions

Previous studies of clays that have been intruded and heated by volcanic rocks (Pytte, 1982; Pytte and Reynolds, 1989) have described transformations of smectite and illite/smectite minerals. In general, where transformations were observed, they corresponded to illitisation, the reaction products being I/S ranging from randomly interstratified minerals (20% of illite) to illite. Studies carried out on sites that have undergone hydrothermal

alterations have also shown illite/smectite mixed-layer minerals evolving according to similar trends (Horton, 1985; Bouchet et al., 1988). However, the results from the present study appear to indicate a different type of reaction.

The smectite-bearing mudstones on Skye are analogous to some host-rocks being considered in other parts of Europe for the disposal of heat-emitting radioactive waste, and might initially be expected to react in a similar way to the above examples. However, the wall rocks did not show any obvious illitisation phenomenon, in fact they turned out to be smectite-enriched.

Toarcian argilites from the Col du Perthus show the formation of illite, but also a swelling mineral (saponite) close to the contact with the intrusion. Although the formation of illite follows that traditionally described in the literature, it is only very limited in extent.

At Orciatico, the wall rock did not show any obvious illitisation phenomenon, again appearing to be smectite-enriched. In fact, illite minerals (i.e. illite stricto sensu and mixed-layered I/S) were consumed by the reaction (as well as chlorite). The Orciatico site can thus be compared to that of the Lùb Score site on the Isle of Skye. Another interesting observation concerning Orciatico site, is the presence of chlorite in the initial rock which has been transformed into chlorite/smectite mixed layer and then into saponite. This is a reverse reaction sequence compared to normal diagenetic reactions (Velde, 1995). It is suspected that short timescales of reaction and localised chemical equilibria are probably account for such observations (in essence, the reaction has been 'frozen' at a state part way through the expected reaction sequence).

In the present study, although the initial clay minerals are different, the three sites show similar reactions:

1 on Skye, an assemblage [R=0 I/S (rich in smectite) + kaolinite + micas] evolves to give dioctahedral (Al) and trioctahedral (Fe-Mg) smectites while kaolinite disappears;

2 at Col du Perthus, from an assemblage of [illite + R=1 I/S (S < 30%) + micas + kaolinite + chlorite], the mixed-layer I/S is enriched in illite while kaolinite disappears. At 5 cm from the contact, the clay is characterised by presence of a metamorphic assemblage and a trioctahedral swelling phase (saponite type);

3 at Orciatico, the initial assemblage [R=1 I/S (S = 30% max.) + illite + chlorite + kaolinite + micas] is replaced by a mixture of dioctahedral (Al) + trioctahedral (Fe-Mg) smectites accompanied by biotite. Other metamorphic reaction products (K-feldspars ± diopside) are also present. Chemical exchanges (fluid circulation) between the wall rock and intrusive rock appear to have taken place.

While literature data suggest the illitisation of mixed-layer minerals, an important additional observation from the sites studied in this investigation (different clay materials and brief and intense thermal events) is the formation of a new assemblage including a swelling smectite-rich phase. Two hypotheses for the formation of this smectite phase may be evoked: *i*) retrograde or 'back' reactions either during the temperature decrease following the major thermal event, or some time afterwards; *ii*) short-duration kinetically-influenced phyllosilicate (I/S series) transformations (Meunier *et al.*, 1998) occurring during the thermal event, and in contrast to the relatively slow mineral reactions that take place during diagenesis. At present, it is not possible to exclude either of these hypotheses without further detailed investigation. What is important however, is that in some circumstances it is possible to form a secondary phase with swelling characteristics, rather than just non-swelling phases. Such an observation has implications when considering repository performance assessment.

The above two hypotheses can be viewed in the light of control by chemical thermodynamics versus reaction kinetics. The former essentially reflects equilibrium

conditions, where phases stable at high temperatures react to form new phases which are more stable at the low temperatures existing after the thermal event. The latter hypothesis reflects non-equilibrium conditions controlled by the rates (kinetics) of reactions, where a particular reaction has been stopped before reaching completion. Partly because clay mineral evolution controlled by reaction kinetics is less well described in the literature, the following paragraphs concentrate on this approach, and aim to show how such processes might have been operating at the analogue sites studied.

In order to highlight changes in the mudstones studied, the chemical compositions of the samples from the three sites have been plotted on the M^{+}-4Si-R^{2+} system (described by Meunier and Velde, 1989). Samples are represented in four main groups: "intrusive rock", "altered host rock", "partially altered host rock", and "unaltered host rock" (Figure 5). For the Skye and Col du Perthus data, the intrusion and the wall rock compositions are clearly disconnected. In the case of the Orciatico data, the thermantite composition area is partially overlapped by those of minette and of Pliocenic clays, suggesting the existence of chemical exchanges during the intrusive phase. Note that because of the presence of pyrite in the clays, the composition areas are slightly shifted towards the R^{2+} pole.

Recently, Meunier et al. (1998) have shown notable differences between observations of reactions resulting from diagenesis and from short-term laboratory experiments. During diagenesis, I/S minerals belong to the illite/montmorillonite series (I/Mo). The literature review made by these authors shows that, under the action of a brief thermal event, the reactions will not have sufficient time to produce illite, but instead a typical assemblage of beidellite + saponite + quartz forms. Beidellite is subsequently susceptible to reaction to form interstratified muscovite/beidellite (Mu/Be).

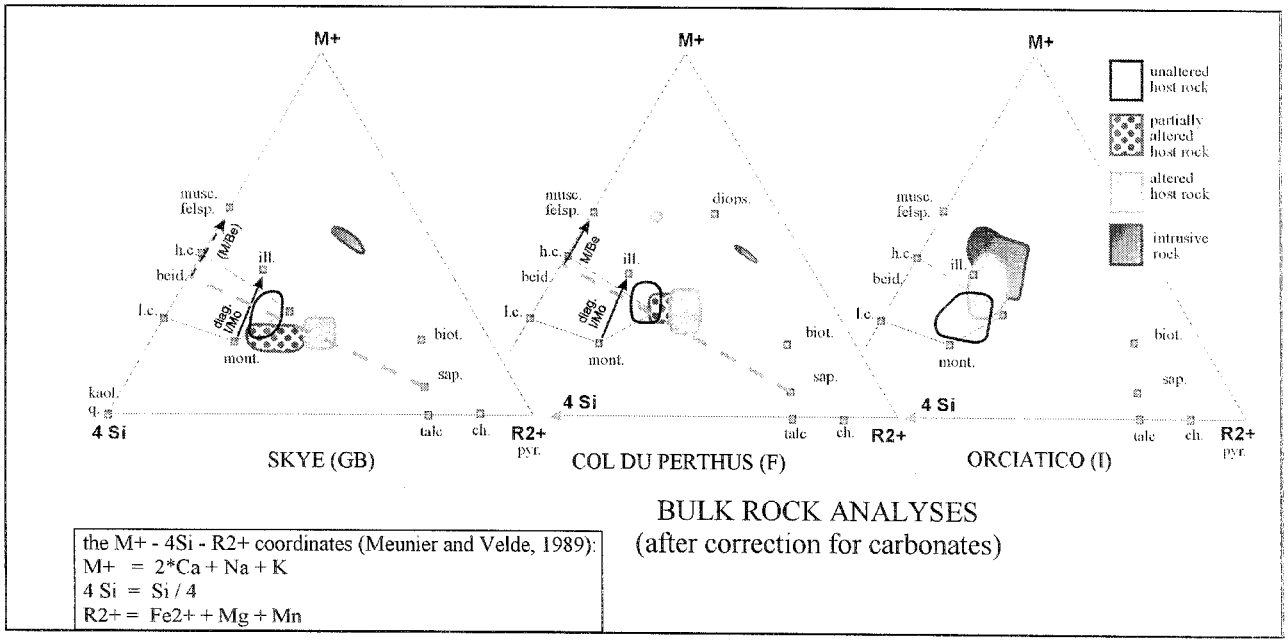

Figure 5: Summary of Skye, Col du Perthus and Orciatico data. Chemical composition of the samples studied is plotted on the M^{+}-4Si-R^{2+} system (iron as Fe^{2+}; CaO content of calcite substracted). The shaded areas represent the unaltered, partially altered and fully altered clay host rocks, and the intrusive rock compositions. The theoretical composition of certain important minerals is also presented. Abbreviations: q: quartz; kaol: kaolinite; beid: beidellite; mont: montmorillonite; h.c.: high charge; l.c.: low charge; ill: illite; musc: muscovite; felsp: felspar; biot: biotite; sap: saponite; ch: chlorite; pyr: pyrite

Considering the theoretical structural formulae for these minerals (see Figure 6), we can describe the reaction to show how a magnesium-bearing mineral (I/Mo) forms two phases, a "purely" aluminous dioctahedral smectite (beidellite) and a magnesian trioctahedral smectite (saponite) [step 2.1 on Figure 6]. As the phyllosilicates produced by the reaction are less Si-rich than montmorillonite, quartz is also produced by the reaction.

Consider now the diagenetic reaction (montmorillonite => I/S) being stopped at a given stage (as a result of geological conditions [step 1 on Figure 6]). The newly formed phyllosilicates appear to crystallise very rapidly compared to illite/smectite (the latter appearing to be the product of a slow reaction). A supply of potassium is necessary to form an interstratified muscovite/beidellite at the expense of beidellite [step 2.2a on Figure 6]. Through the lack of potassium, experiments conducted by Howard and Roy (1985) showed the formation, in an interstratified mineral, of high-charge smectite layers from low-charge smectite layers. As already seen for the smectites, the mica component (muscovite) of the newly formed mixed-layer mineral (Mu/Be, formed from beidellite) does not contain magnesium. Magnesium (in saponite at the first step of the reaction) is included into chlorite at the end of the evolution (if this evolution reaches the possible ultimate step [step 2.2b on Figure 6]. Although supply of magnesium from the intrusion can not be definitively excluded (through chemical exchanges, such as at Orciatico), the migration of this element within the clay under the effect of a thermal gradient has already demontrated (Bouchet *et al.*, 1992), and similar migration of Mg was obtained experimentally by Goffé et al. (1987) at higher temperatures.

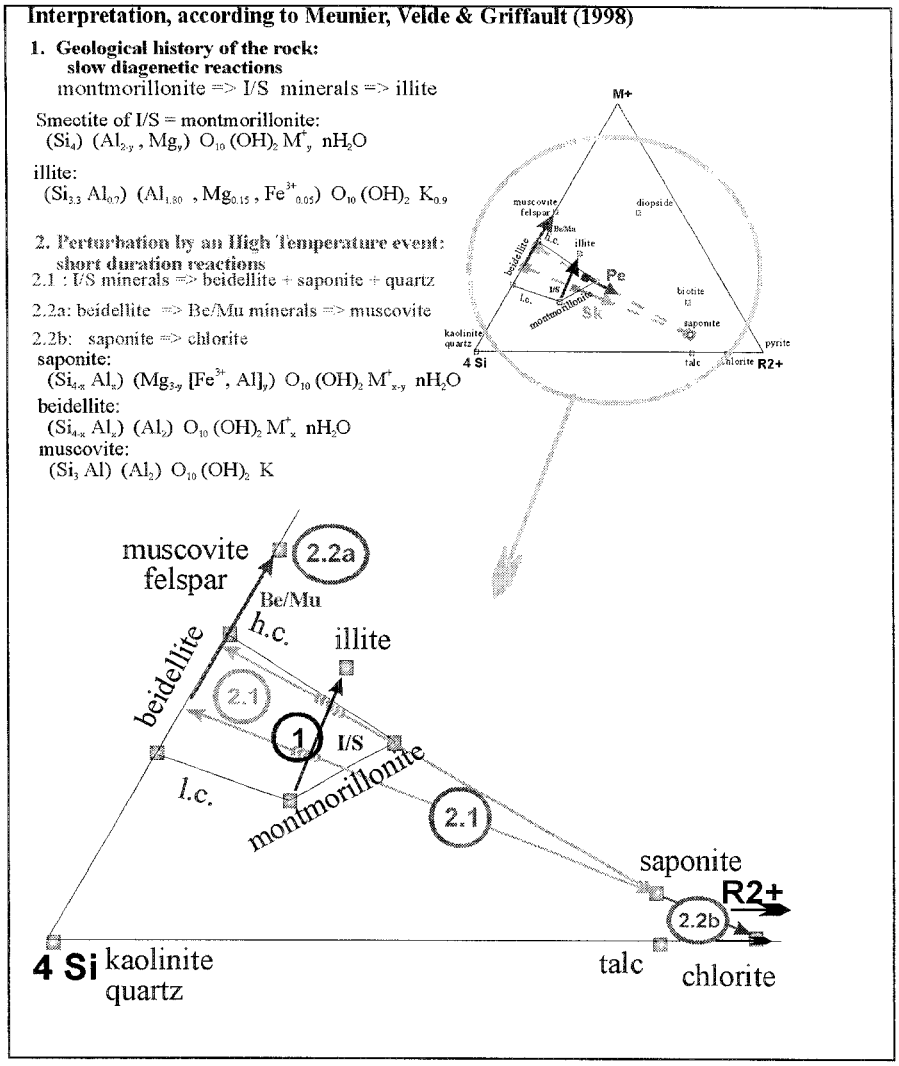

Figure 6. After Meunier et al. (1998)*: Possible evolution of the chemical composition of the I/S minerals plotted in the* M^{+}*-4Si-*R^{2+} *system.*

The data from the Skye and Col du Perthus sites can be interpreted in this way. Near a volcanic intrusion, the heating times are short (compared to geological timescales), and therefore the newly crystallised smectites could be the non-transformed initial assemblages generated under the influence of the magmatic body.

Such a scenario is plotted in Figures 5 and 6. On these, the montmorillonite (smectite as a starting material)-illite line represents compositions of diagenetic I/S minerals (I/Mo, = non altered clay material), whereas the saponite-beidellite line represents the theoretical composition of a recently formed assemblage within the altered wall rock. The beidellite-muscovite line represents the compositions of interstratified minerals (M/Be, in which the smectite is beidellite) which could crystallise later if conditions were favourable (i.e. temperatures remained high and K amount was sufficient). For the Skye site, the presence of such phases was not demonstrated; for the Perthus site, it is supposed that the newly formed micaceous material has a M/Be composition. Nevertheless, it must be noted that discrimination between montmorillonite and beidellite was not achieved in the present study. Therefore, additional work is needed to improve the application of these hypotheses to the Skye and Col du Perthus analogue sites.

Close to the intrusion, physico-chemical measurements confirm the clay mineralogical data (Mg enrichment and notably C.E.C. increase), and phyllosilicate transformations are accompanied by decreasing concentrations of carbonates and quartz. In addition, asymmetrical distribution of the alteration on each side of the intrusions (mainly at the Col du Perthus site, but also to a lesser extent on Skye) highlights the importance of the geometry of the system, i.e. conduction or resistance to the heat-flow from the intrusion, which modifies the duration of reactions occurring at high temperatures. Previous work by Leoni et al. (1986) focused on samples taken from various boreholes drilled in the immediate vicinity of the intrusion, possibly from the thermantite (metamorphosed clay) immediately above the intrusion, where the contact metamorphism of the wall rock can be very intense and produce plagioclases-pyroxenes-biotite hornfels facies. The intensity of the metamorphism and the thickness of altered rock (several meters) observed by Leoni et al. (1986) were much greater than those observed during the present study. The boreholes studied in this investigation concentrated on the edge of the laccolith, while those studied by Leoni et al. (1986) were located nearer the center of the system.

Results from this study indicate that physico-chemical and mineralogical characteristics linked to a short duration, large temperature increase (several hundred degrees), lead to the crystallisation of swelling phases (smectites) with an high retention capacity. At temperatures lower than 100 °C, no major mineral and chemical modifications were observed; indicating that the clay mineralogy of the three sites is quite stable under such temperatures over very long time periods (as under diagenetic conditions), and tends to confirming literature data. Although further work is required to confirm the exact reaction mechanisms operating, these observations could constitute positive points for repository performance assessment. Instead of assumed thermally-induced illitisation and loss of swelling capacity, there may instead be potential for secondary smectite formation.

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III.3. Current Status of Three Major Natural Analogue Projects

III.3.1. Palmottu Natural Analogue Project

Palmottu natural analogue project - geological setting and overview
R Blomqvist, T Ruskeeniemi, GSF (FIN) and J A T Smellie, Conterra AB (S)

Uranium mineralogy with implications for mobilisation of uranium at Palmottu
T Ruskeeniemi, A Lindberg, GSF (FIN); L Perez del Villar, CIEMAT (E); R Blomqvist, GSF (FIN); J Suksi, UH (FIN); A Blyth, UW (CAN) and E Cera, QuantiSci (E)

Hydrogeochemical interpretation of groundwater at Palmottu
P Pitkänen, VTT (FIN); J Kaija, R Blomqvist, GSF (FIN); J A T Smellie, Conterra (S); S K Frape, UW (CAN); M Laaksoharju, Intera KB (S); P Negrel, J Casanova, BRGM (F) and J Karhu, GSF (FIN)

Geochemical modelling of groundwater evolution in the Palmottu natural system
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Redox processes at the Palmottu uranium deposit
E Cera, QuantiSci (E), L Ahonen, GSF (FIN); C Rollin, J Bruno, QuantiSci (E); J Kaija and R Blomqvist, GSF (FIN)

Palaeohydrogeological implications for long-term hydrochemical stability at Palmottu
J A T Smellie, Conterra AB (S); R Blomqvist, GSF (FIN); S K Frape, UW (CAN); A Pitkänen, VTT (FIN); T Ruskeeniemi, GSF (FIN); J Suksi, UH (FIN); J Casanova, BRGM (F); M J Gimeno, CIEMAT (E) and J Kaija, GSF (FIN)

Testing trace element geochemical models at Oklo and Palmottu
J Bruno, D Arcos, E Cera, L Duro, S Jordana, C Rollin, QuantiSci (E); M J Gimeno, L Perez del Villar, J Peña, CIEMAT (E); L Ahonen, GSF (FIN); A Lunkkonen, VTT (FIN) and J Kaija, GSF (FIN)

The migration and fixation of uranium at the Palmottu natural analogue Site
D Read, Enterpris (UK); K Rasilainen, VTT (FIN); C Ayora, CSIC (E) and T Ruskeeniemi, GSF (FIN)

Palmottu natural analogue project – Geological setting and overview

R. Blomqvist[1], T. Ruskeeniemi[1] and J.A.T. Smellie[2]

[1]Geological Survey of Finland
[2] Conterra AB, Sweden

Abstract

The uranium deposit at Palmottu in SW Finland was investigated in order to improve the scientific basis for assessing the long-term performance of a disposal site for high-level nuclear waste in fractured crystalline bedrock. The study entailed assessing the present-day flow situation, and identifying and quantifying the processes related to radionuclide mobilisation and migration.

The Palmottu U-Th mineralisation is hosted by a Proterozoic (1.8 Ga) crystalline bedrock, mainly mica gneiss with granite and granite pegmatite veins. The mineralised part forms a vertical structure that extends to depths of at least 400m. Accordingly, it covers both near-surface oxidative conditions, and low-Eh reduced conditions. Ancient hydrothermal alteration of the uraninite deposit led to substantial re-mobilisation of uranium resulting in the formation of U(IV) silicate (coffinite) Over the last one million years, the site has experienced multiple glaciations during which a proportion of the uranium has been mobilised under oxidising conditions, leading to precipitation of U(VI) silicates (uranophane) at shallow depths. Volumetrically, significant amounts of uranium, mainly as U(IV), are also found in association with fracture coatings such as impure calcites, clays and iron oxy-hydroxides.

A site-specific groundwater flow model was constructed based on an integration of structural, hydrogeological and hydrogeochemical data. The upper 100m of the bedrock is characterised by dilute groundwater of HCO_3 type (the Upper Flow System). Calcium is the dominant cation near the surface changing to sodium in the lower part of this HCO_3 type groundwater zone. High tritium contents indicate a dynamic flow system, which penetrates to a depth of at least 200m in the southern part of the site (the Dynamic Deep Flow System). Below the HCO_3 type water body the groundwater is brackish, of Na-SO_4 or Na-Cl type, and both the hydrochemistry and isotopic results suggest long residence times, up to 10 000 a, and stagnant flow conditions (the Stagnant Flow System). High uranium concentrations (generally from 100-500 ppb) are associated with the oxidative HCO_3 ground-waters in the vicinity of the uranium mineralisation down to depths of 130 m. At greater depths, clearly reducing conditions (-300 mV) prevail, with low uranium concentrations (below 10 ppb).

The fact that the uranium mineralisation extends from an oxidising environment near the bedrock surface down through the redox transition zone into a reducing groundwater environment, allows the study of the full cycle of uranium chemistry under natural conditions. This extends from the interaction of oxidising waters with uranium dioxide ore and converting low solubility U(IV) into the more soluble uranyl ion, followed by transport and retardation processes along water-conducting fractures to deeper, reducing groundwater, where mechanisms such as precipitation/coprecipitation and matrix diffusion were studied.

The Palmottu study confirmed a number of processes responsible for U mobilisation and fixation observed at other natural analogue sites. Additionally, it included some unique features owing to its glacial and post-glacial history. These data were also used to test models and mathematical techniques that will be used to describe the expected behaviour of radionuclides in assessing the performance of high-level nuclear waste repositories in fractured crystalline rock. By demonstrating the very limited dispersion of U over millions of years, it has greatly increased confidence in the safety of spent fuel disposal in crystalline, igneous rocks. However, it has also highlighted the limitations of modelling tools used in repository performance assessment when describing U migration in a complex, natural geochemical system.

Introduction

Natural analogue studies have become an essential part of national and international programmes for the deep disposal of radioactive waste (Chapman *et al.*, 1984; Brandberg *et al.*, 1993; Miller *et al.*, 1994). The Palmottu site, in southwestern Finland, represents the development of natural analogue studies to a fractured crystalline bedrock environment. Results from this site are therefore of considerable benefit to countries considering crystalline bedrock as a disposal option. The site itself is a source of radionuclides, comprising a U-Th deposit in mica gneisses and granites typical of the rocks in the Fennoscandian Shield.

The contribution of the Palmottu Project to the future disposal of high-level radioactive waste is severalfold. For example, for those countries expecting future cooler climatic changes (e.g. Canada, Finland and Sweden), the glacial scenario is potentially a major threat to the bedrock hydrochemical stability and thus repository integrity in these regions. Since Palmottu experienced continental ice margin conditions, a major contribution from the project can be expected in increasing knowledge of the effects of glaciations and related phenomena (*i.e.* permafrost) on the hydrogeochemistry of the system.

The fact that the uranium deposits extend from an oxidising environment near the bedrock surface down through the redox transition zone into a reducing groundwater environment, allows the study of the full cycle of uranium chemistry under natural conditions. This extends from the interaction of oxidising waters with uranium dioxide ore and converting low solubility U(IV) into the more soluble uranyl ion, followed by transport and retardation processes along water-conducting fractures to deeper, reducing groundwater where mechanisms such as precipitation/coprecipitation may be studied. All these data can be used to refine and test models and mathematical techniques that will be used to describe the expected behaviour of radionuclides in assessing the performance of high-level nuclear waste repositories in fractured crystalline rock.

Palmottu has also provided the opportunity of testing site characterisation methodology and investigative techniques. For example, potential contamination effects from borehole activities were minimised thus contributing to the sampling of groundwaters representative of the bedrock environment under investigation.

The Palmottu project was divided into two parts. The objective of the first part was to assess the present-day flow situation of the site and to specify areas where radionuclide transport studies could be conducted (Blomqvist *et al.*, 1998a). The second part of the project was aimed at identifying and quantifying geochemical processes related to mobilisation and migration of radionuclides, and further to radionuclide retardation. An important part of the Palmottu project was the close integration of the study with repository performance assessment (PA). To ensure that this integration was successful, PA expertise was incorporated to the project from the very beginning.

Site characterization

Bedrock geology

The Palmottu site represents a near-surface uranium occurrence located in a Precambrian metasedimentary sequence of rocks in southwestern Finland. The Palmottu occurrence is situated close to the contact with the late-kinematic Perniö granite together with some other uranium showings (Fig 1). The original sediments were clays and sands and intermediate volcanic material deposited in shallow sea basin, possibly related to an island arc system (Mäkelä, 1989). The major sedimentation phase took place 2400-1900 Ma ago (Simonen, 1980). High-grade regional metamorphism at 600-800° C and 4-5 kb (Schreurs and Westra, 1986) provoked a thorough recrystallisation and change in the original mineralogy and destroyed largely the original sedimentary textures. The present lithologies are predominantly mica gneisses frequently containing almandine garnet (Fe-Al silicate) or pyroxene (Ca-Mg-Fe silicates) porphyroblasts as a reflection of the chemical composition of the sedimentary precursors. The culmination stage of the metamorphism was about 1.84 Ga ago (Huhma, 1986, Vaasjoki, 1996), at the same time as the late-kinematic K-granite massiv of the Perniö granite intruded the surrounding sediments. The last thermal event was related to the introduction of dolerite veins 1750-1400 Ma ago (Aro and Laitakari, 1987).

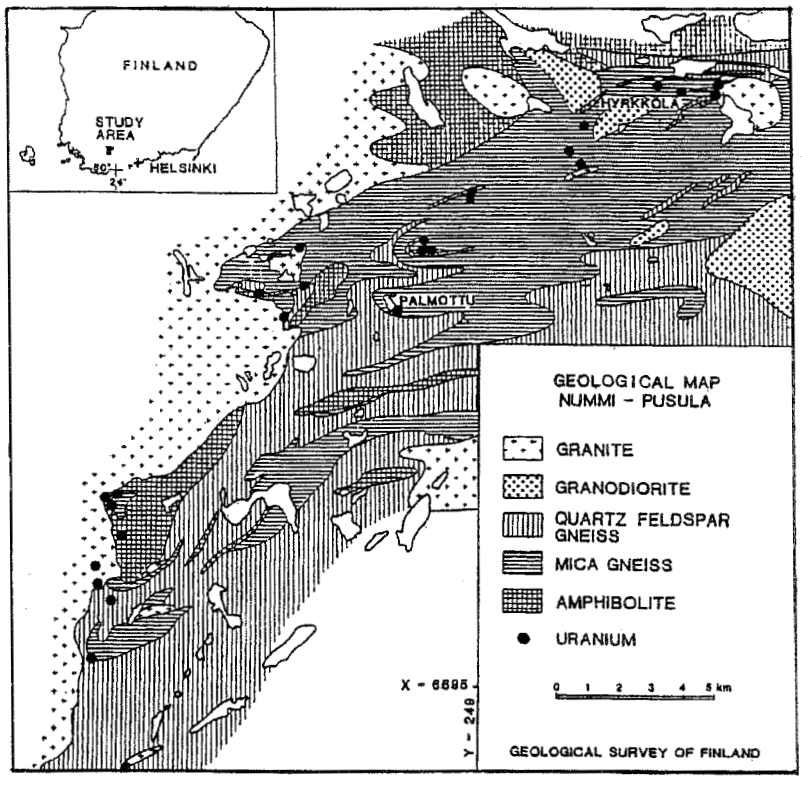

Figure 1. Regional geological map of Palmottu and location of the study site after Räisänen (1986).

During or soon after the peak of the metamorphism, pegmatite veins were intruded into the metasediments (Fig. 2). The veins are usually concordant, *i.e.* parallel to the schistosity. Three different types can be distinguished: 1) a gray, even- or coarse-

grained granite, referred in the text as the Western Granite (WGR), 2) a coarse-grained, heterogeneous pegmatite with deep red hematite pigment, referred to as the Eastern Granite (EGR) and 3) a white or reddish coarse-grained pegmatite.

The main uranium mineralisation is associated with a biotite–rich variety of the latter vein type (type 3, above). However, only few veins contain anomalous amounts of U. The EGR has sporadically high U concentrations, while WGR and the major part of the common pegmatite veins are essentially barren. Uraninite [UO_{2+x}, $0.01<x<0.25$] and monazite [$(Ce,La,Nd,Th)PO_4$] are the primary U-Th minerals in the ore (*c.f.* Ruskeeniemi *et al.*, in this volume). Coffinite [$U(SiO4)_{1-x}(OH)_{4x}$] is a widespread secondary mineral as a hydrothermal alteration product of uraninite. The ore minerals occur as dissemination, no massive parts have been encountered. It is suggested that the pegmatites represent the late-stage residual magmatic fluids of the nearby Perniö granite. Hence, it is likely that the source of uranium at Palmottu is predominantly magmatic, but a proportion may also be derived from the surrounding metasediments by magmatic assimilation or by hydrothermal leaching. The ore estimates suggest around one million tonnes of ore grading at 0.1% U down to depths of 300m (Räisänen, 1986). Later drilling within the Palmottu Project has shown that the mineralisation partly continues to depths below 450 m (Blomqvist *et al.*, 1998a).

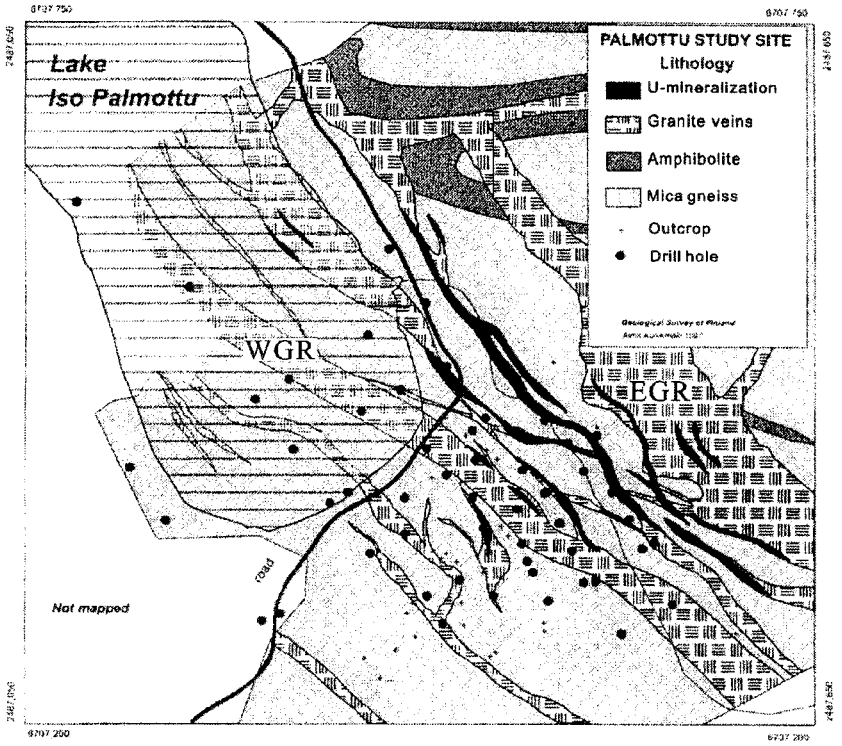

Figure 2. Geological map of the Palmottu site after Kuivamäki, modified from Blomqvist *et al.* (1998b). The major granitic units are the Western Granite (WGR) and the Eastern Granite (EGR).

Due to the long and complex geological history, the bedrock is cut by numerous fracture generations. However, most of the fractures are sealed by precipitation of secondary minerals, mainly calcite and various clay minerals (Ruskeeniemi, 1998). Open, water-conducting fracturing is mainly observed in the upper part of the bedrock

down to 150 m. Subhorizontal fractures, frequently dipping towards the SW or NE, together with variously oriented steeply dipping fractures, form a network of interconnected fractures that allow a dynamic flow system in the upper part of the bedrock. This is a common feature of the Fennoscandian Shield and stress-release following deglaciation is thought to be a contributary factor to their formation. Deeper down in the bedrock open fracturing is rare and, consequently the hydraulic conductivity is generally very low (Blomqvist *et al.,* 1998a).

Since the time of the peak of the metamorphic activities (1.84 Ga ago), erosion has removed some 10-15 km of rock from what is now the bedrock surface. However, the rate of erosion of the crystalline bedrock has been very low during the last 500 Ma, and mainly unconsolidated Palaeozoic sediments were affected. At present, the bedrock at Palmottu is either outcropping or it is covered by Quaternary deposits. Due to repeated glacial erosion, the weathering crust, so typical for non-glaciated terrains, has dominantly been removed and can only be found in well-sheltered depressions of the bedrock. Since the retreat of the last ice cover 10 000 a ago, mechanical and chemical weathering has eroded a negligible amount of the intact rock. Based on resistant minerals of glacially eroded and polished bedrock surfaces, the order of postglacial erosion is not more than 10 mm of intact rock. Additionally, a chemical weathering front may extend to some tens of millimetres into the rock; this is based on colour differences, mostly a red staining caused by oxidation of Fe(II).

Quaternary geology

During the last million years the area has been subjected to several glaciations (Donner, 1995), the last of which (Weichselian Ice Age) ended only 10 000 a ago. It is estimated that the maximum thickness of the continental ice cover in the central part of the Fennoscandian Shield was about 3 km some 20 000 a ago. The weight of the ice depressed the underlying crust by up to 800 m at the centre of the glaciated area (Niskanen 1943; Mörner 1979). At Palmottu, the depression was less, of the order of 300-400 m, but here the isostatic rebound after the deglaciation is still going on at a rate of 4-5 mm/a (Ekman, 1996).

The three ice-marginal formations called Salpausselkä I to III are, together with the esker formations, the most distinctive signs of the retreating ice (Fig. 3). The Salpausselkä formations can be followed for hundreds of kilometres from SW Finland eastwards to Russian Karelia. The ice-marginal formations imply the periods when the retreat of the continental ice cover temporarily stopped for some hundreds of years, caused by slightly cooler climatic conditions. These temporal stops can now be observed as huge accumulations of loose sediments that were deposited in front of the ice cover, composed of partly washed till, gravel and sand. At Palmottu, additionally a large delta formation was deposited next to the Salpausselkä III formation in front of the ice margin. As it was deposited at the level of the Yoldia Sea of that time, the elevation of delta formation is 118 m.

Palmottu is located in a bedrock block surrounded by prominent fracture zones; this block is topographically clearly higher than its surroundings with a present elevation of 106-138 m (Blomqvist *et al.,* 1995). Due to its topographic situation, the highest peaks of the Palmottu area emerged from the proto-Baltic immediately after the retreat of the ice sheet during the Yoldia Sea stage, 10 000 a B.P., as the sea level was

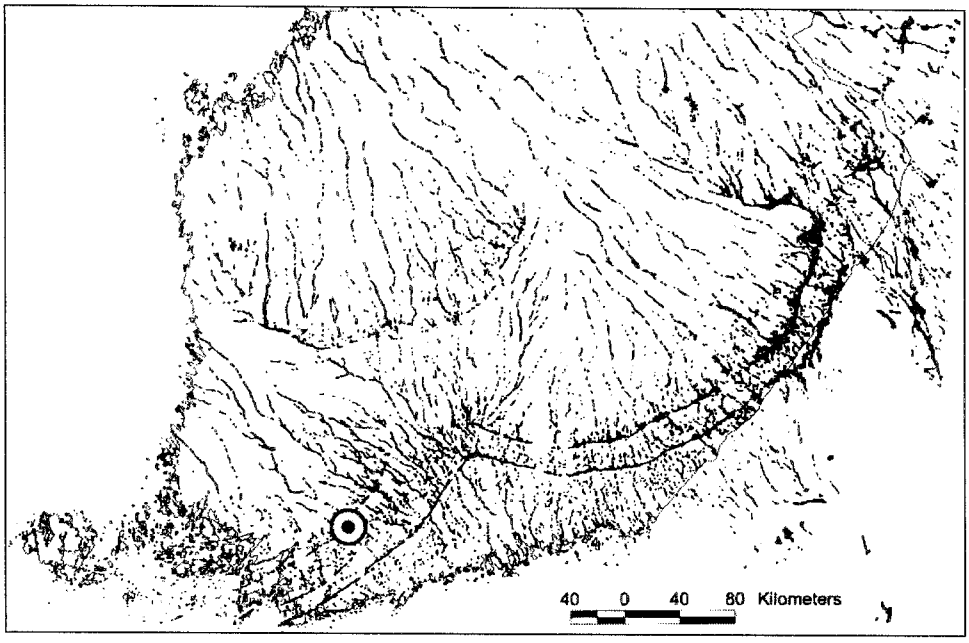

Figure 3. Eskers and ice-marginal formations in Southern Finland (and part of Russian Karelia). The NE trending formations are the Salpausselkä I to III ice-marginal formations (from South to North). Palmottu is located immediately SE from the Salpausselkä III formation (marked with the black dot). The size and shape of the individual glacial lobes are clearly reproduced by the pattern of the ice-marginal formations and the eskers. Data by the Geological Survey of Finland after Kujansuu and Niemelä (1984).

then at an elevation of 118 m (Fig. 4). As the isostatic rebound was at that time still very fast, 4.1 m/100 a, based on shore line displacements (Donner, 1995), the separate islands of the Palmottu area soon formed an integrated part of the main land of that time (part of present SW Finland). This is clearly indicated in the lower part of Figure 4, which shows the Ancylus Lake stage of the proto-Baltic some 9 200 a B.P.

During the Yoldia stage substantial meltwater streams have flushed the Palmottu site. However, it was during the previous Salpausselkä II stage, at the time of deglaciation, that glacial melt water flowing beneath the ice sheet may also have partly intruded into the bedrock, caused by the enormous hydrostatic pressures prevailing below the ice cover. The depleted O-18 values of some of the fracture groundwaters sampled at Palmottu (Blomqvist *et al.*, 1995, 1998a; Pitkänen *et al.*, in this volume; Smellie *et al.*, in this volume) could be interpreted as glacial melt water intrusion.

The eroding and transporting movement of the continental glacier and the subglacial melt-water streams had a drastic impact on the landscape. Most of the loose preglacial formations were removed or reworked. Presently the bedrock of Palmottu region is largely covered by glaciogenic tills or glaciofluvial formations. In the regional lows around the Palmottu block, post-glacial clays deposited during the different stages of the Baltic Sea cover the glaciogenic layers. Soon after the deglaciation, peat started to form on depressions of bedrock. In about 9000 years, a peat thickness of up to 3-4 m was reached, but generally the peat layer is less than 2 m thick at Palmottu. Peat in the vicinity of the exposed U-mineralisation contains several hundreds of ppm of uranium (in ash), and it can be used to assess the biospheric migration of uranium.

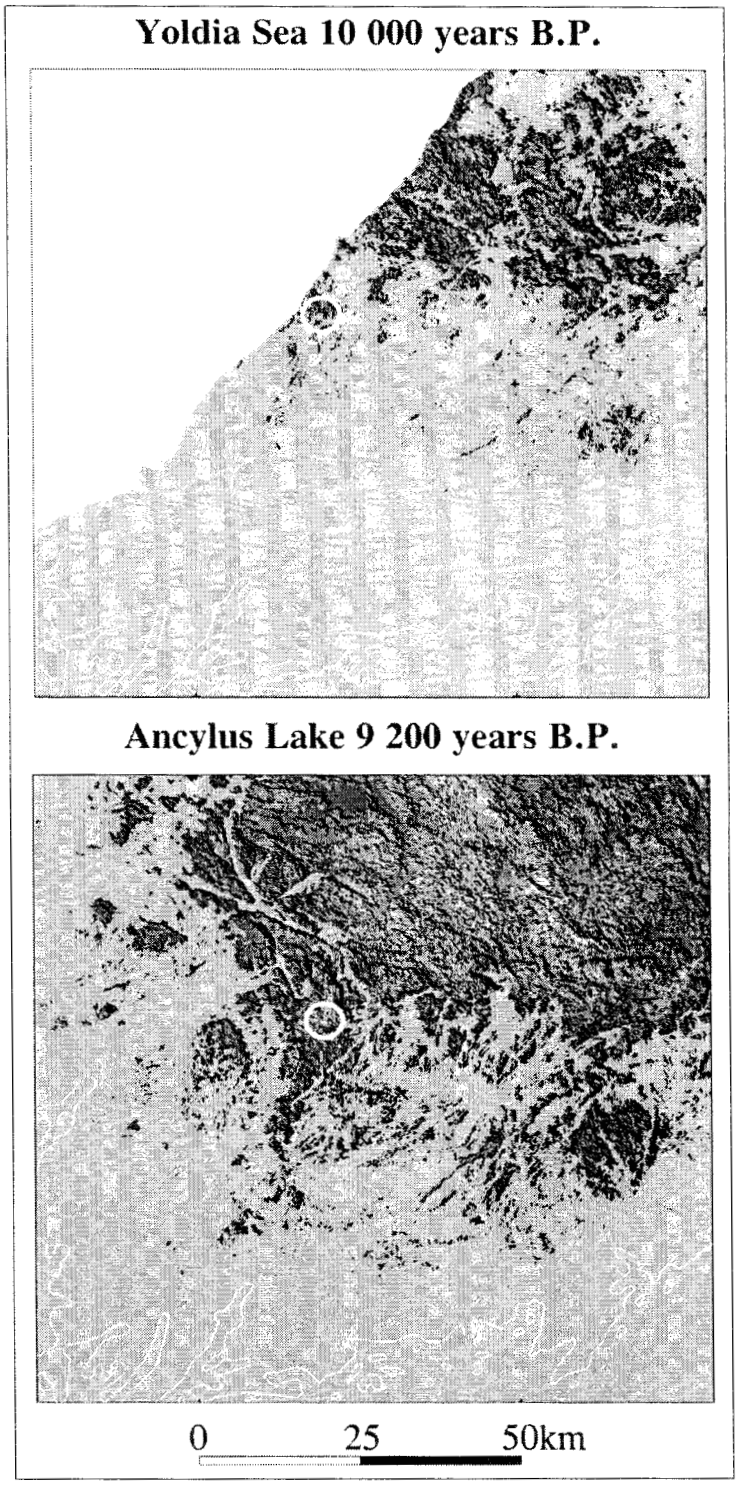

Figure 4. The Palmottu site emerged from the sea as a group of islands immediately after the retreat of the ice sheet 10 000 a ago. After a few hundred years, the Palmottu region formed an integrated part of the main land of that time (part of present SW Finland, the shoreline is also indicated). The figures are mainly based on observations from shoreline displacements, and their construction utilises the isobars of isostatic rebound. Figures by the Geological Survey of Finland based on data from Saarnisto (1971).

Hydrogeology and hydrogeochemistry

The integrated hydrogeological and hydrochemical model of the Palmottu site (Fig. 5) is presented in Blomqvist *et al.* (1998a) and only a brief summary is given in this article. The upper 100 m of the bedrock is characterised by dilute groundwater of HCO_3 type (the Upper Flow System). Calcium is the dominant cation near the surface changing to sodium in the lower part of this HCO_3 type groundwater zone. High tritium contents indicate a dynamic flow system, which penetrates to a depth of at least 200 m in the southern part of the site (the Dynamic Deep Flow System). Below the HCO_3 type water body the groundwater is brackish, of Na-SO_4 or Na-Cl type, and both the hydrochemistry and isotopic results suggest long residence times and stagnant flow conditions (the Stagnant Flow System). The Na-SO_4 type water seems to be restricted to the central mineralised zone of the site, between the Na-HCO_3 and Na-Cl type waters. In the surrounding area, *i.e.* the area westward from the Western Granite, the Na-Cl water type is observed directly below the Na-HCO_3 water. The Eastern Flow System, as a part of the Upper Flow System, is less connected to the central area of the site, and forms a separate flow system serving as a target for the migration analogue study of radionuclides (cf. Read *et al.*, in this volume).

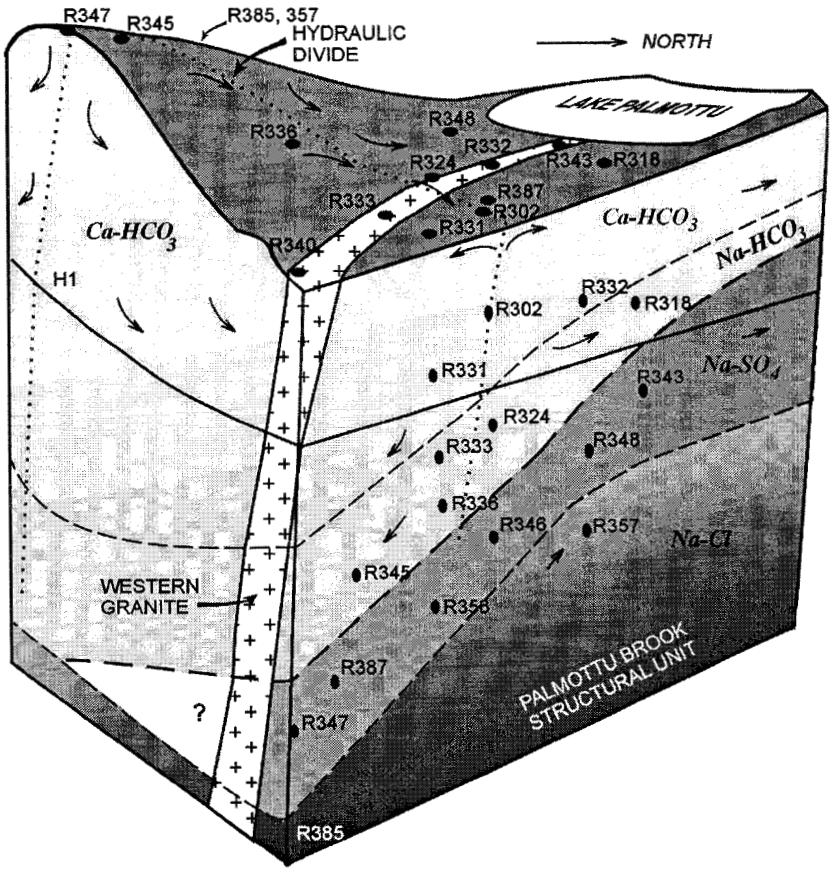

Figure 5. Conceptual hydrogeological model of the Palmottu site (modified from Blomqvist *et al.*, 1998a). The Eastern Flow System is located to the right of the Palmottu brook structural unit, and is not shown in the figure.

Overview of the results of the study

In the following section a short overview is given of the main results from the Palmottu study based on the following information (in this volume): Uranium mineralogy (Ruskeeniemi *et al.*), hydrogeochemistry (Pitkänen *et al.*; Gimeno *et al.*), palaeohydrogeology (Smellie *et al.*), redox processes (Cera *et al.*), migration and fixation of uranium (Read *et al.*), testing of trace element solubility models (Bruno *et al.*), and a first compilation of conclusions relevant to repository performance assessment (PA), (Grundfelt).

Uranium mineralogy with implications for uranium mobility. The main U-bearing ore mineral in the Palmottu U-Th mineralisation is uraninite which occurs as euhedral crystals. Dating of the uraninites gave discordant ages between 1678 and 1741 Ma. Most uraninite grains are altered (along grain boundaries and along microcracks) to U-silicate phases mostly amorphous and resembling coffinite [$(U,Th)SiO_4 \cong nH_2O$] with minor radiogenic galena and other sulphides. Residual silica-rich hydrothermal solutions associated with the uraniferous pegmatites were responsible for most of the alteration which occurred under reducing conditions; a later carbonatisation process contributed also. During alteration considerable amounts of U, Th, and Pb were mobilised from the deposit and consequently high U concentrations have been recorded from calcites and other fracture infillings. In addition, small amounts of uranium silicate or possible uranium silicophosphate (chemically resembling coffinite) have been detected from calcites. Fluid-inclusion geothermometry from a U-rich calcite infilling gave a hydrothermal formation temperature of 285°C implying a minimum age of 1 Ga.

A geologically young, easily soluble secondary U(VI) mineral uranophane [U(VI)-Ca-silicate] is found in the uppermost part of the Eastern Granite, including above the water table. Uranophane occurs in tight to open fractures, and also in microfractures of the intact rock, as tiny bright-yellow crystals and crystalline aggregate. Some of these fractures resemble dilational-type fractures, possibly related to unloading during deglaciation. U-decay series age-dating of two uranophane samples gave ages of 90-120 ka and 189-240 ka. Based on a unique field experiment, conducted in the unsaturated zone of the Eastern Granite, a rapid increase of dissolved uranium in the recharge water was observed within a short time (a few weeks) following heavy precipitation. Since lower pH values characterised the recharge water, the pH dependent dissolution of uranophane was concluded as the most likely uranium source. This conclusion was supported by modelling calculations of uranophane solubility and reaction kinetics.

As a conclusion it can be stated that the major flux of uranium into the fracture network of the bedrock was clearly related to the ancient coffinitisation of the uranium mineralisation. However, with respect to the present-day mobilisation of uranium in groundwaters, the most significant contribution is likely to be derived from the dissolution of the geologically young, easily soluble secondary U(VI) mineral uranophane.

Hydrogeochemical interpretation of groundwater at Palmottu. Four general groundwater types characterise the Palmottu site. Recently recharged, shallow Ca-HCO_3 type groundwater evolves in the upper part of the bedrock into a Na-HCO_3 type

groundwater at increasing depth within a few decades, partly due to Ca to Na ion-exchange processes. Brackish Na-SO_4 and Na-Cl type groundwaters (some thousands of years old) prevail below the HCO_3 groundwater bodies; Na-SO_4 is present only around the mineralised zone whilst Na-Cl is found at greater depths in the surrounding area. The latter groundwater types show distinct glacial isotopic ($\delta^{18}O$) signatures.

Mixing of water types explains largely the changes of SO_4, Cl and Na concentrations. Water-rock interaction is specifically connected to carbon cycling; biogenically produced CO_2 promotes silicate weathering and dissolution of calcite at shallow depths. The heavy $^{87}Sr/^{86}Sr$ ratios measured from the HCO_3 waters are consistent with the dissolution of Rb-rich minerals such as K-feldspar and biotite. Ca to Na ion-exchange maintains calcite dissolution and calcite is saturated in the Na-HCO_3 type water. Minor calcite precipitation and silicate dissolution is likely in the brackish groundwater types, thus buffering pH to around 8.5. Anaerobic oxidation of organic matter in the lower part of the Na-HCO_3 layer and CH_4 oxidation in the brackish groundwater layer using SO_4 as an electron acceptor are considered probable processes based on C and S isotope data.

Geochemical modelling of groundwater evolution in the Palmottu natural system. Geochemical modelling has involved: 1) a statistical evaluation to confirm the major groundwater groups, and 2) reaction path modelling considering both inverse and forward simulations using the PHREEQC code. Mineralogy, redox pairs, and isotopic data have been taken into account in order to support the modelling results. The modelling has helped to define: 1) the different water types involved in the system: Ca-HCO_3 waters, Na-HCO_3 waters, Na-SO_4 waters and Na-Cl waters; and 2) the two main hydrogeochemical processes which are taking place: the weathering of a crystalline basement, responsible for the evolution from the recharge water to the Na-HCO_3 end member; and the mixing of the latter with other deeper, older and more saline waters: Na-SO_4 and Na-Cl waters.

The weathering process has been characterized by the following reactions: (a) dissolution of calcite, plagioclase, uranium oxides and uranophane, (b) biogenic uptake of CO_2 from overburden, (c) ionic exchange, (d) biotite alteration, (e) oxidation of iron sulphides and (f) precipitation of silica, kaolinite, smectite, illite and iron oxyhydroxides. The final result is that the shallower and more dilute Ca-HCO_3 waters evolve towards Na-HCO_3 groundwaters, with an increase of pH and a progressive decrease of Eh. The deep waters have different proportions of the three water types, Na-HCO_3, Na-SO_4 and Na-Cl and are slightly affected by water-rock interaction processes.

Palaeohydrogeological implications for long-term hydrochemical stability at Palmottu. In the Fennoscandian Shield environment the glacial scenario is potentially a major threat to hydrochemical stability and thus repository integrity. The Palmottu study is important in this respect by helping to predict future events during ice margin permafrost conditions since there is clear Quaternary evidence that Palmottu experienced a continental ice margin palaeoclimate and was never submerged subsequently by seawater.

A sizeable $\delta^{18}O$ depleted glacial water component is present in the deep Na-Cl and Na-SO_4 type groundwaters (additionally in some of the deep Na-HCO_3 types). The

presence of glacial water may suggest that the system has been open to the incursion of oxidising waters to at least 400 m. However, it is highly unlikely that the glacial melt waters would retain their oxidation capacity to any great depth because of the buffering capacity of first the overburden and then the bedrock itself.

The SO_4 in groundwaters at Palmottu may result from sulphide dissolution and oxidation during hydrothermal events or by continuous oxidation of sulphide minerals during geological times. A few mechanisms related to glacial or permafrost conditions can be proposed also to explain the high SO_4 concentrations and depleted oxygen isotope signals of the sulphate waters. The mechanisms could involve cyclic freezing of groundwater to generate a saline layer of groundwater in front of an advancing permafrost layer. Irrespective to the origin of these groundwaters, however, the fact that Na-SO_4 groundwaters, and to a lesser extent the Na-Cl type groundwaters, are still present at these depths, underlines the stability of the hydrochemical system over long periods of geological time under low permeable conditions, at least since the last glaciation approximately 10 000 a ago. At greater depths, more applicable to repository depths, conditions would be expected to be more stable.

Redox processes at the Palmottu uranium deposit. On-line redox measurements have been performed at Palmottu in order to ascertain the redox pairs controlling the redox state of the system. By comparing the characteristic reaction times of these redox processes with the residence times of the deep groundwaters, the attainment of redox equilibrium in the system can be assumed. The thermodynamic modelling performed in this natural system indicates two zones with different redox controls: the Western area where the sulphide minerals seem to control the redox potential of this subsystem, and the Eastern area where the uranium mineralisation occurs. In this area the uranium minerals could play an important role as a redox buffer in the reduced area, while the most common redox pair $Fe^{2+}/Fe(OH)_3(s)$ appears to control the redox behaviour in the most oxidised surface zones of the same area.

The gradation of the reducing capacity levels follows the traditional scheme: atmospheric oxidation of organic matter controls the soil and surface redox system, followed by the oxidation of Mn(II) and Fe (II) to Fe(III). At deeper and more anoxic levels, the oxidation of UO_2 to UO_{2+x} controls the redox system close to the ore, while the sulphide/sulphate system is the dominant pair in the most stagnant waters. The origin of these sulphate containing waters in the undisturbed part of the system and its possible connection to oxic melt waters intrusion remains an open question with critical implications of the redox stability of granitic groundwaters at the Fennoscandian shield.

The migration and fixation of uranium at the Palmottu Natural Analogue Site. Alteration of the 1,800 Ma old uraninite deposit at Palmottu has led to substantial re-mobilisation of uranium. A relatively well characterised recharge system in the Eastern Granite area was chosen for a detailed migration modelling exercise. The modelling study consists of two steps, the first involving prediction, the second allowing model refinement. The flow route is assumed to constitute a closed system and to reflect essentially post-glacial events, as it is probable that this latest signal dominates.

A set of hypotheses that are believed to be involved in the mobilisation and fixation of uranium are being tested using a variety of modelling approaches. These range from a simple advection-dispersion-matrix diffusion approach to a fully coupled chemical transport model. An effort is also being made to represent the observed uranium-series disequilibria (USD) observed in fracture coating minerals and associated groundwaters along the flow route.

Uranium concentrations in groundwater rise rapidly from close to zero at the surface to around 150 ppb at 30 m depth. With increasing depth concentrations are thought to be limited according to the solubility versus pH relationships. At greater depths the system approximates steady state with both U concentrations and isotopic ratios likely to be controlled by equilibrium with U-rich fracture minerals. Any accessible UO_2 encountered in this zone will tend to dissolve. Finally, at depths below the model domain (> 200 m), reducing conditions persist and U concentrations of a few ppb reflect solubility control by uraninite.

Preliminary modelling of this system using the coupled chemical transport code RETRASO accounts for the direct and indirect effects of Eh-pH variations on U concentrations. The model predicts the development of a sharp dissolution front, which seems to be borne out by analysis of waters and fracture minerals. The existence of an additional uranium source was also postulated, though this source was not specified. On the basis of surface complexation modelling, it was concluded that an insufficient amount of Fe oxides is present for equilibrium adsorption to play a major role in determining aqueous concentrations. Refinement of the models will now need to take into account the presence of uranophane and the rapid dissolution kinetics of uraniferous phases close to the surface (described above). It is apparent that essentially physical models, such as FTRANS, cannot provide an explicit representation of the processes believed to control U geochemistry. The FTRANS simulations assumed an outward diffusion from the rock matrix around a water-carrying fracture to account for the levels observed. However, it is apparent from the sensitivity studies undertaken that matrix diffusion is not a dominant process in determining U concentrations in the shallow Palmottu groundwaters. Refinement of physical models is clearly needed to take into account the geochemical processes that invariably control such systems.

The Palmottu study has confirmed a number of processes responsible for U mobilisation and fixation observed at other natural analogue sites. Additionally, it includes some unique features owing to its glacial and post-glacial history. By demonstrating very limited dispersion of U over millions of years, it has greatly increased confidence in the safety of spent fuel disposal in crystalline, igneous rocks. However, it has also highlighted the limitations of modelling tools used to quantify repository performance when describing U migration in a complex, natural geochemical system.

Testing of trace element geochemical models at Palmottu. The geochemical behaviour of natural systems is controlled by water-rock interactions. These processes exert a direct control on the intensive geochemical master variables, pH and Eh, as well as on their associated extensive capacities, alkalinity and redox potential, which, in turn, influence the geochemistry of trace metals. Consequently, water-rock interaction processes control the behaviour of the trace components of geochemical

systems. The concentration of trace elements in natural groundwaters may be controlled by dissolution/precipitation of individual solid phases, although in most cases the processes responsible for the observed minor component behaviour involve the main components of the system. Sorption, occlusion or incorporation to the crystalline lattice of major minerals present in the media are processes likely to account for the observed behaviour of trace metals in the geosphere. Co-precipitation and co-dissolution models are able to explain the existing link between major and minor components of the system in a simple fashion. The behaviour of Mn, Sr, Ni, Ba, Zn, U, Th and REE was studied. Some of the results are reviewed below.

Uranium cannot be considered a trace element in the Palmottu system since the solubility of pure U phases, coffinite and oxidised uraninite (U_4O_9) is able to explain the U concentration in these groundwaters. The presence of strontium illustrates the association between a trace component and major minerals. The incorporation of this element to the calcite lattice is a well-known phenomenon and is able to explain the concentrations of Sr found in the studied groundwaters. Furthermore, the fact that the aqueous Ca concentration correlates with that of Sr indicate that these elements have a common mineral source in the systems (Sr-bearing calcite respectively). All REEs behave in a very similar way. The solubility of solid REE phosphates reproduces fairly well not only the REE aqueous concentrations, but also the trend of the data. The overestimation of the concentrations of REEs obtained when assuming equilibrium with $REEPO_4 \cdot xH_2O$ increases when increasing the atomic weight. This may indicate an association of REEs with major phosphate minerals present in the system, such as apatite or monazite, and this association would occur in major proportion as the atomic weight decreases. According to these results a co-dissolution process of REEs with apatite explains the behaviour of this element.

The experimental observations on trace element associations together with the geochemical modelling work performed in Palmottu give additional evidence of the link between trace and major component cycling, particularly C, Fe and P. Fe(III) oxyhydroxide, calcite, and apatite precipitation/dissolution processes appear to be critical to control trace element mobility in the Palmottu system.

Important lessons for PA: A first summing up from Palmottu. An important part of the Palmottu project is the close integration of the natural analogue study with repository performance assessment (PA). The following PA-related areas were specifically addressed: 1) development of scenarios, 2) process identification, 3) testing of transport models for processes, 4) cross-checking of data consistency with natural systems and 5) data collection. The main contributions are within areas 1-3, and this is probably a situation that is common to many studies of natural analogues.

With respect to *scenario development* the main contribution from the Palmottu project will be an increased knowledge of effects of glaciations on the long-term hydrogeochemical stability of the system, essential to predict the performance and robustness of a high-level radioactive waste repository during its expected lifespan. Furthermore, mineralogical and hydrogeochemical observations show that even though a continuous alteration and oxygenating process is proceeding at Palmottu, the site-scale uranium mass balance indicates that the dominant part of the uranium has remained in the primary U(IV) phases, uraninite and coffinite, since its emplacement

some 1.7-1.8 Ga ago. This increases confidence in the long-term stability of spent fuel disposal in crystalline rocks.

In the area of *process identification* the Palmottu project will result in several important outputs, for example, the identification of those geochemical reactions and mixing processes governing the evolution and composition of the migrating groundwater. The modelling results obtained, using several standard geochemical tools, are in good accordance with the known hydrogeochemistry at Palmottu. Furthermore, the field experiment described above from the Eastern Granite area, where uranophane occurs as fracture infilling and a rapid increase of dissolved uranium was observed in the recharge waters within a short time (a few weeks) following heavier precipitation (and lower pH values), it was concluded that uranophane was the most likely source for the uranium. This conclusion was supported by modelling calculations of uranophane solubility and reaction kinetics. A third output is the identification of redox processes. Thermodynamic modelling indicates two zones with different redox controls: the Western Granite where the sulphide minerals seem to control the redox potential, and the Eastern Granite where the uranium minerals could play an important role as a redox buffer in the reduced area, while the most common redox pair $Fe^{2+}/Fe(OH)_3(s)$ appears to control the redox behaviour in the most oxidised surface zones of the same area.

In all these areas of process identification, standard geochemical models, which form an integral part of the site characterisation protocol for the eventual construction of a radioactive waste repository, have been tested with good success.

Testing of transport models at different scales and levels is a part of the scientific process of understanding what is going on in the complete system. The first phase of the project involved a successful integration of geochemical and hydrogeological models for describing the groundwater flow situation of the site. Independent chemical parameters were utilised to establish a realistic flow model of the site. A well-characterised sub-system of the Palmottu site was selected for testing different types of transport models for describing the behaviour of uranium along a selected flow path. The objective of the modelling exercise was to assess and compare modelling approaches for simulating the migration-fixation of U at the site, and to test alternative hypotheses of U behaviour as a means towards constructing a defensible, conceptual model of site evolution.

A predictive modelling exercise was set up to test the capability of predicting trace metal behaviour. The modelling exercise incorporated a component of testing the conceptual understanding of the various trace element systems, but it also included comparison and testing of databases and codes commonly used to calculate radionuclide solubility and transport parameters in repository performance assessments.

Acknowledgements

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Uranium mineralogy with implications for mobilisation of uranium at Palmottu

T.Ruskeeniemi[1], A. Lindberg[1], L. Pérez del Villar[2], R. Blomqvist[1], J. Suksi[3], A. Blyth[4] and E. Cera[5]

[1]Geological Survey of Finland
[2]Ciemat, Spain
[3]University of Helsinki, Finland
[4]University of Waterloo, Canada
[5]Quantisci, Spain

Abstract

One of the targets of the Palmottu Analogue Project is to obtain information on the factors affecting the mobilisation and retardation of uranium in crystalline bedrock; uranium minerals are therefore of particular interest.

Uraninite occurs as euhedral crystals in the Precambrian biotite-rich pegmatites and sheared quartz-biotite veins. Conventional U-Pb dating of the uraninites gave discordant ages between 1678 and 1741 Ma. Most uraninite grains are altered along grain boundaries and along microcracks within the grains. The altered zone is composed of a black heterogeneous mass of uranium silicate phases with minor radiogenic galena and other sulphides. The major uranium silicate is amorphous and chemically resembles coffinite $(U,Th)SiO_4 \cong nH_2O$.

The alteration of the uraninite at Palmottu occurred under reducing hydrothermal conditions. This is indicated by the formation of uranous silicate phases (coffinite) instead of uranyl compounds, and by the occurrence of galena and other sulphides in the altered phase. Residual silica-rich hydrothermal solutions of the uraniferous pegmatites were responsible for most of the alteration and a later carbonatisation process contributed also. Considerable amounts of U, Th, and Pb were mobilised from the deposit during alteration. Consequently, high U concentrations have been recorded from calcites and other fracture infilling. Small amounts of uranium silicate or possible uranium silicophosphate have been detected from calcites. Chemically this mineral resembles coffinite. The common association with pyrite-bearing calcite infilling and the chemical similarity with coffinite suggest that uranium is in a reduced form. Fluid-inclusion geothermometry from a U-rich calcite infilling gave a hydrothermal formation temperature of 285^{B}C. This implies a minimum age of 1 Ga.

Geologically, young secondary uranium minerals are found in the uppermost part of the Eastern Granite, also above the water table. Uranophane (U(VI)-Ca-silicate) occurs in tight to open fractures as tiny bright-yellow crystals and crystalline aggregates, also in semi-closed microfractures. Uranium series dating of two samples gave ages of 90-120 ka and 189-240 ka. Some of the uranophane occurs in thin dilational-type fractures, possibly related to unloading during deglaciation. Based on a unique field experiment, conducted in the unsaturated zone of the Eastern Granite, uranophane seems to be of major importance in controlling the dissolved uranium load of the recharging groundwaters

The major flux of uranium into the fracture network is obviously related to the ancient coffinitisation of the uranium mineralisation, but the present day, high concentrations of uranium of the recharging waters of the Eastern Granite are dominantly due to the dissolution of easily soluble U(VI) minerals, most likely uranophane. Experimental tests to prove/disregard this assumption are presently proceeding.

The Palmottu U-Th mineralisation

Räisänen (1989) distinguished two types of uraniferous veins at Palmottu, the coarse-grained biotite-pegmatites and the sheared quartz-biotite veins. The latter are actually not veins at all, but narrow shear seams frequently located in the contact zones between biotite pegmatites and gneisses. These quartz-biotite seams contain higher uranium concentrations, but they are usually only some tens of centimetres thick. The Eastern Granite forms the third type of mineralised rock. It differs from the common biotite pegmatite by having a strong hematite pigment in plagioclase. It is a common feature for all these host rocks that uranium is mostly associated with the biotite-rich parts of the rocks.

Räisänen (1989) proposed that the pegmatites represent the late-stage residual magmatic fluids of the nearby Perniö granite. Pegmatite melts are rich in volatiles and elements that are not readily incorporated into the lattices of major granite minerals (Evans 1980). Uranium is a typical example of an incompatible element enriched in this kind of systems. A number of uranium showings have been found all along the contact zone of the Perniö granite. It is probable that the source of uranium at Palmottu is predominantly magmatic, but a proportion may also be derived from the surrounding metasediments by magmatic assimilation or hydrothermal leaching.

The main U-Th mineralisation of the site is located under thick Quaternary deposits, up to 15 m thick (Fig. 1). The mineralisation is composed of several, narrow pegmatite veins (2 to 10 m) interlayered with mica gneisses. The Eastern Granite, largely exposed as a minor hill, is sporadically mineralised with uraninite grains observed on the exposed surface of the bedrock. The ore minerals occur as dissemination in the host rock and no massive ore types of uranium have been found. The U and Th concentrations range from negligible values to 0.7% for U and up to 0.1% for Th. The U/Th ratio in the ore is highly variable (0.3-10) due to the uneven distribution of the two major U and Th bearing minerals, uraninite and monazite. In U-rich samples the U/Th ratio tend to cluster around 6-7.

The high activity of phosphate in the magmatic solutions is reflected by the common occurrence of phosphate minerals, apatite and monazite. Hence, it is plausible that uranyl phosphate complexes like $UO_2(HPO_4)_2^{2-}$ played an important role in the formation of the U-Th ore. The coeval formation of the first monazite generation with uraninite suggests that the phosphorus released in the breakdown of uranyl complexes was incorporated in monazite

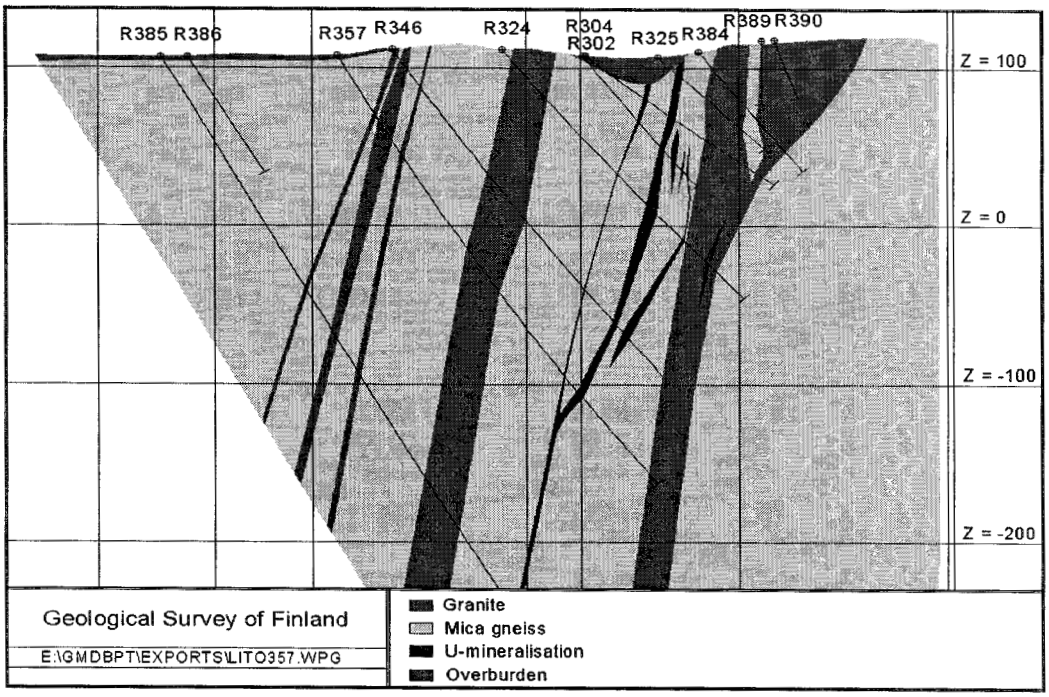

Figure 1. A vertical section showing the general geological setting at Palmottu. The Eastern Granite on the right and the Western Granite on left, are the major granite units. The main U-Th mineralisation is located between them (the narrow, dark veins).

and apatite. The interaction between the pegmatitic melts and the surrounding mica gneisses changed the physico-chemical conditions which contributed to the precipitation of uraniferous minerals. The almost uniform association of uraninite and monazite with biotite implies that the uranyl phosphate complexes became unstable at the early stage of pegmatite crystallisation. The reduction of U(VI) to U(IV) requires a counterpart which is oxidised to maintain the electron balance in the system. At Palmottu the Fe(II)/Fe(III) pair is a likely candidate for this role. Reduced pegmatite melts contain dissolved iron species in which iron is in the ferrous state. Hematite (Fe_2O_3) is an oxide mineral present at Palmottu where the iron is in the ferric state. The strong hematite pigmentation of plagioclase (Ca, Na, Al-silicate) in the mineralised Eastern Granite indicate that there has been large amounts of hematite or ferric iron available during the crystallisation of this silicate mineral.

The mineralised parts of the Eastern Granite caused the anomalies shown by the airborne radiometric maps and initialised the actual start to exploration of uranium during the late 1970's. Consequently, the mineralisation was heavily drilled during early 1980's. About 30 shallow (80-300 m) boreholes are still available for groundwater monitoring and the drill cores of over 60 boreholes are stored in the National Drill Core Archive of GTK. The ore estimates suggest around one million tonnes of ore grading at 0.1% U down to depths of 300m (Räisänen, 1986). Later drilling within the Palmottu Project have shown that the mineralisation partly continues to below a depth of 450 m (Blomqvist *et al.*, 1998).

U-Th minerals

Only a few mineral phases have been observed so far. Uraninite [UO_{2+x}, ($0.01<x<0.25$)] and monazite [$(Ce,La,Nd,Th)PO_4$] are the primary U-Th minerals of the site. Zircon [$ZrSiO_4$] and apatite (Ca-phosphate) contain only negligible amounts of radio- nuclides. Coffinite [$U(SiO4)_{1-x}(OH)_{4x}$] is a widespread alteration product of uraninite; it is a U(IV) mineral which has formed soon after the precipitation of its precursor mineral. An important group of remobilised uranium phases with chemical compositions resembling that of coffinite is found in association with fracture infilling. Minor amounts of thorite [$ThSiO_4$] and thorianite [ThO_2] have been observed in some weathered samples. There are also some indications of U-carbonate, possibly rutherfordine, in microfractures close to altered uraninite grains (Perez del Villar *et al.*, 1997).

The only U(VI) phase identified so far is uranophane [$Ca(UO_2)_2Si_2O_7{\bullet}5H_2O$]. It occurs as fracture infilling, and occasionally also in the weathered rock matrix, in the upper-most part of the uraniferous Eastern Granite, close to the ground surface (Ruskeeniemi *et al.*, 1998). The scarcity of U(VI) minerals is a peculiar feature since part of the mineralised rock is exposed at ground surface. This may be due to glacial erosion that has removed most of the ancient weathered parts of the deposits, and possibly due to the tight nature of the crystalline bedrock that has prevented oxidising waters from penetrating in the mineralisation.

Uraninite UO_{2+x}, $0.01< x < 0.25$ and coffinite $U(SiO_4)_{1-x}(OH)_{4x}$. Uraninite, in the form of euhedral crystals (generally with a diameter less than 0.3 mm) occurs as inclusions in biotites (Ruskeeniemi *et al.*, 1994). Most uraninite grains at Palmottu are visibly altered to a heterogeneous mass essentially composed of uranium and silica. The alteration begins along the grain boundaries or along microcracks within the grains (Fig. 2), hence these two phases form a basically inseparable mixture. The alteration product is amorphous with respect to X-rays; however, based on the chemistry and sophisticated mineralogical techniques it was

possible to confirm that there is coffinite in the mass (R. Ewing and J. Janeczek, pers. comm.). Galena (PbS) is a common constituent of the alteration rim and occurs as relatively coarse grained clusters or veinlets, often exhibiting crystal faces. The lead is radiogenic and derived from uraninite.

The chemical composition of uraninites is relatively uniform with U, Th and Pb as the major elements. Representative analyses give the following range of variations: UO_2 77—82%, ThO_2 5—8%, and PbO 13—18%. The Y_2O_3 content commonly exceeds 1%, also CaO concentrations are around 1%. Palmottu uraninites have high ThO_2 concentrations which are characteristic for pegmatitic mineralisations. The high Pb content is naturally due to the very old age of the mineralisation. The coffinite mass is chemically heterogeneous with uranium (50-74%) and silica (10-25%) always present as major components, whilst thorium and lead contents vary from negligible to over 10% (Ruskeeniemi *et al.*, 1994, Ruskeeniemi, 1998). Microprobe analyses indicate that in addition to the common coffinite there is a Th and P rich variety known as thorian coffinite (J. Janeczek, pers. comm.).

Due to high amounts of Th, Pb and other cations incorporated in the uraninite lattice, it is not possible to evaluate the oxidation state of uranium based on the cell parametres. XPS analyses of the surfaces of uraninite grains revealed oxidation up to composition $UO_{2.43}$ (Bruno *et al.*, 1998). These extremely high values are indicative of oxidation in the air. However, a trend showing decreasing oxidation with increasing depth of the sampling point was observed suggesting in situ variation of the oxidation states in different parts of the mineralisation.

The alteration of the uraninite at Palmottu proceeded under reducing conditions, observed by the formation of uranous silicate phases instead of uranyl compounds, and in the occurrence

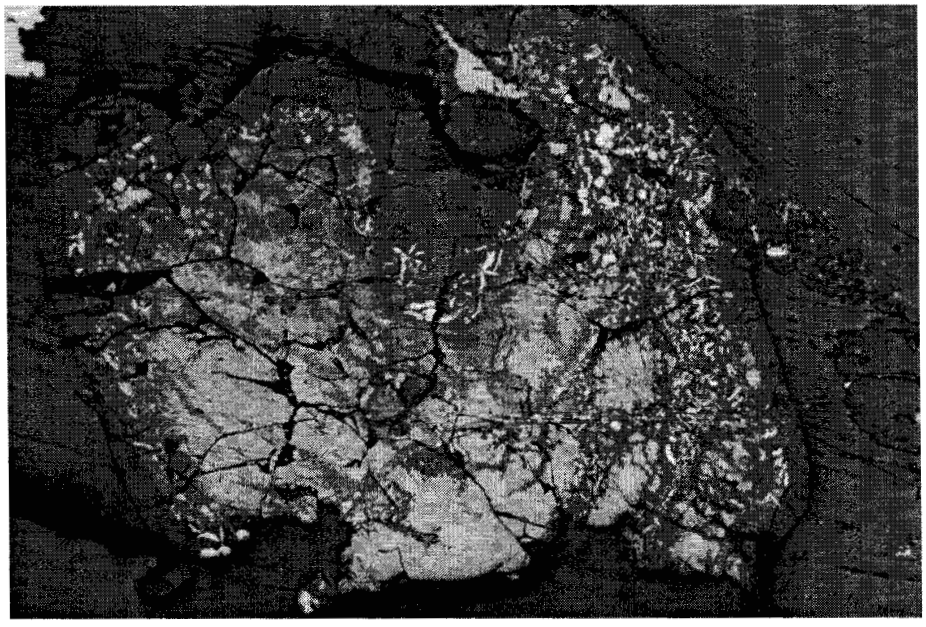

Figure 2. Altered uraninite grain. Fractured and corroded uraninite (light grey) is surrounded by poorly crystalline coffinite. Fine-grained laths and clusters of iron sulphides and galena (PbS) are frequently found in the coffinite mass. The dark background of the image is mainly biotite. The diameter of the uraninite grain is 0.3 mm.

of galena and other sulphides in the altered phases. Evidently the silica-rich residual hydrothermal solutions of the uraniferous pegmatites were responsible for the alteration of the uraninite crystals. At the late stage of crystallisation the magma is only partly solidified allowing relatively free movement of the solutions. This explains why the coffinitisation has been so pervasive.

An important consequence of the coffinitisation process is that large amounts of uranium and radiogenic lead are released. Considering alteration in constant volume, coffinitisation releases 38 g U and 11 g Pb per 100 g of uraninite (Janeczek and Ewing, 1992). At Palmottu both these elements are found dispersed in the rock matrix around the mineralised units of the site and in the fracture infilling (see below).

Conventional U/Pb dating of uraninite+coffinite gave discordant ages of 1678-1741 Ma (Huhma, 1994). These dates are affected by the out-diffusion of radiogenic lead and, hence, they should be considered as indicative of minimum ages of the mineralisation. Chemical model ages for coffinites yield almost a continuous range from around 1.7-1.8 Ga to dates well below 100 Ma (Ruskeeniemi *et al.*, 1994). The young dates indicate either geologically recent deposition of uranium silicate or conditions favouring enhanced out-diffusion of lead.

Monazite (Ce, La, Nd, Th)PO_4. Monazite is commonly accompanied with uraninite and biotite in the pegmatite, but it is also a common accessory of all lithological units of the site. A considerable amount of the REEs and related elements are hosted by monazite which may contain 11-22% of ThO_2, about 25% of Ce_2O_3 and 7-12% of both La and Nd. Gd, Pr and Y concentrations are in the order of 1-3%. The UO_2 concentrations are high averaging 1.4% (Ruskeeniemi *et al.*, 1994, Ruskeeniemi, 1998).

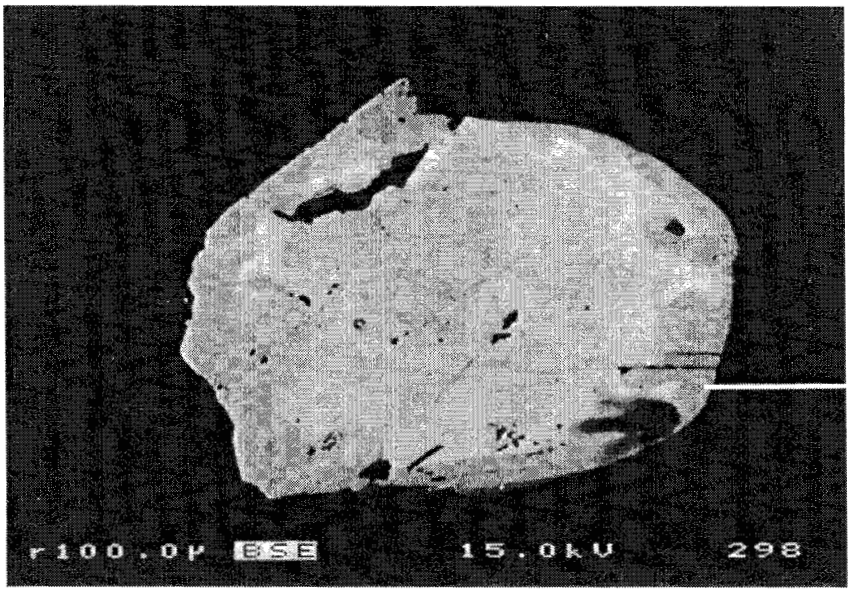

Figure 3. Corroded and recrystallised monazite grain. The core of the grain is monazite(I). The angular, magmatic zoning is only barely seen. Later alteration events have caused the patchy outlook of the grain. In a backscatter image the areas enriched in heavy elements appear lighter. Monazite(II) enriched in Ca, U, Y and P forms a darker rim around the primary grain.

In the mineralisation several monazite generations can be distinguished (Fig. 3). The monazite(I) forms euhedral or slightly rounded crystals, occasionally showing concentric magmatic zoning. This type is considered to represent the primary pegmatitic generation and it is coeval with uraninite. Dating of this monazite gave a concordant age of 1793 Ma, which can be considered as the formation age of the mineralised pegmatites (Vaasjoki, 1996). During later hydrothermal events the monazite crystals have been broken and corroded. Chemical alteration causing irregular zonations or patch-like textures is also frequent. Some grains are mantled with a younger monazite(II) generation characterised by higher Ca, U, Y and P concentrations and lower Th and Si concentrations compared to the primary monazite. Some monazites contain altered uraninite inclusions, demonstrating that they post-date the coffinitisation of uraninite.

Dispersed uranium phases. Dispersed uranium from the U-Th mineralisation can be observed in fracture infilling all over the site (Ruskeeniemi *et al.*, 1994, 1999; Perez del Villar *et al.*, 1997, 1999). High U concentrations have been recorded in association with calcites, kaolinites and iron oxyhydroxides. The highest concentrations of calcite-bearing fractures (exceeding 1000 ppm) have been observed in the upper part of the site, but small amounts of uranium phases have also been found below 400 m.

It is evident that different mechanisms are involved in controlling the fixation of uranium. The high concentrations in calcite bearing infilling can not be explained by incorporation in the lattice of calcite alone. In detailed microanalytical studies small amounts of uranium silicate or possibly uranium silicophosphate particles have been detected from calcite. The particles tend to form aggregates smaller than 10 :m in diameter. Similar material has also precipitated on smectite, pyrite and neo-formed albite, and it is also found in the tight unfractured parts of the rock (in rock matrix) around the mineralised zones. Chemically these tiny particles resemble coffinite (U(IV)-silicate), and their common association with pyrite suggest the reduced form for uranium. Their negligible Th concentration is the major difference compared to the composition of the coffinite around uraninite grains, this feature evidently reflecting the geochemically low mobility of Th. Bulk analyses of some weathered fracture infillings in the Eastern Granite show U concentrations up to several hundreds of ppm (Landström and Tullborg, 1999). However, it is not yet known whether it is a question of sorbed uranium or a discrete uranium phase/phases.

It is has earlier been proposed that the major mobilisation of uranium took place during the coffinitisation of uraninite under hydrothermal conditions (Ruskeeniemi *et al.*, 1994). Recent fluid inclusion studies (Blyth and Frape, 1999) have provided independent and additional support in favour of the hydrothemal concept. Based on the fluid inclusion results, the majority of the fracture calcites were formed under hydrothermal conditions at temperatures from 300 to 150EC. For example, a calcite-dominant fracture infilling which contains more than 1000 ppm of U was formed at 285EC. Such high temperatures have not generally prevailed on the Finnish part of the Fennoscandian Shield since Proterozoic times.

Somewhat contradicting results have been received from uranium series decay (USD) studies. A set of bulk calcite analyses shows that considerable part of the total uranium is in the oxidised form (Suksi *et al.*, 1998). The USD results from the same samples indicate dynamic leaching-accumulation conditions and the calculated USD dates range from 30 to 310 ka (the upper limit of the analytical technique). These recent dates may indicate that mobilisation (reworking) of the dispersed uranium has been a continuous long-term process, probably due

to changing conditions. In comparison, the major part of calcite and other fracture-infilling minerals, may show clear signs of ancient hydrothermal origin. In conclusion, the fracture infilling minerals and the associated uranium compounds may actually represent completely different formation times and conditions of the system.

Uranophane $Ca(UO_2)_2Si_2O_7 \bullet 5H_2O$. Uranophane, a secondary bright yellow U(VI) silicate mineral, is found in the very uppermost part of the Eastern Granite which forms a small hill. It was first detected in borehole R384 at a depth of 40 m and later turned later out to be very common in the upper part of the short boreholes R389 and R390 (cf. Fig. 1; Ruskeeniemi *et al.*, 1998). Uranophane occurs in tight to open fractures as a bright yellow crystalline mass or as rosettes together with minor calcite and/or mixed layer clays (Fig. 4). Many of the uranophane-bearing fractures are above the present groundwater table and in some fractures uranophane infilling exhibit cross-fiber textural types, indicative of dilational-type conditions during crystallisation. Several microprobe analyses from uranophane grains show that it contains 67 - 75 % U_2O_3, 11 - 18 % SiO_2 and 3.7 - 6.1 % CaO. Some analyses also show small amounts of Th, La, Fe, Al and P. Gorman and Nuffield (1955) give very similar values for eleven uranophane samples from different locations; therefore the uranophane from Palmottu seems to be quite typical. Detailed microprobe studies failed to reveal any signs of corrosion in the delicate uranophane needles. Yet, the U-series disequilibrium studies (USD) point to uranium dissolution in one of the samples, although the sample is seemingly intact (Suksi, 1998).

Two uranophane samples were dated by the USD method. The dates obtained for the samples, 90-120 ka and 189-240 ka, respectively (Suksi, 1998), fit well with the interglacial periods of the two latest ice ages. The conventional U-Pb dating gave considerably higher dates from some million to tens of millions of years (Mänttäri, 1999). This latter dating method, however, is not sensitive enough for samples with so low lead concentrations; therefore the results would just confirm the geologically recent ages indicated by the USD data.

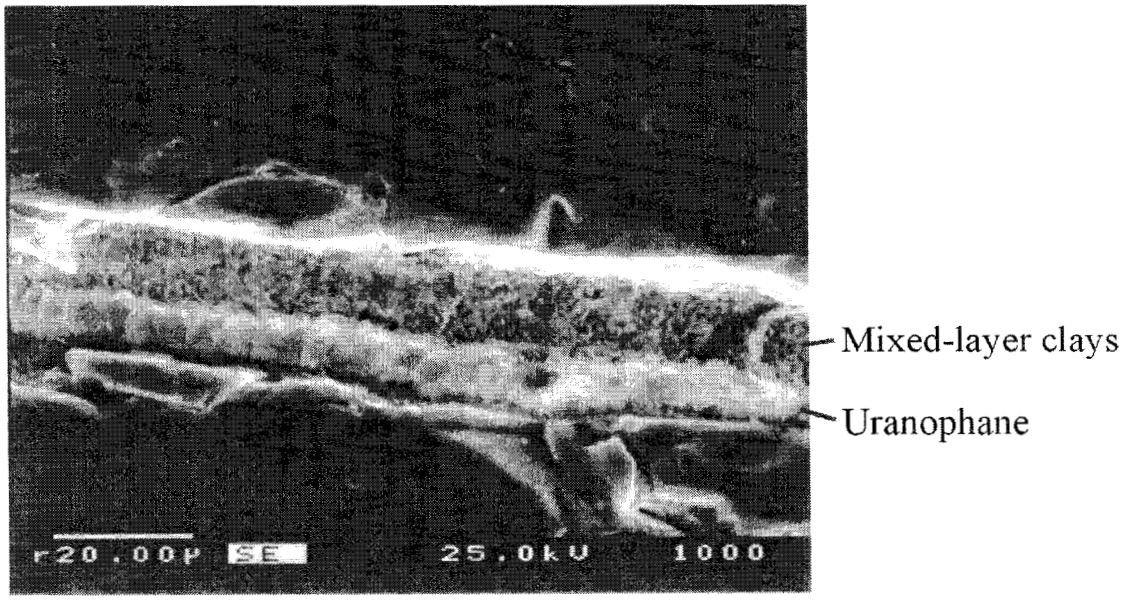

Figure 4. A tight microfracture filled with uranophane and mixed-layer clays. The micro-fracture forms an outlayer (extension) of a partly open fracture, the surface of which is sporadically covered with a thin layer of uranophane. Sample from borehole R390, 6.59 m.

There seem to be two main reasons, why uranophane only occurs in the restricted area of the upper part of the Eastern Granite. The Eastern Granite has in average two to three times higher uranium concentrations compared to the other granites of the site. As the Eastern Granite is largely utcropping, its surface has been subject to continuous flushing of oxidising, low-pH rain water, yielding good physico-chemical conditions for the slow disintegration of U(IV) minerals and the formation of dissolved uranyl phases that subsequently may precipitate as U(VI) minerals. In comparison, the main mineralisation, located outside the Eastern Granite (Fig. 1), is covered by the thick Quaternary deposits that shelter it from continuous infiltration of oxidising surface waters.

Implications for mobilisation of uranium

Considering present-day mobilisation and migration of uranium, it is essential that there is a source of relatively easily soluble uranium and that this source can be reached by flowing groundwater. Groundwater flow in crystalline rocks is predominantly focused within discrete fractures, therefore groundwater does not have a direct access to the major part of the bedrock. In such cases, diffusion is the only possible mechanism to transport uranium. As documented for Palmottu (Suksi, 1999; Suksi *et al.*, 1992), out-diffusion of uranium (from rock to fracture) has taken place in a narrow zone extending up to a few centimetres around many fractures. The diffusion process may involve large volumes but it is quite slow and does not respond quickly to changing conditions. However, during the long run, the bedrock acts as an infinite source of uranium from which diffusion may feed uranium to easily accessible sites for groundwater flow.

Fracture coating and infilling are more attractive sources for uranium due to their close contact to groundwater. At Palmottu considerable amounts of uranium are associated with the fracture-infilling minerals: calcite, kaolinite and iron oxyhydroxide. Dissolution of, or desorption from these minerals could give high uranium concentrations in groundwater, but in a dynamic flow systems the fracture coating or infilling could not maintain a continuous, long-term supply of uranium without additional contribution from other sources (Salas and Ayora, 1998). However, in the fractures of the uppermost part of the Eastern Granite, uranophane is a frequent mineral that potentially constitutes, as described above, a very rich source for uranium with U_2O_3 up to 75 %.

Experimental field work: dissolution of uranophane. A field experiment was established to monitor and study the dissolved concentrations of uranium in the uppermost part of the bedrock of the Eastern Granite where uranophane were known to exist. A borehole packer was installed in borehole R390 at 10.4 m depth, just above the groundwater table during a dry period (Kaija and Blomqvist, 1999). This borehole was originally drilled at a dip of 60° from a flat-lying terasse on the Eastern Granite. Most of the area surrounding the borehole is composed of homogenous non-fractured granite, except for a narrow, distant part of the terasse covered by overburden and vegetation, which could be indicative of a fractured part of the bedrock. A video camera survey of the borehole showed that sub-horizontal fracturing was quite common in the upper part of the bedrock, and seven fractures with small apertures (1 to 2 mm) were detected above the groundwater table. Some of the fractures contained uranophane, often accompanied by calcite.

After approximately 3 weeks following the start of a rainy period, the water table in borehole R390 rose above the packer level so that the first groundwater samples of the "unsaturated

zone" could be taken. Uranium concentrations in these samples were around 100 μg/l, twice the concentration compared to a water-conducting fracture zone in the same borehole at a depth of 27.5 – 33.5 m (Fig. 5). After an additional week, the groundwater table of the "unsaturated zone" had further risen some 5 m, to a level of 5.1 m below ground surface and it remained here for at least 3 weeks. Simultaneously, the dissolved uranium concentrations had increased to 300-350 μg/l. This concentration increase was attributed to increased precipitation (120 mm in four weeks) that introduced low-pH water in the "unsaturated zone" of the Eastern Granite. The pH values of the samples from the "unsaturated zone" were from 6.5 to 7.2 compared to 7.5 to 7.8 for groundwater in fracture zones of boreholes R390 and R 389 at 27.5–33.5 m and 28.5–32.5 m, respectively. The pH values of precipitation were, however, still much lower, from pH 4.9 to 5.8.

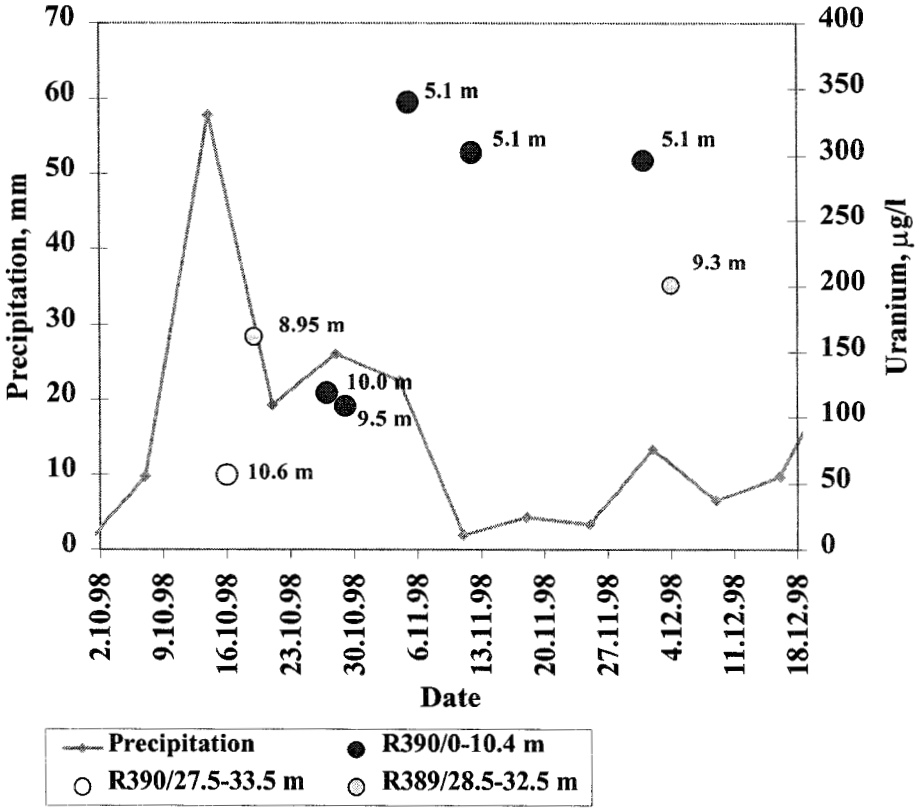

Figure 5. Concentration of dissolved uranium *vs.* time for groundwater from the "unsaturated zone" of borehole R390 (from 0 to 10.4 m) in relation to weekly precipitation. For comparison, the dissolved uranium concentrations of groundwater from the fracture zones 27.5–33.5 m and 28.5–32.5 m of boreholes R390 and R389, respectively, are also given. The figures attached to the observation points indicate depth of groundwater table during sampling time. Modified from Kaija and Blomqvist (1999).

Modelling support for uranophane dissolution. The solubility of uranophane is strongly dependent on the pH of the solution, as summarised by Bruno *et al.*, (1999). Using the solubility product given for natural uranophane by E. Cera (logk = 7.69, *c.f.* Bruno *et al.*, 1999), the solubility of uranium would be of the order of 200 ppb in a surface-close groundwater at Palmottu with pH of 6.5. In water with pH of 5.5, typical for precipitation at Palmottu, the solubility of uranium would be 2000 ppb. The characteristic reaction time (*c.f.* Bruno, 1997) for dissolution of uranophane is variable and strongly dependent on the

parameters used in the calculations, but for natural uranophanes a time interval from one hundred to a thousand days has been calculated. For synthetic uranophane, however, the calculated characteristic reaction time is much shorter, in the order of one day to ten days (Bruno *et al.*, 1999). Accordingly, the modelling results with respect to uranium solubility and reaction kinetics are in good accordance with the experimental results that indicate dissolution of uranophane in the uppermost part of the Eastern Granite at Palmottu.

Summary and discussion. Field experiments performed in the unsaturated zone of the Eastern Granite indicate a sensitive balance between low pH recharge infiltration and increases in dissolved uranium. This indicates access to easily soluble uranium phases along fractures in the unsaturated part of bedrock. The increase in uranium concentrations after such a short mean residence time of approximately 3 weeks, is attributed to the dissolution of uranophane, the only identified U(VI) mineral that has been observed in fractures until now. This interpretation is supported by modelling results of uranophane dissolution and by reaction kinetics. Experimental tests of uranophane dissolution are presently being performed in conditions relevant to Palmottu in order to approve/disregard this hypothesis.

The dissolved uranium concentrations in the recharging groundwater, 300 μg/l, is an extremely low concentration compared to the concentration of uranium in the mineral uranophane, close to 60 wt-%. Therefore only a small portion of uranophane need to be dissolved in order to explain the observed concentrations in water. However, if such a dissolution process would be repeated annually from 10 to 100 times and during a period of some thousand years, the availability of uranophane would soon become a critical issue. On the other hand, the solubility of uranophane is strongly pH dependent (Bruno *et al.*, 1999), decreasing with increasing pH. Therefore, the typical increase of pH with time (and depth) would cause a tendency of re-precipitation of uranium in the upper part of the bedrock, as also pointed out by Read *et al.*, (in this volume) at shallow depths where uranophane presently occurs. As no volumetrically important sources of other uranyl phases have yet been observed, despite of careful micro-analytical work, it is likely that uranium is re-precipitated as secondary uranophane.

During Quaternary times, glacial erosion has strongly affected the Fennoscandian Shield and eroded much of the overburden and weathering layer of the bedrock. Therefore, also the supergene alteration zone of Palmottu may largely have been eroded away. As evidenced by the geologically young dates of uranophane (from 90 to 240 ka), the formation of a "uranophane zone" is presently proceeding at Palmottu and the amount of uranophane may slowly be increasing and expanding due to oxidative alteration of uraninite in supergene conditions (*c.f.* Gorman and Nuffield, 1955).

Conclusions

Emplacement of the uranium mineralisation, coeval with pegmatite formation, took place 1.8 Ga ago with uraninite and monazite being the dominant uranium bearing phases. Since then, it is apparent that the major flux of uranium into the geosphere of Palmottu is related to the hydrothermal alteration of the uranium mineralisation and formation of coffinite and a dispersed uranium pulse some 1.7-1.8 Ga ago. Reworking of all this uranium has continued under variable conditions from that that time and it is still going on, as is evidenced by the uranophane zone of the uppermost part of Eastern Granite. Here uranophane ages of 90-120 ka and 189-240 ka have been received, corresponding to the interglacial periods of the last two glaciations. More recent reworking is evidenced by the comparatively high uranium

concentrations in groundwater at the upper part of the mineralisation, some of which even respond to short-time variation of precipitation.

However, with respect to the site-scale uranium mass balance, it is clear that the major part of the uranium has remained in the ancient U(IV) phases, uraninite and coffinite, since their formation, despite the fact that the mineralisation has been subject to supergene processes for long periods of geological time. The amount of mobilised or dissolved U(VI) in minerals and groundwater is, however, very low compared to U(IV) in uraninite, coffinite and dispersed uranium phases. This demonstrates the overall geochemical stability of the crystalline bedrock over these geological timescales.

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Hydrogeochemical interpretation of groundwater at Palmottu

P. Pitkänen[1], J.Kaija[2], R. Blomqvist[2], J.A.T. Smellie[3], S.K. Frape[4], M. Laaksoharju[5], P. Negrel[6], J. Casanova[6] and J. Karhu[2]

[1]VTT, Finland
[2]Geological Survey of Finland
[3]Conterra AB, Sweden
[4]University of Waterloo, Canada
[5]Intera KB, Sweden
[6]BRGM, France

Abstract

The understanding of hydrogeochemical evolution is essential in order to assess the migration of radionuclides at Palmottu. The objective of this study is to evaluate chemical interaction and mixing processes of groundwater evolution, and also to evaluate the residence time over which such processes have persisted. The following interpretation is based on hydrochemical, isotopic, petrographic and hydrological data. Statistical analyses and geochemical modelling are used in order to determine groundwater types, and the relation between conservative mixing and water-rock interaction.

Four general groundwater types characterise the Palmottu site. Recently recharged, shallow Ca-HCO_3 type groundwater evolves in the upper part of the bedrock into a Na-HCO_3 type groundwater at increasing depth within a few decades, partly due to Ca to Na ion-exchange processes. Brackish Na-SO_4 and Na-Cl type groundwaters prevail below the HCO_3 groundwater bodies; Na-SO_4 is present only around the mineralised zone whilst Na-Cl is found at greater depths also in the surrounding area. The latter two groundwater types show distinct glacial isotopic signatures. Mixing of water types explains largely the changes of SO_4, Cl and Na concentrations. Water-rock interaction is specifically connected to carbon cycling. Biogenically produced CO_2 promotes silicate weathering and dissolution of calcite at shallow depths. The heavy $^{87}Sr/^{86}Sr$ ratios measured from the HCO_3 waters are consistent with the dissolution of Rb-rich minerals such as K-feldspar and biotite. Ca to Na ion-exchange maintains calcite dissolution and calcite is saturated in Na-HCO_3 type water. Minor calcite precipitation and silicate dissolution is likely in the brackish groundwater types, thus buffering pH to around 8.5. Anaerobic oxidation of organic matter in the lower part of the Na-HCO_3 layer and CH_4 oxidation in the brackish groundwater layer using SO_4 as an electron acceptor are considered probable processes based on C and S isotope data.

Introduction

The characterisation of groundwater geochemistry, and the interpretation and understanding of hydrogeochemical evolution form an essential part of assessing radionuclide migration in a natural environment and ultimately the performance assessment of a repository for deep geological disposal of radioactive wastes. Transport of radionuclides in groundwater may be affected by several processes: adsorption, desorption, dissolution and precipitation. In order to understand and characterise these reactions, a model describing the water-rock interaction and mixing controlling the basic hydrochemistry is needed. The ultimate goal is to create a site-specific model that describes the changes in groundwater composition reliably, explains the reasons for these processes and evaluates how long these processes have persisted.

This study represents a continuation of the hydrogeochemical characterisation performed during the first phase of the Palmottu natural analogue project (Blomqvist *et al.,* 1998, and previous work referred therein). During the current, detailed investigation phase many additional hydrogeochemical data have been produced (Kaija, 1998), much of which have been utilised in other related on-going site

evaluations. The data have been described and modelled using several standard geochemical tools including principal component analysis (Laaksoharju *et al.,* 1999; Gimeno and Peña, 1999) and both inverse and forward geochemical modelling approaches (Gimeno *et al.,* in this volume) have been used in the description of data.

Hydrogeological setting

The Palmottu U-Th mineralisation is hosted by Proterozoic (1800 Ma) crystalline bedrock, mainly mica gneiss with granite pegmatite veins, where feldspars, biotite and quartz are the dominant rock-forming minerals with relatively abundant pyrrhotite and pyrite. Due to its complex geological history, the bedrock is cut by numerous fracture generations; most are sealed by precipitation of secondary minerals, mainly calcite and various clay minerals (Ruskeeniemi, 1998). Open, water-conducting fractures are mainly observed in the upper part of the bedrock at depths down to 150 m. At greater depths open fractures are less frequent and, the hydraulic conductivity of the bedrock is correspondingly very low. In the upper part of the bedrock, open fractures form a network composed of subhorizontal fractures, frequently dipping towards the S or NE, intersected by steeply dipping fractures of various orientations. Deeper down, groundwater flow is controlled mainly by discrete, subvertical fracture zones (Blomqvist *et al.,* 1998). The bedrock at Palmottu is largely covered by glaciogenic till or glaciofluvial formations. A large delta formation, located at the margin of the Salpausselkä III end moraine formation, borders the Palmottu site from the west.

The integrated hydrogeological and hydrochemical model of the Palmottu site (Fig. 1) is presented in Blomqvist *et al.,* (1998) and only a brief summary is presented in this volume (Blomqvist *et al.*, in this volume). The upper 100 m of the bedrock is characterised by dilute groundwater of HCO_3 type. Calcium is the dominant cation near the surface changing to sodium in the lower part of this HCO_3 type groundwater zone. High tritium contents indicate a dynamic flow system, which penetrates to a depth of at least 200 m in the southern part of the site. Below the HCO_3 type water body the groundwater is brackish, of Na-SO_4 or Na-Cl type, and both the hydrochemistry and isotopic results suggest long residence times and stagnant flow conditions. The Na-SO_4 type water seems to be restricted to the central mineralised zone of the site, between the Na-HCO_3 and Na-Cl type waters. In the surrounding area, *i.e.* the area westward from the Western Granite, the Na-Cl water type is observed directly below the Na-HCO_3 water.

General hydrogeochemical features

Major chemical trends

With increasing depth the content of total dissolved solids (TDS) increases from less than 100 mg/l for groundwater in the overburden to a maximum of 1600 mg/l in the brackish Na-SO_4 and Na-Cl groundwaters at 300 to 350 m depth (Fig. 2a). Likewise, pH increases with depth from slightly acid conditions in the overburden to pH 7-8 in the Ca-HCO_3 type groundwater in the upper part of the bedrock (Fig. 2b) and further to 7.5-9 in the Na-HCO_3 type groundwater due to dissolution of minerals during its evolution. In the brackish groundwater types pH mainly varies from 8.5 to 9.

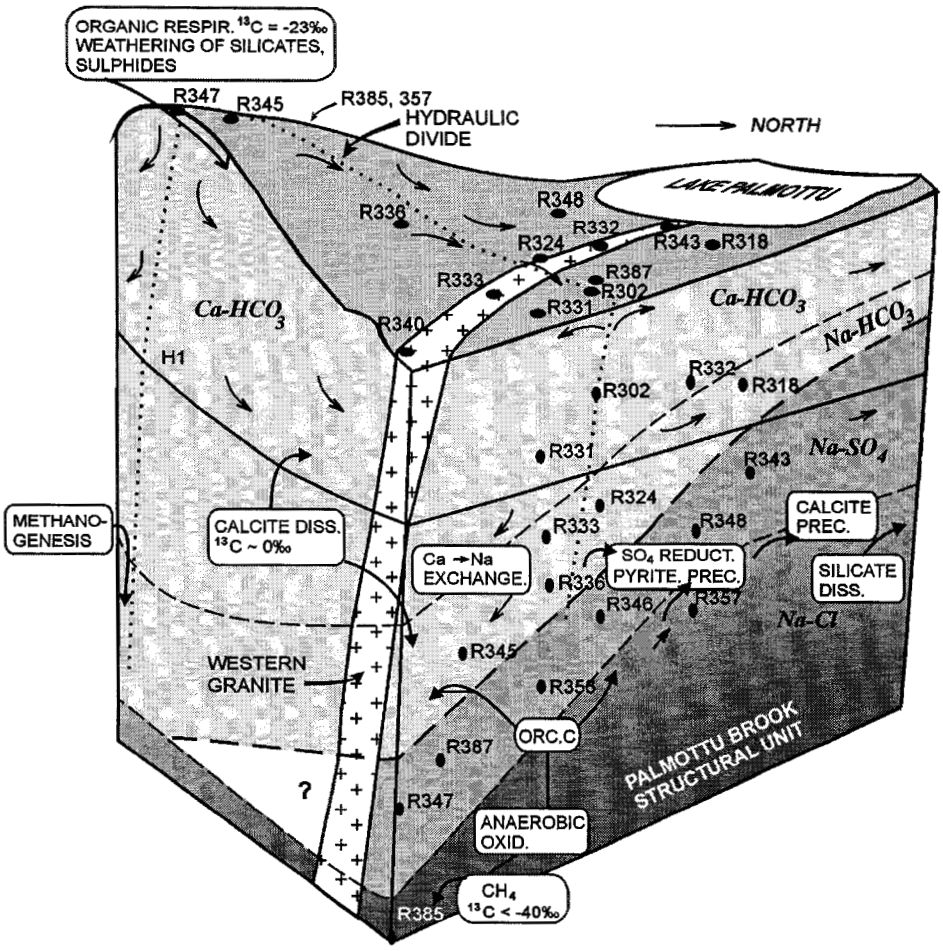

Figure 1. The conceptual hydrogeological model of Palmottu with flow directions indicated by arrows (modified from Blomqvist *et al.,* 1998). The hydrogeochemical processes are described later in the text. Depth extension is about 350 m.

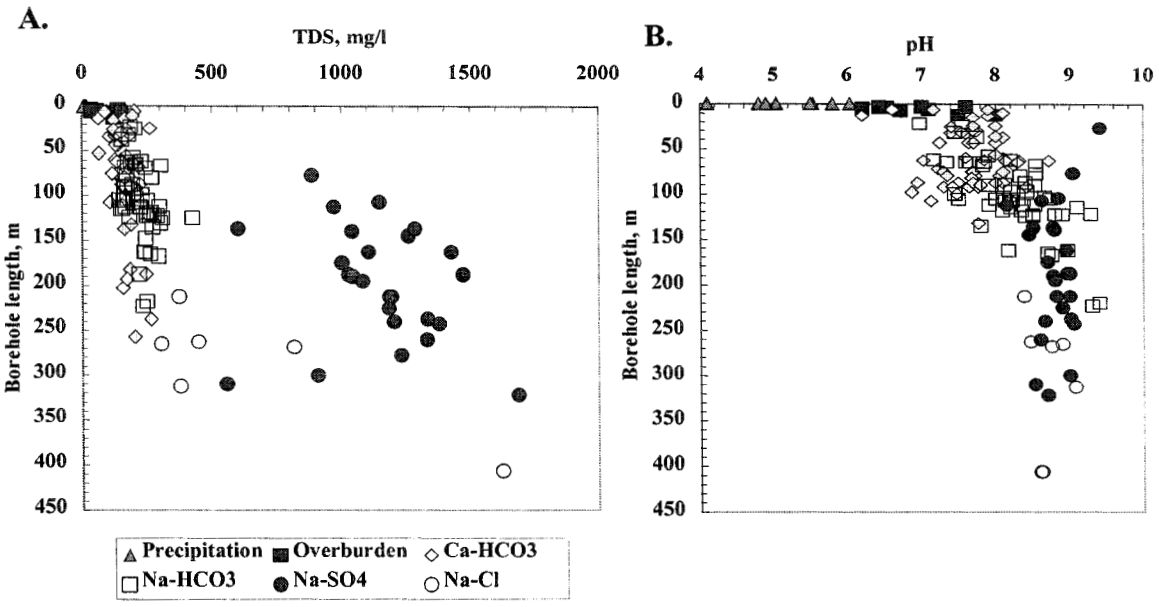

Figure 2. Variation of a) TDS, and b) pH versus borehole length.

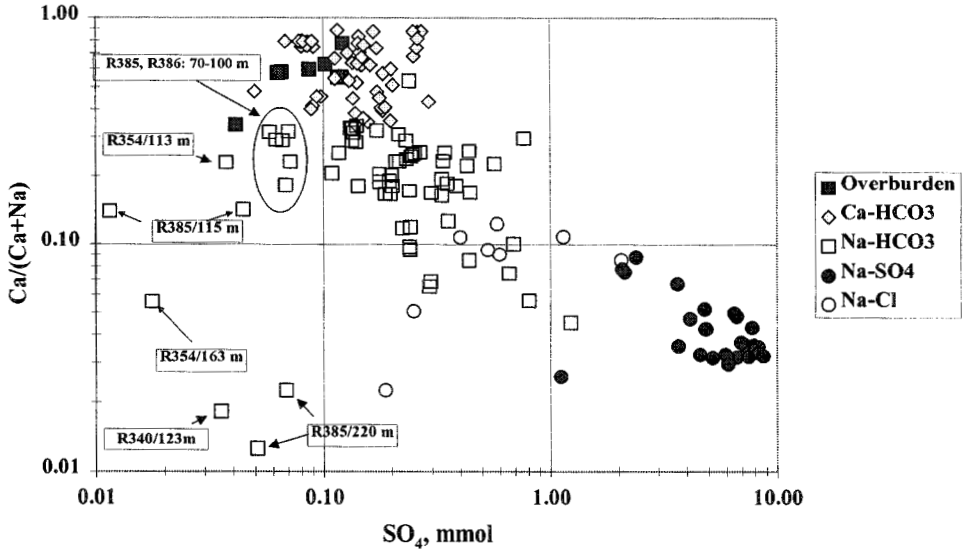

Figure 3. Variation of Ca/Ca+Na ratio versus SO_4. Specified samples are from the area surrounding the U-mineralisation.

The obtained data indicate differences in groundwater chemistry between the central, mineralised zone of the site and the bedrock of the surrounding area (Fig. 3). In the central zone the groundwater changes from a Ca-dominant type in the overburden and shallow bedrock to a Na-dominant type at greater depths together with increasing SO_4. Brackish Na-SO_4 type groundwaters have not been observed from the surrounding area (Fig. 1). The presence of SO_4 in the central area may be explained by the long-term mixing of Na-SO_4 type water from the mineralised zone and/or artificial mixing stimulated by open-hole hydraulic conditions following the drilling activities for uranium exploration in the beginning of the 1980s.

Stable isotope signatures

The δ^2H and $\delta^{18}O$ isotope signatures of the four groundwater types (Fig. 4) indicate a meteoric origin of the water without any palaeoevidence of seawater mixing during post-glacial times. There is, however, a significant depletion in the $\delta^{18}O$ isotope values of the Na-SO_4, Na-Cl and Na-HCO_3 type groundwaters. The local, present-day meteoric groundwater signature can be observed in the shallow bicarbonate water, and isotopic shifts in either direction deeper in the bedrock reflect older changes of climate or in geological conditions. The low values may represent a colder climate recharge, which took place during the retreat of the Weichselian ice sheet about 10 000 years ago (*c.f.* Blomqvist *et al.,* 1998). The increasing depletion of $\delta^{18}O$ in samples compared to modern recharge values should reflect a higher portion of glacial melt water. The isotopic depletion in the Na-SO_4 type water corresponds roughly to a mixing of up to 90 % melt water, if the $\delta^{18}O$ of the glacial melt water is considered to be –19 to –20 ‰, an estimate based on measured values from bedrock groundwaters in Estonia (Ferronsky *et al.*, 1983) and from carbonaceous concretions in Baltic Sea sediments (Karhu, 1988). If the glacial melt water had a $\delta^{18}O$ signature of –25 ‰, as calculated for the water forming the subglacial calcite precipitates (Tullborg and Larson, 1984), the isotopic depletion would then correspond to the mixing of 50 % melt water. The deepest Na-Cl type groundwater shows a slight shift to the right (Fig. 4) which may reflect an increasing contribution of preglacial waters and still higher mean residence time.

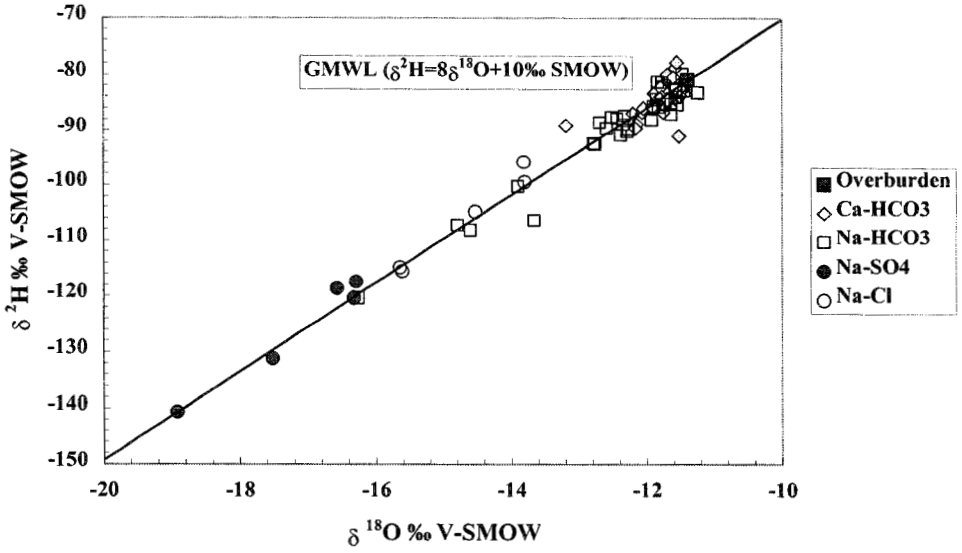

Figure 4. Stable isotope plot (δ^2H and $\delta^{18}O$) for the Palmottu groundwater samples compared to the Global Meteoric Water Line ($\delta^2H = 8 \cdot \delta^{18}O + 10$; Craig, 1961).

Salinity trends

Salinity increase with depth in the Palmottu groundwaters is mainly due to higher concentrations of Na, Cl and SO_4. The chemistry points to two different sources: Na-SO_4 and Na-Cl, neither of which seems to be of marine origin. This latter statement is consistent with the supra-aquatic location of the Palmottu site since the last glaciation (Donner, 1995; Blomqvist *et al.*, in this volume). The SO_4/Cl ratio in the most saline Na-SO_4 type water exceeds by two orders of magnitude the modern Baltic Sea ratio; furthermore, the Br/Cl ratio of brackish water types is about 0.005 (calculated in mmol/l), *i.e.* approximately three times higher compared to sea water. High Br/Cl ratios are common in strongly enriched brines of the Canadian and Fennoscandian Shields (Frape *et al.*, 1984; Nordstrom *et al.*, 1989; Blomqvist *et al.*, 1989; Kamineni *et al.*, 1992; Pitkänen *et al.*, 1999). Such enrichment in Br has been attributed to water-rock interaction, and it is also typical for evaporated seawater which has been concentrated due to the precipitation of halite. Alternatively, formation of such evaporites can be linked to periglacial conditions (*e.g.* Keys and Williams, 1981).

Moreover, there is no realistic process to produce such high concentrations of Cl or SO_4 in the current type conditions that have prevailed since the last glaciation, in which water-rock interaction and salinity enrichment are mainly based on CO_2 and O_2 promoted dissolution. Chloride and sulphate do not have primary minerals in the bedrock of the Palmottu site, but Cl is a typical trace element in hydrous silicates (replacing OH groups) and the mineralisation is rich in iron sulphides, which could be oxidised. However, hydrolysis of silicates, as a source of high salinities, is not a convincing process because it effectively ceases when proton production ends due to the diminishing of carbonic acid (maximum production a few mmol/l). Significant aerobic oxidation of sulphides is considered unlikely below the groundwater table. This reaction would require high amounts of dissolved oxygen. For example, to produce 800 mg/l of SO_4 (the presently observed maximum concentration in groundwaters at Palmottu) from the oxidation of pyrite, would require 500 mg/l of O_2. This value exceeds by a factor of ten the maximum solubility of O_2 in cold, glacial water (45 mg/l at 0° C) (Ahonen and Vieno, 1994). Further salinity enrichment would therefore require additional saline

sources, most likely by mixing with a saline water type existing deeper in the bedrock or formed under specific palaeo conditions (Smellie *et al.*, in this volume).

Groundwater mixing trends

At Palmottu the near-surface bedrock is characteristically fractured and the groundwater flow system tends to be controlled by a complex, interconnected network of fractures. Thus, mixing of different groundwater types may be expected. To complicate the picture, naturally occurring mixing processes may be further enhanced, or changed, during borehole activities such as drilling, cleaning, sampling and testing. The influence of these latter processes have been largely minimised by employing strict procedures during borehole activities, however, the possibility of some adverse effects cannot be totally ruled out in particular with respect to the old exploration boreholes drilled in the 1980s.

Laaksoharju *et al.*, (1999) and Gimeno *et al.*, (in this volume) have addressed in detail groundwater mixing processes using various multivariant techniques (*i.e.* Principal Component Analysis). These studies revealed the groundwater end-members most likely to have undergone mixing in the groundwater system (*e.g.* Fig. 5). It is clear that mixing occurs within the upper dynamic groundwater system where the HCO_3 type waters are dominant. In contrast, the Na-Cl type waters indicate negligible mixing with shallower HCO_3 groundwaters. Also the mixing of Na-SO_4 type water with the bicarbonate waters is limited, according to the bimodal character of the distribution of Na-SO_4 samples (Fig. 5). The conclusions of these modelling results essentially support the findings of the hydrostructural model of the Palmottu site.

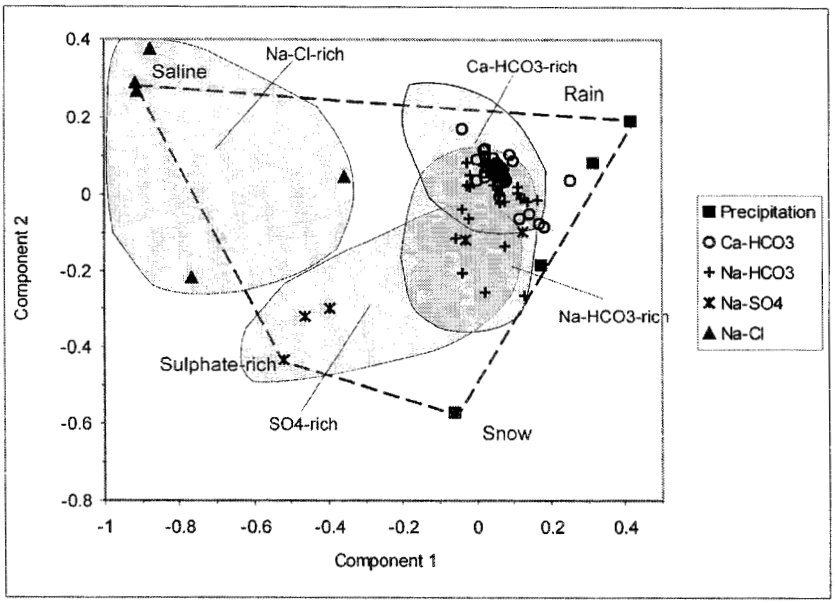

Figure 5. Principal Component Analysis (PCA) plot showing the mixing relationships at Palmottu (Laaksoharju *et al.*, 1999).

Groundwater residence time

The use of tritium data gives a possibility to estimate the effects of isotopic dilution on ^{14}C values of dissolved carbonate (DIC) caused by the dissolution of ^{14}C-free calcite or due to interaction with old organic carbon (*e.g.* peat). No natural tritium levels of groundwater recharged prior to thermonuclear testing in the 1950s are any more detectable in the late 1990s, therefore high tritium concentrations of the shallow groundwaters (overburden and the Ca-HCO_3 type of Fig. 6) at Palmottu are due to recharge during the last 50 years. As the tritium and $\delta^{18}O$ levels of shallow groundwater samples correspond to the values of current precipitation, they can be considered as young groundwater up to 100 %.

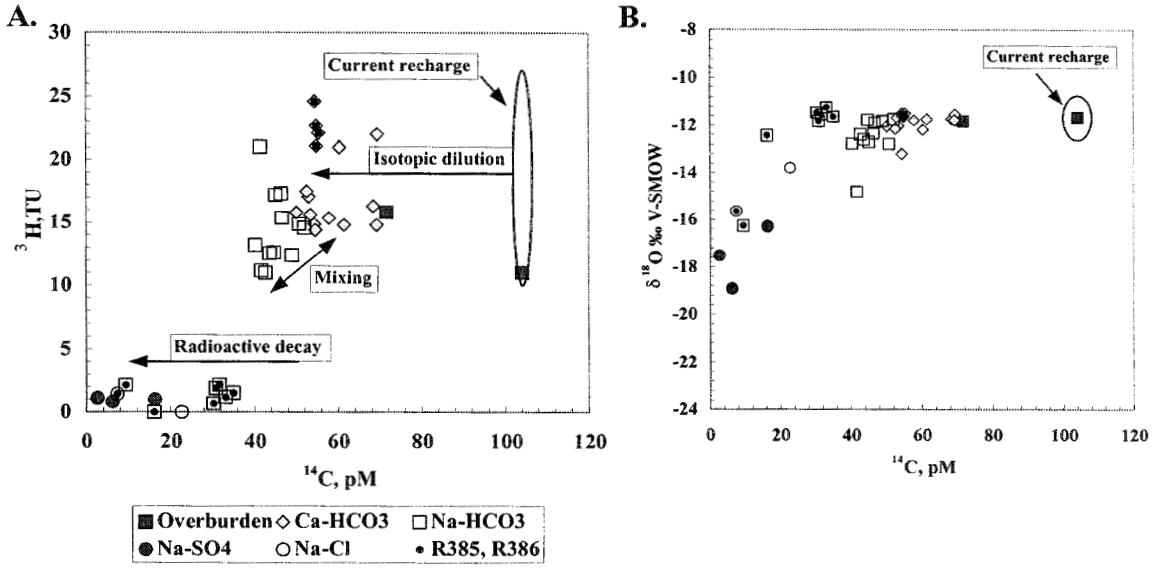

Figure 6. Variation of a) ^3H, and b) $\delta^{18}O$ in water versus radiocarbon of dissolved carbonate at Palmottu. The ^{14}C values of current recharge are based on other sites in Finland (Pitkänen *et al.*, 1996, 1998, 1999).

Some of the Na-HCO_3 water samples of the central area have tritium values comparable to the Ca-HCO_3 water, whereas others show a slight depletion of tritium compared to the Ca-rich water. On the other hand, the Na-HCO_3 samples of the surrounding area (from R385 and R386) contain only traces of tritium. At the same time, all of these Na-HCO_3 samples, except one, represent current recharge values of $\delta^{18}O$. Accordingly their residence times may range widely, from early post-glacial times up to the 1950s.

The ^{14}C values of present-day groundwaters at Palmottu are of the order of 70 to 50 % modern for the Ca-HCO_3 waters and 50 to 40 % modern for the Na-HCO_3 waters (Fig 6a), due to isotopic dilution caused by calcite dissolution. Similar magnitudes of dilution has also been observed at several other sites in Finland (Kankainen, 1986; Pitkänen *et al.*, 1996, 1998, 1999). Calcite has reached saturation in the Na-HCO_3 water (Gimeno and Peña, 1999) suggesting that the input of dead carbon during groundwater evolution can go down to 40 % dilution, and radioactive decay is responsible for the still lower ^{14}C values, for most of the samples that contain only traces of tritium. For estimating the mean residence time of the samples with low ^{14}C values (Fig. 6a), a value of 40 % of modern can be used as an initial value. Then samples with ^{14}C values below 20 % of modern would have a mean residence time of more than the half life of ^{14}C, 5730 years,

and samples with ^{14}C values below 10 % of the order 11 000 years or more. As groundwaters usually are mixtures of younger and older components, waters dating back to the retreat of the ice sheet at Palmottu may be involved in all these low ^{14}C mixtures. This is as also indicated by the $\delta^{18}O$ data of these waters (Figs. 4 and 6b). The possibility of mixing with still older groundwater types is also present; in particular for the groundwaters with very low ^{14}C values (< 10 % modern).

Water-rock interaction

Chemical reactions in a crystalline rock-groundwater environment and under cool climate conditions are essentially connected to the geochemical cycling of carbon. Carbon-related processes also contribute significantly to the concentrations of such ions as Ca, Mg, K and HCO_3, and in pH and redox conditions. The initial increase of alkalinity, pH and calculated saturation indices of calcite (from Gimeno and Peña, 1999) in shallow groundwaters (Figs 2 and 7) have been generally interpreted as a result of fracture calcite dissolution in CO_2-rich recharge water (*e.g.* Nordstrom *et al.*, 1989). A similar interpretation is considered valid for the HCO_3 type groundwater at Palmottu (Blomqvist et al. 1998; Gimeno *et al.*, in this volume).

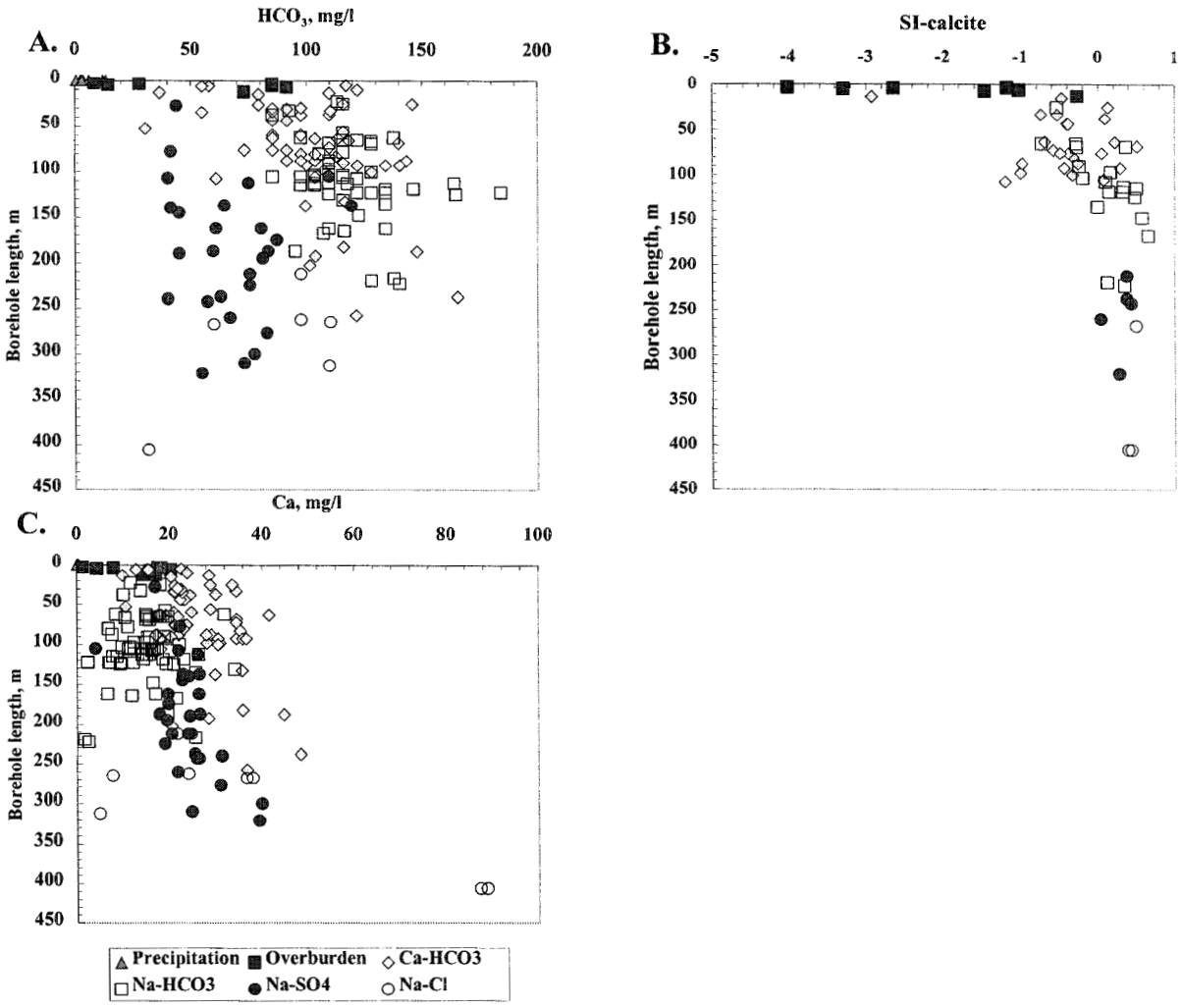

Figure 7. Variation of a) HCO_3, b) saturation indices of calcite, and c) Ca versus borehole length at Palmottu.

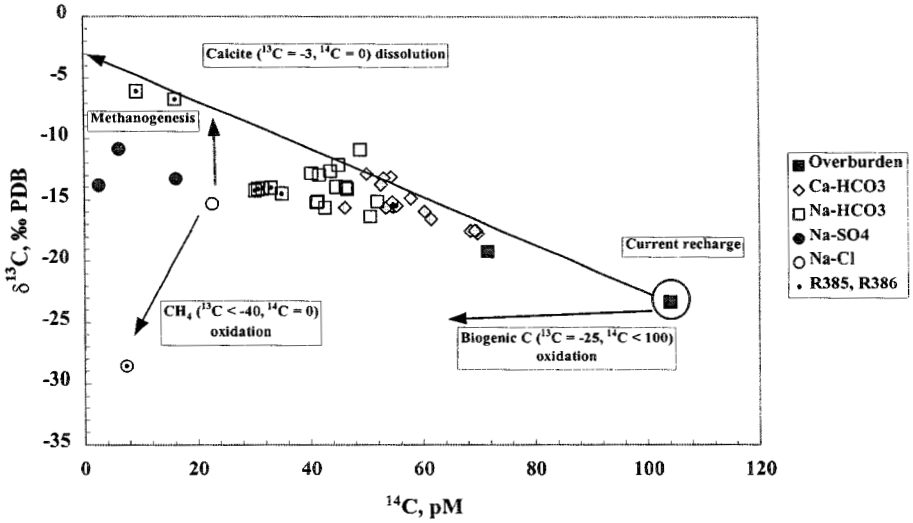

Figure 8. Carbon isotopes of dissolved carbonate with potential processes affecting carbon isotope signatures.

The carbon isotope composition of DIC is a direct reflection of the potential processes affecting the geochemical history of groundwater (*e.g.* Fritz *et al.*, 1989; Plummer *et al.*, 1990; Pearson *et al.*, 1991). Recharging groundwater in the overburden has commonly a low pH and high CO_2 content which predominates over the carbonate ions in the DIC. The uptake of soil-air CO_2, produced by plant root respiration and decay of plant debris, buffer $\delta^{13}C$ values to about –25 ‰; at the same time the ^{14}C content of water will be over 100 % modern, due to present vegetation. The overburden groundwater sample with low $\delta^{13}C$ and high ^{14}C (Fig. 8) also has a low pH (6.2) and alkalinity (15.6 mg/l HCO_3).

The subsequent dissolution of fracture calcites by carbonic acid is the main process that increases $\delta^{13}C$ and decreases ^{14}C in the Ca-HCO_3 groundwater after recharge as radioactive decay is a slow process. The $\delta^{13}C$ values of fracture calcites vary between –8 to +4 ‰ in the upper 100 m of the Palmottu site (Ruskeeniemi, 1998). The calcites are considered generally ^{14}C free because of their age. The $\delta^{13}C$ values of calcites fit well with the trend shown in Figure 8, even though some HCO_3 type groundwaters tend to plot slightly below the pure calcite dissolution line. Respiration of biogenic carbon may decrease ^{14}C but it should clearly retard $\delta^{13}C$ increase. Therefore the effect of biogenic carbon after recharge on DIC is minor in the Ca-HCO_3 water. Silicate dissolution promoted by CO_2-rich water also increases the alkalinity and pH, and it is reflected in the heavy Sr isotopic signature measured from near-surface groundwater samples (Negrel and Casanova, 1999). This indicates a radiogenic Sr source, best explained by the dissolution of Rb-rich phases such as K-feldspar and micas during bedrock infiltration at Palmottu.

The carbon isotope composition appears to increase slightly from the Ca-HCO_3 type to the bulk of Na-HCO_3 type groundwater samples of Figure 8, suggesting further dissolution of calcite, partly supported by the saturation indices (Fig. 7b). The bicarbonate content seems to increase also, whereas Ca decreases (Fig. 7c). Cation exchange may contribute to the observed changes. The uptake of Ca and release of Na

from ion exchange sites in clay minerals causes a gradual dissolution of calcite along the flow route in order to maintain calcite equilibrium.

Groundwater samples from the deep borehole R385 show low ^{14}C values associated with both anomalously high and low $\delta^{13}C$ levels (Fig. 8). Subsurface biological processes can modify the $\delta^{13}C$ of DIC very effectively even when mass transfer is relatively low in these processes. High values are generated when methane production occurs, and very negative values where methane is oxidised and added to DIC (*e.g.* Fritz *et al.*, 1989). Microbial methanogenesis generates CH_4 with significantly depleted $\delta^{13}C$ signatures whereupon it releases CO_2 which is strongly enriched in $\delta^{13}C$. It acts in SO_4-depleted environments (*e.g.* Lovley and Klug 1986; Ferdelman *et al.*, 1997) whereas the simultaneous presence of measurable CH_4 and SO_4 indicates mixing of different waters. In contrast to the methanogenesis, anaerobic oxidation of CH_4 has been thought to occur together with microbial SO_4 reduction (Niewöhner *et al.*, 1998).

The highest $\delta^{13}C$ values (-6 to –7 ‰) in the data (Fig. 8) are obtained from samples representing the surrounding groundwater environment, which is SO_4-poor and therefore has the potential for methanogenesis. In contrast, the lowest $\delta^{13}C$ value (-29 ‰) has been obtained from the deep Na-Cl type groundwater sample with minor CH_4 and SO_4 contents, representing the mixing zone below the brackish Na-SO_4 groundwater body. Minor amounts of dissolved sulphide are also analysed from this sample, which supports the process of anaerobic methane oxidation.

The fact that microbial reduction of SO_4 significantly fractionates $\delta^{34}S$ can be generally used in evaluating the origin and redox processes related to dissolved SO_4. Oxidation of high temperature rock sulphides has been assumed to produce SO_4 with a $\delta^{34}S$ close to zero (*e.g.* Fontes *et al.*, 1989). The shallow Ca-HCO_3 and brackish Na-SO_4 groundwaters both show such $\delta^{34}S$ signatures (Fig. 9), and these values have been interpreted to be derived originally from the oxidation of primary sulphides at Palmottu (Frape *et al.*, 1999).

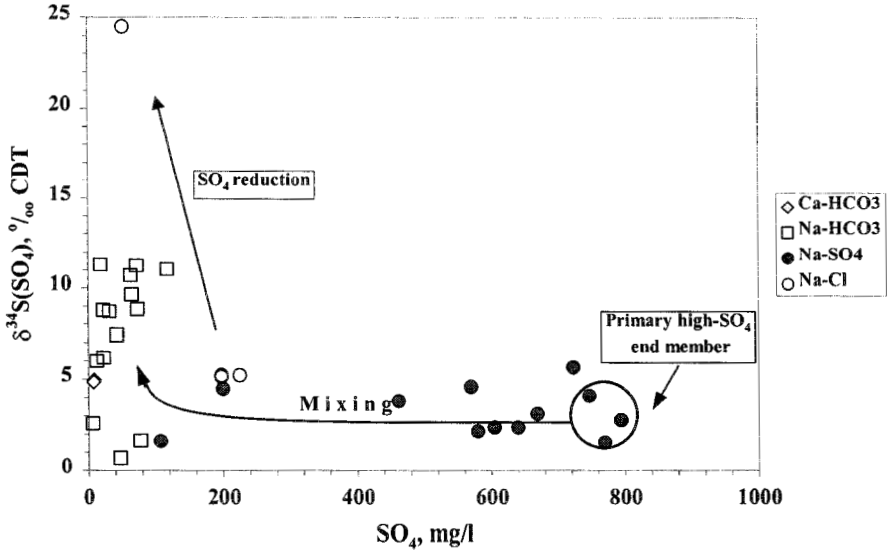

Figure 9. $\delta^{34}S(SO_4)$ values versus SO_4 concentrations. Potential processes affecting the isotope signature are given (modified from Frape *et al.*, 1999).

Microbial reduction of SO_4 elevates $\delta^{34}S$ of the residual SO_4 significantly. The Na-HCO_3 type groundwater shows elevated $\delta^{34}S$ compared to the Ca-HCO_3 and Na-SO_4 groundwaters (Fig. 9). This may reflect ongoing reduction of SO_4 in this water type, following its reception of some primary high SO_4 end-member from Na-SO_4 water. The single, highly reduced $\delta^{34}S$ signature represents the same brackish Na-Cl type water that also shows a low $\delta^{13}C$ signature. This gives further evidence for the interpretation of the deep SO_4-reducing environment in the transition zone between the Na-SO_4 and Na-Cl groundwaters. In contrast, Na-SO_4 groundwater does not show any clear S-isotope signature reflecting SO_4 reduction. The Na-SO_4 water is probably buffered against biodegradable organic carbon. If there is any input of organic carbon, microbes will consume it at the transition zone of the Na-SO_4 water. Therefore the redox conditions will remain stable inside the Na-SO_4 water body.

Furthermore, carbon and sulphur isotope studies indicate mixing between Na-HCO_3 and brackish groundwater types. Additional input of Ca from either of the brackish groundwater types (Fig. 7c) may oversaturate calcite, which will likely precipitate and release protons for silicate dissolution. The low Sr isotope ratios in the deep groundwater samples at Palmottu (Negrel and Casanova, 1999) suggest dissolution of low Rb minerals, particularly plagioclase, thus buffering the pH to around 8.5 in deep samples (Fig 2b). Precipitation of calcite in the transition zone of the Na-HCO_3 may be of great importance for uranium retardation in the system. High concentrations of uranium are typically associated with the HCO_3 waters (*c.f.* Kaija, 1998) and uranium frequently tends to co-precipitate with calcite.

Summary

The conceptual hydrogeological model of Palmottu (Fig. 1) summarises the dominant hydrogeochemical processes of the site. The processes occurring in the overburden during infiltration into bedrock start with biogenic CO_2 input, followed by weathering of silicates and sulphide minerals. Carbon isotope and tritium data indicate that rapid dissolution of fracture calcites is the dominant process in the upper part of the bedrock. This increases pH and alkalinity, thus modifying the groundwater composition to a Ca-HCO_3 type. The groundwater subsequently evolves to a deeper Na-HCO_3 type along the flow within a few decades due to Ca to Na ion-exchange process, which further maintains calcite dissolution. Geochemical modelling has been used to test these geochemical evolutionary processes (Gimeno *et al.*, in this volume).

Brackish Na-SO_4 and Na-Cl groundwaters prevail below the HCO_3 groundwater bodies. The Na-SO_4 type is restricted to the mineralised zone and Na-Cl is found deeper down as well as in the surrounding area, westward from the western granite. The brackish groundwaters show distinct glacial isotopic signatures. Mixing of water types mainly explains the changes in Na, SO_4 and Cl concentrations in the deep Na-HCO_3 type and brackish waters (*cf.* Laaksoharju *et al.*, 1999; Gimeno *et al.*, in this volume); furthermore, mixing activates many of deep processes by disturbing thermodynamic equilibrium. Carbon and sulphur isotope data strongly support microbial reduction of SO_4 in the transition zone of the Na-SO_4 groundwater and either dissolved organic carbon or methane is used as energy sources. Methane is apparent for the transition zone to the deep Na-Cl water. Mixing also seems to promote calcite precipitation by adding extra Ca, and stimulating silicate hydrolysis in the deep groundwater system, thus buffering pH to around 8.5. Methanogenesis is

interpreted as a probable process in the deep, SO_4-poor groundwater system of the surrounding area based on $\delta^{13}C$-data.

Acknowledgements

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Geochemical modelling of groundwater evolution in the Palmottu natural system

M.J. Gimeno, J. Peña and L. Pérez del Villar

Departamento de Impacto Ambiental de la Energía, CIEMAT
Avda. Complutense, 22, 28040, Madrid, Spain

Abstract

A geochemical modelling has been carried out in order to characterise the hydrogeochemical behavior of the groundwaters in the Palmottu natural system.

A statistical approach of hydrochemical data has first been performed as a part of the conventional interpretation process. Secondly, the study has been focused on the reaction path modelling considering both, inverse and forward simulations, using the PHREEQC code. Mineralogy, redox pairs, and isotopic data have been taken into account in order to support the modelling results.

The interpretation of the statistical analysis and the geochemical models has lead to the definition of (a) the different water types involved in the system: Ca-HCO_3 waters, Na-HCO_3 waters, Na-SO_4 waters and Na-Cl waters; and (b) the two main hydrogeochemical processes which are taking place: the weathering of a crystalline basement, responsible for the evolution from the recharge water to the Na-HCO_3 end member; and the mixing of the latter with other deeper, older and more saline waters Na-SO_4 and Na-Cl waters.

Weathering process has been characterized by the following reactions: calcite, plagioclase, uranium oxides and uranophane dissolution, biogenic CO_2 uptake from overburden, ionic exchange, biotite alteration, oxidation of iron sulfides and precipitation of silica, kaolinite, smectite, illite and iron oxihydroxides. The final result is that the shallower and more dilute waters evolve towards Na-HCO_3 groundwaters, with an increase of pH and a progressive decrease of Eh. The deep waters have different proportions of the three water types, Na-HCO_3, Na-SO_4 and Na-Cl, and are slightly affected by water-rock interaction processes.

1. Introduction

The main aim of this work is to define and interpret the water-rock interaction processes responsible for the geochemical evolution of groundwaters and to predict their future behaviour, in relation to the mobilisation of trace elements. Based on the whole set of hydrochemical data a geochemical modelling has been carried out using two different and complementary approaches, the statistical analysis and the geochemical modelling.

From the statistical analysis the main water groups in the system have been separated and their plot on the factorial plane has been very useful for the interpretation of the main geochemical trends. Geochemical modelling has been used to define more specifically the chemical reactions which are taking place in the system, both qualitative

and quantitatively. Finally, these results have been put together with the additional information on mineralogy (Pérez del Villar *et al.*, 1997, 1999; Ruskeeniemi, 1998, in this volume), redox pairs (Cera *et al.*, in this volume) and stable isotopes (Pitkänen *et al.*, in this volume; Frape *et al.*, 1999), in order to integrate them in the global picture and understanding of the system (Blomqvist *et al.*, 1995, 1998).

2. Methodology

One of the approaches which are considered in the application of geochemical models to water-rock interaction studies is, together with the forward and inverse modeling, the statistical approach (Nordstrom and Muñoz, 1994; Drever, 1988).

The technique used here is the Factorial Analysis that consists of a mathematical method that looks for the basic structure inside a big group of bivariate correlations (Siegel and Anderholm, 1994). Therefore, it tries to identify relationships among variables (called factors) and to assign a meaning to each one of these relationships. In this case, the meaning will be of a hydrogeochemical nature.

The statistical analysis carried out in this study has been done using the code SPSS for Windows (3.1) (SPSS Inc., 1994). The data managed in it is the whole hydrochemical data set of the Palmottu waters (precipitation, surface waters, tube and packered groundwaters) compiled, revised and selected by Kaija (1998).

The geochemical modelling has started with the speciation solubility calculations focused on the saturation indexes of the more relevant mineral phases in the system. In order to define the mixing and water-rock interaction processes two kinds of simulations have been performed, which constitute the base of the inverse modelling (mass balance calculations) and the forward modelling (reaction-path or mass transfer simulations).

The main goal of the mass balance models is to evaluate a group of hypothetical reactions that could have taken place in a hydrochemical / hydrogeological system, without any thermodynamic control. Starting with the analytical data obtained in several points of the system these calculations define the reaction model better adjusted to the system. The verification of their thermodynamic consistency is made by applying reaction-path simulations. A combination of both has been used here. PHREEQC (Parkhurst *et al.*, 1998) is the code used to perform all these calculations. The samples used in this study are only the packered ones (Kaija, 1998).

3. Results and discussion

Statistical results

Two main factors have been obtained with which 80% of the variance is explained and they are defined by equations (1) and (2) (Peña *et al.*, 1997, Peña and Gimeno, 1997a, b):

$$F_1 = 0.34[Cl^-] + 0.33[SO_4^{2-}] + 0.31[Na^+] + 0.18[Ca^{2+}] - 0.09[HCO_3^-] \quad (1)$$

$$F_2 = 0.98[HCO_3^-] + 0.14[Na^{2+}] - 0.08[Cl^-] - 0.08[SO_4^{2-}] - 0.06[Ca^+] \quad (2)$$

Factor 1 (saline factor) has been interpreted as an indicator of the progressive mixing between old and saline waters (Na-SO_4 and Na-Cl waters) and the younger and more diluted bicarbonate ones. The negative coefficient for bicarbonate ion supports the logical competition between sulphate and chloride ions, on one hand, and bicarbonate ion on the other hand, in the mixing process.

Factor 2 (bicarbonate factor) can be considered as an indicative of the evolution state in a weathering process of a crystalline rock. High values of this factor will correspond to samples that have evolved in the weathering process without any influence of mixing.

These equations are used to obtain the values of the factors for each sample, values that are plotted in the aforementioned factorial plane (Fig. 1). All the waters fit very well in two main trends, the first one increasing with the increase of factor 2, that is bicarbonate, and the second one evolving with the decrease of the bicarbonate factor and the increase of the saline one. As a result, the existence of 4 groups of waters can be separated: (a) Ca-HCO_3 waters, (b) Na-HCO_3 waters, (c) Na-SO_4 waters and (d) Na-Cl waters.

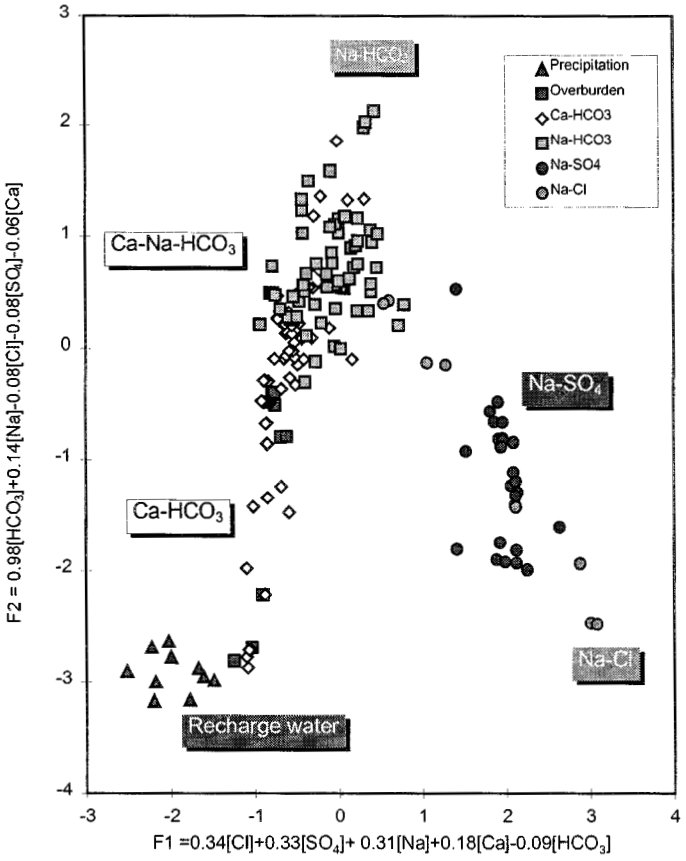

Figure 1. Plot of the different waters in a factor diagram. The factors express the weight for the different elements.

Taking into account the meaning of the 2 main factors, the whole set of Palmottu waters seems to be related by water-rock interaction and mixing processes in the following way: the evolution from the meteoric and surface waters (rain, snow, lakes, springs, water from the overburden) towards the bicarbonate ones is driven by the weathering process; and then the more or less evolved bicarbonate waters mix with the saline end-members.

Once this basic hydrochemical frame has been established, the rest of the important parameters in the system, pH, Eh, depth, electrical conductance, or trace element concentration, can be evaluated.

The weathering process from the recharge waters to the Na-HCO_3 ones, progresses with depth. In general, the increase in depth is associated to the presence of saline waters, except in some places where the presence of a dynamic deep flow system (towards the SE zone) allows the progress of the weathering process towards the more evolved Na-HCO_3 waters. In the same way, total dissolved solids (TDS) increases monotonically during weathering progress and therefore during the increase of Factor 2 (bicarbonate), but when mixing starts, there is an exponential increase of the amount of dissolved solids.

With respect to pH values, they also increase as the weathering process progresses until it reaches equilibrium with calcite. At this point, pH is more or less buffered in the more saline waters increasing towards more alkaline values in the more evolved Na-HCO_3 waters. On the other hand, Eh evolves almost parallel to depth and reverse to pH, starting with the more oxidant values in the shallower waters and going down towards more reducing values as weathering progresses as well as saline waters start to prevail. The results obtained from the redox modelling (Cera *et al.*, in this volume), are in a good agreement with this evolution. They fit very well in the aforementioned general trend of the whole set of waters: from the shallow zone, in which $O_{2(g)}/H_2O$ pair seems to be the main control, to the deepest one, with sulphides/sulphates as controlling pair. The intermediate zone is mainly controlled by iron ($Fe^{2+}/Fe(OH)_{3(s)}$), except in the U-rich zones, where Uraninite/$U_3O_{7(s)}$ is the control of the redox state (Ahonen *et al.*, 1994).

Summing up, there are three main groups of waters: (1) the Ca-HCO_3 waters, shallow, diluted, oxidant and acidic and characteristic of the "Dynamic Upper Flow System"; (2) the Na-HCO_3 waters, characteristics of a Dynamic Deep Flow System, more concentrated and progressively deeper, more alkaline and more reducing; and (3) the saline waters (Na-SO_4 and Na-Cl types), typical of a Stagnant Deep Flow System, the most concentrated, alkaline and reducing ones. The evolution from the first to the second group is driven by weathering, and the relationship between the second and the third groups is by means of mixing.

Geochemical modelling results

Speciation-solubility calculations

With respect to the distribution of species in the system, the results indicate some general trends for the major and trace elements. Major cations (Ca, Mg, Na, K) are mainly as free ions (>95 %) except in the most evolved bicarbonate waters where calcium is also associated with carbonate ligands ($CaCO_3^0$). In the saline waters there are some significant proportion of those cations associated with sulphate.

Chloride and silica are always in the form of Cl^- and H_4SiO_4, respectively. Carbon appears as bicarbonate ion (HCO_3^-) in most of the waters except in the more acidic ones (recharge water) where the proportion of aqueous CO_2 become predominant. Sulphate (SO_4^{2-}) is the dominant form for sulphur, except in the most reducing waters where the dominant species are HS^- and H_2S^0.

The trace elements show different speciation behaviours. Ba^{2+} is always the dominant species for barium but in saline waters there can be significant proportion of $BaSO_4^0$. The same is valid for strontium, mainly in free form but also associated to sulphate in saline waters and to carbonate ligands in the sodium bicarbonate waters. Manganese and zinc appear as free ions and, in an important proportion, associated to carbonate. In the most reducing waters, the dominant species for zinc is $Zn(HS)_2^0$. Aluminium is in the form of $Al(OH)_4^-$ in most of the waters and only in the acidic ones its predominance is transferred to $Al(OH)_2^+$ and $Al(OH)_3^0$.

The behaviour of iron is more complex. Fe(II) forms dominate in most of the waters, as free form or associated with carbonate. Even in the most reducing waters the dominant form is $Fe(HS)_2$. Only in the oxidant waters Fe(III) dominates the speciation and mainly associated to OH^-, as $Fe(OH)_3^0$. Concerning uranium speciation it is mainly associated with carbonate ligands as U(VI), except in the more reducing waters where uranium (IV)-hydroxide is the dominant species.

The saturation state of the waters with respect to the most feasible and reactive mineral phases in the system (Pérez del Villar *et al.*, 1997, 1999; Ruskeeniemi, 1998) indicates that waters evolve towards equilibrium with calcite: dissolving it in the shallower zones and precipitating in the deeper ones. With regard to the rest of the studied carbonates (Mg, Mn, Zn, Ba and Sr) all the waters are undersaturated although the trend to approach to equilibrium is similar to calcite. The reverse trend is shown by $Fe(OH)_3$ which is, in general, oversaturated in the shallower waters and undersaturated in the deeper ones.

Those results are indicative of a process in which calcite (and carbonates in general) in the fracture fillings is dissolved by meteoric waters flowing through these fractures. Waters progressively increase their pH and become enriched in calcium and bicarbonate up to the saturation point of calcite. Then a steady state keeps the system in equilibrium with carbonates and buffers the pH. At the same time, the iron released by acid meteoric water from other fracture filling minerals (mainly sulphides) is able to precipitate as Fe(III)-oxyhydroxides, up to the point that more reducing conditions prevent their precipitation.

Plagioclase is clearly dissolving in the system, whereas silica is close to equilibrium showing a practically constant or stationary behaviour. Aluminosilicates (kaolinite, illite and smectite) are both, oversaturated in the shallow part of the system, and undersaturated in the deepest part. This result leads to the consideration that silica is in a steady state controlled by silicate dissolution, which supplies silica to the solution, and the precipitation of secondary silica phases, which removes silica from it. Furthermore, plagioclase dissolution may supply the Na content observed in the more evolved bicarbonate waters, and indirectly contributes to the increase of bicarbonate in solution. The cycle is closed by the precipitation of aluminosilicates as secondary minerals.

Uraninite is clearly undersaturated in the shallow waters but it is in equilibrium in samples from the uranium rich zone, and even oversaturated in the deepest waters. On the contrary, uranophane (Ruskeeniemi *et al.*, in this volume; Pérez del Villar *et al.*, in prep) is always undersaturated. The saturation state of waters with respect to uranophane seems to indicate that a UO_2^{6+}-Ca silicate like uranophane can be an active uranyl phase in the system. Assuming this hypothesis, a lower equilibrium solubility can be envisaged and therefore, it could be explained that samples saturated in uranyl-Ca-silicate are the less saturated in uraninite, and *vice versa*.

These results could also explain the continuous process of oxidation and dissolution of uraninite due to the entry of meteoric waters and the almost simultaneous neoformation of uranophane, either by precipitation far away of the primary source term

(uraninite) or by *in situ* transformation of uraninite and/or coffinite (Pérez del Villar, *et al.*, in prep.). More rainy periods could increase the dissolution of uranophane, or other U(VI) phases, releasing uranium to solution. During dryer times, a re-precipitation of secondary U(VI) phases would take place in the unsaturated zone (Ruskeeniemi *et al.*, in this volume).

Mass balance calculations and forward simulations

Concerning the simulation of the weathering process, it has started with a mass balance calculations (Gimeno and Peña, 1997, Gimeno *et al.*, 1998). The first approach was done with two extreme waters: one representative of the recharge water (OT1) and the other representative of the Na-HCO_3 waters (sample from the interval between 122 and 128 meters depth in the borehole R346). They were used as initial and final water in the mass balance calculations. Although they are not actually connected by a flow line, they can be indicative of a general process in the system and they will be used as reference samples.

The following constraints were considered in the calculations: C, S, Ca, Al, Si, Mg and Na. Calcite and CO_2 were included as plausible phases for carbon, and gypsum for sulphur. The alumino-silicate reactions were modelled using chalcedony, plagioclase (An-37) and kaolinite. Finally, the ionic exchange processes as additional sources and sinks of Na, Mg and Ca, have also been used.

For this set of phases and constraints several models have been found indicating three different main possible reactions: (a) calcite dissolution and Na/Ca exchange; (b) plagioclase dissolution and Na/Ca exchange; and (c) plagioclase dissolution and calcite precipitation. These different models indicate the possibility to establish two steps in the weathering of the system. In order to define these steps, two mass balance calculations have been performed among them:

First step

- initial water: representative of recharge waters (OT1)
- final water: representative of an intermediate stage in the weathering evolution (sample from the interval between 72 and 84 meters depth in the borehole R386, a calcium-sodium bicarbonate water).

Second step

- initial water: the final one in the previous balance (R386, 72-84)
- final water: representative of the most evolved waters in the weathering process, (sample from the interval between 122 and 128 meters depth in the borehole R346, a sodium bicarbonate water).

The constraints and plausible phases in these calculations were the same as before and several models have been found in each step. Two are the most plausible from a thermodynamic point of view (eq. 3 and 4). In the model for the step one, the predominant reactions are: plagioclase and calcite dissolution, ingassing of CO_2, precipitation of gypsum and the exchange of Na and Mg by Ca (eq. 3).

The model for the second step differs mainly in the calculated mass transfer for plagioclase (higher amount of plagioclase is dissolving now), and in the presence of calcite as a product of the reaction (eq. 4). Moreover, gypsum is dissolving, and there are important amounts of silica and kaolinite precipitating.

Step 1:

Water OT1 + 1.9e-7 plagioclase (An-37) + 3.9e-4 $CO_{2(g)}$ + 7.9e-4 calcite + 1.2e-3 Na_2-exchange + 9.3e-5 Mg-exchange -------> Water R386 (72-84m) + 1.863e-5 gypsum + 7.179e-4 Ca-exchange (3)

Step 2:

Water R386 (72-84m) + 1.5e-3 plagioclase (An-37) + 1.6e-3 $CO_{2(g)}$ + 2.8e-4 gypsum + 1.6e-4 Mg-exchange --> Water R346 (122-128m) + 4.3e-4 calcite + 1.0e-3 kaolinite + 1.8e-3 chalcedony + 1.6e-4 Ca-exchange (4)

One of the main conclusions from these results is that even though primary silicate minerals (feldspars, quartz, etc.) predominate in the mineralogy of the massif, the mass balance modelling indicates that reactions with these minerals are secondary to those of the more reactive (although volumetrically less important) carbonates, and secondary aluminosilicates.

In order to check these chemical models, some forward simulations were performed using those reactions as the driving force for the evolution from one end-member to the other. The result is the state of the solutions in different stages (10 steps simulations) of the evolution process. With these compositions and applying the factor equations (1) and (2), the position of each solution stage was calculated and plotted over the factorial plane (Fig. 2; black diamonds for the simulation of weathering 1; and scarlett and pink diamonds for the two steps: weathering 1a and 1b). The comparison between the theoretically calculated solutions and the real samples is clearly seen in Figure 2.

The variation of pH and Eh in the different processes have also been checked. The disagreements observed in Eh are mainly due to the fact that there are not complete data for all the samples. The problem with pH is a bit more complicated. The pH evolution calculated in the first step of theoretical weathering shows a higher increase (up to 9) than the real values (up to 8.4). This minor disagreement can be due to the fact that some other processes are taken place. For example, the presence of protonation-deprotonation processes could be feasible in the system and they can easily low the pH to the observed values. The pH evolution in the second weathering step fits better with the observed results. Concerning the saturation state of the minerals of interest in the system the calculated values fit very well with the real ones.

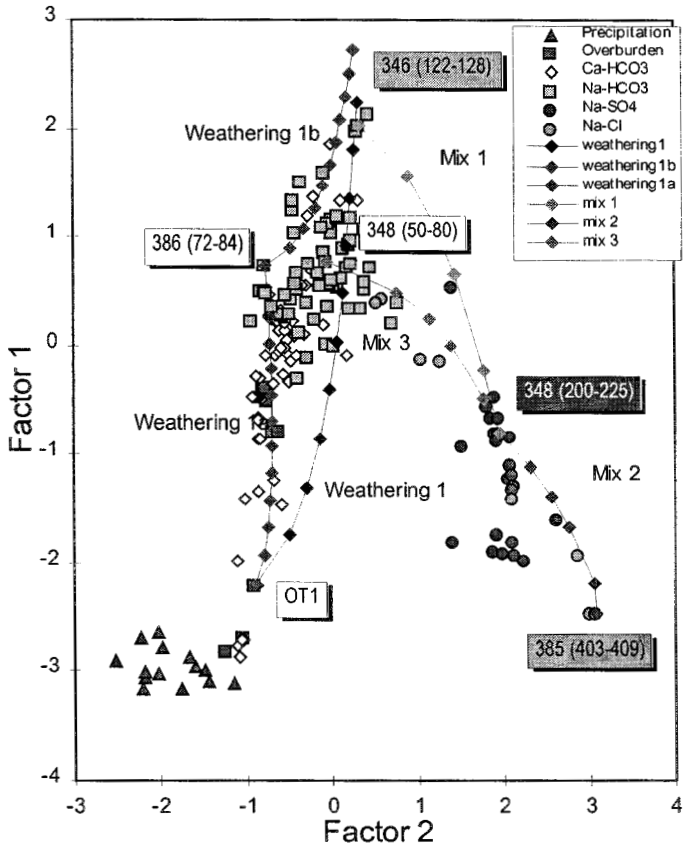

Figure 2: Plot of the solutions obtained from the theoretical simulations of weathering and mixing on the factorial plane, and comparison with the real waters. The samples in the boxes are the selected end-members for simulations.

With regard to the mixing processes, the theoretical calculations have been performed only by a forward approach, assuming that no significant chemical reactions are taking place. Following the criteria of Wigley and Plummer (1976), the aqueous solution has been considered as the reference system and the simulations have been made in closed system, considering the mixing process as a lineal combination of the end members concentration according to the mixed proportions.

The simplified structure of the model has been defined with the most representative samples of the end-members:

Mix 1: Na-HCO_3 waters, R346(122-128), and Na-SO_4 waters, R348(200-225).

Mix 2: Na-SO_4 waters, R348(200-225), and Na-Cl waters, R385(403-409).

Mix 3: Ca-Na-HCO_3 waters, R348(43-95), and Na-SO_4 waters, R348(200-225).

The simulation procedure consists in a simple mixing process between the aforementioned end members. It has been divided in five steps and the solution state in each of the mixing proportions has been obtained. With these calculated chemical compositions, the position of each solution has been plot on the factorial plane (Fig. 2; light blue

diamonds for Mix 1, dark blue diamonds for Mix 2 and grey diamonds for Mix 3) and also compared to the real samples.

The results obtained for the evolution of several parameters are coherent with the process of simple mixture of the used endmembers, even in the case of pH. Only in waters closer to the Ca-Na bicarbonate group (first steps in Mix 3), the theoretical values of pH are lower than the real ones. It has been interpreted as a consequence of the presence of some chemical reactions (dynamic equilibrium with calcite) not considered in the theoretical simulations.

In general it could be said that almost all the major elements show a conservative behaviour during the mixing process. This fact reduces the possibility of important influences of heterogeneous processes. Consequently, the development of the mixing phenomenon could be considered as defined by closed system conditions for these elements, as it was initially assumed.

4. Summary and conceptual model

The interpretation of the geochemical modelling and the statistical analysis leads us to think that two main hydrogeochemical processes are taking place in the system: (1) the weathering of a crystalline basement taking place along the upper flow system and the dynamic deep flow system, responsible for the waters on the line between the recharge water and the Na-HCO_3^- end member (Fig. 3); and (2) the mixture of the previous waters with other deeper, older and more saline ones, Na-SO_4 and Na-Cl waters, located in a stagnant deep flow system. Some mixing between these two saline endmembers has also been found (Fig. 3).

Taking into account the geochemical models and the mineralogical data, the weathering process has been characterised by the following reactions: calcite, plagioclase, uranium oxides and uranophane dissolution, biogenic CO_2 uptake from overburden, ionic exchange (involving Ca, Na, H^+) biotite alteration, pyrite and / or other sulphides oxidation and precipitation of silica, kaolinite, smectite, illite and iron oxihydroxides. The final result is that the shallower and more diluted waters evolve towards the Na-HCO_3 end member, with an increase of pH and a progressive decrease of Eh.

Waters resulting from the mixing process have different proportions of the three end members, bicarbonate and saline waters, being slightly affected by water-rock interaction processes.

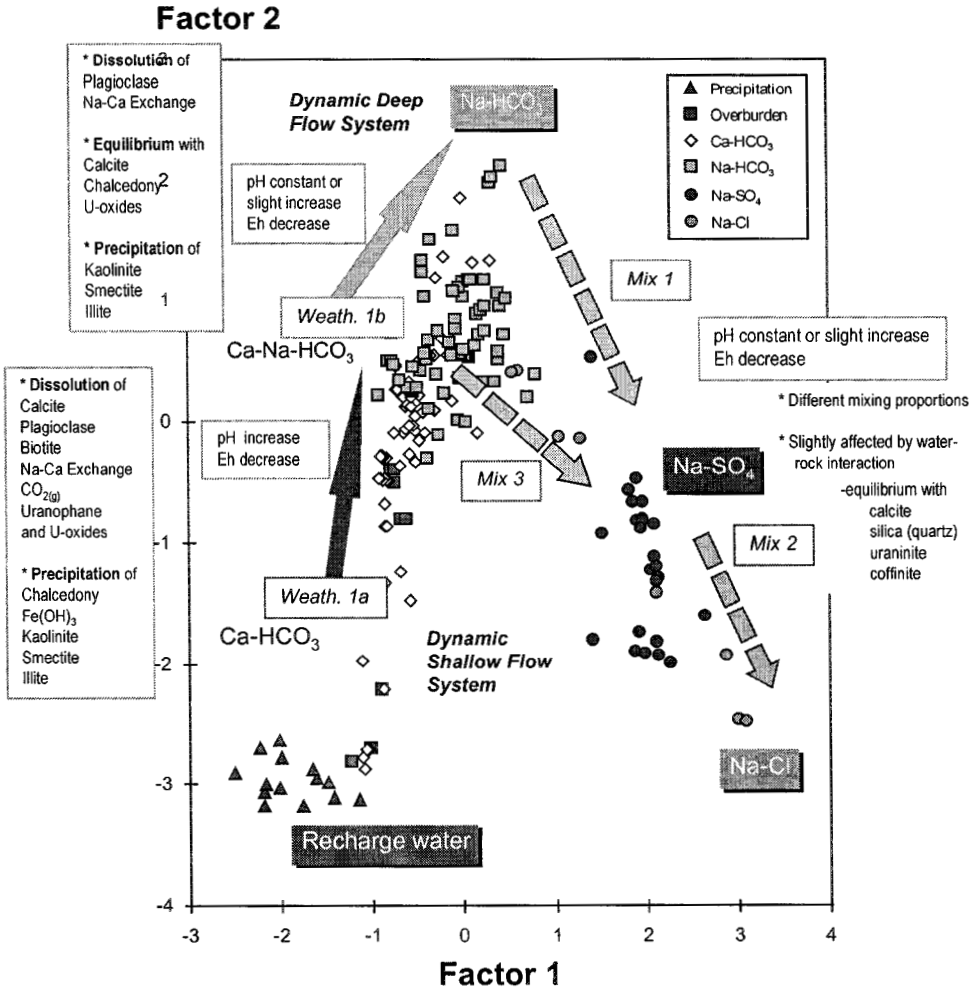

Figure 3: Factorial plane with the waters and the main chemical reactions.

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Redox processes at the Palmottu uranium deposit

E. Cera[1], L. Ahonen[2], C. Rollin[1], J. Bruno[1], J. Kaija[2] and R.Blomqvist[2]

[1] QuantiSci, Spain

[2] Geological Survey of Finland

Abstract

The redox chemistry of a geochemically stable environment such as the Palmottu system has been investigated based on extensive field measurements. The solid phases controlling uranium concentrations in groundwater, as well as the processes controlling its concentration in the redox transition zone have been studied.

On-line redox measurements have been performed at Palmottu in order to ascertain the redox pairs able to control the redox state of this system. By comparing the characteristic reaction times of these redox processes with the residence times of these deep groundwaters we can assume that redox equilibrium is attained in this system. The thermodynamic modelling performed in this natural system indicates two zones with different redox controls: the Western area where the sulphide minerals seem to control the redox potential of this subsystem, and the Eastern area where the uranium mineralisation occurs. In this area the uranium minerals could play an important role as a redox buffer in the reduced area, while the most common redox pair $Fe^{2+}/Fe(OH)_3(s)$ appears to control the redox behaviour in the most oxidised surface zones of the same area.

The gradation of the reducing capacity levels follows the traditional scheme: oxidation of organic matter by air controls the soil and surface redox system, followed by the oxidation of Mn(II) and Fe (II) to Fe(III). At deeper and more anoxic levels, the oxidation of UO_2 to UO_{2+x} controls the redox system close to the ore, while the sulphide/sulphate system is the dominant pair in the most stagnant waters. The origin of these sulphate containing waters in the undisturbed part of the system and its possible connection to oxic melt waters intrusion remains an open question with critical implications of the redox stability of granitic groundwaters at the Fennoscandian shield.

This study confirms the previous investigations of the Cigar Lake uranium ore deposit, where we could establish that the presence of UO_2 plays a key role controlling the redox capacities and intensities of the system (Cramer and Smellie, 1994). This has obvious implication when determining the redox behaviour of the near field of a spent fuel repository.

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1. Introduction

The geochemical stability of a Nuclear waste repository largely depends on the appropriate conditions for the stability and performance of the successive barriers of the repository system. Geochemically stable conditions are partially defined in terms

of various intensive parameters, e.g., pH and Eh. However, the capability of the disposal system to react against chemical disturbances is not completely described by the intensive parameters, because their persistence depends on the associated extensive parameters. Alkalinity and redox buffering capacities are two of the main chemical conditions required in a geological system to ensure that both the internal and external perturbations do not disturb the performance of an engineered barrier system.

The present nuclear waste disposal programs have had a large impact on the studies of redox conditions of the deep bedrock as well as in the development of redox measurement technologies (Wikberg, 1987, Ahonen et al. 1995). In redox electrolyte-poor groundwaters, stable potentials are not readily attained, and measuring times of several weeks may be required. Otherwise, different types of electrodes may have dissimilar response to dissolved redox electrolytes, in such cases the electrodes may be sensitive to different pairs or they may give mixed potentials. When similar values are displayed, the different electrodes are probably in equilibrium with the same pair, which in that case is potential-determining.

The work performed has been focused on the measurement and understanding of the redox processes taking place in the Palmottu system as well as the study of its main redox buffer capacities. In addition, and because of the key role of uranium in defining the redox chemistry in Palmottu, the geochemical behaviour of uranium and its relationship to redox properties has been also studied. The solid phases controlling the uranium in groundwater in the Western and the Eastern systems as well as the processes controlling its concentration in the redox transition zone have been studied.

2. Selection of the redox field data to perform the modelling work

Three campaigns were carried out at the Palmottu site and different measuring-instrument assemblies were used in the redox measurements. In the first campaign during 1992-1994, double packer equipment constructed and developed at GTK (Geological Survey of Finland) was used. Since 1996, when new research boreholes were available, the mobile field laboratory of SKB (The Swedish Nuclear Fuel and Waste Management Company) was used for redox-potential measurements and groundwater sampling in the new boreholes. In 1997, a new water-sampling and redox-measurement device was developed to fit the slim observation tubes (12 mm) of the packered boreholes. Redox-measurements using this device were done in 1998. A complete description of the redox measurements methodologies and sampling devices used in the different campaigns will be given by Ahonen et al. 1999).

Three different electrodes, platinum, glassy-carbon and gold, were used with the SBK mobile field laboratory and the redox measurements were obtained both on surface and down-hole by the three electrodes. Quasi-continuous measures were taken for different time periods by using this equipment. GTK used a platinum foil electrode with Ag/AgCl as reference one. With this device, only measurements on surface were taken. In this case, punctual measurements were taken at different time intervals and during different time periods depending mainly on the time necessary to reach stable potentials.

Redox potentials measured with platinum and gold in reducing conditions displayed a rather systematic pattern: in situ gold electrode measurements were systematically from 100 mV to 400 mV higher than platinum ones, while on the surface-measurements both electrodes showed, in general, rather similar values. This could indicate that down-hole electrodes displayed mixed potentials, in which the reaction of the electrode material contributed to the electron exchange. In addition, the gold electrode reached slightly higher potentials than the glassy-carbon and platinum ones. This behaviour agreed with the results obtained by Wikberg (1987). In his work, he performed measurements on surface and down-hole by using these three electrodes and he noticed the same behaviour for the gold one. In another study by Grenthe et al. (1992), the authors observed that the sulphide concentrations in the groundwaters have an effect on the redox-potential readings of gold electrode, while platinum electrode was less affected. In particular, the presence of this compound increases slightly the potentials measured by using the gold electrode. Whitfield (1974) observed that potentials measured by platinum electrode shifted to lower values due to the formation of platinum sulphide on the electrode surface in prolonged measurements. Sulphides are present in the Western area of the Palmottu system, and, as we will see later, they have an important role on the redox behaviour in this system. Hence we can assume that the sulphidisation of the 'in-situ' gold electrode - possibly also of platinum electrode - has contributed to the anodic currents on these electrodes, and they display an electrode-specific mixed potential. However, this behaviour seems to be less important for surface electrodes due to the shorter measurement times involved.

The potentials measured with the platinum electrode during the 96 campaign were very low compared to the ones measured in the following campaign. The measured potentials agreed quite well with the redox potentials calculated by assuming the H_2/H_2O pair This is a quite common behaviour for Pt foils, which are sensitive to $H_2(g)$ and become a proton electrode in the presence of hydrogen gas. The gas-phase analysis indicated that the three uppermost sections contained $H_2(g)$ in measurable amounts: 41.5 %, 1.8 %, and 0.004 % in sampling sections 94-100 m, 112-118 m and 217-223 m respectively, while in other sections, hydrogen concentration of the gas phase was below the detection limit (30 ppm).

In general, a good agreement was observed between surface and down-hole measurements for the three electrodes. The data indicate an agreement within ± 50 mV between both types of measurements. The same kind of comparative field measurements (down-hole and on surface) were carried out by Wikberg (1987) in his seminal work concerning redox measurements in deep groundwaters. His results indicate that down-hole measurements were more stable and were attained more rapidly than those on surface. These observations were discussed in Grenthe et al., (1992). They explained the different behaviour by indicating the high sensitivity of surface measurements to the oxygen intrusion into the measuring chamber. The present redox data obtained at Palmottu would indicate that much better control on potential oxygen intrusion has been attained in the measuring chamber located at the surface in these measurements than in the ones performed by Wikberg (1987). This could have important implications in the redox measurement methodology to be used in future site investigations.

The selection of redox values representative of the redox potentials measured in field in all sampled sections has been performed according to several criteria. Mean

values have been calculated by considering the same range of time for all the measures in each section. The selection of this range has been based on the stability of the redox potential. The values reached on surface and down-hole agree in general quite well indicating the stability of the system and give confidence on the measures obtained. The low standard deviations of the redox and pH measurements indicate the goodness of the field measurements as well as the stability of the sampled system. The redox and pH data selected to perform the modelling work is displayed in Table I. The same data has been projected to a cross section presented below in order to have a general overview of the redox system in Palmottu (Fig.1).

Table I. Mean values and standard deviations of the redox potentials and pH used for the modelling calculations.

Borehole	Section (m)	Eh (mV)	stan dev. (mV)	pH	stan dev.
302	90-95	-55		8.4	
302	80-95	-34	6	8.0	
318	50-80	52	14	7.7	0.3
324	95-101	5		6.9	
325	38-81	345	11	7.6	
335	45-81.5	141	0	8.7	
337	80-100	22	3	7.7	0.1
346	65-71	-11		8.1	
346	122-128	-75		8.4	
346	240-246	-92		9.1	
348	200-225	-70		8.8	
384	29.5-56.5	413	6	7.7	
384	56.5-94	454	18	6.8	0.2
387	119-127	-326	3	8.8	0.1
387	257-264	-198	8	8.6	
387	304-339	-292	32	8.6	0.1
385	112-118	-322	5	8.6	0.1
385	217-223	-345	11	9.4	0.1
385	403-409	-326	11	8.4	0.1
386	72-84	-284	23	8.5	0.0

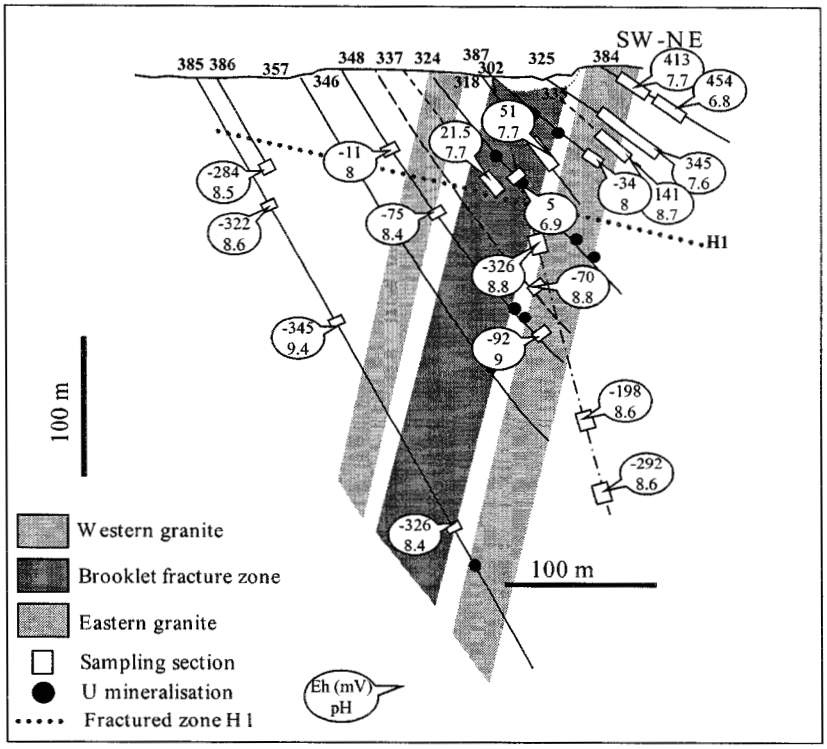

Figure 1. Vertical cross section , SW-NE, showing the Eh and pH values measured in field.

As we can observe in the cross section, there are two differentiated areas according to the measured redox potentials. The oxidised area, which corresponds to the most superficial part of the system, over the sub-horizontal fractured structure (H1), and the reduced area, below this sub-horizontal unit, corresponding to the deeper part of the system. In addition two different ranges of potentials have been measured in both areas. The most oxidised area, with potentials between 300 and 450 mV corresponds to the superficial groundwaters from the Eastern part of the system, while the less oxidised potentials ranging between 0 and 150 mV approximately have been measured in deeper sections than the previous one.

In the deepest areas of the system below the sub-horizontal unit, there are also two different redox ranges. The most reduced potentials have been measured in the Western area and out of the fractured zone in the Eastern part, while the less reduced ones have been measured in shallower sections, and close of this sub-vertical fractured unit, where the U mineralisation occurs.

The Palmottu system can be divided into different hydrogeological units (Blomqvist et al., 1998), and consequently, we can expect different processes to be responsible of the redox behaviour in each unit.

3. Evolution of Eh, pH and uranium concentrations with depth

As we can observe in the following graphs, in general the Eh (Fig. 2) and the U concentrations (Fig. 3) measured in groundwaters decrease with increasing depth, while the measured pH (Fig. 4) slightly increases. This general trend of increasing alkalinity and reducing capacity with depth, is given both in the Western and the Eastern areas of the system.

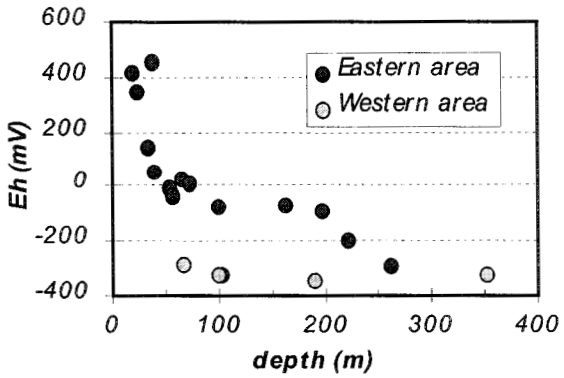

Figure 2. Evolution of redox potential with depth.

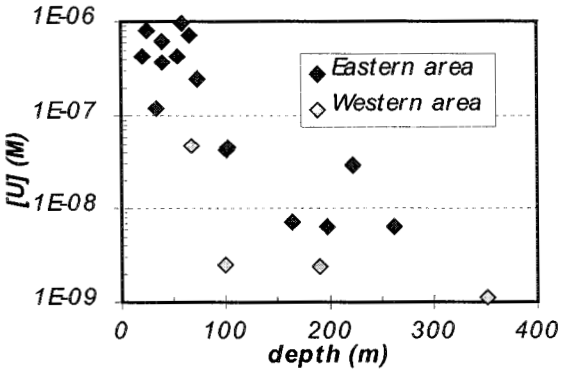

Figure 3. Evolution of uranium concentrations with depth.

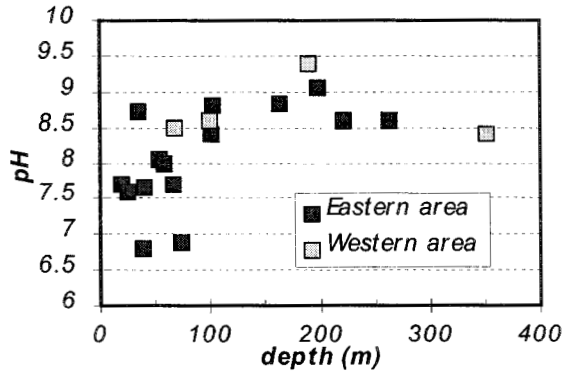

Figure 4. Evolution of pH with depth.

The Eh decrease with depth reflects the transition from the oxidised to the reduced area in the system. This decrease of the redox potential leads to the stabilisation of the U(IV) when increasing depth with the consequent decrease of the concentration of this element in the groundwaters. In addition the slight increase of pH when increasing depth is an indication of the different water types determined in the different sections and of the evolution of these waters from the shallowest part to the deepest one. However, the redox potential is the main factor controlling the behaviour of uranium in the system. This is clearly shown in Figure 5 where a direct relationship between the logarithm of the measured uranium concentrations and pe is observed.

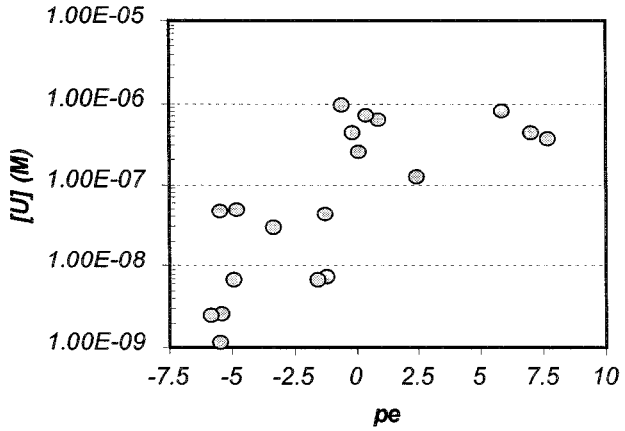

Figure 5. Plot of the uranium concentrations in groundwaters versus pe.

4. Thermodynamic modelling of the redox processes

Two differentiated oxidising areas have been determined in the Eastern part of the system according to the redox potentials measured: the very oxidising waters, mainly associated with the upper part of the Eastern granite, and the moderately oxidising waters at depths of around 100 meters.

The Eastern granite subsystem constitutes an active groundwater infiltration path. The recharging oxic groundwaters with Eh-values around 400 mV have been observed at depths of some tens of meters, the redox potential being decreasing downwards. The measured Eh-values of oxic waters have generally not observed to reach the thermodynamic equilibrium of O_2/H_2O pair, which is about (1200 - 59pH) mV (or pe = 20.75-pH), but the apparent potentials are about 300 mV lower.

In the near-surface oxic waters, major reduction of oxygen is due to biological processes. In aqueous systems containing organic material, the reduction of O_2 is observed to occur first by oxidation of organic matter (aerobic respiration) with an apparent pe^o=13.8 (Stumm and Morgan, 1996). This pe^o can be considered equivalent to the apparent log k_{app} value for the reaction of oxygen reduction to water in the presence of organic matter according to equation 1.

$$0.25O_2(g) + H^+ + e^- + \text{organic} \Rightarrow 0.5H_2O + CO_2 \quad (1)$$

with

$$k_{app} = 1/([H^+] \times \{e^-\}_{app} \times pO_2^{0.25}) = 10^{13.8} \quad (2)$$

and

$$E_h^{app} = 59.16 \times \log \{e^-\}_{app} \quad (3)$$

We calculated both the equilibrium potentials and apparent potentials of oxygen reduction and compared them with measured ones (Fig. 6). The atmospheric partial pressure of oxygen (pO_2=0.21 atm) has been considered in both approaches. The results establish that reduction of the atmospheric oxygen to water in presence of organic matter is controlling the redox potential in the shallowest waters.

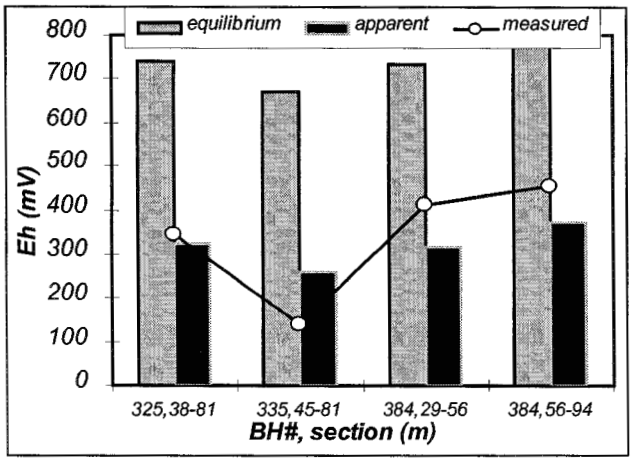

Figure 6. Measured and calculated redox potentials assuming the $O_2(g)/H_2O$ redox pair with and without presence of organic matter.

Deeper in the bedrock the amount of organic material decreases, and respiratory oxidation of organic compounds become less important, while the role of chemolitotrophic microorganisms may become more important. These organisms derive their energy from oxidation of inorganic compounds, mainly iron, sulphur, and manganese, and are able to assimilate inorganic carbon (CO_2) as the sole source of C for cellular synthesis. Iron is one of the main components of the bedrock, also in Palmottu. Oxic water, probably associated with biological processes may oxidise dissolved iron to their solid oxides, which in turn buffer the redox conditions.

According to this, the most probable redox buffer governing the potentials at depths of around 100 meters, corresponding to the less oxidised waters is the $Fe^{2+}/Fe(OH)_3(s)$ redox pair. In the next graph (Fig. 7) the measured redox potentials are compared with the calculated ones according to the redox buffer previously established. The calculated redox potentials when assuming the iron system reproduce satisfactorily the measured redox potentials within ±35 mV.

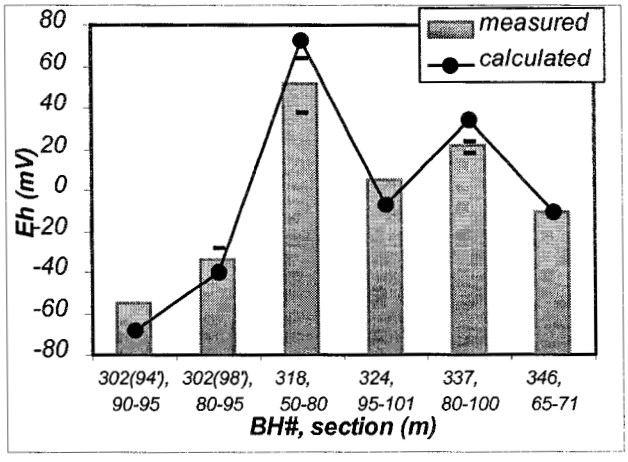

Figure 7. Measured and calculated redox potentials assuming the $Fe^{2+}/Fe(OH)_3(s)$ redox pair.

In the shallowest sections Fe oxy-hydroxides have been identified in general in all the fractures fillings. In addition, U(VI) silicates have also been detected indicating

the oxidant nature of this area. The oxidised minerals identified in this zone corroborate the previous assumptions to explain the different redox potentials measured in the shallowest part of the system. In this sense, the redox buffering role of ferric-oxy-hydroxide is well established in granitic groundwaters (Grenthe et al., 1992).

Two differentiated ranges of redox measurements have been collected under the sub-horizontal unit, below 100 meters depth, in the reduced area. The redox potentials measured in this area are displayed in a Eh/pH diagram (Fig. 8). Two differentiated trends are observed responding to different redox controls. The same graph shows the redox controls that most probably govern the redox system in this area according to the field measures obtained. As we can observe in this graph, the less reduced redox potentials measured in the shallower sections below the sub-horizontal unit in the Eastern zone, where the uranium mineralisation occurs, agree satisfactorily with the redox potentials given by the phase transition uraninite/U_3O_7(s). This is an indication that this surface oxidation is mainly responsible for the reducing capacity in this area. The role of uranium minerals in the mineralised area of the Palmottu system has been yet extensively studied (Ahonen et al., 1993, Bruno et al., 1996). On the other hand, in the deepest sections, out of the mineralised area, the most reduced redox potentials agree with the sulphide /SO_4^{2-} system as it can be seen in the same graph.

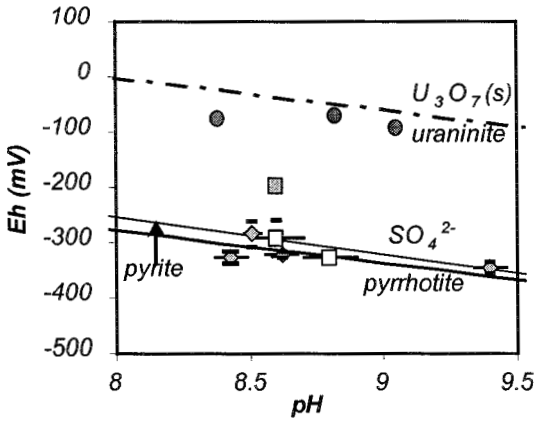

Figure 8. Eh/pH diagram showing the redox potentials measured in the reduced zone of the system. Squares and circles correspond to the Eastern system and diamonds to the Western one. The uncertainty in the measures is indicated by error bars. The uraninite/U_3O_7 and sulphide/SO_4^{2-} phase boundaries are also displayed, dashed and solid lines respectively.

There is one data point (grey square) corresponding to bore hole 387 section 257-264 which does not respond to any redox couple considered in this system. The location of this section, the mineralogical information and the redox potentials measured in the surrounding area lead us to suspect that this redox measure is not totally representative of the sampled groundwater. The expected redox potential in this area corresponds to the one given by the sulphide /sulphate system.

The calculated redox potentials when assuming the uranium system (Fig. 9) reproduce satisfactorily the measured redox potentials (within ±35 mV). In Fig. 8, we have also plotted for comparison the measured U concentration in groundwaters and

the calculated ones when assuming the equilibrium between uraninite and $U_3O_7(s)$. The agreement obtained is quite satisfactory and a good indication that these U-minerals play a critical role as redox controls of the system.

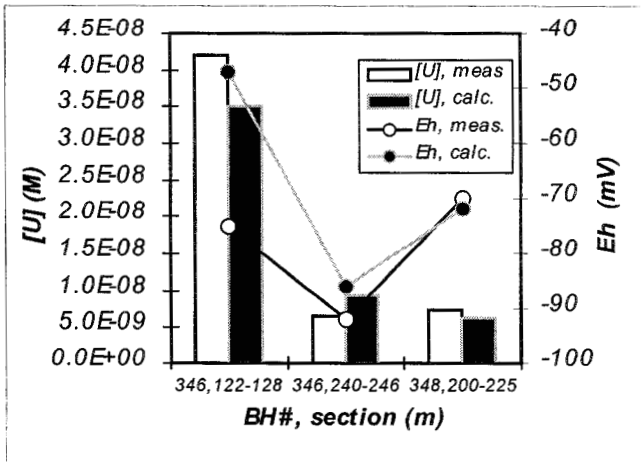

Figure 9. Measured and calculated redox potentials assuming the uraninite/$U_3O_7(s)$ redox pair.

In addition, the same agreement between measured and calculated redox potentials is observed when considering the sulphide system in the deepest waters (Fig. 10). Two different redox buffers pyrite/SO_4^{2-} and pyrrhotite/SO_4^{2-} have been considered for the sulphide/sulphate redox controls. Both redox buffers have been selected according to the mineralogical information gathered from fracture fillings.

These groundwater samples are located in the Stagnant Flow System and are mainly of Na-SO_4 type. The association of sulphate with a glacial melt component may indicate oxidation of sulphide minerals by dilute, oxygen-rich melt water intruded into the bedrock (Blomqvist et al., 1998), but this process is not expected taking into account the large amounts of oxygen required for the reaction to proceed. However, the oxidation of sulphide to sulphate could occur by reaction with the Fe(III) triggered by the oxidation of Fe(II) by melt water at the shallowest parts of the system (Guimerà et al., 1999). On the other hand, Pitkänen et al. (1999) do not exclude the reduction of sulphate in the deeper parts of the bedrock. The low ^{13}C signature in bore hole 385 in the deepest section indicates the presence of hydrocarbons. This could imply methane oxidation during microbially mediated sulphate reduction (Fritz et al., 1989). Bacteria able to mediate this process have been identified by Pedersen et al. (1999) in Palmottu. The low redox values determined as well as the mineralogical and groundwater information supports the feasibility of this process in the bedrock.

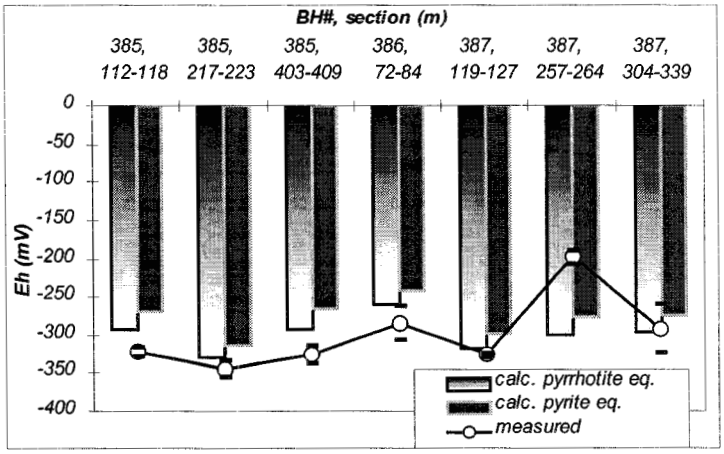

Figure 10. Measured and calculated redox potentials assuming the sulphide comp./SO_4^{2-} redox pair.

As we can observe in the previous figure (Fig. 10), the calculated redox potentials when assuming equilibrium with pyrrhotite or pyrite are quite close to the measured ones, in addition both the measured and the calculated data follow the same trend. However, the results seem to indicate that in general the measured potentials are closer to the calculated ones when assuming equilibrium with pyrrhotite. This result is reasonable taking into account that pyrrhotite is a more redox labile solid phase than pyrite.

5. U controls in the Palmottu system

According to the different redox pairs controlling the redox behaviour in the oxidised and reduced areas of the system, it is expected that the uranium control in groundwaters will be exerted by different processes according to the redox transition studied. In this sense, a thermodynamic study has been performed in order to elucidate the geochemical behaviour of this trace element associated to the different redox pairs controlling the system. As we will see, the results obtained in this work agree satisfactorily with the results of the blind prediction modelling (BPM) exercise (Bruno et al., 1999).

As we have previously seen, the redox control in the shallowest groundwaters is given by the O_2/H_2O redox pair. According to the oxidant character of these groundwaters, it is expected that U(VI) solid phases control the concentration of this element in this zone. The saturation indexes calculated based on groundwater composition indicate that uranophane is close to saturation in most of the groundwater samples analysed. Consequently, several U(VI) solid phases have been taken in the calculations. In addition, taking into account that calcite is slightly undersaturated in all samples studied, we have also assumed a co-dissolution process of uranium with this carbonate. The results of the thermodynamic calculations are given in Figure 12.

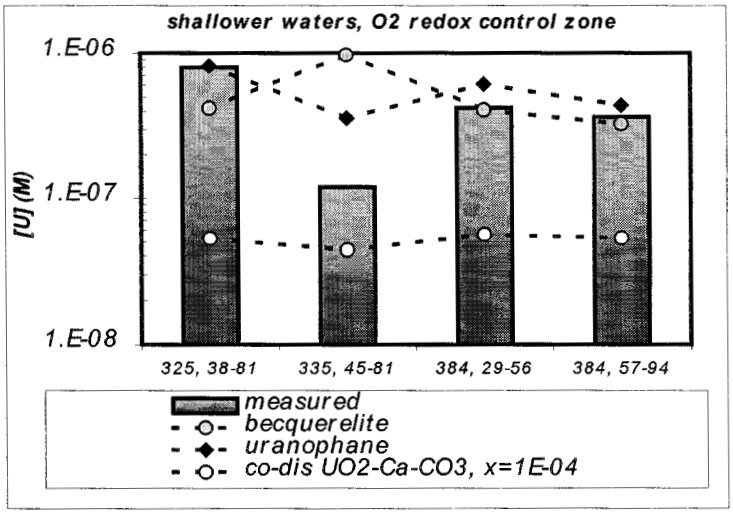

Figure 11. Uranium concentrations measured and calculated by considering uranophane, becquerelite and a mixed uranium-calcium-carbonate as limiting the solubility of uranium in the shallowest groundwaters.

The results show a good agreement between calculated and measured data when considering an U(VI) pure solid phase limiting the concentration of uranium in these groundwaters. The presence of U(VI) silicates in this zone confirm the selection of uranophane as limiting solid phase in these waters. The presence of uranophane in this area is not surprising taking into account the ubiquitous occurrence of this mineral in natural systems (Smith, 1984). The calculated uranium concentrations when considering the co-dissolution approach do not reproduce the measured values.

According to the redox control exerted by the iron system in the shallow area above the sub-horizontal unit, it is expected that U(VI) solid phases would again control the measured uranium concentrations in groundwaters. The thermodynamic modelling confirms this assumption. However, a co-precipitation process of uranium with iron oxy-hydroxides has been also considered. This process has been taken into account based on both, the role of the iron system in this zone and the association of uranium with iron oxy-hydroxides controlling the release of this trace element in shallow and oxidising groundwaters of other natural systems (Bruno et al., 1996a, 1996b). The results of the modelling are given in Figure 11.

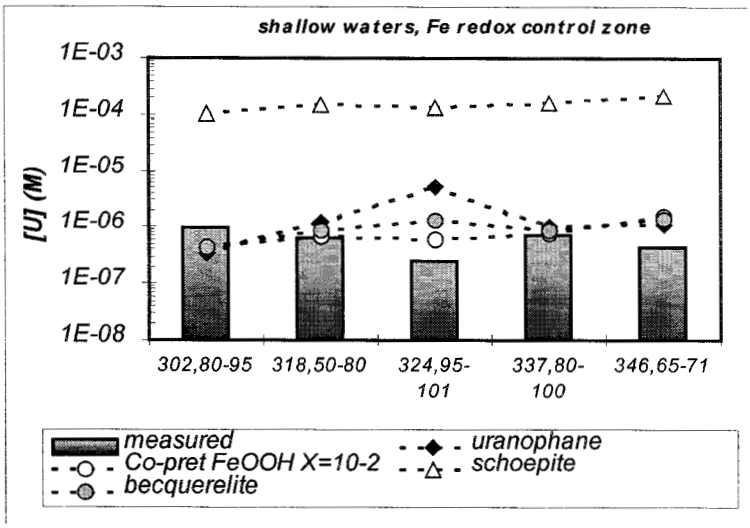

Figure 12. Uranium concentrations measured and calculated by considering uranophane, becquerelite, schoepite and a co-precipitation approach limiting the solubility of uranium in these groundwaters.

Measured uranium concentrations are reproduced when considering a pure solid phase or the co-precipitation approach limiting the uranium concentrations in groundwaters. However the molar fraction of uranium in iron oxy-hydroxides has been estimated because of the lack of mineralogical information. In this sense, this value has been selected just to fit the calculated values to the measured ones.

Finally, the redox potentials measured in the deepest part, in the reduced area, as well as the low uranium concentrations determined indicate the possible role of U(IV) solid phases limiting the concentration of this trace element in this zone. The role of uranium oxides in the area of the system where the U-mineralisation occurs has been previously established. In the present calculations, uraninite and coffinite have been considered as solubility-controlling phases in the deepest sections, where the sulphide system is exerting the redox control. The results are given in Figure 13.

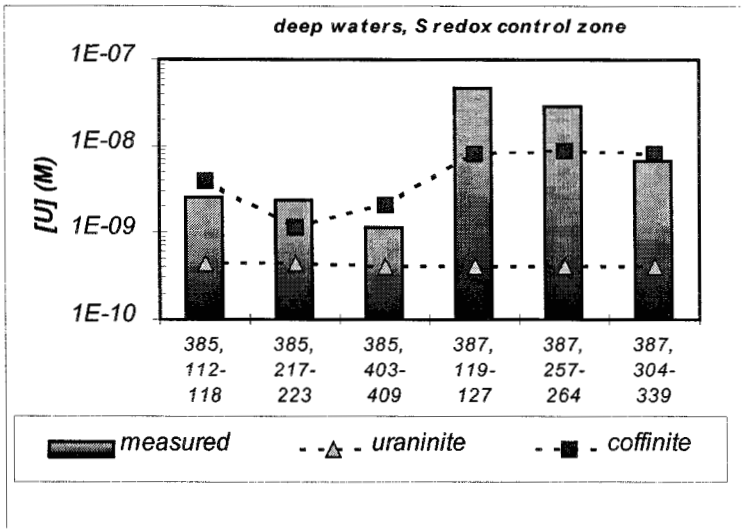

Figure 13. *Uranium concentrations measured and calculated by considering uraninite and coffinite limiting the solubility of uranium in these groundwaters.*

The calculated solubility of coffinite agrees quite well with the measured uranium concentrations in deep groundwaters, particularly it better reproduces the observed trends in the measured uranium concentrations. The fact that this mineral has been identified in the deep areas of the system as alteration product of uraninite under reducing conditions (Blomqvist et al., 1995) corroborates the modelling hypothesis.

6. Discussion

As we have previously stated, the redox potential in the Palmottu system decreases when increasing depth. The transition from an oxidised to a reduced zone observed in this system can be explained by the electrochemical evolution sequence (Freeze and Cherry, 1979). This sequence refers to the tendency for the redox potential of any groundwater system to decrease as the water moves along its flow paths. The Palmottu system is a good example of the existence of the electrochemical sequence based upon reliable redox field measurements.

The initial redox conditions reflect high concentrations of dissolved oxygen, with redox potentials around around 450 mV. However, the redox potentials decrease as the water infiltrates through the soil zone. The consumption of oxygen in this zone will vary depending on numerous factors, such as the soil structure, porosity, permeability, nature and distribution of organic matter, etc. The oxidation of organic matter commonly removes most of the dissolved oxygen and Fe(III) replace it as the predominant oxidant. However, as we have previously pointed out, in the aerobic areas there are also other reactions like the oxidation of ammonia, manganese, ferrous ion, sulphides etc. that consume oxygen. Even though these processes may consume only a small portion of the total oxygen relative to oxidation by organic matter, they can have a major effect on chemical evolution of the water. Such is the case of the evolution of groundwater system studied in Palmottu where these processes happen as water moves deeper into the groundwater flow system. In this sense the iron system plays also a key role controlling the redox potential in the shallow areas corresponding to the Upper and Dynamic Deep Flow Systems, where the inflowing oxygen is transformed into Fe(III).

Otherwise Stumm and Morgan (1996) state that in closed aqueous systems containing organic material and the other nutrients necessary for growth of bacteria, the reduction of SO_4^{2-} to HS^- and H_2S may occur when sufficiently low redox levels are reached. This is the process expected in the deepest areas of the Palmottu system, corresponding to the Stagnant Flow System, characterised by groundwaters with long residence times.

The effect of the uranium minerals buffering the redox system in the Palmottu zone where the uranium mineralisation occurs indicates the important role of these minerals on the redox capacity of this system.

From the previous modelling work we can extract that active solid phases constitute a large pool of redox buffering capacity, provided that the necessary time is given to reach redox equilibrium. This time to reach equilibrium can be assessed by using the concept of characteristic reaction times of slow processes and compare them to the residence times of the water in the system under consideration.

The characteristic reaction times for the most relevant geochemical redox processes considered in the present work are given in Table II. These reaction times can be compared to the residence times of groundwaters studied in the Palmottu system, these times are included in the same table.

Table II. Characteristic reaction times for relevant geochemical redox processes (Data taken from Bruno, 1996) and residence times of groundwaters in the Palmottu uranium deposit.

Characteristic reaction times	
Reaction Type	**Log τ_{char} (s)**
Homogeneous redox reactions	
One electron transfer	3-8
Multielectron transfer	8-11
Heterogeneous redox reactions	
One electron transfer	2-4
Multielectron transfer	9-11
Residence times in Palmottu	
	log τ_R (s)
Shallow groundwaters (Dynamic flow system)	9
Deep groundwaters (Stagnant flow system)	11

By comparing the characteristic reaction times of the redox processes with the residence times of Palmottu groundwaters it is possible to extract the following:

In the oxic shallow groundwaters corresponding to the Dynamic Flow System, where the redox chemistry was basically controlled by the oxygen and the iron redox systems. The waters have residence times (10^9 s) longer than the characteristic reaction times of the redox processes involved (ranging between 10^2 and 10^8 s), and therefore, redox equilibrium may be attained and redox potentials may be measured (Grenthe et al., 1992).

In the deep anoxic media, corresponding to the Stagnant Flow System, the potential redox pairs are given by the uranium and the sulphur systems. The redox processes have characteristic reaction times between 10^9 and 10^{11} seconds which are comparable to the residence time of the deep groundwaters in Palmottu (10^9 s). Consequently, equilibrium may also be attained. In this sense the fact to use a thermodynamic approach to model the measurements of the redox potentials in the whole Palmottu system appears to be appropriated.

This sequence is also reflected in the processes controlling the concentration of uranium in groundwaters. While U(VI) pure or mixed solid phases are limiting the

concentration of uranium in oxidising groundwaters, in the reduced ones, the solubility control is exerted by U(IV) pure solid phases.

7. Conclusions

The reproducibility and consistency of the results obtained with the various redox measurement methodologies used indicate the robustness of actual redox measurement technologies when applied to site characterisation. Consequently, it is possible to obtain a reproducible and consistent representation of the redox condition of the groundwaters by using the proper site characterisation techniques.

The redox potentials measured in the Palmottu system show two differentiated areas. The oxidised one, corresponding to the shallowest part of the system, above the sub-horizontal unit, and the reduced one, below this unit, corresponding to the deepest part. The redox potential decrease with depth shows the transition from the oxidised area to the reduced one.

The most oxidised groundwaters, with redox potentials ranging between 300 and 450 mV have been explained by biologically mediated oxygen reduction. In the shallow groundwaters, with redox potentials ranging between 0 and 150 mV, the iron system is controlling the redox potential.

The comparison of the characteristic reaction times of the redox processes involved in the Palmottu system, with the residence time of the groundwaters let to establish thermodynamic equilibrium criteria in all the redox system.

In the reduced area of the Palmottu system, where the U-mineralisation occurs, the uranium minerals play a key role buffering the redox capacity in this subsystem. There is a clear analogy between this system and the spent fuel/water interface. Otherwise, in the deepest area, where the Stagnant Flow System is located, the sulphide system is exerting the redox control of the zone.

According to this redox evolution with depth, the uranium concentrations in groundwaters are limited by different processes. Consequently, in the shallow areas, above the sub-horizontal unit, the U(VI) solid phases, mostly the uranyl silicates are controlling the concentration of this trace element in the shallow groundwaters. While in the deep area, below this unit, U(IV) solid phases, oxides and silicates, are exerting the solubility control of this trace metal in the aqueous system.

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Palaeohydrogeological implications for long-term hydrochemical stability at Palmottu

J.A.T. Smellie[1], R. Blomqvist[2], S. K. Frape[3], P. Pitkänen[4], T. Ruskeeniemi[2], J. Suksi[5], J. Casanova[6], M.J. Gimeno[7] and J. Kaija[2]

[1]Conterra AB, Sweden
[2]Geological Survey of Finland
[3]University of Waterloo, Canada
[4]VTT, Finland
[5]University of Helsinki, Finland
[6]BRGM, France
[7]Ciemat, Spain

Abstract

In the Fennoscandian Shield environment the glacial scenario is potentially a major threat to hydrochemical stability and thus repository integrity. The Palmottu study is important in this respect by helping to predict future events during ice margin permafrost conditions since there is clear Quaternary evidence that Palmottu experienced a continental ice margin palaeoclimate and was never submerged subsequently by seawater.

Palmottu is characterised by an upper, dynamic groundwater flow system, with typical bicarbonate groundwaters which can be partly explained by mixing processes, but nevertheless show a clear evolutionary trend from Ca-HCO_3 types to deeper Na-HCO_3 types. At greater depths, where low permeable conditions prevail, Na-Cl and Na-SO_4 type groundwaters are present. A sizeable $\delta^{18}O$ depleted glacial water component is present in the deep Na-Cl and Na-SO_4 type groundwaters (additionally in some of the deep Na-HCO_3 types). The presence of glacial water may suggest that the system has been open to the incursion of oxidising waters to at least 400 m. However, it is highly unlikely that the glacial melt waters would retain their oxidation capacity to any great depth because of the buffering capacity of first the overburden and then the bedrock itself; this is supported by mineralogical evidence.

The SO_4 groundwaters at Palmottu may be explained by sulphide dissolution and oxidation during hydrothermal events creating an *in situ* residual sulphate fluid/solid. Continuous, long-term oxidation of sulphide minerals during geological times can also have contributed to the character of SO_4 waters. During recent glacial melting and unloading, $NaSO_4$ groundwaters may have been formed from the breakdown of solid mirabilite ($Na_2SO_4 \cdot 10H_2O$) formed under permafrost conditions and mixed with glacial melt water as observed today. In addition, the generation of a more saline front under the permafrost layer would further enrich sulphate concentrations. These cyclic processes have increased gradually the amount of sulphate to presently observed levels. Irrespective to the origin of these groundwaters, however, the fact that Na-SO_4 groundwaters, and to a lesser extent the Na-Cl type groundwaters, are still present at these depths, underlines the stability of the hydrochemical system over long periods of geological time under low permeable conditions, at least since the last glaciation approximately 10 000 a ago. At greater depths, more applicable to repository depths, conditions would be expected to be more stable.

Introduction

With respect to the deep geological disposal of radioactive wastes, a key question is whether the future safety and performance of a repository system can be evaluated over periods of time extending from thousands to hundreds of thousands of years. Specifically, in the case of the reference scenario (*i.e.* assuming canister degradation), it is necessary to predict the long-term release of radionuclides from the repository to the biosphere (*e.g.* KBS-3, 1983). Modelling must demonstrate that the rate of

radionuclide release, and consequently the radiological risk, will not be suddenly increased to unacceptable levels within and beyond a 10 000 a period.

Performance assessment modelling is normally based on estimates of present-day groundwater fluxes and solutes through various parts of the system being modelled. The drawbacks from this approach are that a purely hydraulic flow model is validated (*i.e.* only valid for short-term predictions), and the extrapolations for longer time periods (> 10 000 a) are vague. A more realistic approach is to try to understand the fluid history of the host rock medium by using mineralogy, hydrochemistry and isotope geochemistry to trace past events, which can provide the basis to predict future groundwater trends (*i.e.* palaeohydrogeology).

There is clear Quaternary evidence that Palmottu experienced a continental ice margin palaeoclimate and was never submerged subsequently by seawater (*e.g.* Donner 1995, also Blomqvist *et al.*, in this volume). The main glacial processes influencing the palaeo-evolution at Palmottu, and therefore potentially influencing the hydrochemical stability of the groundwater system, have been permafrost and the near-vicinity of the ice margin.

Hydrochemistry and isotope geochemistry

The conceptual groundwater flow model of Palmottu site is presented in Blomqvist *et al.* (1998); also, in this volume). The model comprises: 1) a Dynamic Upper Flow System (100 m depth) characterised by a young (tens of years) Ca-HCO_3 type groundwater, 2) a Dynamic Deep Flow System (to at least 200 m depth) characterised by an older (hundreds to a few thousands of years), more evolved Na-HCO_3 type groundwater, and 3) a Stagnant Deep Flow System characterised by a Na-SO_4 and/or Na-Cl type groundwater at least down 350 m depth.

Hydrochemical characterisation and geochemical modelling of the Palmottu system essentially support the groundwater flow model (Laaksoharju *et al.*, 1999; Gimeno *et al.*, in this volume; Pitkänen *et al.*, in this volume). Both mixing and water/rock interaction characterise the dynamic groundwater flow regimes. There is a clear geochemical evolution from the shallow Ca-HCO_3 type to the deeper Na-HCO_3 type groundwater, but there is no evidence to date that this evolutionary trend links in with the groundwaters of the Stagnant Deep Flow System, although the Na-Cl type groundwater might be an expected long-term evolved end-member. Chemical and isotopic data suggest that some mixing continues to within the waters of the Stagnant Deep Flow System.

At Palmottu there appear to be two main features that are potentially relevant to understanding past perturbation of the hydrochemical system: a) the presence of glacial water component at depth, and b) the presence of Na-SO_4 type groundwater at depth.

Glacial water component

There is a sizeable $\delta^{18}O$ depleted groundwater component that may represent glacial melt water associated with both the Na-SO_4 and Na-Cl type groundwaters, and additionally in some of the deeper Na-HCO_3 type groundwaters (Blomqvist *et al.*,

1995, 1998; Pitkänen *et al.*, in this volume). This is clearly seen from the $\delta^{18}O$ values plotted against borehole length in Figure 1, where $\delta^{18}O$ values less than –12 ‰ signify colder climate recharge conditions compared to present ones. The extreme $\delta^{18}O$ value of –19 ‰ obtained at Palmottu is close to the expected isotopic value of glacial melt water (*c.f.* Ferronsky *et al.*, 1983; Pitkänen *et al.*, in this volume), and $\delta^{18}O$ values lighter than –15 ‰ would already have a sizeable glacial water component. It is possible that these glacial waters were introduced under high hydraulic pressures at the margins of the ice mass during glacial melting and retreat, and mixed with existing groundwaters. Subsequently (*i.e.* during the last 10 000 a), the glacial component has been flushed out from the upper part of the highly permeable bedrock, but has been retained in the low permeable parts of the deep bedrock, mostly below 200 m depth.

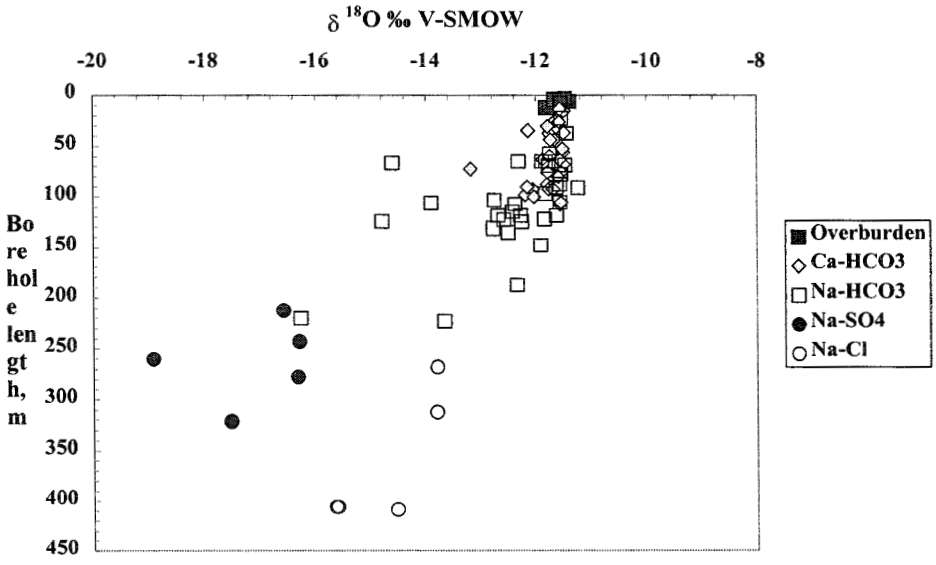

Figure 1. $\delta^{18}O$ plotted against borehole length at Palmottu.

Na-SO_4 type groundwaters

The presence of Na-SO_4 type groundwaters makes Palmottu unique since there is no other recorded occurrence from a crystalline rock environment in the open literature. It appears to be restricted to the area of uranium mineralisation in the central part of the Palmottu site, located between the Na-HCO_3 and Na-Cl type groundwaters (Blomqvist *et al.*, 1998).

Basically three hypothesis can be considered to explain the presence of sulphate in these groundwaters: 1) Sulphide dissolution and oxidation during hydrothermal events creating an *in situ* residual sulphate fluid/solid, 2) Continuous, long-term oxidation of sulphide minerals during geological times including oxidation of sulphide minerals due to the incursion of oxygen-rich meltwaters, and 3) Enrichment of sulphate waters by freezing under permafrost conditions. It is possible that a combination of all three mechanisms have been involved in creating the observed sulphate concentrations.

The fact that the SO_4 groundwater type at Palmottu has been found only in association with the uranium mineralisation suggests that its composition is site-specific and not

the normal product of water/rock interaction. These brackish Na-SO_4 groundwaters show low $\delta^{34}S$ signatures most likely derived from the oxidation of primary sulphides associated with the mineralisation (Frape *et al.*, 1999). Further support for the association with hydrothermal activity includes: a) the potential of U-reduction and S-oxidation exists within the mineralised area (Bruno *et al.*, 1998), b) widespread hydrothermal alteration of plagioclase with replacement by clays, mica and iron oxide and corrosion of matrix sulphide phases, pyrrhotite and pyrite, is observed (Ruskeeniemi *et al.*, 1998), c) Sr-isotope signatures in the Na_2SO_4 waters are similar to these in hydrothermal plagioclases and uranium-rich secondary calcites (Negrel and Casanova, 1999), d) fluid inclusions in the secondary calcites indicate hydrothermal temperatures, frequently from 100 to 250°C (Blyth and Frape, 1999), and e) the calculated water of formation from the secondary calcite fluid inclusions fall within the range of hydrothermal/magmatic fluids.

There appears to be reasonable evidence, therefore, to show that the origin of the sulphate is closely related to the uranium mineralisation, and that sulphate-forming processes may have been active over geological timescales. The amount of sulphate, however, is greater than what would be expected from hydrothermal reactions alone (Pingfang Shi, pers. comm., 1999). Furthermore, it is considered unlikely that oxidation of sulphides under present conditions or even in the case of melt water penetration could produce any significant amounts of sulphates due to the small amount of dissolved oxygen available (c.f. Pitkänen *et al*, in this volume). To explain the measured concentrations would require some additional mechanism to be invoked, and presently the cyclic enrichment of sulphate by freezing under cold climate or permafrost conditions is considered a viable explanation. The basis of this hypothesis is the formation of solid mirabilite ($Na_2SO_4 \cdot 10H_2O$) in fractures (or possibly at the surface) resulting from the freezing of waters initially containing some sulphate. Present-day analogous processes can be observed to be occurring at the edge of the Antarctic ice sheet (*e.g.* Matsubaya *et al.*, 1979; Keys and Williams, 1981). At Palmottu, during glacial melting and unloading, Na-SO_4 groundwaters may have been formed from the breakdown of mirabilite and mixed with glacial melt water (Blomqvist *et al.*, 1998). A similar effect is achieved also without the intermediate solid phase by just removing ice from the water and driving a concentration front deeper down. These freezing mechanisms would conveniently explain the association of Na-SO_4 groundwaters with $\delta^{18}O$-depleted cold climate recharge waters (Figure 1). Furthermore, the depth of the Na-SO_4 groundwaters is well within the range of reported permafrost occurrences in Russia and Canada (Yershov, 1998; Brown, 1970). A freeze out explanation to the Na-SO_4 groundwaters is also supported by: a) the oxygen in the sulphate is in isotopic equilibrium with the associated oxygen in the water phase (Frape *et al.*, 1999), and b) calculation of the molar ratios of the Na-SO_4 groundwaters is a precise fit to the mirabilite formula.

In conclusion, a plausible explanation for the character of the Na-SO_4 groundwaters is that there have been initially ancient sulphate groundwaters of hydrothermal origin associated with the uranium mineralisation. Subsequent glacial events over thousands of years may have resulted in the freezing of these waters during permafrost conditions further enriching the sulphate water. These cyclic processes have increased gradually the amount of sulphate to presently observed levels.

Mineralogy

The major low-temperature fracture mineral phases at Palmottu that may indicate past changes in groundwater chemistry are calcite and iron oxyhydroxides. Of restricted occurrence, but of great importance, are uranophane that have been observed close to the bedrock surface (Ruskeeniemi *et al.*, 1998; also, in this volume).

Calcites have been observed at all depths studied; most are hydrothermal or magmatic in origin (>100° C) dating back to at least 1.0 Ga. Younger calcites are also present, but they tend to be fine-grained, characterised by multiprocess compositions and, generally devoid of fluid inclusions (Ruskeeniemi, 1998). Uranium-decay series model ages from younger calcites selected from the upper 100 m of the bedrock suggest that uranium mobilisation/deposition may have occurred periodically during the last 30-350 ka (Suksi *et al.*, 1998) reflecting palaeoclimatic changes.

Most iron oxyhydroxides occur as poorly crystalline goethite and are restricted to the upper 60-70 m of the bedrock. They appear to be the latest fracture filling phase, forming on older mineral coatings such as calcite, or directly on the fracture surfaces (Ruskeeniemi, 1998). Uranium-decay series measurements on these phases suggest uranium mobilisation/deposition over the last 1 Ma or so (Suksi *et al.*, 1998).

Small amounts of pure uranophane (U(VI)-Ca-silicate) occur in sealed, sub-horizontal dilation-type fractures, in the upper 30 m of the Eastern Granite. Textural fabric patterns suggest slow growth in an open void system that may have resulted from stress-release during glacial unloading. Subsequently, following unloading and destressing, the fractures have become sealed, preserving the uranophane from groundwater contact (Ruskeeniemi *et al.*, in this volume). Uranium-decay series measurements of two uranophane samples gave geologically young ages of 90-120 and 189-240 ka, respectively (Suksi, 1998; Ruskeeniemi *et al.*, in this volume), which suggests that the formation of a "uranophane zone" is presently proceeding at Palmottu. The range of dates corresponds with those of calcite and appears to represent warmer interglacial periods of the past.

Conclusions and PA-implications

The presence of glacial water in the deep Na-Cl and Na-SO_4 type groundwaters may suggest that under high hydraulic pressures, expected to prevail at the ice margins during glacial melting and retreat, the melt water can be forced down to depths in the order of 350 m, *i.e.* close to repository depths. However, it is highly unlikely that the glacial melt waters would retain their oxidation capacity to any great depth because of the buffering capacity of first the overburden and then the bedrock itself; this is supported by mineralogical evidence.

The present SO_4 groundwaters at Palmottu may be explained by sulphide dissolution and oxidation during hydrothermal events creating an *in situ* residual sulphate fluid/solid. Continuous, long-term oxidation of sulphide minerals during geological

times is also a potential SO_4 producing process. Surface/near-surface freeze out of saline/brackish fluids under permafrost conditions with possible emplacement of the resulting SO_4 groundwaters to depth during glacial unloading and retreat could be a significant factor. Alternatively, or in addition to freeze out processes in fractures extending to greater depth could also contribute to the present groundwater character. These cyclic glacial freeze out processes accompanied by the incursion of glacial water have increased gradually the amount of sulphate to presently observed levels. Irrespective to the origin of these groundwaters, however, the fact that Na-SO_4 groundwaters, and to a lesser extent the Na-Cl type groundwaters, are still present at these depths, underlines the stability of the hydrochemical system over long periods of time, under low permeable conditions, up to the last glaciation, close to 10 000 a ago. At greater depths, more applicable to repository depths, conditions would be expected to be more stable.

In contrast to hydrochemical studies which tend to be most influenced by the latest events, *i.e.* the last glaciation, mineralogical studies of fracture phases, namely calcite and uranophane, indicate that systematic events related to previous interglacial periods may have affected the site. However, their effect on the long-term stability of the hydrochemical system still needs further study.

Acknowledgements

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Testing trace element geochemical models at Oklo and Palmottu

J. Bruno[1], D. Arcos[1], E. Cera[1], L. Duro[1], S. Jordana[1], C. Rollin[1], M.J. Gimeno[2], L. Pérez del Villar[2], J. Peña[2], L. Ahonen[3], A. Luukkonen[4] and J. Kaija[3]

[1]QuantiSci, Spain
[2]Ciemat, Spain
[3]Geological Survey of Finland
[4]VTT, Finland

ABSTRACT: We present the results obtained from the modelling of the main processes governing trace element behaviour at the Oklo fossil reactor system in Gabon and the Palmottu uranium deposit in Finland. The results are discussed in the light of the mineralogical data on the occurrence of trace elements in the sites. Following the pattern indicated by former studies, trace element mobility and retardation are controlled by their co-precipitation and co-dissolution with more dynamic mineral phases of the system, particularly Fe(III) oxy-hydroxides and calcite.

1 INTRODUCTION

The geochemical behaviour of natural systems is controlled by water-rock interactions. These processes exert a direct control on the intensive geochemical master variables, pH and Eh, as well as on their associated extensive capacities, alkalinity and redox potential, which, in turn, influence the geochemistry of trace metals. Consequently, water-rock interaction processes control the behaviour of the trace components of geochemical systems. The concentration of trace elements in natural groundwaters may be controlled by dissolution/precipitation of individual solid phases, although in most cases the processes responsible for the observed minor component behaviour involve the main components of the system. Sorption, occlusion or incorporation to the crystalline lattice of major minerals present in the media are processes likely to account for the observed behaviour of trace metals in the geosphere. In principle, the models intended to explain this coupled behaviour are complicated and need of a large number of parameters generally lacking in the geochemical literature. In other cases, the processes of dissolution and precipitation of solid phases present long characteristic times (see Bruno, 1996), which prevents the attainment of equilibrium in systems with shorter residence times and causes kinetics to play a significant role in those environments.

Co-precipitation (Bruno et al., 1995) and co-dissolution (Bruno et al., 1998) models are able to explain the existing link between major and minor components of the system in a simple fashion. These models have been succesfully applied to both, lab and natural systems, and have proven to reproduce the concentration of uranium, strontium, manganese, zinc and several other trace metals in diverse geological environments. Particularly, in granitic media (El Berrocal, Toledo, Spain), clayey media (Cigar Lake, Canada), hyperalkaline environments (Maqarin, Jordan) etc., (see Bruno et al., 1998, and references therein).

In this work we present a further extension of this modelling by reporting on the main findings from the geochemical model testing undertaken at two Natural Analogue sites: the Oklo fossil reactor system in Gabon and the Palmottu uranium deposit in Finland.

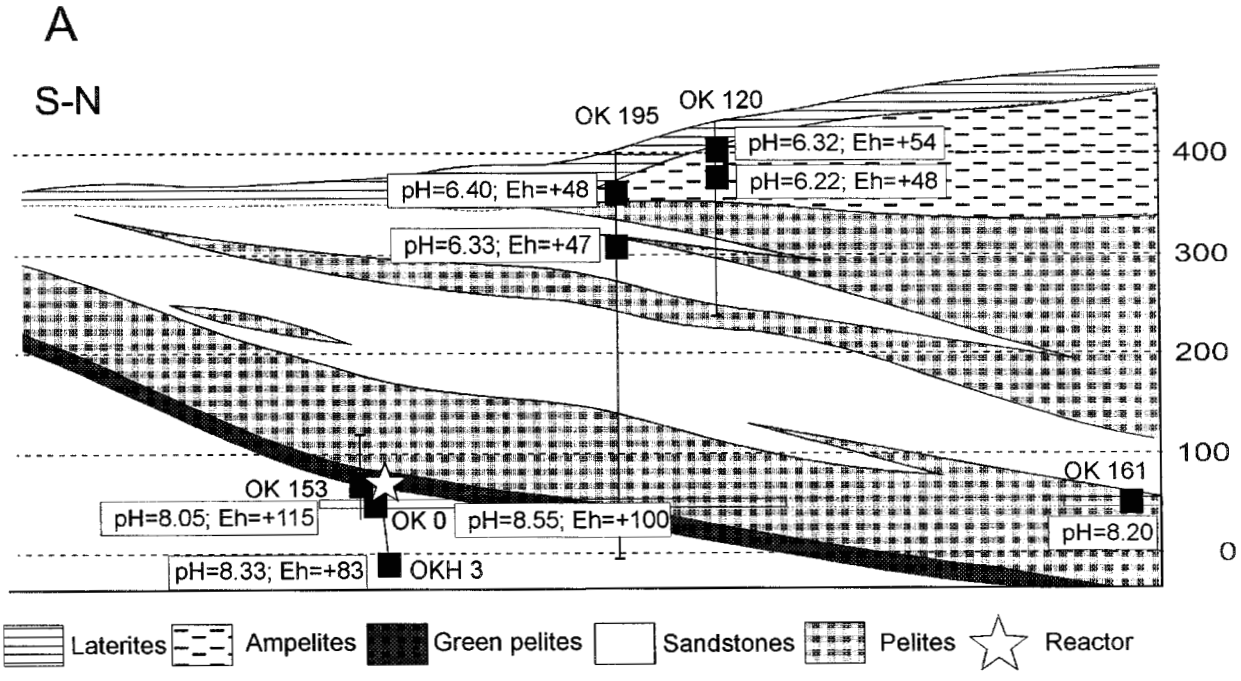
This work is not only focused on testing the conceptual and mathematical models on trace element behaviour, but also constitutes a check on the consistency of thermodynamic databases and geochemical codes.

2 THE OKLO AND PALMOTTU GEOCHEMICAL SETTINGS

2.1 The Oklo natural analogue system

The fossil natural nuclear reactor systems of Oklo (Gabon) are located in the Precambrian Franceville basin. This sedimentary basin is composed of two main formations, a lower sandstone and an upper pelitic unit. Most of the uranium ores are related to a pelitic level at the top of the sandstone formation. The ores consist of uraninite associated to organic mater and sulphides in a quartz and phyllosilicate (illite and chlorite) matrix. Two different uranium deposits have been identified. The most important is Oklo, which contains 16 nuclear reactors, being the Okélobondo reactor the one considered here. This deposit is located at the northwester edge of the Franceville basin, along the basement uplift of Mounana. An additional reactor has been identified in the Bagombé uranium deposit in the southern part of the Franceville basin (Naudet 1991). The location of these unique fossil reactors prompted the study of these systems as analogues to the disposal of spent nuclear fuel.

In Figure 1 we include an schematic cross section with the main geological units of the Okélobondo and Bagombé systems. Also the groundwater samples selected for the study of the trace metals geochemistry are indicated in the figure.



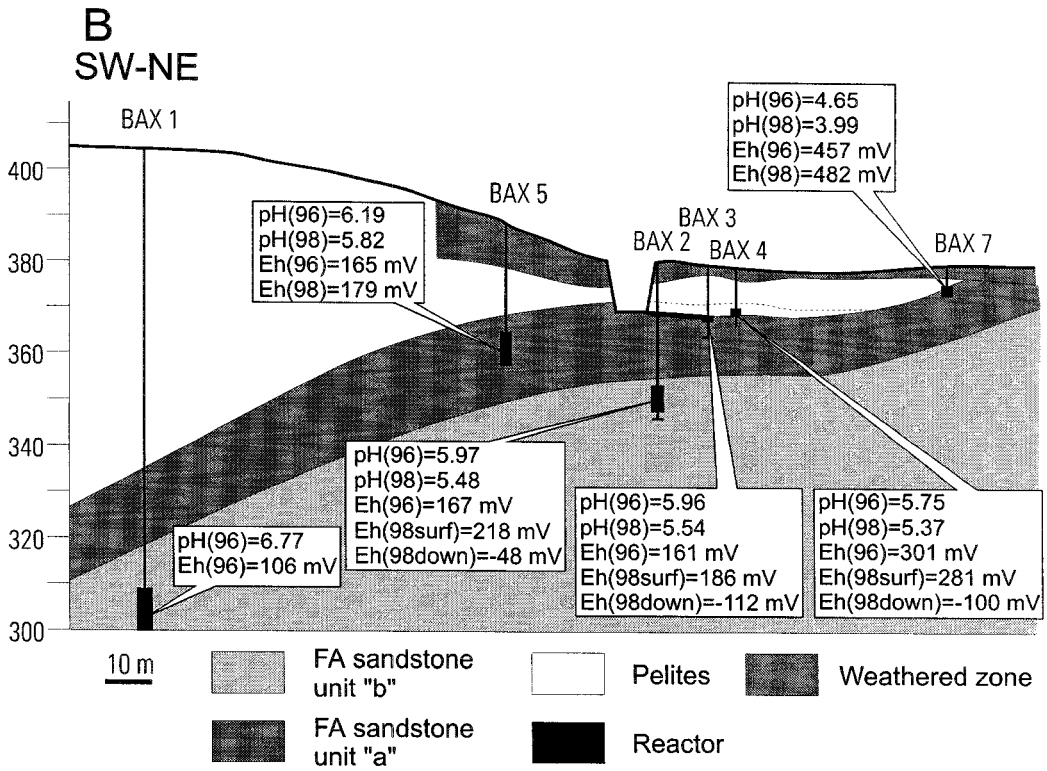


Figure 1. Cross section of the Okélobondo (A) and Bagombé (B) systems. Black squares indicate the location of the groundwater samples selected for the study. Groundwater pH and Eh values are also presented.

2.2 The Palmottu uranium deposit

The Palmottu uranium deposit occurs within a zone of metamorphosed supracrustral and sedimentary rocks that extends from SW Finland into central Sweden. This region is characterised by granites and highly metamorphosed migmatitic rocks (Blomqvist et al., 1995; 1998). The Palmottu U-Th mineralisation is related to the latest stages of the orogenic events in Finland about 1.8-1.7 Ga. The U-Th deposit is located in the contact zone of a late orogenic granite and the highly metamorphosed rocks suggesting a link between the magmatic activity and the mineralisation process. Nevertheless it is still not clear whether the source of uranium was magmatic or it was related to a hydrothermal leaching of the metasediments.

The uranium ore consists of an irregular discontinuous body, which is approximately 400 m long and between 1 and 15 m thick. Within this body U and Th are associated to biotitic-pegmatite dykes and quartz-biotite veins up to a few decimetres-thick. Thorium is mainly found incorporated to uraninite and monazite, whereas all uranium occurs as uraninite and uranium silicates (Blomqvist et al., 1995). A schematic view of the system studied and the groundwater samples selected for the trace element study is presented in Figure 2.

Figure 3 summarises in a Piper diagram the main geochemical data of the Oklo and Palmottu samples used in the trace element geochemical modelling of these systems.

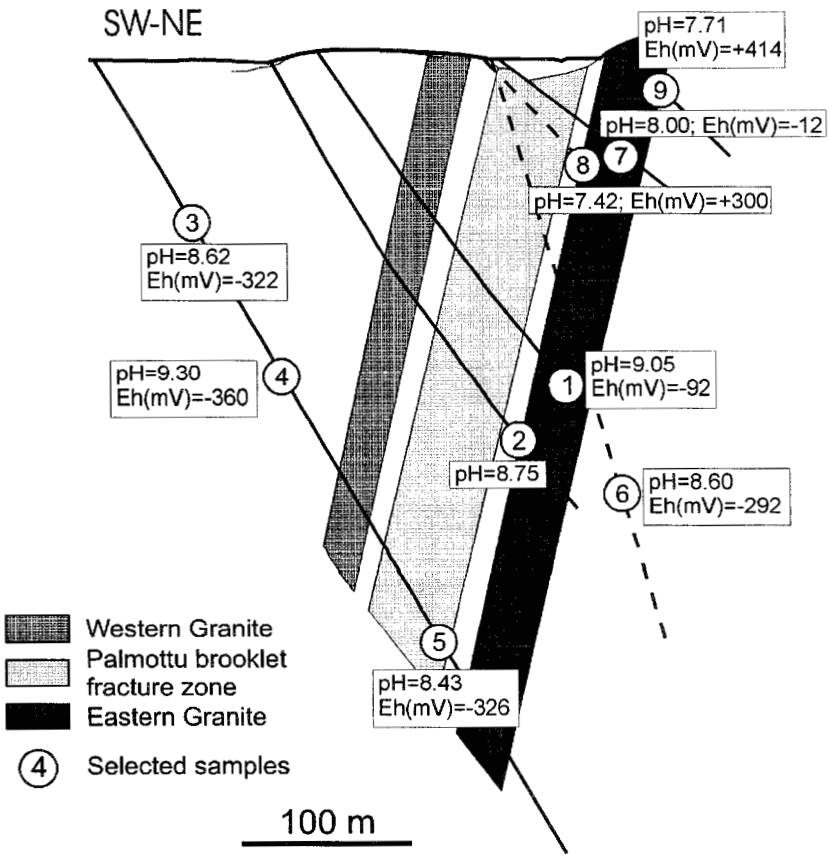


Figure 2. Cross section of the Palmottu system with the location of the groundwater samples selected for the trace elements study.

2.3 Groundwater chemistry

The groundwater samples selected from Oklo are all of the Na-Ca-HCO_3-type. They can be classified in three groups: surface waters, presenting acidic pH values; waters sampled in sandstones, with near neutral pH and relatively reducing redox potentials and a third group of waters, sampled in the vicinity of the reactors and presenting larger alkalinity and oxidising redox potential.

The Palmottu groundwater samples are also classified according to three different groups (Gimeno et al., 1999). The shallow Ca-Na-HCO_3-type waters, which are diluted, slightly acidic and oxidant; the Na-Cl-SO_4 type waters, sampled at larger depths and presenting more reducing redox potentials and larger TDS values; and finally the deepest samples, of Na-Cl type and of a very reducing character.

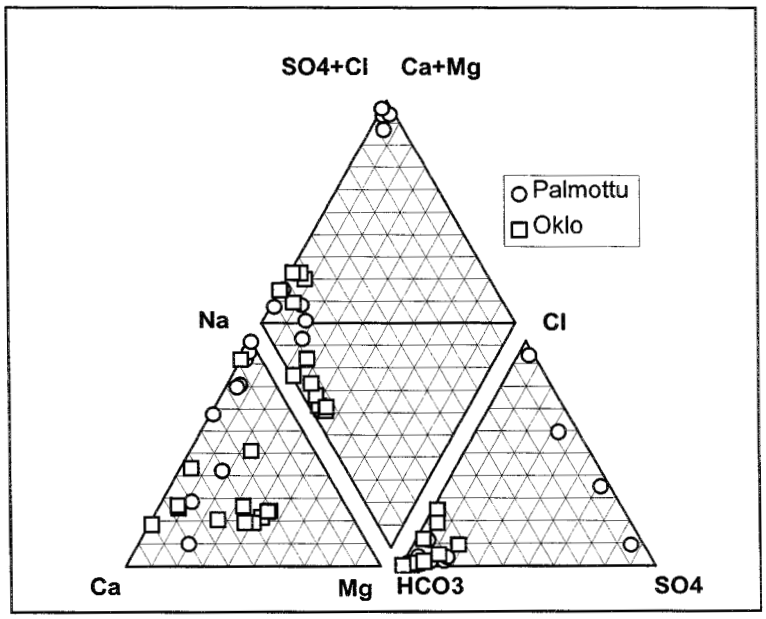


Figure 3. Piper diagram integrating the chemical water data of the Oklo and Palmottu samples used in the modelling exercise.

3 MODELLING RESULTS AND DISCUSSION

The behaviour of Mn, Sr, Ni, Ba, Zn, U, Th and REE was studied in both, Oklo and Palmottu environments. However, and for the sake of brevity, in this paper we will only present some of the results. For extensive explanation of the procedures and results obtained, the reader is referred to the original reports of the projects (Bruno et al., 1998; Duro and Bruno, 1998; Duro et al., 1999a, 1999b).

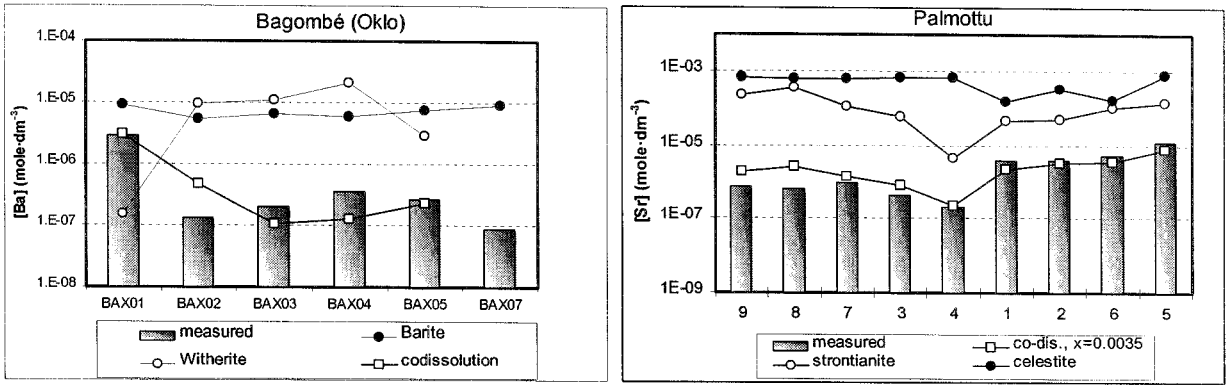
In general, we consider that an element is a trace component of a solution when its aqueous concentration does not exceed 10^{-6} mol/dm^3. By the inherent trace character of these elements, it is very unusual to find them at concentrations large enough as to cause the precipitation of a pure phase of those metals. For this reason, the most common processes able to explain their behaviour must consider their interaction with the major and more active components of the system, mainly the minerals forming the fracture fillings, which are easily available for water-rock interactions.

As an example, we can study the case of uranium in Oklo and Palmottu (see Figure 4b). Although being a trace element in groundwaters, U cannot be considered trace in the Palmottu system, which is illustrated by the fact that the solubility of pure U phases, coffinite and oxidised uraninite (U_4O_9) is able to explain the U concentration in these groundwaters. The same conclusions can be drawn from the study of the Oklo system, although U seems to be associated to Fe(III)-oxyhydroxides in the oxidised parts of the system and a co-precipitation model is able to explain its behaviour in the samples located close to the reactor OK84 in Okélobondo (see samples OK0(96) to OKH3(96) in Figure 4b).

Ba in Bagombé and Sr in Palmottu illustrate the association between trace components and major minerals (see Figure 4a). The incorporation of these elements

to the calcite lattice is a well-known phenomenon (Deer et al., 1964; Tesoriero and Pankow, 1996) able to explain the concentrations of Ba and Sr found in the studied groundwaters. Furthermore, the fact that the aqueous Ca concentration correlates with those of Ba and Sr indicate that all these elements have a common mineral source in the systems (Ba or Sr-bearing calcite respectively)

a)



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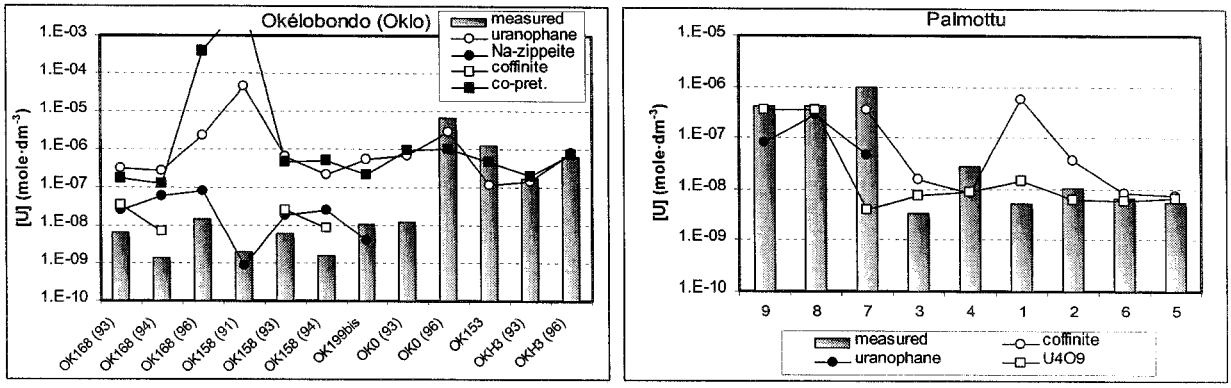

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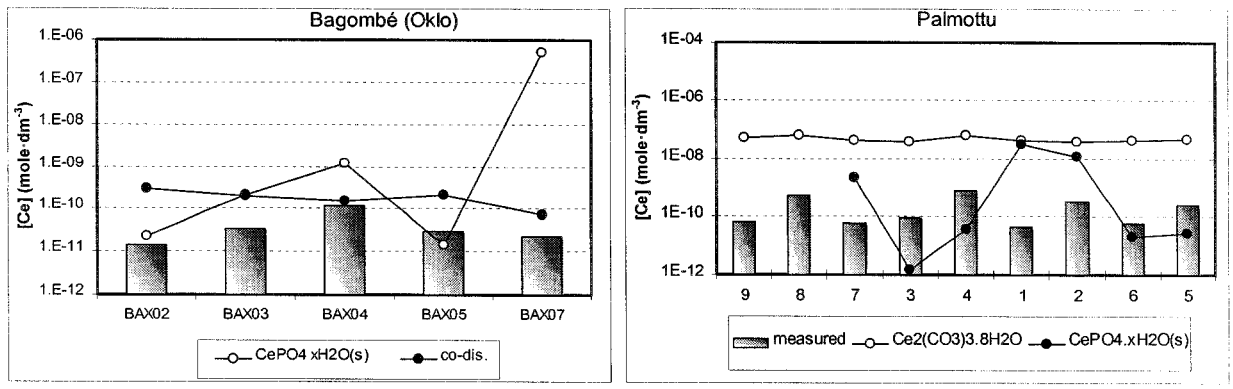

Figure 4. Selected results the solubility calculations performed in Oklo and Palmottu. Cerium has been selected to represent all the REE as they behave all in the same way.

All REE behave in a very similar way. The solubility of solid REE phosphates reproduces fairly well not only the REE aqueous concentrations, but also the trend of the data (Fig. 4c). The overestimation of the concentrations of REE obtained when assuming equilibrium with $REEPO_4 \cdot xH_2O$ increases when increasing the atomic

weight. This may indicate an association of REE with major phosphate minerals present in the system, such as apatite or monazite, and this association would occur in major proportion as the atomic weight decreases. This observation is supported by mineralogical data in Jones et al. (1996).

In order to systematise this observation, in Fig. 5 we have plotted the difference between the measured REE concentration and the $REEPO_4 \cdot xH_2O$ calculated solubility for all the REE included in the analysis and for all the selected samples from Babombé (Oklo) and Palmottu.

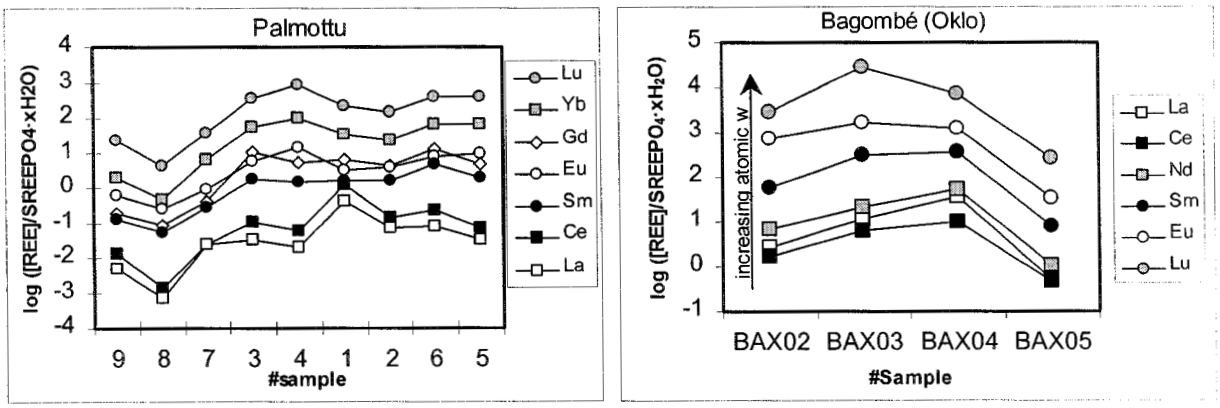

Figure 5. Difference between the measured REE concentrations and the calculated concentrations by assuming equilibrium with pure $REEPO_4 \cdot xH_2O$.

According to these results a co-precipitation process in Bagombé and a co-dissolution process in Palmottu of REE with apatite will be able to explain the behaviour of these elements in both systems respectively.

4 CONCLUSIONS

The experimental observations on trace element associations together with the geochemical modelling work performed in Oklo and Palmottu give additional evidence of the link between trace and major component cycling, particularly C, Fe and P.

Fe(III) oxy-hydroxide, calcite, and apatite precipitation / dissolution processes appear to be critical to control trace element mobility in natural environments.

The co-precipitation/co-dissolution modelling approaches previously proposed give a simple but consistent representation of the fate and mobility of trace metals in natural water systems.

5 ACKNOWLEDGEMENTS

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The migration and fixation of uranium at the Palmottu Natural Analogue Site

D Read[1], K Rasilainen[2], C Ayora[3] and T Ruskeeniemi[4]

[1] Enterpris, University of Reading, UK
[2] VTT Energy, Espoo, Finland
[3] CSIC, Barcelona, Spain
[4] GTK, Espoo, Finland

Abstract

Alteration of the 1,800 ma old uraninite deposit at Palmottu has led to substantial re-mobilisation of uranium. A proportion of the original ore body has been altered hydrothermally resulting in the formation of U(IV) silicate (coffinite) around the primary UO_2 crystals. During the last one million years, the site has experienced multiple glaciations in connection with which a proportion of the uranium has been mobilised under more oxidising conditions, leading to precipitation of U(VI) silicates (uranophane) at shallow depths. Volumetrically significant amounts of U are also found in association with fracture coatings, mainly impure calcites, clays and iron oxy-hydroxides. Finally, at the surface, post-glacial peat constitutes an additional sink as is typical of U deposits in northern Europe.

A relatively well-characterised recharge system was chosen for a detailed migration modelling exercise. The postulated flow route, identified on the basis of tracer tests and supporting information, is in the upper, oxidising part of the bedrock and is intersected by six drill holes. Comprehensive analyses of packered sections from these and for surface recharge provide seven reference points for the calculations. The modelling study consists of two steps, the first involving prediction, the second allowing model refinement. The flow route is assumed to constitute a closed system and to reflect essentially post-glacial events, as it is probable that this latest signal dominates.

A set of hypotheses that are believed to be involved in the mobilisation and fixation of uranium are being tested using a variety of modelling approaches. These range from a simple advection-dispersion-matrix diffusion representation to a fully coupled chemical transport model. Preliminary results are presented here. An effort is also being made to represent the observed uranium-series disequilibria (USD) along the flow route, evident in data for groundwater and fracture coating minerals.

The Palmottu study has confirmed a number of processes responsible for U mobilisation and fixation observed at other natural analogue sites. Additionally, it includes some unique features owing to its glacial and post-glacial history. By demonstrating very limited dispersion of U over millions of years, it has greatly increased confidence in the safety of spent fuel disposal in crystalline, igneous rocks. However, it has also highlighted the limitations of modelling tools used to quantify repository performance when describing U migration in a complex, natural geochemical system.

Introduction

The main purpose of the Palmottu study is to develop an understanding of the mechanisms via which uranium migrates through crystalline bedrock and the timescales on which such processes operate. In this respect, it shares a number of features with other natural analogue investigations, for example Poços de Caldas (Chapman *et al.*, 1991), which addressed oxidation of a supergene uraninite-pitchblende deposit in highly altered, igneous rocks. There are similarities also with Koongarra (Murakami *et al.*, 1997), in terms of the formation of secondary silicate mineralogy, and Broubster (Read *et al.*, 1993), where emphasis was

placed on organic complexation by peat. However, Palmottu is unique in making the influence of palaeoclimatic changes a central aspect of the investigation.

In the main, our interest centres on:
- the length of time over which U migration has been occurring
- the amount of U lost from the system
- the direction of U movement now and in the past

In order to address these questions, it is first necessary to establish the phases that control uranium concentrations at Palmottu, where the role of groundwater composition in maintaining aqueous levels is obviously an important factor. This is the focus of the current paper. Evolution of groundwater chemistry is described in an accompanying paper (Pitkänen *et al.,* in this volume).

Geochemical models have been applied extensively in previous natural analogue investigations. For the most part, their use has been restricted to so-called 'blind prediction' of trace metal solubility. This procedure, developed first within the CEC CHEMVAL Project (Read, 1990), is essentially a test of the completeness and adequacy of the thermodynamic database. To date, there has been no structured attempt to use analogue data to critically examine the fundamental concepts underlying geochemical transport models used routinely in nuclear waste research. This may account for the relative absence of natural analogue information in published assessments (*e.g.* Nirex, 1992) and the low credence attached to such assessments by the geoscientific community (*e.g.* Haszeldine and Smythe, 1996). Within the Palmottu Project an attempt has been made to:

- assess and compare diverse modelling approaches for simulating the migration-fixation of U at the site, with emphasis on the representation of hydrogeologic and geochemical processes
- test alternative hypotheses of U behaviour as a means towards constructing a defensible, conceptual model of site evolution.

The models range from a state of the art coupled chemical transport code (Saaltink *et al.*, 1998) to a standard advection-dispersion-matrix diffusion model employed previously in assessment calculations (Intera, 1983). An outline of the modelling exercise is given below following a brief description of the system and the model domain.

Description of system and postulated migration route

The U-Th mineralisation is hosted within Proterozoic (1800 Ma) mica gneiss with granite pegmatite veins. The U-rich ore is associated with the veins and forms a vertical structure extending to at least 400m. The main U/Th-bearing minerals are uraninite, which has been extensively altered during hydrothermal activity to U(IV) silicate, and monazite. Subsequent mobilisation has led to uranium enrichment in fracture minerals, mainly impure calcites, clays and iron oxides (Blomqvist *et al.*, 1998). A discrete U(VI) silicate, uranophane, has now been identified in the uppermost 50 m of mineralised granite together with an amorphous and, as yet uncharacterised, uraniferous phase of high solubility (cf. Ruskeeniemi *et al.*, in this volume).

Hydrogeologically, Palmottu is thought to comprise an oxidising, Dynamic, Upper Flow System (<100 m) dominated by young Ca-HCO_3 waters, a Dynamic, Deep Flow System (mainly Na-HCO_3) and a Stagnant Deep Hydrogeological System containing waters with a Na-SO_4 or Na-Cl composition (Blomqvist *et al.*, 1998, Pitkänen *et al.*, in this volume). The ^{18}O values of the latter indicate a substantial glacial recharge component introduced some 10,000 years ago. High dissolved uranium concentrations (100-500 ppb) are associated with the HCO_3 groundwaters in the vicinity of the uranium mineralisation down to depths of 130m. This region forms the focus of the migration study. At greater depths, clearly reducing conditions prevail and U concentrations rarely exceed 10 ppb.

Migration modelling focuses on the well-defined Eastern Flow System, for which a complete data set is available. The data comprises a structural model of the bedrock (Paananen *et al.*, 1998), the results of groundwater flow modelling (Koskinen and Kattilakoski, 1997), groundwater and fracture mineral chemistry (Kaija, 1998; Ruskeeniemi, 1998; Ruskeeniemi *et al.*, 1998), *in-situ* video logging (Paulamäki *et al.*, 1997) and the interpretation of a hole–to–hole tracer test (Gustafsson *et al.*, 1998). Recent analyses of samples taken from two shallow boreholes, drilled in autumn 1998, have led to a greatly improved understanding of uranium behaviour at the site.

A transport section was defined for modelling purposes on the basis of the tracer test results and head data from hydraulic testing which indicate the existence of hydrogeologic connections between a number of boreholes in the Eastern Flow System (Paananen *et al.*, 1998). The transport domain is described in detail in Read *et al.*, (1999) and it is shown in cross-section in Figure 1. Rainwater falling on the topographic high to the north east is assumed to constitute the only source of recharge after which water and dissolved constituents migrate towards borehole R318 along a series of interconnected fractures. Rain water and groundwater analyses (sampled in 1998) for each of the packered sections are given in Appendix 1.

The modelling exercise focuses on identifying the dominant solid phases responsible for supplying and removing uranium to/from the system under both present day conditions and in the geological past.

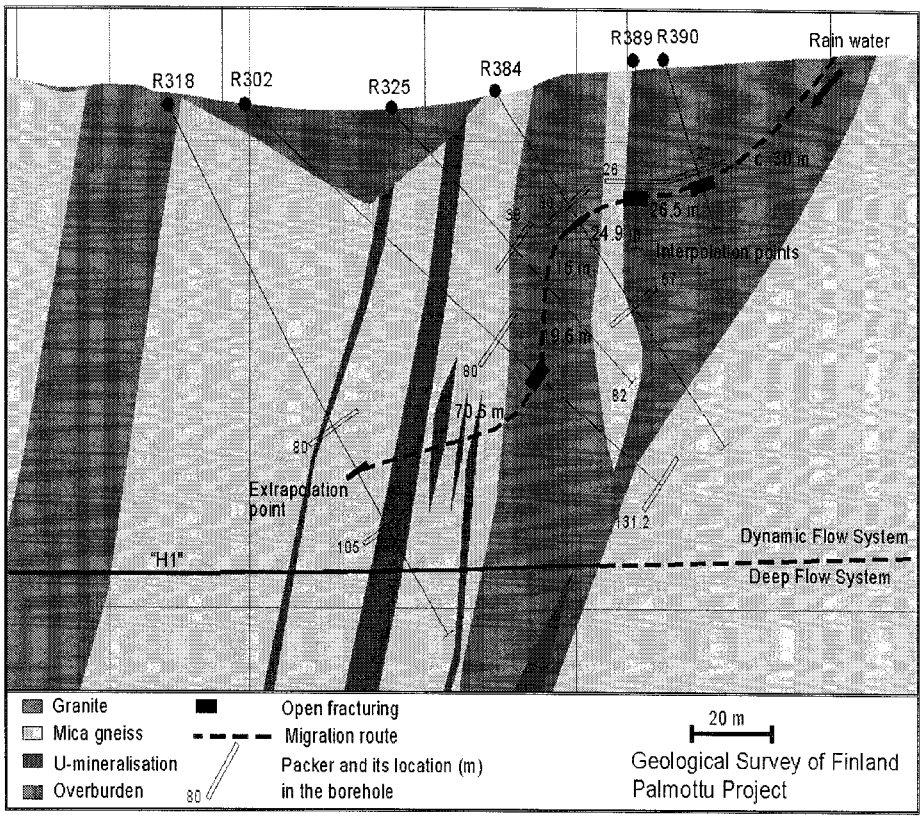

Figure 1. Cross-section of the postulated migration route (Read *et al.*, 1999).

Mobilisation and fixation of uranium

As summarised in Read *et al.*, (1998), previous workers have considered a number of processes when attempting to explain the means by which U concentrations in Palmottu groundwater are maintained, including:

- diffusion from the rock matrix
- adsorption/desorption onto/from Fe oxyhydroxides
- dissolution of primary U(IV) minerals
- dissolution of readily mobilised U associated with fracture calcites
- mixing of water bodies

To the above could be added the dissolution of secondary U(VI) minerals, as observed, for example, at Koongarra (Murakami *et al.*, 1997), though none had been identified at the start of the exercise.

An additional complication at Palmottu is the marked effect of seasonal changes in recharge, which strongly influence uranium concentrations; the latter increasing markedly after rainfall. Finally, the cause of disequilibrium apparent in uranium series measurements (Suksi *et al.*, 1999) needs to be resolved.

Each of the above hypotheses is being tested in a two-phase modelling programme incorporating both interpolation (prediction of concentrations for R389 and R390) and extrapolation (R318) of measured data (Read *et al.*, 1998). Initial simulations were carried out 'blind' as no hydrochemical or mineralogical information was available for the two shallow boreholes (Figure 1) at that time. This modelling phase is now complete and the results are summarised below. The modelling tools employed were RETRASO (Saaltink *et al.*, 1998; Salas and Ayora, 1998), a 2D coupled heat, flow and reactive solute transport code and FTRANS (Intera, 1983), a finite element code employing conventional equilibrium partitioning of solutes to account for adsorption onto fracture surfaces and the rock matrix. These studies have helped to constrain the range of feasible interpretations that can be placed on the Palmottu data.

Diffusion from the rock matrix

The potential effect of rock matrix diffusion (RMD) was examined by Nordman and Rasilainen (1999) using the FTRANS code. Assuming U to be reversibly sorbed onto (unspecified) phases in the matrix and taking an earlier measured Kd of $0.03 m^3 kg^{-1}$, these authors undertook a sensitivity study in which Kd, groundwater velocity and matrix diffusion parameters were varied. The initial U concentration in the pore water was also varied (1500ppb and 300ppb) to provide predictions of U concentration in flowing groundwater as a function of migration distance. Figure 2 gives the results for an initial U concentration in the matrix of 1500ppb.

Figure 2. Calculated U concentrations in Palmottu groundwaters (Nordman and Rasilainen, 1999). Initial U concentration in pore water is 1500 ppb. 'Base' means base case, 'Lv' means low groundwater velocity, 'Hv' high groundwater velocity, 'HKd' high Kd, 'LKd' low Kd, 'LDe' low diffusivity, 'LAl' low all parameters, and 'Mix' high Kd and low diffusivity. Measured U concentration ranges are shown in the order: R390, R389, R384, R302, R318.

The results appear reasonable, particularly as they represent calculations performed 'blind', clustering around the measured values. There is, however, a major uncertainty associated with the initial U concentration in the matrix pore water for which no measurements are available or planned. In order to create a sufficiently large concentration gradient between the rock matrix and water flowing in the fractures, it was necessary to specify a matrix concentration for U of 1500 μgdm^{-3}. This is unrealistically high and would lead to precipitation of secondary U(VI) minerals. Assuming a more realistic value of 300 ppb would lower predicted concentrations by a factor of five from those shown in Figure 2 and correspondingly reduce the model fit. It would also, of course, reduce the intensity of outward diffusion from the matrix.

It must be kept in mind that the simulations described were not based on measured data for samples taken from the flow route. Nevertheless, with a diffusion coefficient in the region of $10^{-13}m^2s^{-1}$, U levels in groundwater would not show a rapid response to seasonal recharge and the effect of recharge would be a further lowering of concentration rather than the increase observed. Further, groundwater analyses indicate particularly high variability for drill hole R302 in the middle of the route. It was concluded therefore that RMD does not exert a dominant influence on aqueous uranium.

Adsorption/desorption onto/from Fe oxyhydroxides

This study, described by Salas and Ayora (1998), also addressed equilibrium sorption but differs from the above in that the adsorbent was specified (amorphous $Fe(OH)_3$ on fracture surfaces) and the adsorption-desorption reactions were represented explicitly by chemical mass action laws.

The model adopted was that proposed by Waite *et al.* (1994), encompassing strong and weak sorption sites with estimated concentrations of $1.8x10^{-3}$ mol/mol Fe and 0.2 mol/mol Fe, respectively. Assuming a $Fe(OH)_{3(am)}$ volume fraction of 0.01 in Palmottu fractures gives site concentrations of $5.4x10^{-4}$ mol dm^{-3} and $6.0x10^{-2}$ mol dm^{-3}. Since the proportion of $Fe(OH)_{3(am)}$ in Palmottu fractures is not known, sensitivity calculations were performed for scoping purposes. The results of the calculations after 1 year of elapsed time are plotted in Figure 3.

The amount of U(VI) in solution is about $7.0x10^{-7}$ mol kg^{-1}, a value within the same order of magnitude as those measured in boreholes R384 and R302. The infiltration water, containing around $2.0x10^{-9}$ mol kg^{-1} U, flushes out the U sorbed initially. Subsequently, U is desorbed from the $Fe(OH)_{3(am)}$ surfaces to the new equilibrium concentration. As the infiltration water percolates through the column, U(VI) species are progressively desorbed from the $Fe(OH)_{3(am)}$ surface and a front of dilute water advances to greater depths. Without replenishment from an additional source, most of the sorbed U species will have been removed after 10 years and the U concentration in the fracture will be similar to the inflow (Salas and Ayora, 1998).

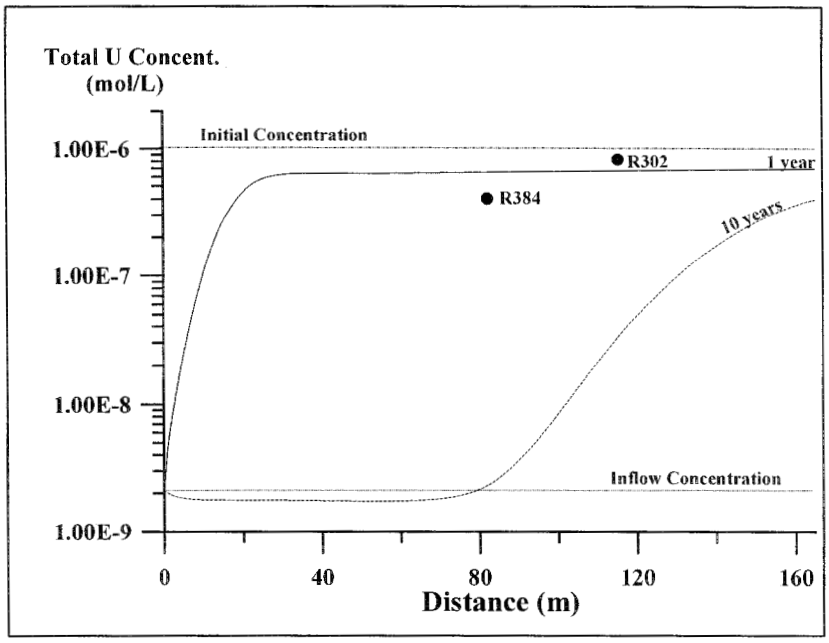

Figure 3. Distribution of U concentration in solution: SCM model (Salas and Ayora, 1998). The time required for the U(VI) species to completely desorb from the $Fe(OH)_{3(am)}$ surface is linearly dependent on the number of initial sites (or $Fe(OH)_{3(am)}$ molar fraction). Therefore, unreasonably high amounts of $Fe(OH)_{3(am)}$ would be required for adsorption to be responsible for the U concentrations measured over periods longer than about 10 years.

Dissolution of primary U(IV) minerals

Uraninite is the ultimate source of U in the Palmottu system and the dominant ore mineral. There is no doubt that dissolution of UO_2 has been active for a considerable length of time and that this process may well be responsible for aqueous levels at depth. However, the extent to which its oxidation influences concentrations in the relatively shallow zone chosen for migration modelling is less certain. This issue has been addressed from both an experimental and theoretical viewpoint. As the former is described in an accompanying paper (Cera *et al.*, in this volume), only the modelling study (Salas and Ayora, 1998) is discussed here.

A series of models has been constructed based on differing assumptions concerning the assemblage of minerals undergoing dissolution along the transport path and the kinetics of dissolution. Each model considers the role played by potential redox buffers; Fe^{2+}-Fe^{3+}, U^{4+}-UO_2^{2+}, H_2S-SO_4. The outcome, as described in Salas and Ayora (1998), is a sequence whereby Eh control evolves from dissolved O_2 in surface waters, through the iron couple in an intermediate zone to the U^{4+}-UO_2^{2+} pair at greater depths. Dissolution of uraninite is predicted to occur at a sharp front that moves downstream as the source is exhausted. According to the calculations, aqueous U concentrations should peak around 80m depth before decreasing to a constant value (Figure 4). This certainly matches the trend observed. However, predicted U levels are some three orders of magnitude lower than those measured in boreholes R384 and R302; a fact that led the authors to postulate the existence of an additional uranium source.

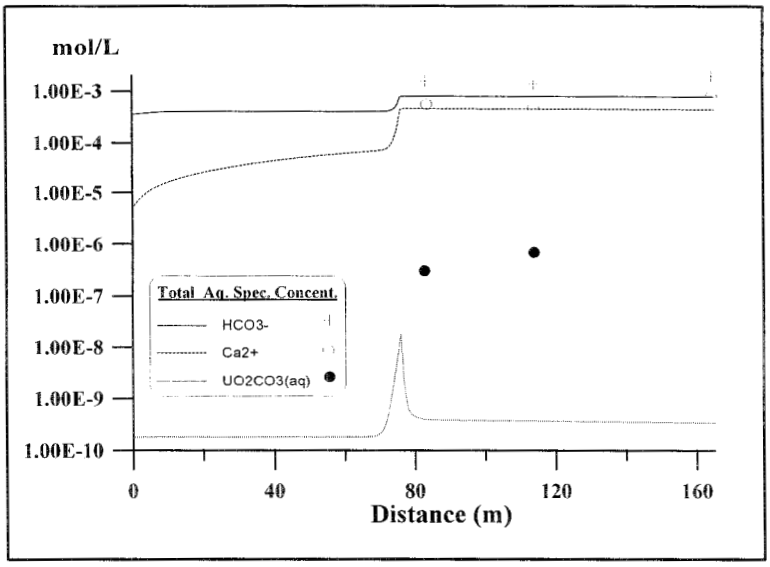

Figure 4. Solute concentration resulting from model B_1 (Salas and Ayora, 1998).

Dissolution of fracture calcites

Fracture coatings at Palmottu, mainly impure calcites, contain a substantial inventory of uranium. Concentrations decrease with depth and higher values, some in excess of 1000ppm, are confined to the upper 100m. Rare earth element patterns indicate at least two generations of calcite, only one of which appears to be U-rich. In terms of major element chemistry, Salas and Ayora (1998) conclude that dissolution of calcite (and uraninite) 'seems to account for the general trend of pH, Eh, HCO_3 and Ca values measured in the R384, R302 and R318 boreholes' (Figure 1).

When examined in detail it is apparent that calcite, itself, cannot constitute a significant uranium source. The U is located in microcrystalline phases associated with the calcite that, unfortunately, are too fine-grained to allow quantitative analysis. Nevertheless, recent mineralogical studies have provided an indication of the dominant oxidation state, albeit on a limited sample set, and the relative isotopic abundance of $^{234}U/^{238}U$. In groundwaters, the latter is fairly constant and close to unity in the upper part of the flow route (R390, R389, R384) but shows a significant increase towards R302 and decreases again towards R318 (Suksi *et al.*, 1999). This U series information forms an important reference for the modelling studies. In addition, it has important implications for building an overall conceptual understanding of the site, as discussed in the final section.

Mixing of water bodies

The well-developed stratification of water bodies at Palmottu militates against extensive mixing as discussed by Pitkänen *et al.*, in this volume. It is clear, at least for the transport domain studied (Figure 1), that simple mixing cannot explain either the distribution of aqueous U concentrations with depth or the variation in isotopic ratios. Contrary to expectation, flushing with fresh recharge does not cause dilution, a feature that can only be accounted for by mineral dissolution. Given relatively constant major element composition,

mixing should also result in a monotonic increase in U levels with depth. This is obviously not the case (cf. Appendix 1).

The use of numerical models to test hypotheses in the manner described above has played an important role in the development of a conceptual model for Palmottu. Current interpretations and the lessons learnt from this approach are outlined below.

Discussion

Based on current knowledge (Ruskeeniemi *et al.*, in this volume, Read *et al.*, 1999), at least three and, possibly, four main phases are believed to control uranium signatures in Palmottu groundwaters; 'amorphous' readily soluble U-phase(s), crystalline uranophane, U-rich fracture fillings, which may or may not have the same composition as the uranophane, and uraninite. The near surface (R390, R389) is a highly active zone in which aqueous U levels fluctuate in response to oscillations in the water table and concomitant dissolution and re-precipitation of amorphous U(VI) minerals. These fine-grained materials may be U(VI) silicates as found at slightly greater depths or other soluble minerals such as U(VI) sulphates. Modelling calculations are being performed in order to shed light on the relative stability of potential alternatives.

Uranium concentrations in groundwater rise rapidly from close to zero at the surface to around 150ppb in R389. With increasing depth concentrations are thought to be limited according to the solubility versus pH relationships described by Bruno *et al.* (1999) and, consequently, U levels fall slightly towards R384. At greater depths (R302, R318) the system approximates steady state with both U concentrations and isotopic ratios likely to be controlled by equilibrium with U-rich fracture minerals. As these are mostly found in tight fractures, the concentrations measured may be influenced, to some extent, by recent drilling. Any accessible UO_2 encountered in this zone will tend to dissolve. Finally, at depths below the model domain, reducing conditions persist and U concentrations of a few ppb reflect solubility control by uraninite (Cera *et al.*, in this volume).

Preliminary modelling of this system using the coupled chemical transport code RETRASO (Saaltink *et al.*, 1998) accounts for the direct and indirect effects of Eh-pH variations on U concentrations (Salas and Ayora, 1998). The models predict the development of a sharp dissolution front, which seems to be borne out by analysis of waters and fracture minerals. These authors also postulated the existence of an additional uranium source, though this source was not specified. On the basis of surface complexation modelling, it was concluded that an insufficient amount of Fe oxides is present for equilibrium adsorption to play a major role in determining aqueous concentrations. Refinement of the models will now need to take into account the presence of uranophane and the rapid dissolution kinetics of uraniferous phases close to the surface.

It is apparent that essentially physical models, such as FTRANS (Intera, 1983), cannot provide an explicit representation of the processes believed to control U geochemistry. The FTRANS simulations assumed an outward diffusion from the rock matrix around a water-carrying fracture to account for the levels observed. This appeared to be a reasonable assumption as there is likely to be very little advection outside fracture zones owing to the

low permeability of the matrix (*c.f.* Siitari-Kauppi *et al.*, 1999). Thus, of the processes tested in this exercise, matrix diffusion is the only means by which mobile U within the rock matrix could reach flowing groundwater (if changes in the stress state of the rock mass are ignored). However, it is apparent from the sensitivity studies undertaken that matrix diffusion is not a dominant process in determining U concentrations in the shallow Palmottu groundwaters. Refinement of physical models is clearly needed to take into account the geochemical processes that invariably control such systems.

One of the planning criteria used in repository performance assessment is that the results obtained should be 'conservative', *i.e.* key performance indicators, for example, the source term and far-field concentrations, should be over-estimates. At Palmottu, as with other sites, it is evident that, once mobilised by breakdown of UO_2, uranium can be fixed and concentrated by a variety of mechanisms. These include the formation of secondary minerals and organic complexation. Such 'sinks' act to limit U migration but also constitute secondary sources for groundwater. The resulting source terms tend to be much greater than those associated with the primary mineralisation, in the case of Palmottu by around two orders of magnitude. Performance assessments have (so far) ignored secondary sources 'downstream', the implications of which will depend on the inventory, timescale and exposure scenario envisaged. It is probable, however, that any model based on dispersion rather than re-concentration of activity will not be conservative over at least part of the model domain.

An understanding of the groundwater flow field is the first requirement for migration modelling. Unfortunately, no matter how detailed the investigation, hydrogeological techniques cannot provide more than a brief 'snapshot' in time. It is now accepted that the necessary information on evolution of groundwater systems can only be derived using geochemical (including isotopic) methods. Not surprisingly, models that account explicitly for these chemical processes have proved more successful than purely physical representations when applied to natural analogue sites.

The Palmottu study has made a substantial contribution to our understanding of uranium behaviour in a glaciated environment, a key feature being the depth to which oxidising conditions have promoted migration. By demonstrating very limited dispersion of U over millions of years, it has also greatly increased confidence in the safety of spent fuel disposal in crystalline rocks. At Palmottu, neighbouring drill holes are much closer than would be expected at a potential repository site and allow quantitative comparison of modelled and measured data. This has provided a valuable test of the applicability of diverse modelling approaches to a real and complex site. Limitations in the modelling tools currently used to quantify repository performance have been highlighted and should help focus further research in this area.

Acknowledgements

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Appendix 1. Analytical data for rainwater and packered-off drill hole sections (Read *et al.*, 1999)

Sample	DATE	Secup m	Seclow m	pH field	pH lab.	Eh mV	E.C. mS/m	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	Cl mg/l	SO_4 mg/l	HCO_3 mg/l	Sr µg/l	Th µg/l	U µg/l
Rainwater	8.7.98	-	-	4.9	5.2	-	1.0	0.13	<0.1	<0.40	0.61	<0.2	0.53	3.1	0.51	<0.02	0.05
R390	29.10.98	0	12	6.61	-	-	11.5	15.3	1.67	2.85	2.54	1.9	8.16	57.97	45	0.0336	109
R390	16.10.98	27.5	33.5	7.7	7.6	310	15.6	22.6	3.35	3.4	1.78	1.2	7.53	85.42	63.2	<0.0005	56.6
R389	19.10.98	28.5	32.5	7.75	7.6	300	15.5	22.7	3.55	3.47	1.95	1.27	7.86	91.52	61.5	0.0008	162
R384	17.7.98	30	57	7.71	7.7	414	16	22.5	3.78	3.6	1.69	1.28	7.93	85.4	63.2	0.0007	101
R325	24.9.98	38	81	7.6	-	345	15.5	21.1	3.37	3.37	1.59	1.28	8.37	85.4	61.2	0.005	188
R302	3.6.98	80	131.2	8.0	8.2	-12	20.1	15.8	3.99	18.8	1.01	1.42	12.9	85.4	83.6	<0.02	228
R318	14.4.98	80	105	7.42	7.9	-	18.8	30.6	3.63	16.8	1.16	3.43	19.4	122	55.7	0.0054	96.8

Uranium series						
R390	29.10.98	0	12		^{238}U	$^{234}U/^{238}U$
				U	109	1.06
R390	16.10.98	27.5	33.5		^{238}U	$^{234}U/^{238}U$
				U	41±1.7	1.23±0.07
				>0.45 µm	0.0285±0.0075	0.912±0.393
R389	27.10.98	28.5	32.5		^{238}U	$^{234}U/^{238}U$
				U	150±3	1.06±0.03
				U(VI)	136±4	1.06±0.04
				U(IV)	14±0.3	1.06±0.03
				>0.45 µm	0.564±0.023	1.07±0.06
R384	9.6.98	30	57		^{238}U	$^{234}U/^{238}U$
				U	88.9±3.6	1.11±0.03
				U(VI)	82.6±3.7	1.09±0.07
				U(IV)	8.68±0.16	1.08±004
				>0.45 µm	0.166±0.015	1.28±0.17
R325	24.9.98	38	81		^{238}U	$^{234}U/^{238}U$
				U	188	1.15
R302	9.6.98	80	131.2		^{238}U	$^{234}U/^{238}U$
				U	214±9	1.96±0.12
				U(VI)	201±10	1.94±0.14
				U(IV)	8.9±0.32	1.84±0.09
				>0.45 µm	0.162±0.017	1.94±0.23
R318	6.10.98	80	105		^{238}U	$^{234}U/^{238}U$
				U	54.2±1.2	1.55±0.04

III.3.2. OKLO - Natural Analogue Phase II project

Natural fission reactions: Unique geological objects
F Gauthier-Lafaye, CNRS (F)

Dissolution studies of Oklo uraninite samples
I Pérez, I Casas, I de Pablo, UPC (E); L Duro and J Bruno, QuantiSci (E)

Retention processes of uranium and REE in the Bangombé natural reactor Zone, Gabon
M Del Nero, CNRS/IN2P3 (F); S Salah, A Clément and F Gauthier-Lafaye, CNRS (F)

Sensitive High Resolution Ion Microprobe (SHRIMP) Pb, U, Nd and Sm Isotopic data from the natural reactor site of Bangombé
G Brake, S Salah and F Gauthier-Lafaye, CNRS (F)

Modelling of uranium transport at Bangombé (Oklo, Gabon)
B Madé, E Ledoux, EMP/CIG (F); C Ayora, J Salas, CSIC (E) and I Gurban, Intera KB (S)

Geochemical environment around Okélobondo reactor zone (Gabon)
R Mathieu and M Cuney, CREGY-UMR GZR (F)

Reactive transport modelling around the Okélobondo uranium Deposit (Oklo, Gabon)
J Salas and C Ayora, CSIC (E)

NATURAL FISSION REACTIONS : UNIQUE GEOLOGICAL OBJECTS

F. GAUTHIER-LAFAYE

E.O.S.T.

Centre de Géochimie de la Surface. CNRS.

1 rue Blessig, 67084 Strasbourg Cedex. France.

INTRODUCTION

When we first discovered the uranium isotopic anomaly at Oklo in 1972, the first studies, which were mainly conducted by the French Atomic Energy Commission, tried to demonstrate that this anomaly was due to the occurrence of nuclear fission reactions which were active 2,0 billions years ago. This has been well documented during the first Oklo meeting which held in Libreville in 1975. Then, and until the beginning of the eighties, scientists focused their efforts to understand this nuclear phenomenon and its effects on the host rocks. At that time, little case was given to the use of these natural nuclear reactors as analogues for nuclear waste.

We had to wait until the first European programme to really recognise that Oklo is an ideal location to test predictions relating to the migration of various radionuclides, including fission products, in a geological environment. This programme started in 1991 and ended in 1995.

In the meantime, researches on the Natural Analogues were developed in the European Nuclear Fission Safety Programme during the years 94-98. And it was considered that Oklo is a good

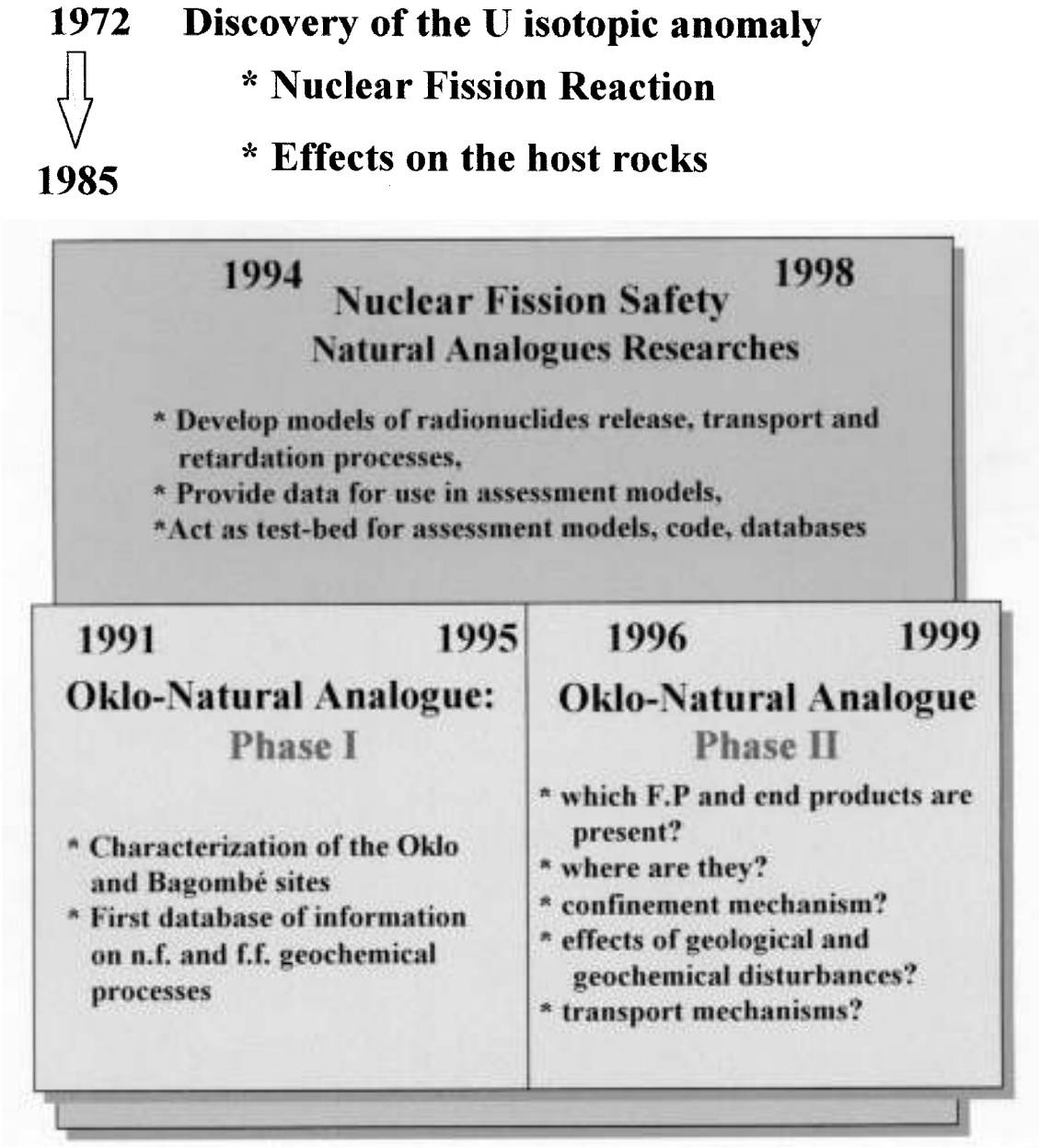

Fig. 1 : Main objectives of the various programs on the natural fission reactors of Oklo

Natural Analogue and that it can help in that programme and mainly for the Performance Assessment aspects.

There is not a direct analogy between a natural reactor and a deep repository for high level radioactive waste. Therefore we cannot expect direct application of our results. But, by working on Natural reactors we can rise several important questions like : do we know all the mechanisms we do have to take into account in order to understand the behaviour of radionuclides in a geological environment? And do the models we are using for repositories are able to predict what we are measuring at Oklo? What kind of parameters are missing or wrong? For these kind of questions, the Natural Analogues may give some answers

And for example, during the phase II, the Oklo project has to address several questions valid for both high and low temperature processes such as :

1- which fission products and end-products are still present?
2- where have they been retained and in which form?
3- what are the confinement mechanisms and for how long have they been active?
4- what were the effects of geological and geochemical disturbances on the confinement?
5- what is the transport mechanism and for how long has it been active?

PRESENTATION OF THE REACTORS

Here, I would like to present the various reactors and mostly to explain why the fission reactors of Gabon are so unique and why we have only very little chance to find other natural reactors in the world. And also I would like to discuss what are the main parameters which are responsible for the stability of the reactors which lasted at least 2.0 b.y.

In Gabon, all reactors are located in the Franceville basin. We know 15 reactors. 14 are located in the Oklo-Okelobondo deposit and 1 in the Bangombé deposit.

All the reactors of Oklo-Okelobondo are mined or not any more accessible because the open pit and the underground mine are now closed. Therefore the only reactor which remain in is natural environment is the reactor of Bangombé.

This is the reason why we asked to preserve this reactor and its environment. And it has been decided by the Gabonese government and the COGEMA not to mine the reactor and the uranium deposit of Bangombé. This site is therefore preserved for future studies.

NATURAL FISSION REACTORS : UNIQUE GEOLOGICAL OBJECTS

For which reasons the natural reactors of the Franceville basin are so unique and why we have little chances to find other reactors in the world ? There are 2 main reasons for that :

1- because there is only one time in the past for the formation, and

2- because the reactor have been preserved to any destruction due to geological events such as orogenesis. And this is because the Franceville basin is located on a very stable craton.

Lets go back to the first reason : the age of the reactor which is close to 2 b.y. Why the age is so important?

Because there is only one moment in the history of the earth when the isotopic and geological conditions can be completed. What are these conditions?

The curve figure 2 presents the evolution of the 235/238 U ratio versus the time. This ratio is 0.72 today but two billions ago had a value up to 3.7. This value is even higher than the value of the fuel in PWR nuclear plan. And it can be seen that it can be even much more higher after 2.0 b.y.

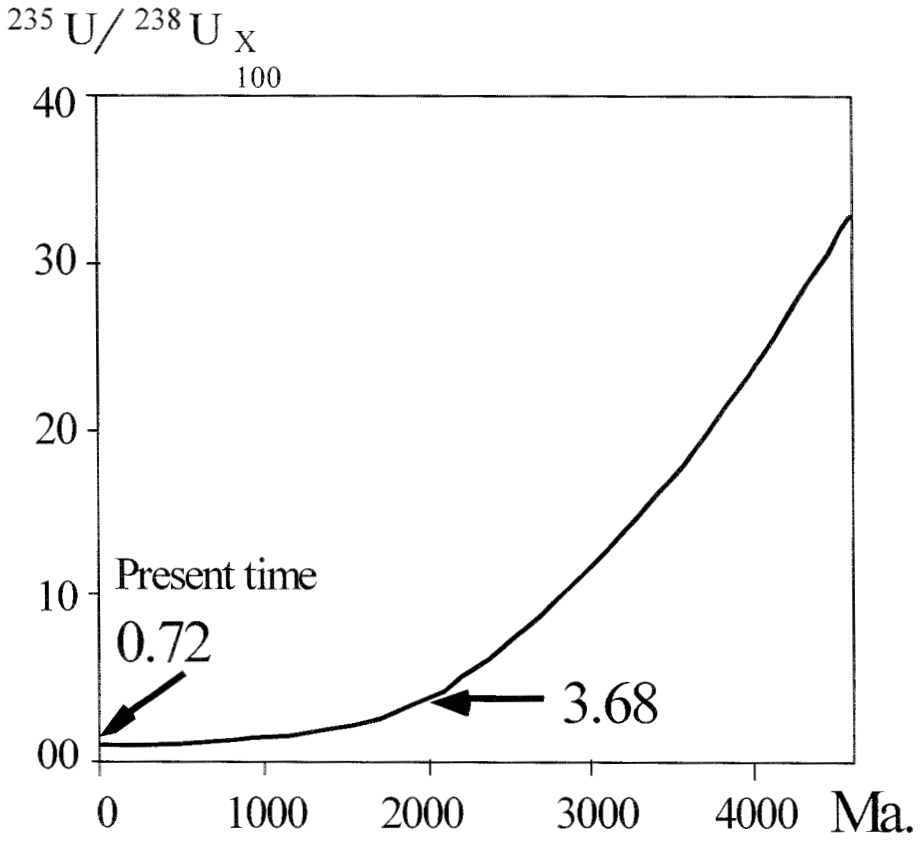

Fig. 2 : Evolution of the $^{235}U/^{238}U$ ratio *versus* time

This curve explains why it is difficult to imagine fission reactors before 2.0 b.y. The amount of fissile ^{235}U is too low, and in that condition, to have fission reaction, it is necessary that the other geological and geochimical conditions was even more favourable : such as for example the porosity and the low content of neutron poisons such as Boron and REE, but also V.

From this curve an other question arise : why don't we have natural reactors older than 2.0 b.y? This is mainly for geological reasons. To have fission reactions, we not only need high content of fissile U but also a critical mass, that is to say a high uranium content in a certain volume. It has been shown that at Oklo it was needed 10% of uranium in 1 cubic meter of rock.

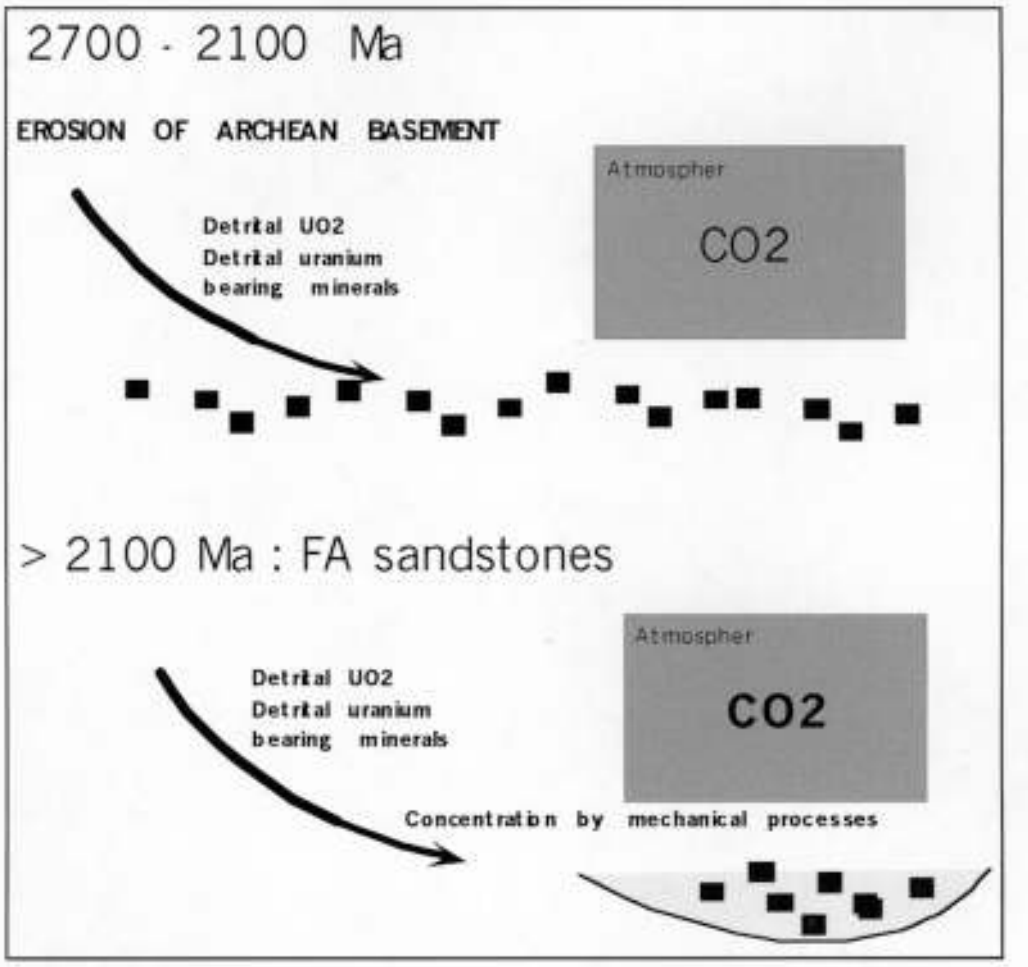

Fig. 3: Behaviour of Uranium in relation with the composition of the atmosphere : 2700 – 2100 Ma

Therefore, how to get such uranium content at that time and why not before?

Oklo can be considered as the first high grade uranium ore and it occurred at a very specific and UNIQUE time in the evolution of the atmosphere : when oxygen content started to increase in the atmosphere. And this was due to the development of the photosynthesis which first started in the sea and oceans.

This time corresponds to the deposit of very important black shales series having very high content of organic carbon.

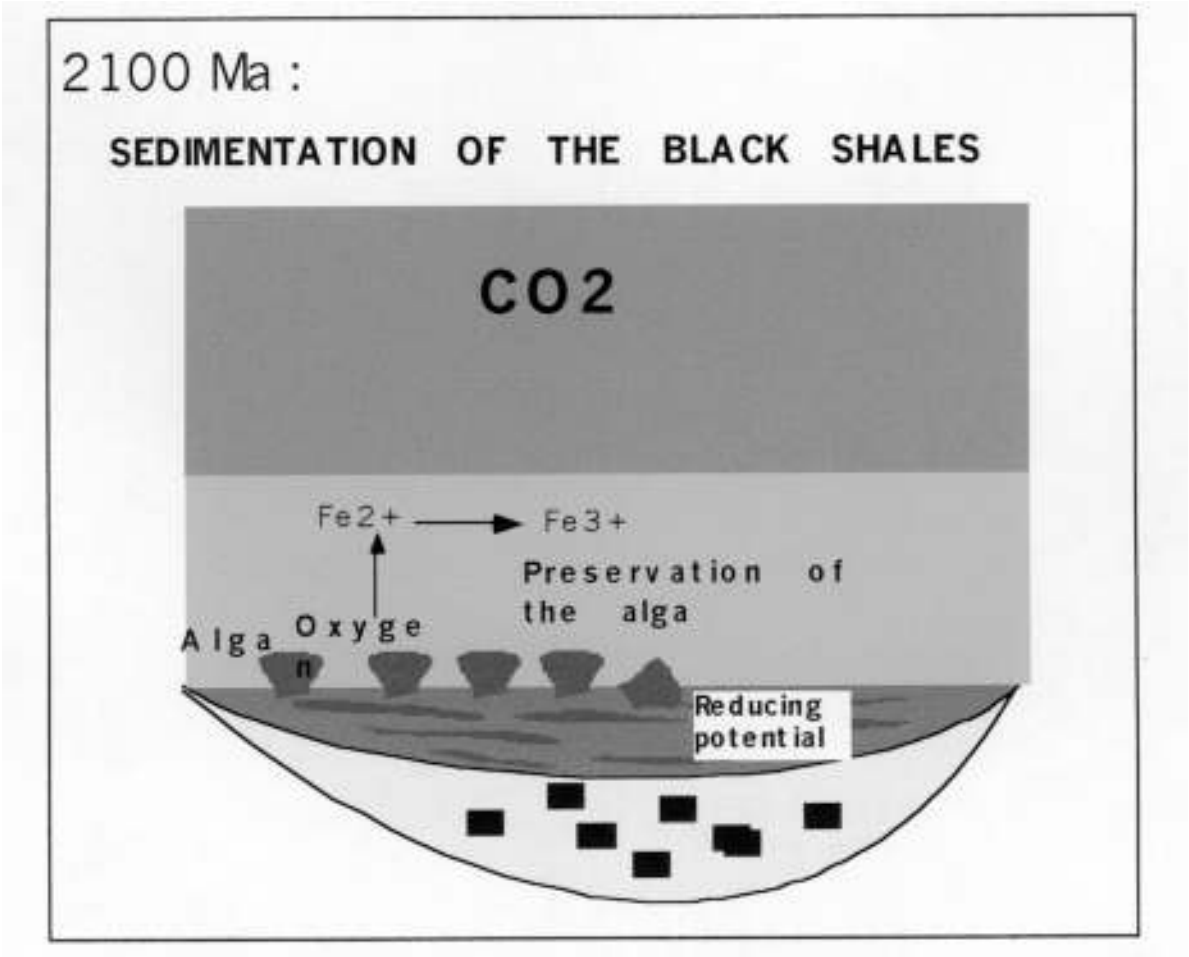

Fig. 4: Deposition of the black shales and appearence of oxygen which is cosumed for iron oxidation. Preservation of detrital uranium bearing minerals.2100 Ma.

At Oklo these rocks are very well represented by the FB black shales which thickness may reach 1000 meters. And of course, the black shales are good source rock for petroleum which migrate into the sandstone reservoirs. Note that organic matters in the reservoir rocks of the Franceville basin are always mineralised with uranium.

So, what is the relation between the change of the atmosphere composition and the formation of high grade uranium ore?

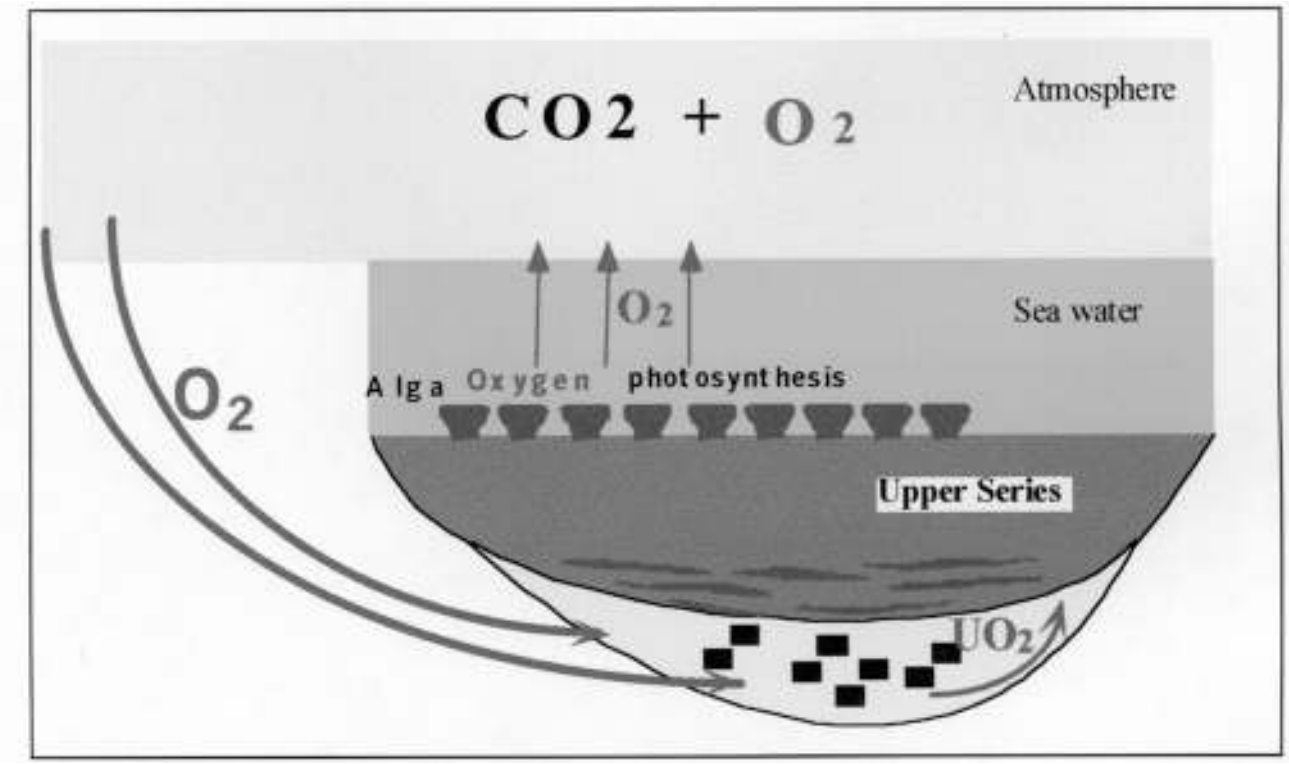

Fig. 5: Appearance of oxygen in atmosphere. Uranium is now mobilised in solution.

The result of the change in the atmosphere composition is a change in the process or mechanism of migration and concentration of uranium. First the mobilisation of uranium was mainly mechanic (by sedimentological processes). Uranium was first eroded from the archean basement as detrital uraninite or uranium bearing minerals (Fig. 3). Because there was not oxygen in the atmosphere, uranium was stable and has been concentrated in the basal conglomerates and sandstones of the Franceville by sedimentary processes. The first uranium concentration at that time should have been sedimentary deposits similar to those of Whitewatersrand (South Africa)

After the deposition of the FA sandstones started the deposit of the FB black shales with the development of photosynthetic algae (Fig. 4). Therefore, oxygen started to be produced but it is quickly used to oxidise the iron in solution. The result is that very little oxygen is released in the atmosphere. And this is important because this prevent the alga to any oxidation and they are therefore preserved in the sediments. This makes the main difference between these old black

shales and the more modern one, where most of the alga are oxidised and then destroyed before their burial.

We have therefore in the FB black shales a very important reserve of potential petroleum (and of course of reducing potential)).

Then there is the deposit of the upper series and the oxygen started to be released in the atmosphere, all available iron in the water being precipitated (Fig. 5).

This is really a revolution for the earth.

For the uranium geochemical behaviour, this means that now, water which migrates through the FA sandstone reservoir and which contains detrital uranium minerals can oxidise these minerals and that uranium can now be transported IN SOLUTION (Fig. 6).

In the meantime, the FB black shales reach the oil window and the generated petroleum which migrated in the FA sandstones and was accumulated in tectonic traps.

The uranium occurred when the oxidised uranium bearing fluids met the reduced conditions in these petroleum traps. We see therefore that the formation of these deposits at this particular time is the result of the conjunction of several events which ARE UNIQUE in the history of the earth.

The result of this history is the mineralization of a 7 meters thick layer of sandstone at Oklo. The initial uranium ore, before criticallity, contains : -60- 80 % of quartz, 5-10 % of clays and in some places, 10 % of uranium with, of course, quite high $^{235}U/^{238}U$ ratio compared at today and low content in elements such as B, V and REE which are poison for neutrons.

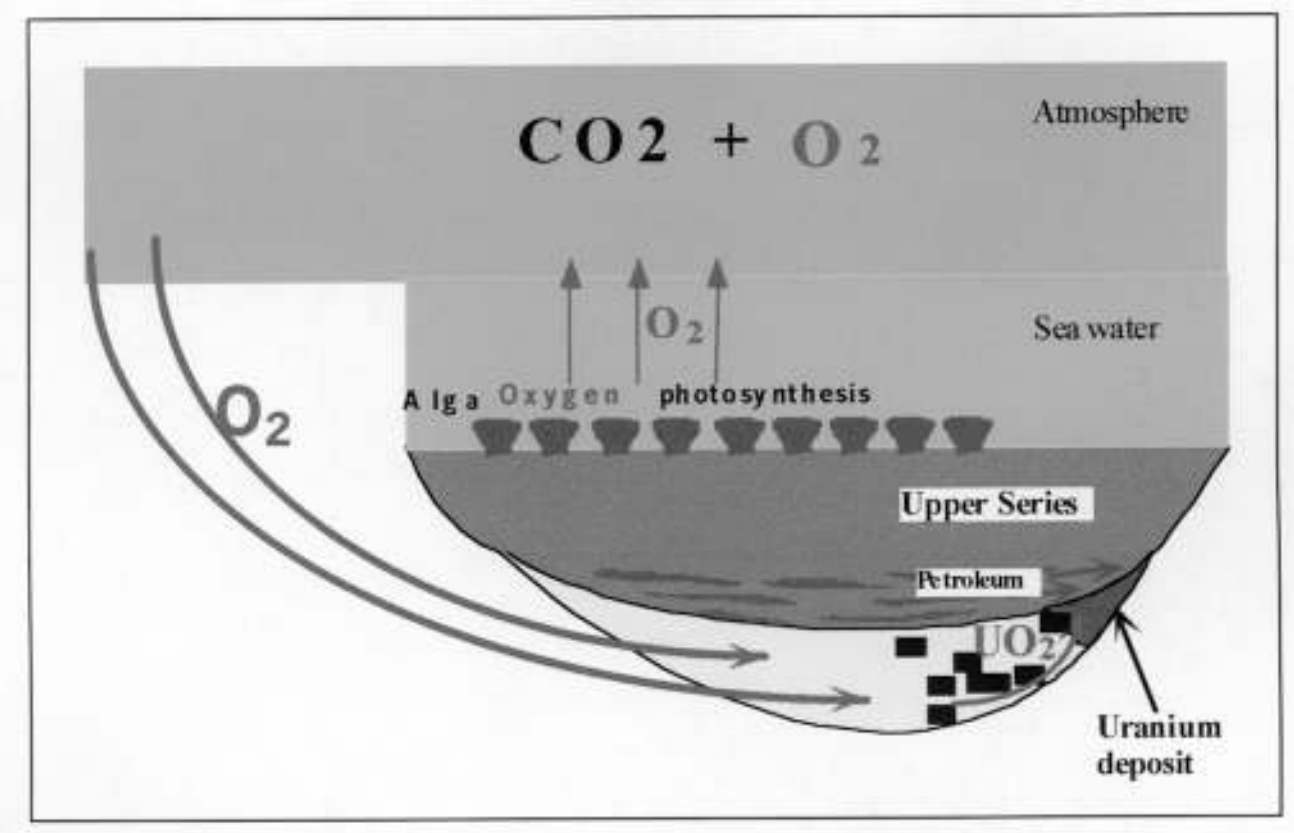

Fig. 6 : Formation of uranium deposits in hydrocarbon traps.

The final stage is represented by the core of the reactor, which is surrounded by clays. There are no more sandstones in the mineralised layer. This is because 80 % of the silica moved out from the reactor during the hydrothermal alteration due to the functioning of the fission reactions. The result is the increase of the uranium content in, the RESIDUAL ROCK. This process finally, allows the formation of the fuel that will be used by the reactor. It is the reactor itself which forms its own fuel.

After the fission reaction there are 4 main events which contributed to the migration of the radionuclides. The first one is the fission reactions themselves, and the second one is a tectonic event which occurred soon after the fission reactions. It is responsible for the main tectonic structure which affect the sediments, and the third event is the intrusion of dolerite dykes which cross the Francevillian series. And then the major process responsible for migration of radionuclides is the present time weathering which seems to have started 500 000 years ago.

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Dissolution Studies of Oklo Uraninite Samples

Isabel Pérez, Ignasi Casas and Joan de Pablo
Universitat Politècnica de Catalunya, Avd. Diagonal 647, H-4, 08028 Barcelona (Spain)

Lara Duro and Jordi Bruno
QuantiSci S.L., Parc Tecnològic del Vallés, 08290 Cerdanyola (Spain)

Summary

The kinetics of dissolution of four uraninite samples of the Oklo site has been determined using continuously stirred tank flow-through reactors, under oxidising conditions, at 25°C and as a function of the total bicarbonate concentration in the range from $2.7 \cdot 10^{-3}$ to $30 \cdot 10^{-3}$ mol dm^{-3}. The uraninite samples came from reactor zones 9, 10 and 13. The fourth sample came from the surroundings of reactor zone 9, what is known as "argile de pile". Samples were characterised before the experiments using x-ray powder diffraction (XPD), x-ray photoelectron spectroscopy (XPS), inductively coupled plasma-mass spectroscopy (ICP-MS) and scanning electron microscopy (SEM). The specific surface area of the samples was determined by the BET methodology.

The dependence of the uranium dissolution rates of the four samples on the total bicarbonate concentration has been rationalised based on a mechanism of surface oxidation and complexation developed from previous studies of synthetic uranium dioxide dissolution studies. The rates of dissolution have been compared with previous information taken from the literature of uraninite, UO_2 and spent nuclear fuel studies performed under similar experimental conditions.

The release of some of the minor elements associated to the uraninite samples has been followed (Nd, Mo, Ba, Cs, Sb, Yb,...) and, when possible, the dependence of their rate of dissolution on the total bicarbonate concentration of the test solutions has been determined.

1. Introduction

Knowledge on spent nuclear fuel dissolution mechanisms is a basic requisite to predict with some confidence the future behaviour of high level radioactive wastes in a deep geological repository. In order to better understand the thermodynamics and kinetics of such dissolution processes, laboratory studies are currently being performed using both spent nuclear fuel as well as chemical analogues such as non-irradiated uranium dioxide, Simfuel, etc. At the same time, natural and anthropogenic analogues are studied to improve the confidence on the conceptual models and numerical tools to be used in the future to predict the behaviour of the repository.

Among the natural analogue sites being studied, the natural fission reactors from the Oklo site constitute a unique opportunity to study the geochemical behaviour of a fossil spent nuclear fuel. This implies that laboratory studies of Oklo uraninite samples can give information on both the

dissolution behaviour of the uranium dioxide matrix and also of some of the fissiogenic minor elements.

In the present work four uraninite samples from different locations of the Oklo site have been investigated to study their basic kinetic dissolution processes. The solid samples selected correspond to reactor zones 9, 10 and 13, and the fourth one comes from the "argile de pile" surrounding reactor zone 9.

The influence of the bicarbonate concentration on the dissolution mechanisms has been established to determine the effect of this important complexing agent of uranium (VI). The kinetic studies have been performed by using flow reactors and keeping the test solutions in contact with air. For each experiment the dissolution of the minor elements has been followed to the maximum extent permitted by the analytical techniques used.

2. Experimental

2.1 Uraninite samples

We have studied selected uraninite samples from reactor zones 9, 10 and 13 (R9, R10 and R13, respectively) as well as an additional sample from the "argile de pile" of reactor zone 9 (AP9). The samples were previously characterised by means of x-ray powder diffraction (XPD), x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and inductively coupled plasma – mass spectrometry (ICP-MS). A summary of the XPD observations is presented in Table 1. The bulk of the samples showed a certain contribution of U(VI), with an average stoichiometry of approximately $UO_{2.25}$. The XPS characterisation indicated that oxidation of the surface was at similar levels than the ones measured for the bulk of the solid. The chemical composition of the samples, determined by ICP-MS, is presented in Table 2.

Samples to be studied in the flow reactors were crushed and sieved and the fraction between 100 to 300 μm was selected to perform the experiments. The specific surface area of these powdered samples was determined by means of the BET method. The values obtained are presented in Table 3.

Table 1.- *Summary of the main minerals identified by XPD.*

R9	***AP9***	***R10***	***R13***
Uraninite	*Uraninite*	*Uraninite*	*Uraninite*
Galena	*Galena*	*Galena*	*Galena*
Quartz	*Quartz*	*Chlorite*	
	Chlorite		
	Illite		

Table 2.- *ICP – MS analyses of the four uraninite samples used in the experiments. Values are given as μg of each element per gram of uraninite.*

	R9	***AP9***	***R10***	***R13***
Nd	2686.9	590.2	608.2	2855.4
Rh	131.65	5.25	26.41	184.22
Cs	0.1	13.77	13.06	1.97
Sr	23.9	23.7	76.5	118.7
Ba	189.5	1129.8	382.6	145.7
Mo	519.4	155.9	134.3	309.4
Sb	12.75	24.37	3.38	4.47
Bi	185.78	2.28	8.46	460.08
Rb	0.74	78.09	8.36	4.4
Yb	36.38	12.1	3.13	0.87
Pb	933.6	1314.1	184.7	1260
Ru	5.63	0.11	2.44	9.92
Te	39.79	3.58	10.28	44.57
U	$6.9 \cdot 10^5$	$2.45 \cdot 10^5$	$3.09 \cdot 10^5$	$6.9 \cdot 10^5$

Table 3.- *Specific surface area ($m^2\ g^{-1}$) determined by the BET method for the four uraninite samples.*

	Specific surface area
R9	0.821 ± 0.007
AP9	0.409 ± 0.007
R10	2.40 ± 0.02
R13	0.031 ± 0.004

2.2 Test solutions

The composition of the test solution included NaCl (5 mM), Na_2SO_4 (10 mM) and varying quantities of $NaHCO_3$ (2.7, 8, 15, 20 and 30 mM). The test solutions were in all cases kept in contact with air.

2.3 Kinetic studies (flow experiments)

The continuously stirred tank (CST) flow-through reactors were selected as a useful tool to determine rates of dissolution preventing possible secondary phase formation. The reactors were built in polymethacryllate with an inner volume of 25 ml (see Fig. 1). A known weight of solid (which varied from 0.3 to 0.5 g for the different experiments) was put into the reactor, with a plastic holder that kept it away from the stirrer. The test solution was circulated through the CST flow-through reactor by means of a peristaltic pump. The appropriated performance of the experimental system was tested by plotting the measured uranium concentration at the output versus the reciprocal of the flow rate. The linear behaviour (see Fig. 2) indicated the ideal response of the system in the experimental range. Based on these results we selected a flow rate of 0.1 ml min^{-1} for most of the experiments. This flow rate implies a test solution residence time of 250 min

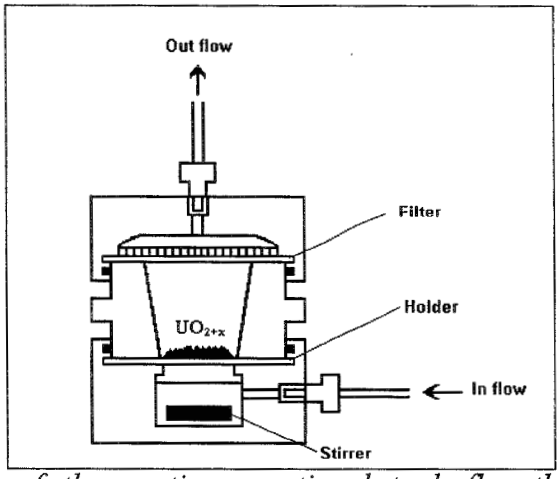

Figure 1. *Schematic view of the continuous stirred tank flow-through reactor used in the experiments.*

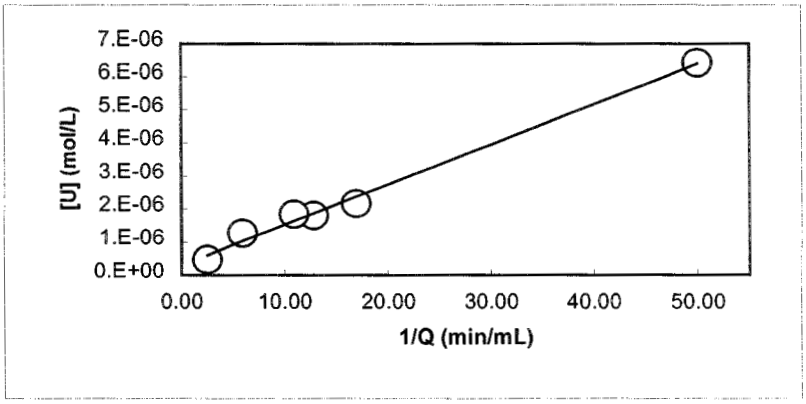

Figure 2. *Plot of the uranium concentration at the output of the reactor as a function of the reciprocal of the flow rate.*

The pH was monitored on-line using a combined glass electrode previously calibrated with commercial buffer solutions (pH 4 and 7). The values ranged between 8.2 and 8.8, depending on the bicarbonate concentration of the test solution. Aliquots of the output solution were taken to determine the concentration of the dissolved species. Before sampling the output solution passed through an on-line filter of 0.45 μm pore size. At each sampling the flow rate was determined from the weight of solution collected over a period of time.

2.4 Analyses

The total uranium concentration in solution was determined by using the Scintrex uranium analyser. The concentration of the minor elements was determined by means of the ICP-MS technique. Uranium was also analysed with this technique and a good concordance with the Scintrex determinations was obtained.

3. Results and Discussion

The rate of dissolution of each element and for each sample (mol s^{-1}) was calculated from the steady-state concentrations determined in the output solutions (mol dm^{-3}) times the experimental flow rate (dm^3 s^{-1}). They were subsequently divided by the total surface area of the solid inside of

the reactor (m^2) to give normalised dissolution rates (mol s^{-1} m^{-2}). In Fig. 3 we present an example of the typical behaviour observed in the experiments, where the dissolution rates of the different elements were normalised to their initial content in the solid phase in order to be readily compared. The number of trace elements determined for each experiment was dependent on the detection limit of the analytical technique.

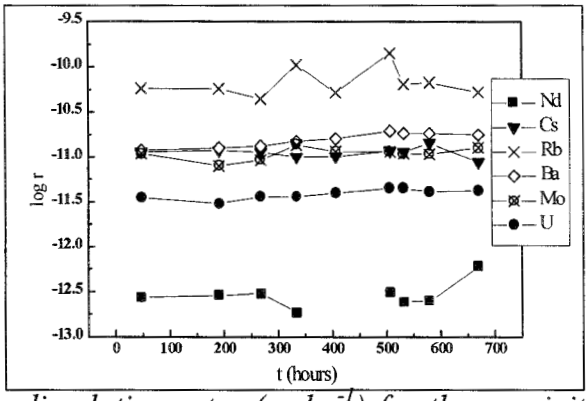

Figure 3. *Logarithm of the dissolution rates (mol s^{-1}) for the uraninite sample R10. Bicarbonate concentration of test solution is 2.7 mM.*

The results obtained from the different experiments showed the constancy of the dissolution rates determined for most of the elements which, in some cases, were practically invariable for as long as almost 800 hours. This constancy was indicative of the good behaviour of the reactors, as well as of the constancy of the solid phase composition. A similar set of experiments was completed for the four uraninite samples.

3.1. Uranium dissolution rates

In Figs. 4 and 5 we present the normalised uranium dissolution rates determined for samples R10 and R13, respectively, as a function of the total bicarbonate concentration. Results obtained from samples R9 and AP9 are presented together in Fig. 6.

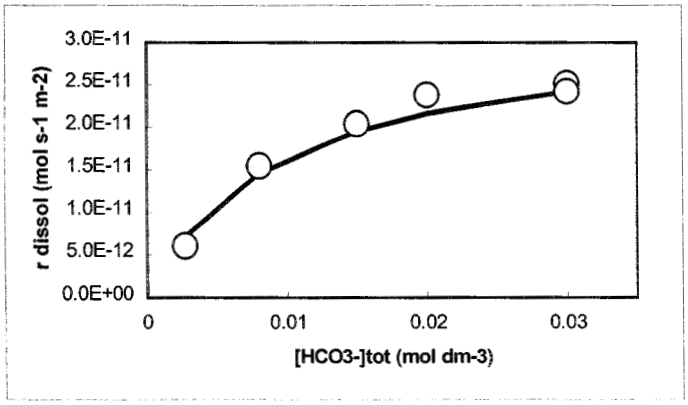

Figure 4. *Normalised uranium dissolution rates (open dots) determined for uraninite sample R10 as a function of the total bicarbonate concentrations. Full line corresponds to calculated dissolution rates (see text).*

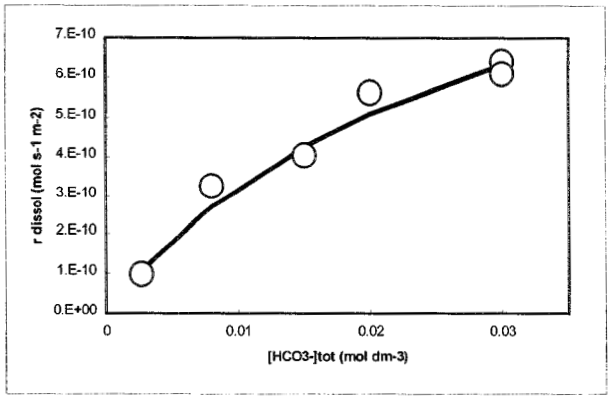

Figure 5. *Normalised uranium dissolution rates (open dots) determined for uraninite sample R13 as a function of the total bicarbonate concentrations. Full line corresponds to calculated dissolution rates (see text).*

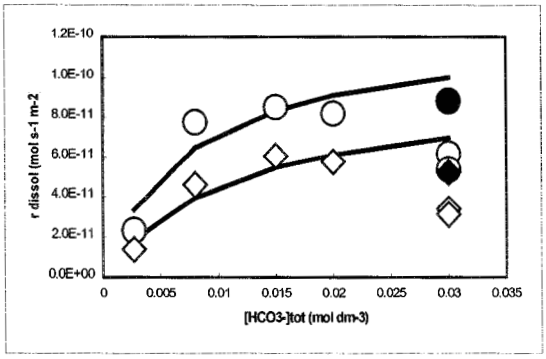

Figure 6. *Normalised uranium dissolution rates determined for uraninite samples R9 (diamonds) and AP9 (circles) as a function of the total bicarbonate concentrations. Full lines correspond to calculated dissolution rates (see text). Full dots correspond to experiments performed at higher flow rates (see text).*

In all cases a similar dependence of the uranium dissolution rate on the total bicarbonate concentration is observed. In the experimental range studied we observed an increase of the rates of dissolution with the bicarbonate concentration until a certain levelling off was attained. A similar behaviour has been observed in experiments performed with synthetic uranium dioxide reported in a previous work [1]. In that work, a mechanism for the bicarbonate promoted oxic dissolution of UO_2 was proposed, which included three steps described as follows:

Step 1: Oxidation of the surface of the solid

$$>UO_2 + O_2 \quad \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} \quad >UO_3$$

Step 2: Surface coordination of U(VI) by HCO_3^-

$$>UO_3 + HCO_3^- \quad \overset{k_2}{\rightarrow} \quad >UO_3\text{-}HCO_3^-$$

Step 3: Detachment (dissolution) of the product species

$$>UO_3\text{-}HCO_3^- \quad \rightarrow \quad \text{“U(VI)(aq)”}$$

The assumption of a fast detachment of the carbonate surface complex (step 3) agrees with the solid surface analysed by XPS.

This mechanism results in the following kinetic equation:

$$r = \frac{k_1 \cdot k_2 \cdot \{> UO_2\}_{tot} \cdot [O_2] \cdot [HCO_3^-]}{k_{-1} + k_2 \cdot [HCO_3^-] + k_1 \cdot [O_2]} \quad (1)$$

where k_1 and k_{-1} correspond to the forward and backward reactions of equilibrium step 1, respectively, and k_2 corresponds to the surface complex formation step 2; $\{>UO_2\}$ corresponds to the total number of surface sites, which could not be determined in our case due to the low amount of uraninite available so, we used a value found in the literature for different oxides of 10^{-6} mol m^{-2} [1]; $[O_2]$ corresponds to the concentration of dissolved oxygen, calculated from the Henry's constant of this gas in water at 25°C; finally, $[HCO_3^-]$ accounts for the total experimental bicarbonate concentration.

The bicarbonate promoted oxic dissolution model has been tested on the present experimental data by comparing the observed dissolution rates with the ones calculated by using Equation (1). The best agreement between the experimental and model data is presented in Figs. 4, 5 and 6, where the calculated rates are presented as full lines. The best values (obtained from a trial an error approach) for the calculated rate constants are presented in Table 4.

The value of the rate constants can be discussed in the following terms. The value of k_1 (oxidation of U(IV) sites to U(VI) sites) is dependent on the initial oxidation degree of the solid under study and consequently very much dependent on the specific uraninite sample. On the other hand, the estimated values of k_{-1} and k_2 correspond to processes that are not dependent on the specific uraninite sample. It is particularly encouraging to see the good agreement obtained among the different samples for the calculated value of k_2, which corresponds to the detachment of the surface bicarbonate complex. We have to remember that, due to the low amount of sample, it was not possible to determine the right surface coordination number for each uraninite sample. Probably, a better comparison among the various samples would have been achieved if the number of coordination sites would have been known.

Table 4.- *Calculated values obtained by fitting equation (1) to the experimental data obtained with the four uraninite samples. The calculated rates are shown as full lines in Figs. 4, 5 and 6.*

	Oklo R10	***Oklo R13***	***Oklo R9***	***Oklo AP9***
k_1	*0.12*	*4.72*	*0.36*	*0.47*
k_{-1}	*0.09*	*0.31*	*0.134*	*0.08*
k_2	*10.03*	*10.72*	*11.70*	*10.37*

Finally, it was observed that for samples R9 and AP9, a decrease of the dissolution rate took place for the highest total bicarbonate concentration of the study (see Fig. 6). Because these two experiments were the ones where the highest uranium concentrations were measured, we suspected the precipitation of a secondary uranium phase. To check this point, the experiments at 30mM total bicarbonate concentration were repeated at faster flow rates, 0.2 and 0.3 ml min^{-1}. We observed that as we increased the flow rate the dissolution rate was also increasing, and at 0.3 ml min^{-1} flow rate

we obtained results again very close to the theoretical calculations (see full dots in Fig. 6). This was interpreted as an indication of the precipitation of a secondary phase in the experiments performed with the slowest flow rate. This phenomenon was suppressed when the residence time of the test solution inside of the reactor was reduced by increasing the flow rate. Although, experiments with uraninite samples R10 and R13 were also performed at 0.2 and 0.3 ml min^{-1} flow rates, no significant effect on the uranium dissolution rates was observed in these cases. This indicates that true uranium release rates were measured in these experiments which corresponded to the dissolution of the uraninite matrix.

The uranium rates of dissolution obtained for the Oklo uraninite samples were also compared with uranium dissolution rates obtained under similar experimental conditions for other uraninite samples [3, 4 and 8] as well as for synthetic uranium dioxide [2] and spent nuclear fuel [5]. The experimental information is presented altogether with the actual Oklo data in Fig. 7.

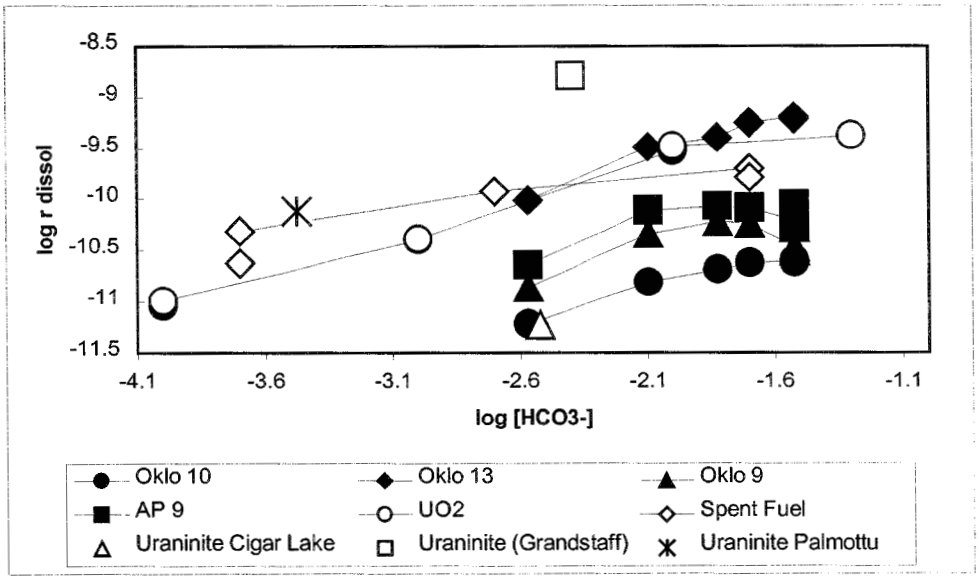

***Figure** 7. Normalised uranium dissolution rates determined in this work for Oklo uraninite samples, compared with results found in the literature for synthetic UO_2 [2], spent nuclear fuel [5] and uraninites [3, 4 and 8] under similar experimental conditions.*

As seen in Fig. 7, the uranium dissolution rates of the Oklo samples are lower than, or equal to, as in the case of sample R13, to the values corresponding to synthetic uranium dioxide and spent nuclear fuel. The values corresponding to the sample R13 are greatly influenced by the low specific surface area determined for this sample. Regarding the values corresponding to other uraninite samples, it is interesting to see the very good concordance obtained with the value determined (in a batch system) for an uraninite sample from the Cigar Lake ore deposit [3]. The value obtained with the Cigar Lake sample agrees remarkably well with the dissolution rate determined for the Oklo sample R10 for the same both total bicarbonate and oxygen concentration. In both cases, the uraninite sample corresponds to a relatively deep and unaltered location. However, the rates determined by Grandstaff [4] are much higher than any other value given in Fig. 7. According to the description of this sample, the uraninite used by Grandstaff corresponds to a highly altered, oxidised uraninite. Finally, the dissolution rate of a uraninite sample obtained from the Palmottu site is seen to correspond fairly well with the values obtained for the spent nuclear fuel, closer to the ones obtained in the present work from sample R13.

In the overall, the obtained bicarbonate promoted oxic dissolution rates obtained for the various types of uranium oxides (synthetic UO_2, spent nuclear fuel and uraninites) are within one order of

magnitude. This indicates that the rates and mechanisms are basically the same for all types of materials independently of their origin and history. This has clear implications for the use of natural uraninite dissolution data to understand the long-term behaviour of the spent nuclear fuel matrix under repository conditions.

3.2. Experimental dissolution rates of the minor elements

The logarithm of the dissolution rates of all the elements determined for the different uraninite samples as a function of the logarithm of the total bicarbonate solution are presented in Figs. 8 to 11 for samples R10, R13, R9 and AP9, respectively.

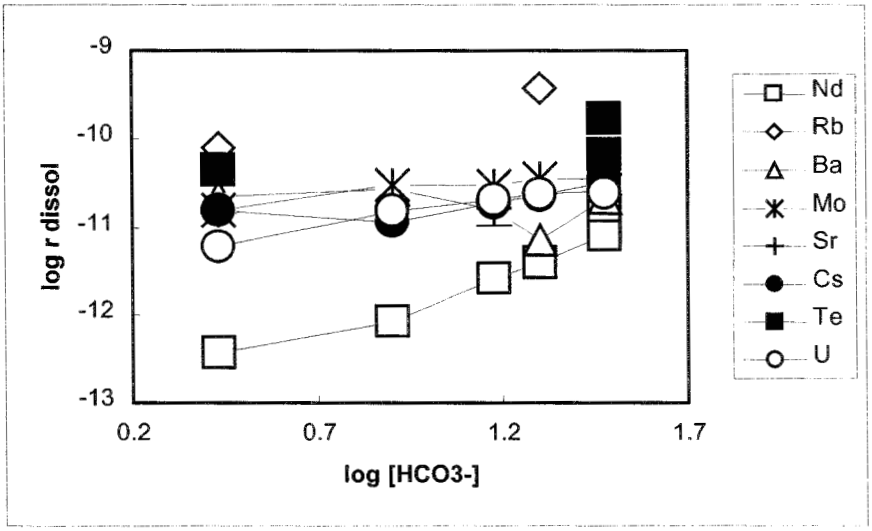

Figure 8. *Logarithm of the dissolution rates as a function of the logarithm of the total bicarbonate concentration for all the elements determined for sample R10.*

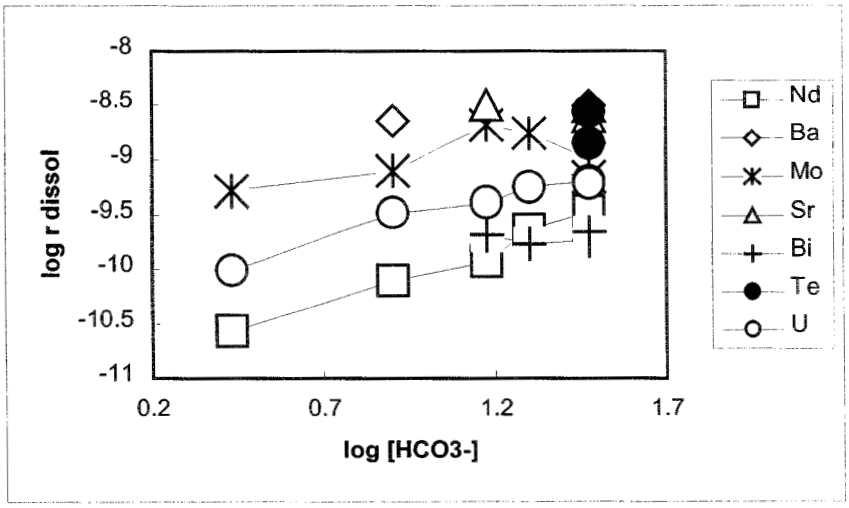

Figure 9. *Logarithm of the dissolution rates as a function of the logarithm of the total bicarbonate concentration for all the elements determined for sample R13.*

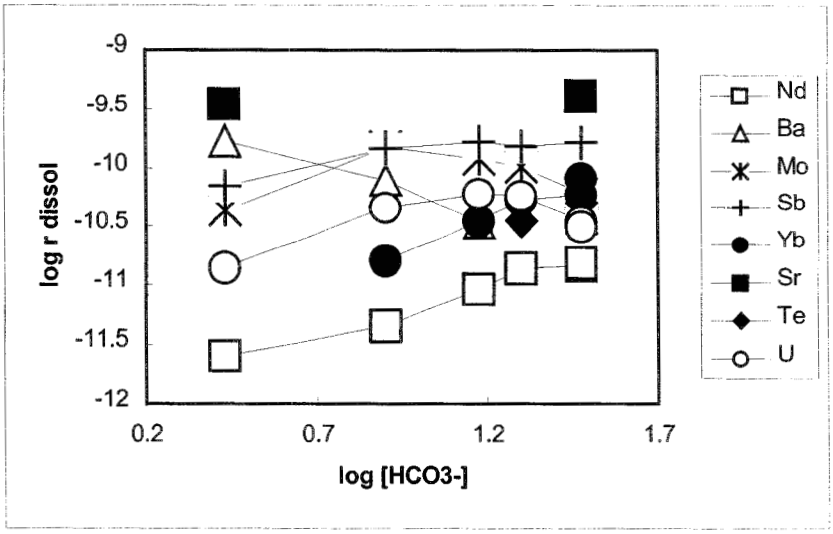

Figure 10. *Logarithm of the dissolution rates as a function of the logarithm of the total bicarbonate concentration for all the elements determined for sample R9.*

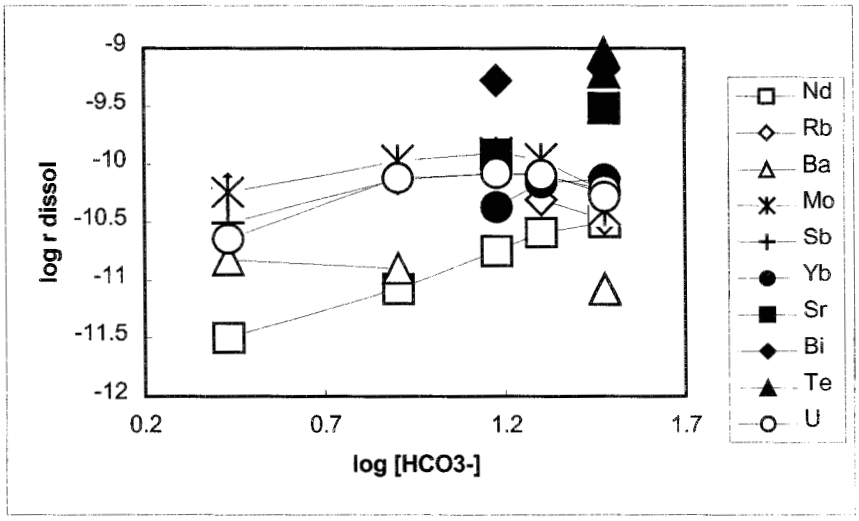

Figure 11. *Logarithm of the dissolution rates as a function of the logarithm of the total bicarbonate concentration for all the elements determined for sample AP9.*

The main observations extracted from the data presented in Figs. 8 to 11 can be summarised as follows.

Neodymium – The behaviour of neodymium is consistent throughout all the experiments performed and for all the samples studied. In all cases this element showed a normalised dissolution rate lower than the one corresponding to uranium and with a very close linear behaviour with respect to the total bicarbonate concentration of the test solutions. These results indicate a non-congruent dissolution of neodymium with respect to the uraninite matrix. Although Nd is one of the REE's considered to be stable within the uraninite structure and, consequently, would be expected to be found retained by the uraninite matrix, this observation does not correspond with the behaviour observed in the leaching experiments. Rather, experimental results point to a source or secondary sink for Nd different to the original uraninite. In this sense, careful characterisations of the minerals surrounding the uraninite grains proved that phosphate minerals as well as clays were very effective retaining neodymium [6]. In addition, the characterisation of these minerals indicated that most of

this Nd was from fissiogenic origin. So, it may be expected these accessory minerals to be the main source or sink of the neodymium found in solution rather than uraninite.

Another mechanism that could account for these lower Nd concentrations would be due to a thermodynamic control instead of a kinetically controlled dissolution mechanism. Calculations performed with the available neodymium database showed that no precipitation should be expected at the lowest total bicarbonate concentrations used in the experiments. However, at the highest total bicarbonate concentrations, it appears the possibility of formation of a solid neodymium carbonate. The formation of such a precipitate it is not congruent with the overall dissolution behaviour observed for Nd. Instead, a decrease of the dissolution rate should be observed at the highest total bicarbonate concentrations if such a phase would form (see the uranium dissolution rates for samples R9 and AP9). Anyway, we checked the possibility of such solid phase being formed by varying the flow rate of the test solution in the same way as we did for uranium. In this case, a clear relationship between the flow rate and the measured Nd concentration in the output solution was found, resulting in equivalent dissolution rates (see Fig. 12). This observation was found to be consistent for all the solid samples studied (with a slight discrepancy for sample R10) and it gives confidence to the conclusion of accessory minerals being responsible of the measured Nd concentration rather than the precipitation of a secondary solid phase.

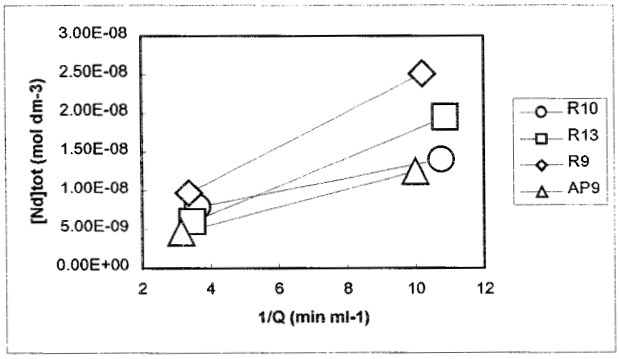

Figure 12. *Effect of the flow rate on the steady-state neodymium concentrations for a total bicarbonate concentration of 30 mM.*

Molybdenum – The dissolution behaviour observed for molybdenum was found to be relatively close to congruent dissolution with the uraninite matrix, mostly for samples R10 and AP9. The largest discrepancy between the dissolution rates of molybdenum and uranium was found for the sample R13. In Table 5 we present the values calculated from the experimental data of the U to Mo normalised dissolution rates ratio given for each sample and for each total bicarbonate concentration.

Table 5.- *U to Mo normalised dissolution rates ratios calculated from the experimental data for all the uraninite samples and for the different total bicarbonate concentrations of the test solutions.*

	R10	***R13***	***R9***	***AP9***
2.7 mM	*0.33*	*0.2*	*0.3*	*0.42*
8 mM	*0.24*	*0.3*	*0.34*	*0.75*
15 mM	*0.61*	*0.13*	*0.52*	*0.96*
20 mM	*0.57*	*0.4*	*0.67*	*0.61*
30 mM	*0.66*	*0.6*	*0.52*	*1.1*

Except in one case (sample AP9 in 30mM bicarbonate), the dissolution rate of molybdenum is found to be consistently slightly higher than the rate of dissolution of uranium. Also, the closest to congruency values are determined for the sample AP9. In addition to the values presented in Table 5, it was observed that the trend of the molybdenum dissolution rates as a function of the bicarbonate concentration seems to follow a similar dependence as the one observed for uranium, stressing the possibility of having congruent dissolution. However, these observations are in contradiction with what is generally observed in the characterisation of the uraninites of Oklo, where molybdenum is generally found segregated from the uraninite matrix in the form of oxide inclusions. However, the dissolution of the Mo oxide inclusions could follow a similar bicarbonate promoted oxic mechanism as uranium dioxide, which would result in the same dissolution behaviour.

Caesium – This element was only detected in measurable quantities in the experiments performed with the sample R10. This is not surprising because of the volatility of this element, which made uraninite unable to retain it in its structure. In fact, elements such as Rb, Sr, Ba and Cs were almost totally removed in practically all the reactors. However, Hidaka et al. [7] have estimated that around 5% of these elements were retained in the core of reactor 10. The chemical characterisation of the samples showed the sample R10 to be the richest in Cs, together with the sample AP9 (see Table 2). Anyway, we never found Cs in measurable amounts in the leaching solutions of the "argile de pile" sample.

Amazingly enough, the dissolution rates of Cs determined for the sample R10, showed a very close congruency with the uranium release rates (see Fig. 8). If we consider the experimental determinations made for all the total bicarbonate concentration test solutions studied, we calculate an average U/Cs dissolution rate ratio of 0.8 ± 0.3. Whereas, if we do not consider the value determined at 2.7 mM bicarbonate, which is the one showing the largest discrepancy between U and Cs release rates, we calculate a ratio of 0.9 ± 0.2. In any case, it is clear the congruency shown by these two elements, as it would be expected being caesium of fissiogenic origin and considering that the remaining found in the solid sample R10 is assumed to be retained in the uraninite structure. This has clear implications for the long-term behaviour of the remaining Cs on the spent nuclear matrix which is not part of the easily accessible fraction.

Barium – Although, this element was measured in many of the samples, there was a great uncertainty on the analytical measurements. For this reason, we could not draw any quantitative conclusion on the behaviour of this element.

Antimony – This element was found in the leaching solutions of samples R9 and AP9, which are the ones that also showed the highest concentration of this element in the chemical characterisation of the solid samples (see Table 2). It is observed that the normalised dissolution rate of Sb follows very closely the release rates of Mo and, consequently, it is not far away from congruency with respect to uranium. Unfortunately, we could not find any information about the characterisation and distribution of this element in the uraninite samples of Oklo. However, based on the chemical knowledge available for this element, we may assume that Sb could likely be found in the form of oxide inclusions. Although this remains to be proved, such assumption would agree with the dissolution data, and with a similar bicarbonate promoted oxic mechanism as uranium dioxide and molybdenum, which would result in the same dissolution behaviour.

Ytterbium – This rare earth-element was only found in detectable quantities for leached samples of uraninites R9 and AP9, and only for the highest total bicarbonate concentrations studied. Although, their dissolution rates are quite close to the ones of uranium, the trend of ytterbium data does not seem to follow the same trend observed for the uraninite matrix dissolution. Rather, they seem to

follow the same dependence on bicarbonate found for neodymium though, with higher dissolution rate values. With the few data available it is very difficult to extract any unambiguous conclusion, but we tend to believe that ytterbium source is more likely to be the same of neodymium, that is, accessory minerals as phosphates or clays.

4. Conclusions

A suitable experimental setup has been developed to determine the kinetics of dissolution of four Oklo uraninite samples extracted from reactor zones 9, 10 and 13 and from the "argile de pile" of reactor zone 9. Using this experimental methodology, the dependence of the rate of dissolution of the uraninite samples on the total bicarbonate concentration in solution has been established. This dependence has been rationalised by using the same mechanism for the bicarbonate promoted oxic dissolution previously developed for experiments performed with synthetic uranium dioxide. Also, the use of a flow system together with the different tests made to ensure the absence of secondary phase precipitation indicate that the uranium release can be taken by itself as indicator of the uraninite matrix dissolution.

The data obtained from the Oklo samples has been compared to dissolution data obtained with other uraninites (Cigar Lake and Palmottu), synthetic uranium dioxide and spent nuclear fuel. In the overall, the obtained bicarbonate promoted oxic dissolution rates obtained for the various types of uranium dioxides: synthetic UO_2, spent nuclear fuel and uraninites are within one order of magnitude. This indicates that the rates and mechanisms are the same for all types of materials independently of the origin and history. This has clear implications for the use of natural uraninite dissolution data, as the one obtained in Oklo, to understand the long-term behaviour of the spent nuclear fuel matrix under repository conditions.

The correlation between minor elements and uranium releases has encountered the difficulty of matching the microscopic solid phase characterisations with the overall contributions observed in the leaching experiments, mainly due to the degree of heterogeneity of the samples studied. However, some observations of interest have been made. Neodymium has been found in all cases to be dissolved in a non-congruent way with uranium. It has been concluded that the most likely source of this element must be accessory minerals as phosphates or clays, according to mineralogical characterisations of the samples. Molybdenum has shown a dissolution behaviour close to congruency, especially for the uraninite sample AP9. This would indicate that, in spite of the fact that uranium and molybdenum are in different sources, the operating dissolution mechanisms are the same. Caesium, although only detected in the study of sample R10, has shown a clear congruent release with the uraninite matrix, giving normalised dissolution rates almost identical as the ones determined for uranium. This has clear implications for the long-term behaviour of the remaining Cs of spent fuel inventory, which does not correspond to the so called "instant release fraction".

5. Acknowledgements

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RETENTION PROCESSES OF URANIUM AND REE IN THE BANGOMBE NATURAL REACTOR ZONE, GABON

Mirella Del Nero[1], Sonia Salah[2], Alain Clément[2] and François Gauthier-Lafaye[2]

[1] Institut de Recherches Subatomiques, CNRS/IN2P3, 23 rue du Loess 67037 STRASBOURG Cedex, FRANCE.
[2] Centre de Géochimie de la Surface, CNRS, 1 rue Blessig, 67084 STRASBOURG Cedex, FRANCE.

Abstract

Experimental studies have been undertaken in order to provide new insights into the relative efficiency of the different mineral phases and sorption processes for the control of U and REE retention in the weathered zones surrounding the natural nuclear reactor at Bangombé (Oklo, Gabon). A sequential extraction technique was used to identify the major U- and REE-containing minerals in the samples. Concerning U sorption processes in the weathered zone at Bangombé, the extractions provide valuable complementary information to mineralogical observations [4] and to uranium isotope exchange experiments [5] which allowed to evaluate the role of adsorption processes on oxides and clays in the partition of U between solid and solution phases of the weathered zone.

In the U-rich iron crust rocks close to the reactor, the fraction of total uranium adsorbed at mineral surfaces is small. A large part of U and a significant proportion of HREE are associated to Fe-oxihydroxides, to minor P-rich phases, and to Mn-oxihydroxides. A possible mechanism for U and HREE retention is an incorporation into the structure of ferric phosphates occurring as surface precipitates on Fe-oxihydroxides. Traces of autunite-like mineral are also present in the zone. For the clayey samples in the weathering profile, it may be inferred that several processes and minerals contribute significantly to U and REE retention: adsorption processes occurring mainly at clay surfaces, association with traces of Mn-containing carbonates (and traces of Mn- and Fe-oxihydroxides for U) and heavy minerals. A significant proportion of total U is adsorbed at mineral surfaces and is thereby easily accessible to weathering solutions.

1. Introduction

Because it is located at a very shallow depth (12 m from the surface), the natural reactor at Bangombé is of particular interest to elucidate the role of present-day weathering in the partition of uranium and fission products. Recent weathering of the Bangombé reactor contributes to the distribution of uranium and fission products into the surrounding rocks [1-3]. Moreover, Bangombé represents a unique tool to study U and FP migration / retention processes under different geochemical conditions. Strong Fe- and Mn- oxihydroxides accumulations occur few meters above the reactor.

Supergene weathering of black shales resulted mainly, close to the surface, in the formation of rubefied pelites, made up of illite, kaolinite and oxihydroxides.

At Bangombé, emphasis was put on the role of clays, phosphates, and/or manganese and iron minerals in the containment of actinides and fission products [2, 3]. However, no detailed experimental studies have so far been undertaken to identify precisely the sorption processes responsible for U and REE retention in the weathered rocks. In this work, we attempted to identify the major U- and REE-containing minerals in the samples using a sequential extraction technique. Clayey and Fe- and Mn-rich samples were examined. Concerning U sorption processes in the weathered zone at Bangombé, the extractions provide valuable complementary information to mineralogical observations [4] and to uranium isotope exchange experiments [5] which allowed to evaluate the role of adsorption processes on oxides and clays in the partition of U between solid and solution phases of the weathered zone. The present study provides an insight into the relative efficiency of the different mineral phases and sorption processes for the control of U and REE retention in the weathered zones surrounding the natural reactor at Bangombé.

2. Material, methods and experimental procedures

2.1 Material

Detailed descriptions of the rock sequence of the Bangombé reactor zone can be found in [1, 3]. Rock samples were collected from a bore-hole (bax08) which intersects the reactor core. Bulk samples were analysed for their chemical composition by ICP-AES and ICP-MS. X-ray diffraction analyses were performed on the bulk samples and on the oriented clay fraction of the samples (<2μm). Rock subsamples were also examined by scanning electron microscope (SEM).

Three clayey samples (noted bax08-5.1, bax08-6.2 and bax08-6.4) were taken in the uppermost rubefied pelites, at a depth from the surface of 5.1, 6.2 and 6.45 meters respectively. The Fe and Mn contents of the white clayey samples bax08-6.2 and bax08-6.4 are very low (1.7 wt% and 3.3 wt% Fe_2O_3 for bax08-6.2 and bax08-6.4 respectively, and <0.01 wt% Mn_3O_4 for both samples). For the ocher clayey sample bax08-5.1, the Fe and Mn contents are equal to 5.8wt% Fe_2O_3 and 0.07 wt% Mn_3O_4. The uranium content is lower than 10 ppm for all clayey samples and is representative of U contents of the uppermost rubefied pelites. X-ray diffraction analyses reveal the presence of clay minerals, quartz and small amounts of hematite and biotite. The clay fraction of the samples (< 2 μm) is mainly made up of illite and minor amounts of kaolinite. Traces of heavy minerals (ilmenite) and rhodocrosite have also been observed in samples collected in the rubefied pelites.

Two samples (noted bax08-10.3 and bax08-10.2) were collected in the zone of iron crusts and red pelites, located at the base of the black shale layer, at a depth of 10.3 and 10.2 meters, respectively. The rocks are black/red colored and contains hard iron concretions. The major minerals detected by X-ray diffraction analyses are goethite, clays, hematite and quartz. The clay fraction (<2 μm) is composed by illite and

kaolinite. An interstratified clay (illite / smectite) also occurs in bax08-10.3. Minor amounts of chlorite are present in bax08-10.2. The Fe content of the bulk samples is very high (51.60 wt% and 35.5wt% Fe_2O_3 for bax10.3 and 10.2, respectively) and the U content amounts to ≈360 ppm for bax08-10.3 and ≈540 ppm for bax08-10.2. Although no crystalline phosphate minerals were detected by XRD analyses, the P content is equal to 1.3 wt% and 0.48 wt% P_2O_5 for bax08-10.3 and bax08-10.2 Detailed examinations of subsamples by SEM revealed the presence of coatings of ferric phosphates on iron oxihydroxides as well as traces of autunite-like minerals in the red pelites [4].

2.2 Extraction experiments on Bangombé samples

The sequential extraction procedure was conducted in three steps. Extractant solutions were prepared as described in [6].

A one gram subsample of crushed bulk rock was contacted with 40 ml of a Morgan reagent (1 M sodium acetate + acetic acid solution at pH = 5) in a polyethylene tube, in order to remove exchangeable elements and carbonate minerals. For each rock sample, the Morgan extraction was conducted on three individual solid subsamples. The tubes were sealed and gently shaken in a rotating shaker in a temperature test chamber at 298 K for 4 hours. After shaking, the samples were filtered (0.22 μm) and the residual solids were washed with 10 ml of Morgan reagent. The 50 ml extractant solutions were analysed by ICP-MS and ICP-AES. The residual solids were then washed with 100 ml ultrapure water and were dried to constant weight. One of the residual solid subsample was taken for X-ray diffraction analyses whereas the others were submitted to the next extraction step. The second extraction step was carried out using 40 ml of Tamm extractant (acid oxalate solution), which can dissolve amorphous Fe-, Al- and Si-minerals and secondary U-minerals and may partly attack ferrous chlorite, biotite or illite. The individual tubes were shaken in the dark in the temperature test chamber at 298 K for 4 hours. After shaking, a filtration procedure was conducted as described above. One of the residual solid subsample was taken for X-ray diffraction analyses whereas the other subsample was gently shaken with 40 ml of a citrate / dithionite / bicarbonate (CDB) solution, at 358 K during 30 minutes, in order to remove crystalline iron oxihydroxides. After filtration of the sample, and washing and drying of the residual solid, the CDB treatment was repeated.

After the second CDB extraction, the remaining solid was washed with ultrapure water, dried, weighted and taken for X-ray diffraction analyses and for chemical analyses in order to check for possible element losses on tube walls and on filters during the experiments.

3. Experimental results

3.1 Clayey samples in the rubefied pelites

An insight into the relative efficiency of the constitutive minerals of the rocks for U and REE retention is provided by the sequential extraction experiments. For bax08-5.1 about 60% of the initial U content is released by dissolution of crystalline Fe-

oxihydroxides and of Mn-phases, presumably Mn-oxihydroxides and Mn-containing carbonates (Fig. 1), which are present in small amounts in the rock. HREE are partly removed by dissolution of Mn-containing carbonates (up to ≈30% of the initial HREE contents removed), whereas LREE are not efficiently extracted (Fig. 2).

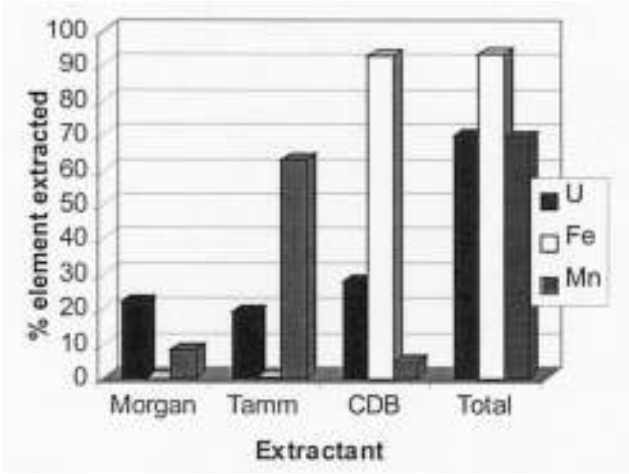

Figure 1 : Distribution of U, Mn and Fe amongst extracted phases for the sequential extraction experiments on the ocher clay sample bax08-5.1 collected in the zone of rubefied pelites, in the upper part of the weathering profile at Bangombé. Results are reported to the initial bulk sample weight and are given in percent of element of untreated bulk sample.

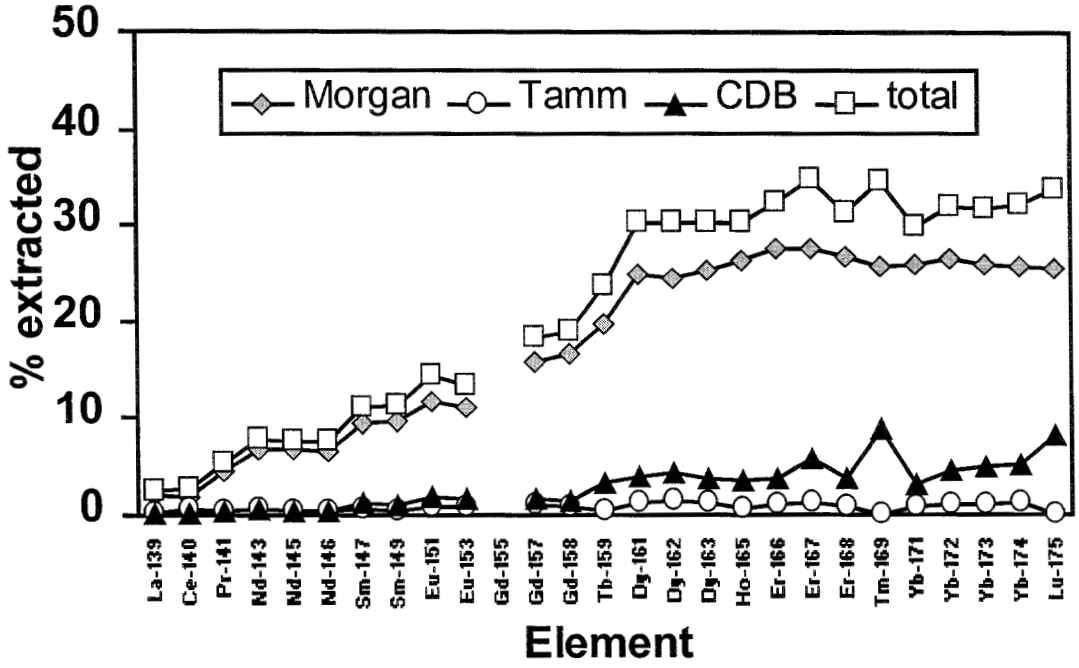

Figure 2 : Distribution of REE amongst extracted phases for the sequential extraction experiments on the ocher clay sample bax08-5.1 collected in the zone of rubefied pelites, in the upper part of the weathering profile at Bangombé. Results are reported to the initial bulk sample weight and are given in percent of element of untreated bulk sample.

For the white clayey samples bax08-6.2 and bax08-6.4, the percentages of initial U and REE in the residual solid are high for both clayey samples (>60% of the initial U contents in residue) [5]. Non-extracted elements may remain partly strongly adsorbed onto insoluble clays, like illite and kaolinite, or associated to traces of non-extracted biotite or heavy minerals. The extracted part of U is due to partial attack of biotite for bax08-6.2, and also to dissolution of traces of Mn-oxihydroxides and of crystalline Fe-oxihydroxides for bax08-6.4 [5].

Although the distribution of U and REE amongst mineral phases cannot be precisely inferred from our extraction experiments, our data suggest that, for the Fe- and Mn-poor white clays, the greatest part of both U and REE are associated to residual clays illite, kaolinite and biotite and/or to heavy minerals [5]. However, beside the major clay components, several traces of minerals may contribute significantly to the retention in the clayey samples, depending on the rock composition. For the Fe- and Mn-containing samples, U is mainly associated to Mn-phases and to crystalline Fe-oxihydroxides. Although a significant part of HREE is sorbed on Mn-containing carbonates, REE are mainly found in residual clays and heavy minerals.

The extraction experiments provide complementary information to U isotope exchange experiments performed on the white clayey samples bax08-6.2 and bax08-6.4 [5]. The $^{238}U/^{233}U$ exhange experiments allowed to measure both the adsorption of ^{233}U and the desorption of ^{238}U on the sample bax08-6.2 and bax08-6.4. The relationship obtained between the percentages of ^{233}U sorbed and ^{238}U released in solution leads

indeed to an estimation of the proportion of uranium taking part in adsorption / desorption processes in the sample [6]. Because the removal of ^{238}U was proportional to ^{233}U in solution throughout a wide range of solution composition, it could be inferred that a desorption process was mainly responsible for ^{238}U release in our experiments. A mean value of the amount of ^{238}U participating in adsorption / desorption processes was found to be equal to ≈0.9 µg/g of solid for bax08-6.2 and ≈1.4 µg/g of solid for bax08-6.4 (≈ 22 % and 23% of the initial U content of the samples). This indicated that a significant part of U occurs at mineral surfaces in the uppermost white clayey rocks at Bangombé. Illite may be the major components for U adsorption on the bax08-6.2, as suggested by surface complexation modeling of U adsorption [5].

3.2 Fe-rich samples in the red pelites

U and HREE in bax08-10.2 were efficiently removed by the extractions. The greatest part of extracted U and HREE is related to the CDB treatment, that dissolved ≈85% of the initial P and ≈50% of the initial Fe contents of the sample (Figs. 4 and 5). The fraction of elements removed by Morgan and by Tamm is also significant, presumably due to a contribution of Mn-oxihydroxides and Mn-containing carbonates. For bax08-10.3, which is richer in P than bax08-10.2, the greatest part of extracted U and HREE are dissolved by CDB with P-rich phases and crystalline iron components [5]. Nevertheless, our experiments suggest that U and HREE are related to Fe- and Mn-oxihydroxides and to P-rich phases in the red pelites.

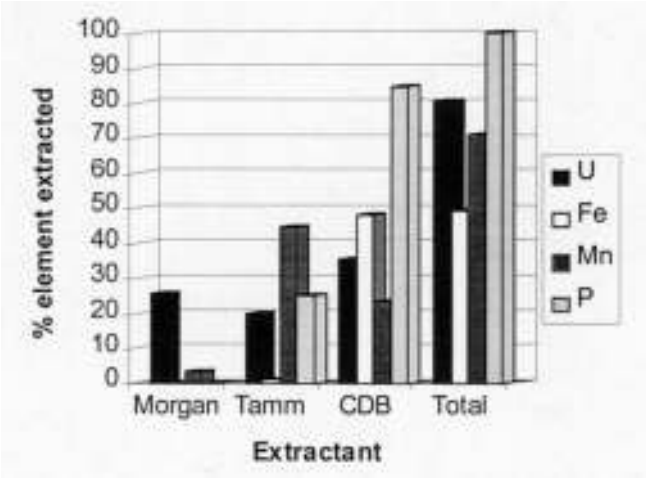

Figure 3 : Distribution of U, Mn, P and Fe amongst extracted phases for the sequential extraction experiments on Fe-rich sample bax08-10.2 collected in the zone of red pelites above the reactor at Bangombé. Results are reported to the initial bulk sample weight and are given in percent of element of untreated bulk sample.

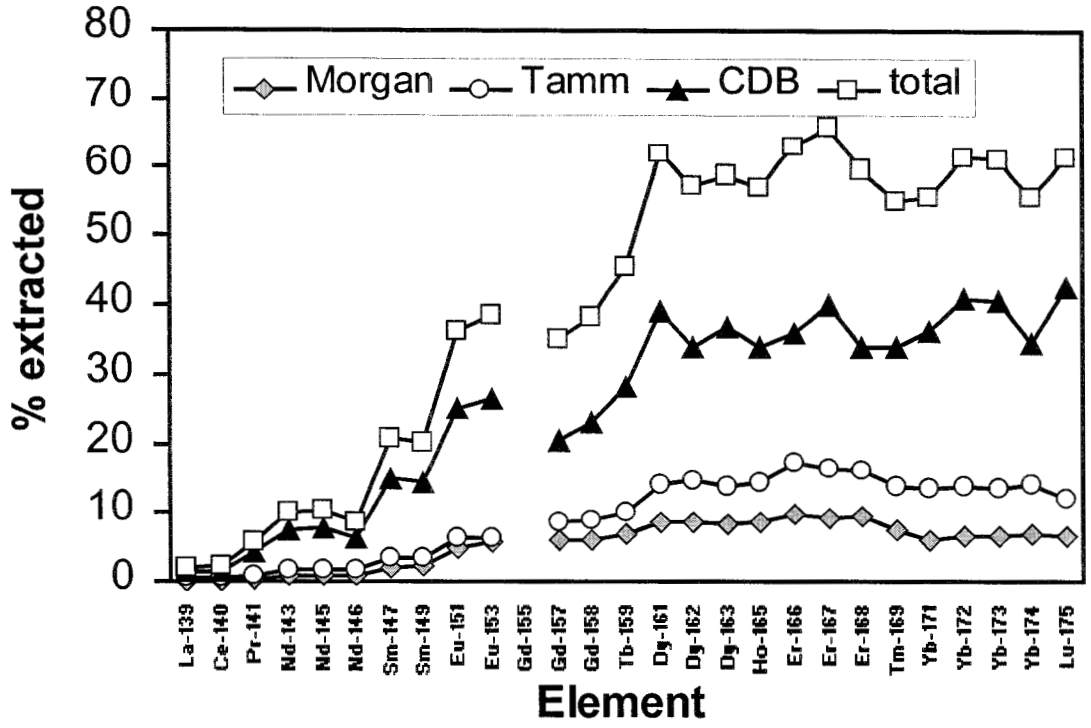

Figure 4 : Distribution of REE amongst extracted phases for the sequential extraction experiments on the Fe-rich sample bax08-10.2 collected in the zone of red pelites above the reactor at Bangombé. Results are reported to the initial bulk sample weight and are given in percent of element of untreated bulk sample.

From our U isotope exhange experiments [5], ^{238}U available for desorption was estimated to be equal to ≈9 µg/g of solid for bax08-10.3. Although this value is higher than those obtained for clayey materials, it represents only a few percents of the initial U content of the Fe-rich sample. These results indicated that adsorption at mineral surfaces is not a significant process for U retention in the U-rich ferruginous layer close to the reactor.

Many experimental and modeling studies on well-defined mineral/solution systems have evidenced that uranyl ions may be sorbed at the surface of iron oxihydroxides and clay minerals by formation of surface complexes. Studies on minerals or rocks have also provided evidence for the incorporation of U into Fe-oxihydroxides [7] Concerning Bangombé samples, our results suggest that the fraction of U associated to both Fe-oxihydroxides and residual clay minerals is considerably higher than U taking part in adsorption / desorption processes. This is consistent with an incorporation of U in the structure of iron oxihydroxides.

The influence of phosphate ligands in solution on the mechanisms of U and REE sorption remains so far poorly known. Payne et al. [8] suggested the formation of a ternary surface complex involving both U and P at the ferrihydrite surface. They pointed out, however, that a mechanism of surface precipitation of ferric phosphate with a stronger efficiency for U scavenging than the original ferrihydrite is also possible.

Concerning our extraction experiments for the Fe-rich sample, significant amounts of U, REE and P are removed by the CDB treatment. SEM examinations of solid subsamples and of thin sections of rocks collected in the red pelites above the reactor revealed the presence of P-rich iron coatings (presumably ferric phosphates) on crystalline Fe-oxihydroxides and of traces of autunite-like mineral [4]. Our studies highlight thus the role of uranyl phosphates on the retention of U and HREE in the iron crust layers located near the reaction zone at Bangombé. They also suggest that ferric phosphate surface precipitates on iron oxides may be efficient traps for uranium and REE.

4. Conclusions

Major findings of our study on U and REE sorption in rock samples collected in the weathered zones around the Bangombé reactor are summarized as follows.

1. For the U-poor white clayey samples in the weathering profile, it may be inferred that U and REE are mainly associated to clays and traces of heavy minerals. U isotope exchange data indicated that adsorption is a significant process that controls the behavior of U in these water/rock systems [5). A significant proportion of total U is thus easily accessible to weathering solutions. Our experiments and surface complexation modeling studies suggested that illite may be the major adsorptive component in white clays [5].

2. However, when present in the clayey rocks, minor amounts of Mn-phases and Fe-oxihydroxides may also significantly control the distribution of U and HREE. In the more Mn- and Fe-rich uppermost ocher clays, U is mainly distributed amongst crystalline iron oxihydroxides and Mn-phases (oxihydroxides and carbonates). HREE are also partly retained by Mn-containing carbonates.

3. In the U- and P-rich red pelites close to the reactor, the fraction of total uranium adsorbed at mineral surfaces is low. A mechanism of U retention is an incorporation into the structure of iron oxihydroxides and/or of minor phosphate phases. Our studies highlight the role of uranyl phosphates and of ferric phosphate precipitates at Fe-oxihydroxides surfaces on the retention of U and HREE. Mn-phases may also significantly contribute to U and HREE sorption in samples containing smaller amounts of phosphate phases.

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Sensitive High Resolution Ion Microprobe (SHRIMP) Pb, U, Nd and Sm isotopic data from the natural reactor site of Bangombé

G. Bracke, S. Salah and F. Gauthier-Lafaye

Ecole et Observatoire des Sciences de la Terre (EOST)

Centre de Geochimie de la Surface – CNRS (UMR7517)

1, rue Blessig, F - 67084 Strasbourg Cedex, France

H. Hidaka

Department of Earth and Planetary Systems Science

Hiroshima University

Higashi-Hiroshima 739-8526, Japan

1 Introduction

The unique, natural fission reactions that occurred 2 Ga ago at Oklo and Bangombé, Gabon, allow us to study fission product migration due to weathering by using isotope compositions as tracers. The Bangombé reactor is located close to the surface at 10 m depth and has been exposed to surface weathering conditions. This reactor is being studied as part of the OKLO-Natural Analogue Phase II project.

These fission reactions have lead to changes in the isotopic ratios of natural elements as a result of the:

a) depletion of isotopes due to fission and neutron capture and subsequent decay (e.g. ^{235}U, ^{149}Sm)

b) accumulation of nonradioactive isotopes which are the endmembers of a decay chain of fission products (e.g. ^{143}Nd)

Isotopic analysis makes it possible to distinguish between fissiogenic and natural components, to trace migration of fission products and to date geological events.

Determination of the isotopic composition of a number of elements in natural fission reactors has been carried out by conventional mass spectrometry such as Thermal Ionisation Mass Spectrometry (TIMS), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and secondary ion mass spectrometry (SIMS). Isotopic measurements by SIMS are especially effective in investigating distribution profiles of fission products on the microscopic scale, such as within individual mineral grains and along grain boundaries. A Sensitive High Resolution Ion Micro-Probe (SHRIMP), which was developed at the Australian National University and installed at Hiroshima University, has been used widely for U-Pb dating of minute areas (20 to 30 μm) of minerals in geological samples. The advantages of SHRIMP, namely its high mass resolution, high sensitivity

and high spatial resolution, make it suitable for the investigation of the detailed distribution of fission products.

Reported here are isotopic data for U, Pb, Nd and Sm from selected samples of the drill core BAX 08 of the Bangombé site obtained by SHRIMP which gives some insight into the geological history of the Bangombé site and migration of fission products.

U / Pb:	Uranium-lead and lead-lead dating
U:	the ratio $^{235}U/^{238}U$ decreases during the course of the fission reaction
Nd / Sm	their isotopic compositions act as tracers for fission products and provide information on fissiogenic and neutronic parameters

2 Objective

Our objectives are to determine isotopic ratios on a microscopic scale and within vairous minerals in order to date geological and mineralisation events at the Bangombé site and possibly to trace the migration of fission products which has occurred.

3 Methods

Samples

All thin sections are from the drill core BAX 08 and are listed in Table 1. The location of the drill core and the mineralogical log is depicted elsewhere (Salah et. al., 1999). Each thin-section was investigated by optical and scanning electron microscopy prior to analysis by SHRIMP. After removal of the carbon coating, the thin sections were cut and gold-coated for ion probe examination.

Analytical Methods

Isotopic measurements of thin-section samples were performed by SHRIMP II at Hiroshima University. A few nA of O_2- primary ion beam focussed onto a 10 to 200 µm spot was used for sputtering the polished section. The mass resolution (m/∂m) was normally set to 5500 at 1 % of the peak height using a 80 µm wide source slit and a 100 µm wide collector slit. Generally 10 sets of Pb, U, Nd, and Sm isotopic data were taken per analysis. A quadratic drift correction was applied. In order to save analytical time, U and Pb analyses were separated from the analytical routine for Nd and Sm. A synthetic uraninite containing 5000 ppm Nd was used as a standard.

4 Results

Uraninites

Lead isotope data with apparent ages for all uraninites are given in Table 2. The corresponding uranium isotope compositions and Pb/U ratios are given in Table 3. The apparent lead-lead age of most uraninites is between 1.68 - 1.95 Ga. Some sample spots of a uraninite vein of approx. 2 mm length, which was found within a nodule of organic matter at 12.35 m, have younger apparent ages of 1.12, 1.19, 1.27, 1.40 and 1.45 Ga. The sample spots of this uraninite vein analysed by SHRIMP are depicted in Figure 1.

Most uraninites plot above the concordia (Figure 2). Only three uraninites (12.13 m, 12.35-U and 12.63 m) could give a discordia intersecting the concordia at the age of the uranium mineralisation (Figure 3). The discordia of the uraninite vein does not intersect the concordia and lies above. Thus we do not obtain an age. This indicates a possible lead gain at the time of mineralisation and a possible recent uranium loss.

We have to consider that likely a lead gain occurred at the time of mineralisation of the uraninite. We further have to consider that this lead was strongly radiogenic due to the primary uranium mineralisation. If we assume that this lead was uniform in its isotopic composition then a Pb-Pb isochron can be applied on the data from the uraninite vein. This isochron is depicted in Figure 4 and gives an age of 766 ± 85 Ma.

The slightly elevated uranium isotope ratios of 0.00735-0.00743 (normal 0.00725) in the uraninite vein are possibly caused by instrumental fractionation (Table 3).

Rare Earth Elements

All sample spots have higher ratios of $^{143}Nd/^{146}Nd$ than the normal value of 0.707 and lower ratios of $^{149}Sm/^{147}Sm$ than the normal value of 0.921 (Table 4). The isotope ratios in the uraninite vein of 0.766 - 0.794 for $^{143}Nd/^{146}Nd$ and 0.826 - 0.858 for $^{149}Sm/^{147}Sm$ indicate clearly the presence of fission products.

A single REE bearing mineral with a diameter of approx. 10 µm has been observed in a fracture filling at 13.15 m by scanning electron microscopy. The presence of fission products is indicated in the REE-mineral by a $^{143}Nd/^{146}Nd$ ratio of 0.756 ± 0.023 and a $^{149}Sm/^{147}Sm$ ratio of 0.861 ± 0.013.

Galena, Hematite, Pyrite, Organic Matter

The lead isotope compositions of galena, their apparent ages and T2-ages using a T1-age of 1.97 Ga are given in Table 5. Except for three sample spots at 11.83 m, all apparent ages for galena are in the range of 1.87-2.1 Ga. Assuming that the mineralisation of the uranium deposit took place at 1.97 Ga (=T1) we obtain an age for lead separation from uraninite (=T2) of 0.02 to 0.27 Ga.

Table 6a-c shows lead and uranium isotope data, their apparent ages and T2-ages using a T1-age of 1.97 Ga for hematite, pyrite, phosphates and organic matter. Most apparent ages range from 1.85 to 2.21 Ga. One hematite sample at 13.15 m has an apparent age of 1.39 Ga. The T2-ages, which refer to lead separation from uraninite and incorporation in these minerals, range from 0.03 to 0.14 (Pyrite, Phosphate, Organic Matter) and from 0.21 to 0.48 Ga (hematite).

An isochron using hematite, omitting the outlier (13.15 m), gives an age of 2064 ± 160 Ma (Figure 5). A discordia can not applied on hematite. The low U content resulted in large uncertainity in Pb/U ratios.

5 Discussion

All samples are strongly enriched in ^{206}Pb and ^{207}Pb due to the primary uranium mineralisation. Several events affected the deposit after mineralisation (fission reaction, dolerite intrusion, weathering), which greatly complicate the uranium-lead and lead-lead-dating.

Nevertheless, the isotope data obtained on a microscopic scale allow us to date the uraninite vein in the organic matter at 12.35 m by a lead-lead isochron at 766 Ma ± 85 Ma. This may be related to the dolerite intrusion which occurred at that time in the Francevillian basin and led to thermal and tectonic stress.

The lead-lead isochron is considered to be a true isochron because:

a) the optical microscope shows a distinct uraninite vein inside organic matter

b) the correlation is distinct

c) recent uranium loss (weathering) would not affect the lead-lead isochron

d) radiogenic lead gain at the time of mineralisation would not affect the lead-lead isochron

The lead-lead isochron on hematite gives 2064 Ma ± 160 Ma. It does not seem likely that hematite captured large amounts of radiogenic lead from the primary uranium deposit recently. Oxidizing conditions may have led to a uranium loss. Therefore, this isochrone age may represent the formation age of hematite.

T2-ages obtained on galena and the other minerals using a T1-age of 1.97 Ga support a separation of lead from uraninites starting less than 500 Ma ago. This would be consistent with the uplift of the Francevillian basin and a subsequent beginning of alteration and weathering. The T2-ages obtained on pyrite, phosphate, organic matter and on some galenas range from 20 to 140 Ma. They may be the result of a variation in degree and intensity of alteration and weathering on the different minerals. The T2-ages can provide an rough estimation for these processes only.

The Nd and Sm isotope data indicate low amounts of fission products in the uraninite vein at 12.35 m. It is likely that the fission products were trapped in the uraninite vein at the time of mineralisation. The uraninite vein did not take part in the fission process as it does not contain an anomalously low $^{235}U/^{238}U$-ratio and contains only low amounts of fission products.

6 Conclusions

A geologic event lead to mineralisation of an uraninite vein at 766 ± 85 Ma, which trapped fission products.

T2 ages indicate separation of lead beginning less than 500 Ma ago. The younger T2 ages from 20 to 140 Ma may be related to the beginning of alteration and weathering effects.

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8 Tables

Table 1: Short description of thin-sections

depth [m]	description
9.13	clay with hematite veins
9.18	clay with hematite veins
9.40	clay with hematite veins
10.30	red clay with hematite veins
10.90	reactor clay
11.08	sandstone
11.83	sandstone
12.13	sandstone
12.35	sandstone
12.63	sandstone
13.15	sandstone with hematite

Table 2: Lead isotope composition of uraninites

Sample spot	207/206	±	206/204	±	207/204	±	208/207	±	207*/206*	app. Age (Ga)
11.08-2U	0.1272	0.0002	1688	43	215	5	0.1962	0.0053	0.1193	1.95
11.08-2U1	0.1082	0.0022	2676	153	289	11	0.1469	0.0035	0.1031	1.68
11.08-2U2	0.1130	0.0032	1902	332	214	31	0.2001	0.0230	0.1058	1.73
11.08-2U3	0.1174	0.0016	2244	114	263	10	0.1640	0.0053	0.1114	1.82
11.83-Z1U1	0.1132	0.0007	2149	144	243	16	0.1736	0.0051	0.1069	1.75
11.83-Z2U1	0.1174	0.0003	2568	71	302	9	0.1457	0.0004	0.1122	1.84
11.83-Z3U1	0.1169	0.0003	2598	57	303	6	0.1441	0.0007	0.1117	1.83
11.83-Z4U1	0.1028	0.0004	3439	101	353	9	0.1256	0.0021	0.0988	1.60
12.13-3-U	0.1176	0.0001	2420	46	285	5	0.1517	0.0011	0.1121	1.83
12.13-z1U1	0.1044	0.0010	2796	225	298	23	0.1449	0.0042	0.0997	1.62
12.35-u	0.1198	0.0005	2584	163	310	21	0.1480	0.0022	0.1146	1.87
12.35-u3	0.1101	0.0003	2651	121	291	14	0.1445	0.0009	0.1050	1.72
12.35-u4	0.1082	0.0006	2779	92	300	8	0.1394	0.0014	0.1033	1.68
12.35-u5	0.0787	0.0003	7325	265	578	22	0.0724	0.0006	0.0768	1.12
12.35-u6	0.0820	0.0006	6062	96	497	10	0.0847	0.0011	0.0797	1.19
12.35-u7	0.0953	0.0004	3359	150	321	14	0.1272	0.0037	0.0912	1.45
12.35-u8	0.0921	0.0004	4389	158	398	22	0.1060	0.0010	0.0889	1.40
12.35-u9	0.0856	0.0005	5020	188	430	18	0.1019	0.0012	0.0828	1.27
12.35-u10	0.1177	0.0006	2644	46	312	6	0.1447	0.0006	0.1126	1.84
12.35-u11	0.1201	0.0005	2469	89	296	11	0.1465	0.0009	0.1147	1.88
12.63-3a-U	0.1117	0.0042	221	18	25	1	1.4120	0.0652	0.0472	0.06

* corrected for common lead using $^{206}Pb/^{204}Pb$ = 15.16 and $^{207}Pb/^{204}Pb$ = 15.19 (all tables)

± 2 sigma (mean) (all tables)

Table 3: Isotope composition of U and Pb/U ratio of uraninites

Sample spot	235U/238U	±	207Pb*/235U	±	206Pb*/238U	±
11.08-2U	0.00733	0.00006	7.22	0.27	116	4
11.08-2U1	0.00734	0.00004	0.67	0.01	9.63	0.02
11.08-2U2	0.00732	0.00003	0.65	0.05	9.65	1.01
11.08-2U3	0.00732	0.00003	0.88	0.05	13.6	1.0
11.83-Z1U1	0.00728	0.00010	0.41	0.02	5.69	0.15
11.83-Z2U1	0.00723	0.00003	1.54	0.10	23.3	1.7
11.83-Z3U1	0.00683	0.00003	2.78	0.03	44.8	0.7
11.83-Z4U1	0.00727	0.00005	6.77	0.74	89	11
12.13-3-U	0.00662	0.00003	11.9	0.4	202	3
12.13-z1U1	0.00659	0.00003	0.23	0.01	3.58	0.21
12.35-u	0.00742	0.00006	0.32	0.00	5.11	0.05
12.35-u3	0.00737	0.00004	0.80	0.01	11.4	0.1
12.35-u4	0.00739	0.00008	0.55	0.02	7.54	0.27
12.35-u5	0.00735	0.00003	0.26	0.01	2.76	0.09
12.35-u6	0.00735	0.00006	0.30	0.01	3.25	0.14
12.35-u7	0.00738	0.00004	0.54	0.03	6.60	0.38
12.35-u8	0.00743	0.00004	0.33	0.01	3.90	0.06
12.35-u9	0.00741	0.00006	0.29	0.02	3.26	0.19
12.35-u10	0.00742	0.00004	1.06	0.02	15.7	0.6
12.35-u11	0.00742	0.00005	0.58	0.02	8.93	0.25
12.63-3a-U	0.00713	0.00008	0.08	0.01	0.76	0.08

Table 4: Nd and Sm isotope composition of uraninite

Spot	149Sm/147Sm	±	143Nd/146Nd	±	145Nd/146Nd	±
10.30-REE	0.874	0.009	0.742	0.010	0.496	0.008
10.90-Clay-REE	0.609	0.074	0.814	0.025	0.539	0.010
10.90-Clay-REE2	0.516	0.032	0.894	0.032	0.561	0.017
12.35-REE1	0.833	0.003	0.792	0.002	0.534	0.002
12.35-REE2	0.829	0.006	0.788	0.009	0.534	0.004
12.35-REE3	0.841	0.002	0.782	0.003	0.525	0.002
12.35-REE4	0.858	0.006	0.766	0.004	0.516	0.001
12.35-REE5	0.841	0.007	0.775	0.008	0.516	0.003
12.35-REE6	0.826	0.008	0.784	0.012	0.529	0.005
12.35-OM1	0.876	0.025	0.751	0.012	0.511	0.008
12.35-OM2	0.834	0.040	0.782	0.012	0.532	0.020
12.35-OM3	0.833	0.007	0.782	0.003	0.529	0.002
12.63-REE1	0.865	0.019	0.747	0.024	0.491	0.010
12.63-REE2	0.900	0.018	0.753	0.020	0.503	0.004
12.63-ZR-REE	0.884	0.012	0.747	0.008	0.495	0.004
13.15-REE	0.861	0.013	0.765	0.023	0.502	0.009
Standard 1	-	-	0.729	0.004	0.484	0.003
Standard 2	-	-	0.725	0.006	0.489	0.004
Standard 3	-	-	0.726	0.002	0.484	0.001
normal value	0.921	-	0.707	-	0.483	-

Table 5: Lead isotope composition of Galena (#NV = negative value)

Spot	206Pb/204Pb	±	207Pb/204Pb	±	207Pb/206Pb	±	208Pb/207Pb	±	207Pb*/206Pb*	app. Age (Ga)	T2 (T1=1.97 Ga)
9.18-k2-pb1	1304	5	182	1	0.1404	0.0003	0.2296	0.0008	0.1302	2.10	0.27
10.90-gal1	1622	14	217	3	0.1335	0.0007	0.1970	0.0012	0.1253	2.03	0.13
10.90-gal2	1614	61	216	9	0.1339	0.0008	0.1991	0.0017	0.1257	2.04	0.14
10.90-gal3	1643	77	220	8	0.1344	0.0019	0.1978	0.0038	0.1263	2.05	0.16
11.08-0gal	1652	45	220	6	0.1330	0.0007	0.1952	0.0009	0.1250	2.03	0.12
11.08-2gal1	1587	40	215	5	0.1353	0.0002	0.1918	0.0022	0.1270	2.06	0.18
11.08-2gal2	1928	84	258	9	0.1331	0.0007	0.1653	0.0038	0.1263	2.05	0.16
11.08-2gal4	2097	26	281	4	0.1339	0.0007	0.1548	0.0009	0.1276	2.07	0.20
11.08-2gal5	1973	27	268	4	0.1359	0.0005	0.1627	0.0011	0.1292	2.09	0.24
11.08-2gal6	2239	42	288	4	0.1278	0.0007	0.1521	0.0012	0.1219	1.99	0.03
11.08-Pb	2322	42	282	5	0.1216	0.0004	0.1502	0.0004	0.1159	1.89	#NV
11.08-Pb2	1950	42	265	6	0.1359	0.0013	0.1654	0.0007	0.1291	2.09	0.24
11.08-Pb3	1993	24	265	4	0.1336	0.0008	0.1647	0.0006	0.1270	2.06	0.18
11.83-Z3Gal1	2865	170	314	19	0.1101	0.0010	0.1369	0.0025	0.1054	1.72	#NV
11.83-Z3Gal2	6946	331	535	27	0.0772	0.0003	0.0852	0.0005	0.0752	1.07	#NV
11.83-Z3Gal3	2209	41	286	7	0.1308	0.0015	0.1555	0.0019	0.1247	2.03	0.11
11.83-Z4Gal1	2185	104	277	12	0.1276	0.0008	0.1542	0.0011	0.1214	1.98	0.02
11.83-Z3Gal5	6780	603	516	44	0.0754	0.0010	0.0803	0.0012	0.0733	1.02	#NV
12.35-Pb1	2573	91	310	13	0.1198	0.0015	0.1421	0.0033	0.1146	1.87	#NV
12.35-Pb2	1980	59	268	11	0.1348	0.0006	0.1580	0.0015	0.1282	2.07	0.21
12.63-3a-Pb	2009	99	269	14	0.1335	0.0003	0.1622	0.0013	0.1270	2.06	0.18

Table 6a: Lead isotope composition of Hematite

Hematite	206/204	±	207/204	±	207/206	±	208/207	±	235U/238U	±	207*/206*	app. Age (Ga)	T2
9.13-k1-hem	1051	33	159	5	0.1510	0.0004	0.2729	0.0010	0.00736	0.00009	0.1386	2.21	0.48
9.18-k2-hem	1170	70	168	8	0.1439	0.0008	0.2406	0.0032	0.00706	0.00063	0.1326	2.13	0.33
9.40-k1-hem	1483	16	206	2	0.1386	0.0002	0.2158	0.0011	0.00743	0.00008	0.1297	2.10	0.25
9.40-k1-vein	1462	78	204	14	0.1396	0.0015	0.2155	0.0019	0.00743	0.00041	0.1306	2.11	0.28
10.30-k4-fe	1900	155	264	21	0.1393	0.0006	0.2107	0.0016	0.00744	0.00007	0.1323	2.13	0.32
10.30-k4-fe2	1957	73	274	10	0.1397	0.0007	0.2098	0.0022	0.00741	0.00008	0.1330	2.14	0.34
10.30-k2-hem	1636	106	232	12	0.1392	0.0004	0.2115	0.0023	0.00743	0.00009	0.1313	2.12	0.30
10.30-k2-mnpb	1837	47	249	7	0.1354	0.0002	0.2089	0.0004	0.00757	0.00022	0.1282	2.07	0.21
13.15-vk13-Fe	1834	136	176	12	0.0957	0.0006	0.2260	0.0155	0.00741	0.00013	0.0883	1.39	#NV

Table 6b: Lead isotope composition Pyrite (Py) and Phosphates (P)

Pyrite / Phosphate	206/204	±	207/204	±	207/206	±	208/207	±	235U/238U	±	207*/206*	app. Age (Ga)	T2
11.08-2Py1	1944	33	258	5	0.1323	0.0010	0.1629	0.0015	-	-	0.1256	2.04	0.14
11.08-Py	333	30	54	4	0.1616	0.0023	0.6786	0.0384	0.00882	0.00036	0.1220	1.98	0.03
11.08-Py1	1898	39	251	6	0.1320	0.0011	0.1733	0.0011	-	-	0.1250	2.03	0.12
11.08-Py2	73	13	22	3	0.3080	0.0251	1.6891	0.1025	0.00845	0.00067	0.1192	1.94	#NV
12.35-P1	1160	148	145	17	0.1245	0.0016	0.2527	0.0232	0.00719	0.00007	0.1130	1.85	#NV

Table 6c: Lead isotope composition of Organic Matter

Org. Matter	206/204	±	207/204	±	207/206	±	208/207	±	235U/238U	±	207*/206*	app. Age (Ga)	T2
11.08-3OM1	1660	75	220	10	0.1326	0.0004	0.1896	0.0035	0.00672	0.00011	0.1246	2.02	0.11
11.08-3OM2	1700	62	226	8	0.1333	0.0004	0.1901	0.0018	0.00671	0.00012	0.1256	2.04	0.14
11.08-3OM3	1578	38	208	5	0.1332	0.0010	0.1976	0.0025	0.00699	0.00012	0.1247	2.03	0.11
11.08-3OM4	1525	63	202	9	0.1327	0.0003	0.2017	0.0038	0.00664	0.00006	0.1240	2.02	0.09

9 Figures

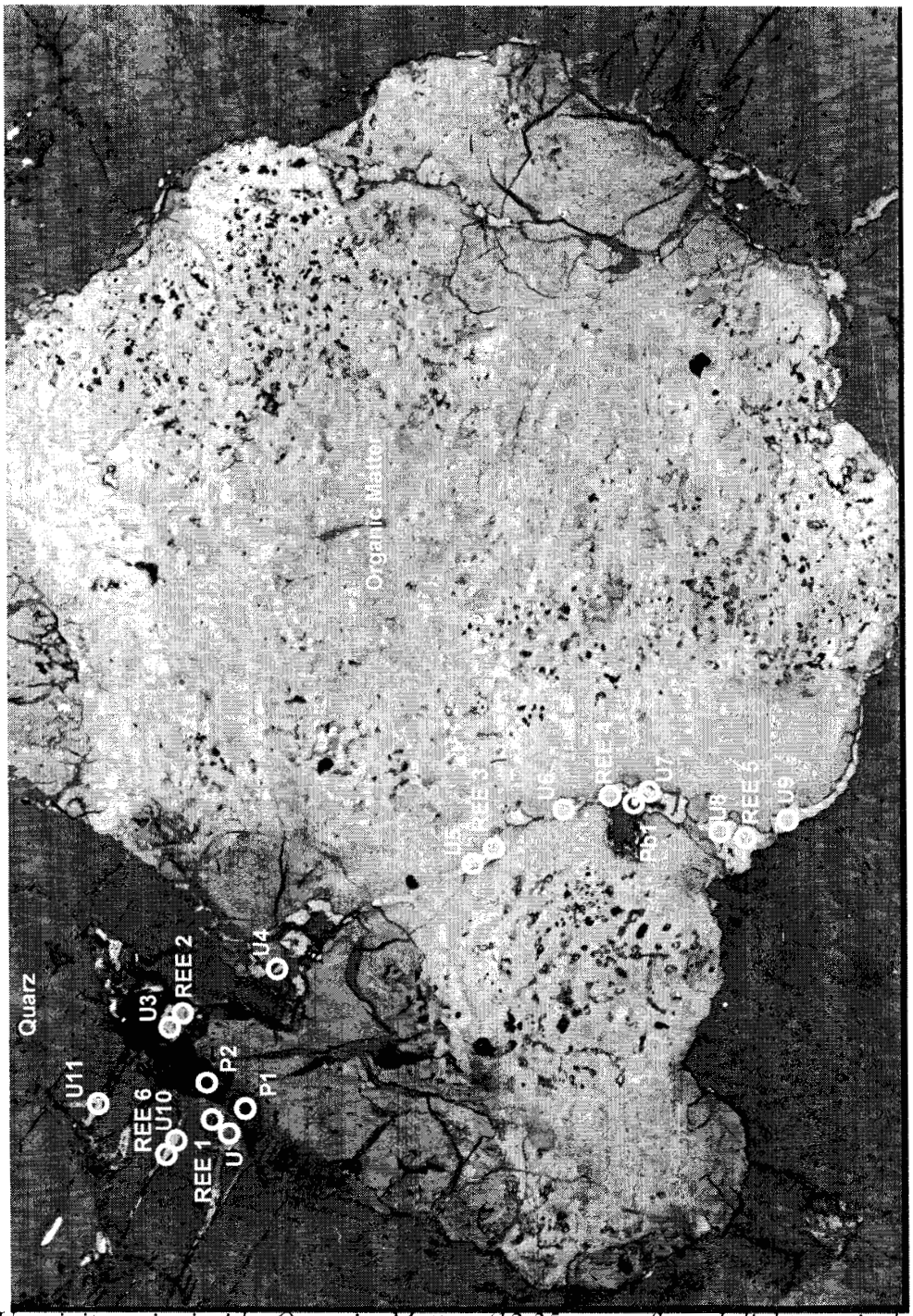

Figure 1: Uraninite vein inside Organic Matter (12.35 m, reflected light, optical microscope, diameter approx. 3 mm)

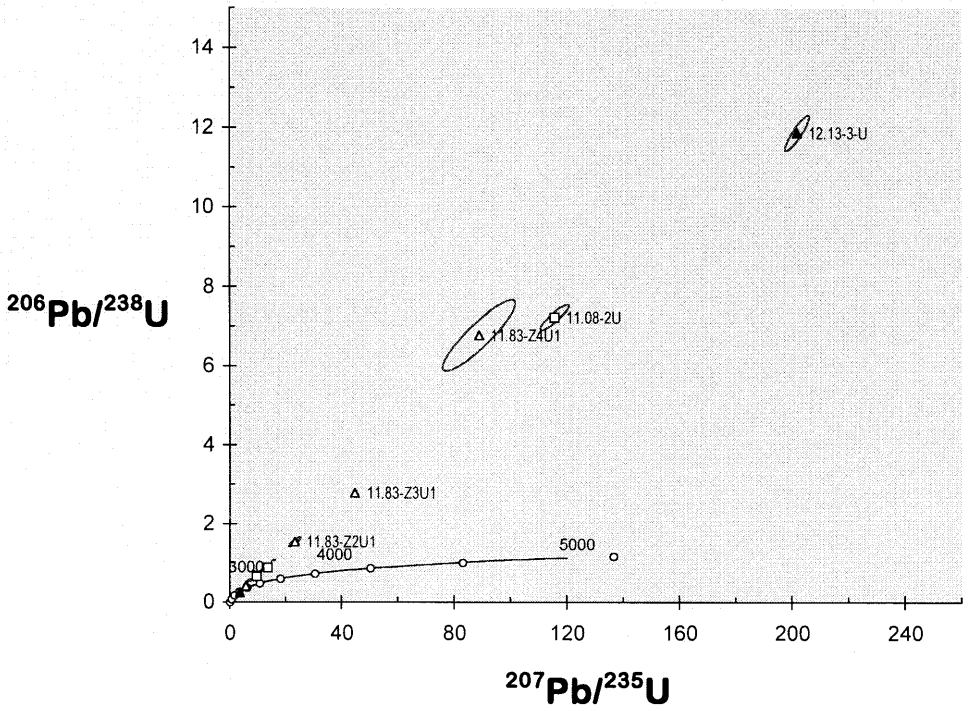

Figure 2: discordia plot of uraninites

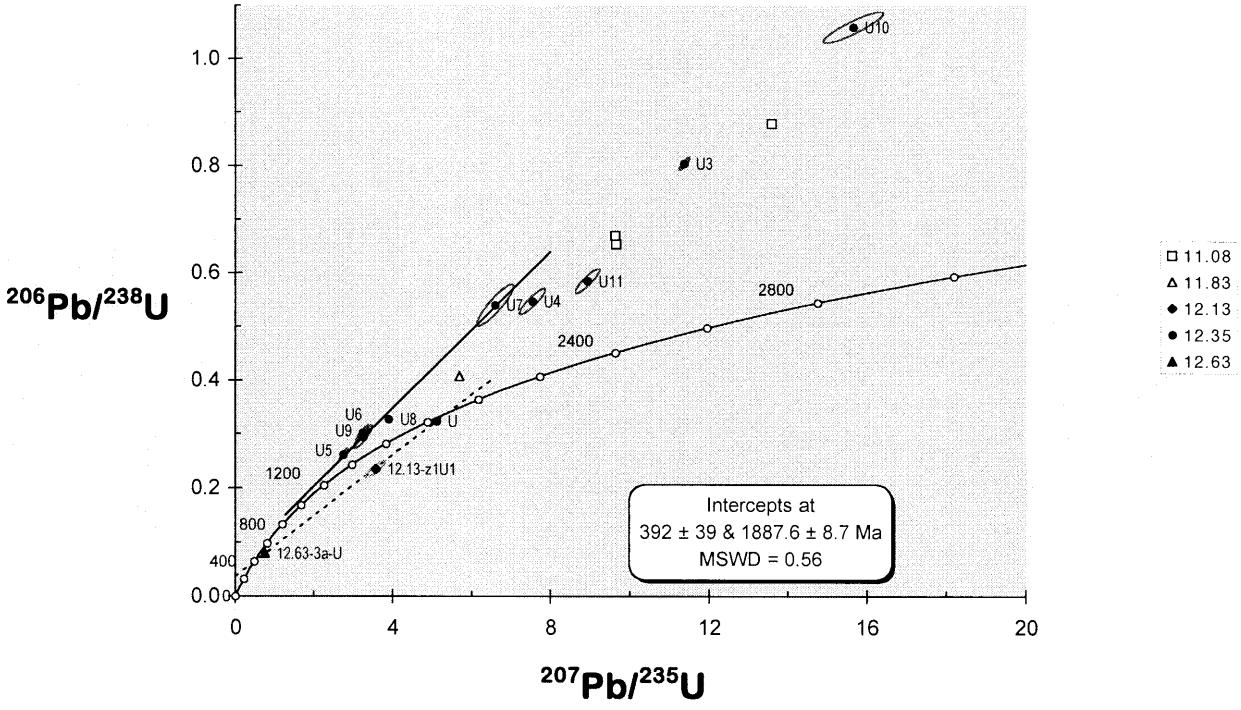

Figure 3: discordia plot of uraninites - enlarged

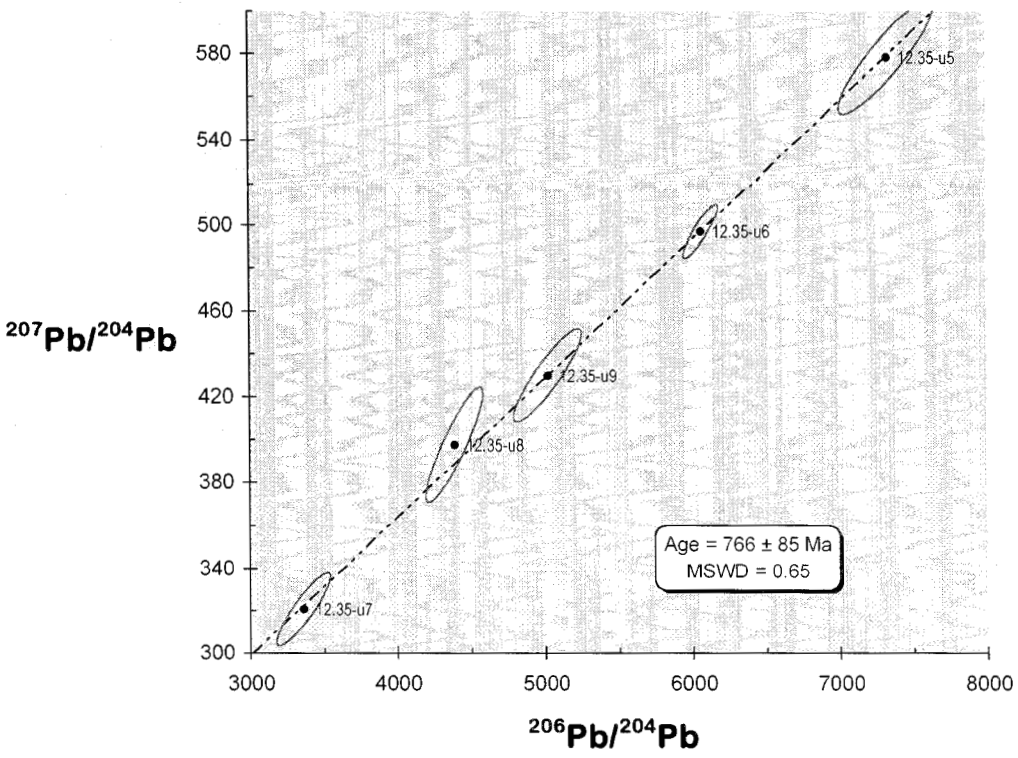

Figure 4: Pb-Pb isochron of uraninite vein at 12.35 m

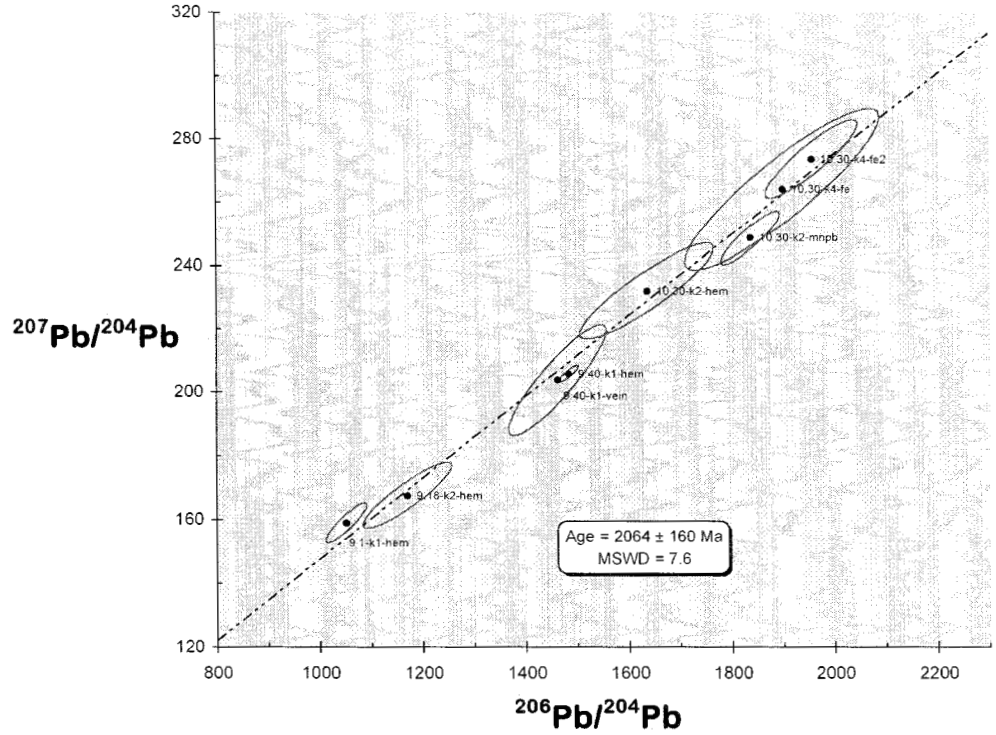

Figure 5: Pb-Pb isochron of hematite

Modelling of Uranium Transport at Bangombé (Oklo, Gabon)

B. Madé and E. Ledoux
Ecole des Mines de Paris, CIG, UMR Sisyphe, Fontainebleau, France

C. Ayora and J. Salas
Institut de Ciencies de la Terra, CSIC, Barcelona, Spain

I. Gurban
Intera KB, Stocholm

1. Introduction

The aim of this study is to describe the geochemical behaviour of uranium at Bagombé using a coupled reactive transport modelling approach. The calculations have been carried out with the coupled transport equations/chemical reactions code, HYTEC-2D developed by Ecole des Mines de Paris, Centre d'Informatique Géologique (Salignac, 1998). This coupled code takes into account numerous geochemical phenomena according to the local equilibrium assumption as aqueous complexation, redox reactions, adsorption on mineral surfaces, ionic exchange, dissolution-precipitation of minerals, coprecipitation reactions...

The results of the uranium behaviour modelling on the Bangombé site can be divided into two stages :

Stage 1 : Presentation and comparative description of the geochemical landscapes of Bangombé site for the campaigns of March 1993, July 1994 and September 1996 (Ledoux and Madé, 1997).

Stage 2 : Description of the coupled reactive transport modelling of uranium around the reaction zone using HYTEC-2D. Calculations with the water analysis of March 1993 campaign have been carried out through two steps :

- Several tests evaluate the sensibility to the presence or not of a buffer redox zone (equilibrium Fe^{II}-Fe^{III}) on the uranium behaviour around the reaction zone. The influence of the precipitation of secondary minerals (uranium solid phases, clays minerals, Al- Fe- oxi-hydroxides...) allows to understand their effects on the reactor existence.
- Description of the chemical parameters controlling the coffinite precipitation in the reaction zone. The presence of coffinite as secondary mineral in the reactor is directly connected with the aqueous silica concentration when the aqueous uranium concentration is controlled by the equilibrium with respect to uraninite.

In conclusion, the main parameters controlling the geochemical behaviour of uranium around the reaction zone are characterised. The sensibility of simulations results are exposed according to the modelling approach retained.

2. Geochemical landscapes of Bangombé site

The characterisation of the evolution of the geochemical behaviour of dissolved uranium over time is based on the campaigns of March 1993, July 1994 and September 1996 during which groundwater was sampled at Bangombé and analysed for major and trace elements and isotopes (Ledoux and Madé, 1997).

The saturation index of Bangombé waters are calculated with speciation CHESS code (van der Lee, 1997). A geochemical landscape can be drawn from the results of saturation index with respect to coffinite, uraninite, ferrihydrite, siderite, chalcedony and calcite for the different boreholes. For the campaign of March 1993, all groundwater samples are in equilibrium with chalcedony and are undersaturated with respect to calcite.
From the geochemical modelling (with CHESS code) of the situation observed in 1993, the groundwater leaching the Bangombé reactor zone could possibly be the result of the mixing of deep reduced water (sampled in BAX01), closed to equilibrium with uraninite and coffinite, and oxidised surficial water (sampled in BAX06), showing low content in U. The result of this mixing was observed in borehole BAX05 which appeared as undersaturated with regards to these U^{IV} minerals. Within the reactor zone, the groundwater became more reduced and showed equilibrated with uraninite and coffinite under redox buffered conditions regulated by Fe^{II}/Fe^{III} ratio through an equilibrium with siderite and ferrihydrite. Due to these reduced conditions the reactor zone was in situation of precipitating U, which explained the preservation of the within the weathered zone. Nevertheless, the isotopic ratio $^{235}U/^{238}U$ of dissolved U within the reactor (BAX03) was significantly depleted (0,683 %).
The modelling of the isotopic ratio plume (with METIS code ; Goblet, 1986) was made possible by introducing a source term of depleted uranium in the area of the reactor, mixing with a background of isotopically normal uranium. This model was able to explain the depleted ratio of 0,7201% measured in borehole BAX04 groundwater immediately above the reactor.

In 1996, the geochemical landscape remains similar apart from the fact that in general the waters look more oxidised, the U content of deep water has decreased and the U content of shallow waters has increased. This low content of deep waters comes together with a high oversaturation in $Fe(OH)_3$ which might induce coprecipitation or sorption of U. The U content within the reactor zone seems always controlled by uraninite and coffinite and the redox buffer Fe^{II}/Fe^{III} appears still active. BAX04 water is more oxidised and thus more undersaturated with respect to U minerals which probably indicates a more important contribution of surface water. BAX07 water downstream the reactor shows oxidised water as well.

Comparing the results of three analytical campaigns between 1993 and 1996, it appears that the redox buffered conditions identified within the reactor zone have been preserved although the redox potentials were regularly increasing. This might be the consequence of the intrusion of the boreholes through the geological medium. Surficial water could thus be mixed with deep water which becomes more able to dissolve uranium. This increase of U content is more evident in the shallow boreholes located inside the uranium ore body than in the deep ones where the solid phase in not able to compensate the undersaturation in U of the oxidised

water. The depletion of U can be due to coprecipitation or adsorption of aqueous U with ferric hydroxide or adsorption on clay minerals (Ledoux and Madé, 1997).

The chemical compositions of waters from March 1993 campaign (BAX03, BAX05 and BAX06 boreholes) have been retained to carried out the reactive transport modelling around the reactor zone.

3. HYTEC-2D modelling of the reaction zone (campaign 1993)

The geochemical behaviour of uranium and trace elements around the reaction zone at Bangombé has been carried out using an approach based on the reactive transport modelling. The calculations with HYTEC-2D code can help to understand the factors affecting the weathering of the rocks (sandstones, pelites and reactor...).
HYTEC-2D code take into account of numerous geochemical phenomena as aqueous complexation, redox reactions, adsorption on mineral surfaces (Fe and Al oxi-hydroxides, clays minerals...), ionic exchange, dissolution of primary minerals and precipitation of secondary minerals, coprecipitation of trace elements... The chemical reactions in HYTEC-2D model is based on the local equilibrium assumption.

3.1 Description of the hydro-geochemical system

The hydro-geochemical system studied in the reactive transport modelling is obtained from geochemical landscape of March 1993 campaign. The chemical compositions of aqueous solutions of the reaction zone, the sandstone and the pelites are characterised by the BAX03, BAX05 and BAX06 boreholes, respectively. The preliminary assumptions for the coupled transport equations/chemical reaction modelling are given by Gurban (1996) and Gurban *et al.* (1996). All groundwater samples are close to the equilibrium with chalcedony.
The BAX03 borehole is situated in the reactor zone, this groundwater is slightly oversaturated with respect to uraninite and coffinite, and on the other hand is in equilibrium with respect to siderite and ferrihydrite those one control the value of redox potential (Fe^{II}/Fe^{III}).

The rock matrix around the reactor zone is rich in organic matter and may act as a buffer zone against the atmospheric oxygen. Thus, the role of the redox buffer (Eh = 26 mV) protecting the reactor zone can be represented by two geochemical systems : (1) the organic matter (as graphite) or (2) the Fe^{II}/Fe^{III} redox couple defined by siderite/ferrihydrite equilibrium.
The both systems, organic matter and iron minerals, acting as a redox buffer might coexist in the matrix. There is an abundance of organic matter around the reaction zone (Bros *et al.*, 1993), however in groundwater, the kinetic reaction of the Fe^{2+}/Fe^{3+} couple are fast and this latter probability controls the value of the redox potential.

For the HYTEC-2D modelling, the control of the redox potential is based on the Fe^{II}/Fe^{III} redox couple defined by siderite/ferrihydrite equilibrium. The simulation results obtained have been compared with M3 results (Gurban *et al.*, 1998).

From 13 base components (H^+, Ca^{2+}, Na^+, K^+, Mg^{2+}, Al^{3+}, UO_2^{2+}, Fe^{2+}, Cl^-, HCO_3^-, $SiO_2(aq)$ and $O_2(aq)$), 117 chemical species and 62 minerals were generated.
The aqueous complexation reactions, redox reactions and precipitation/dissolution reactions were particularly investigated. The sorption on the surface minerals and the colloids were ignored at this stage of the modelling.

The local geochemical system is defined by four distinctive zones with the following characteristics :
- SANDSTONES : this domain is in equilibrium with chalcedony. The chemical composition of the aqueous solution is given by the borehole BAX05 (pH = 6.57 and Eh = 147 mV).
- PELITES : in this domain, the chalcedony controlling the aqueous silica concentration and the illite controlling the aqueous aluminium concentration are in equilibrium. The chemical composition of the aqueous solution is given by the surficial borehole BAX06 (pH = 5.64 and Eh = 277 mV).
- REACTOR : chalcedony (aqueous silica concentration), "argile de pile" (aqueous aluminium concentration) and uraninite (concentration of aqueous uranium) are the minerals in equilibrium. The chemical composition of the aqueous solution in the reactor zone is given by the borehole BAX03 (pH = 6.69 and Eh = 26 mV).
- REDOX BUFFER : this domain is in equilibrium with chalcedony and is defined from two iron minerals : siderite (ferrous carbonate) and ferrihydrite (ferric hydroxide). The chemical composition of the aqueous solution in the redox buffer zone is given by the borehole BAX05 with the uranium concentration in equilibrium with respect to uraninite.

3.2 Modelling of reaction zone without buffer redox zone

Without precipitation of secondary minerals

The pH value in the sandstone and in the reactor zone is uniform and close to the pH of the borehole BAX05 (pH = 6.57). The Eh value in the reactor zone increase from 26 to 100 mV under the percolation of oxidising water with BAX05 chemical composition. The total aqueous concentration of uranium in the reactor zone increases from 8.36×10^{-10} mol/l, the aqueous uranium concentration in equilibrium with respect to uraninite, to 9.9×10^{-8} mol/l. The oxidation of uraninite can be explain the aqueous uranium plume observed behind the reactor.

With precipitation of secondary minerals

The Eh value in the reactor zone increase from 26 to 60 mV, the pH decrease from 6.69 to 6.6. These evolution results are similar to their describe above. However, the precipitation of secondary solid phase in the reaction zone forces the Eh value at 60 mV (Eh = 100 mV without minerals precipitation).

In the reactor, the aqueous concentration of uranium is equal to 1.2×10^{-9} mol/l. The U aqueous concentration and the Eh value is controlled by the equilibrium with respect to the secondary mineral $UO_{2.25}$. The equilibrium equation of $UO_{2.25}$ is described in database by the following relation:

$$UO_{2.25} + 4\ H^+ = U^{4+} + 0.125\ O_2(aq) + 2\ H_2O$$

or

$$UO_{2.25} + 2.5\ H^+ = 0.5\ U^{4+} + 0.5\ UO_2^+ + 1.25\ H_2O$$

with equilibrium constant equal to log K = -11.785 and -4.819, respectively. The $UO_{2.25}$ mineral is a mixed phase with two uranium oxidation state, U^{IV} and U^{V}.
In the reactor, we can show the uraninite dissolution ($4x10^{-6}$ mol/l) and the $UO_{2.25}$ precipitation ($4.2x10^{-6}$ mol/l).

3.3 Modelling of reaction zone with buffer redox zone (siderite/ferrihydrite equilibrium)

Without precipitation of secondary minerals

When we consider the presence of a redox buffer zone, the water reaches equilibrium with respect to specific solid phases siderite ($FeCO_3$) and ferrihydrite ($Fe(OH)_3$). These phases act as a "redox buffer" maintaining an Fe^{2+}/Fe^{3+} equilibrium in the aqueous solution. This matrix protects the uraninite in the reaction zone from potential dissolution by oxidising water (chemical composition of borehole BAX05).

An increase of the pH is observed downstream the reactor (Fig. 1) varying in the sandstone from 6.6 to 6.8 and varying in the reaction zone from 6.69 to 6.86. This increasing of pH is consistent with the siderite dissolution of the redox buffer zone (aqueous concentration of HCO_3^- increases). The Eh value in the reactor zone change from 26 to 100 mV (Fig. 1). In the redox buffer zone in front of reactor zone, the Eh increase from 135 to 147 mV. Behind the reactor, the Eh describe a reductive plume.
The figure 2 shows the evolution of the amount of siderite and ferrihydrite in the redox buffer zone. Under the oxidising groundwater from the sandstones (chemical composition of BAX05 borehole), the ferrous mineral siderite is destroyed. The total aqueous concentration of uranium in the reaction zone increase from $8.4x10^{-10}$ mol/l (tot U(aq) in equilibrium with Uraninite at 26 mV) to $5.7x10^{-7}$ mol/l (tot U(aq) in equilibrium with Uraninite at 100 mV). The impact of the redox buffer zone on the uranium transport can be observed. Thus, a diminution of the uranium transport downstream the reactor is observed (Fig. 3). This plume of depleted uranium can be explain the anomaly ratio $^{235}U/^{238}U$ characterising an isotopic signature from the reactor zone.

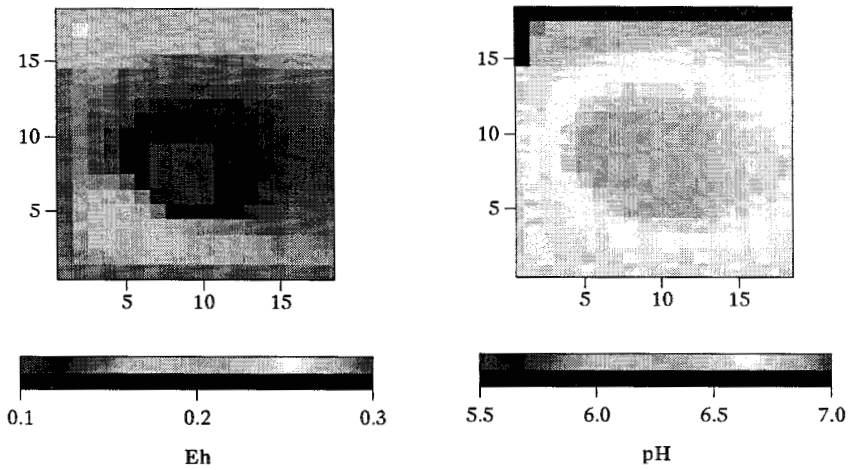

Figure 1 - Evolution of Eh and pH values around the reaction zone (with redox buffer).

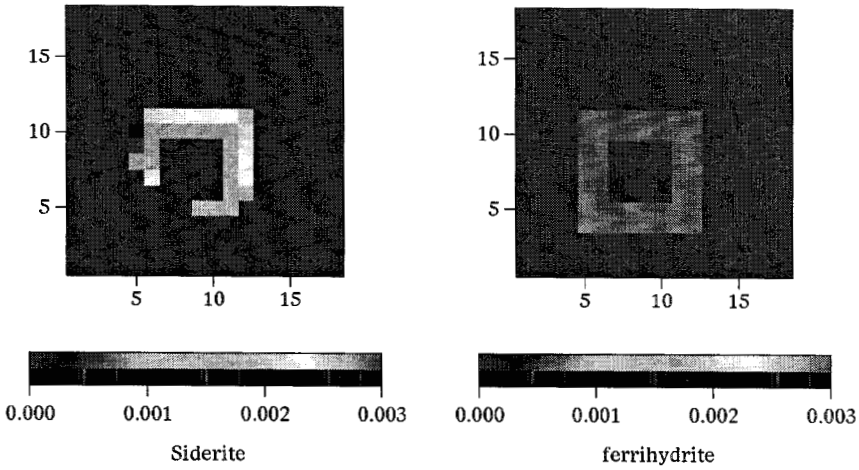

Figure 2 - Evolution of amount of siderite and ferrihydrite (mol/l) in the redox buffer zone.

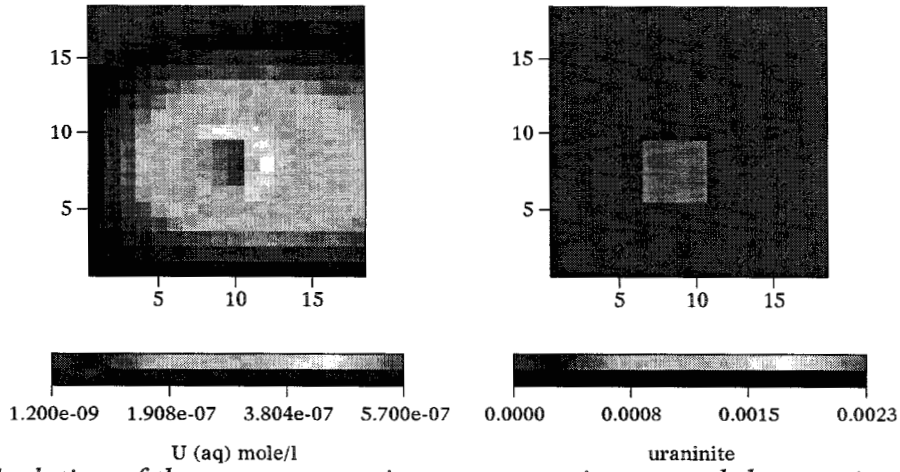

Figure 3 - Evolution of the aqueous uranium concentration around the reaction zone (mol/l). Uraninite concentration in the geochemical system (mol/l).

With precipitation of secondary minerals

A part of the redox buffer zone is destroyed characterising by the siderite dissolution (Fig. 2). The Eh value in the reactor zone increases from 26 to 40 mV and the pH from 6.69 to 6.86 (Fig. 4). This increasing of pH value can be connected with the siderite dissolution releasing bicarbonate ions (HCO_3^-). The aqueous concentration of U (Fig. 5) is similar with the case controlled by the equilibrium with respect to $UO_{2.25}$ mineral (tot U(aq) = 1.25×10^{-9} mol/l). The "illite de pile" controls the aqueous aluminium concentration in the reactor. A precipitation of illite, containing Fe^{3+} ions, is simulated at the boundary between pelites and sandstones. This illite formation can characterise a redox front.

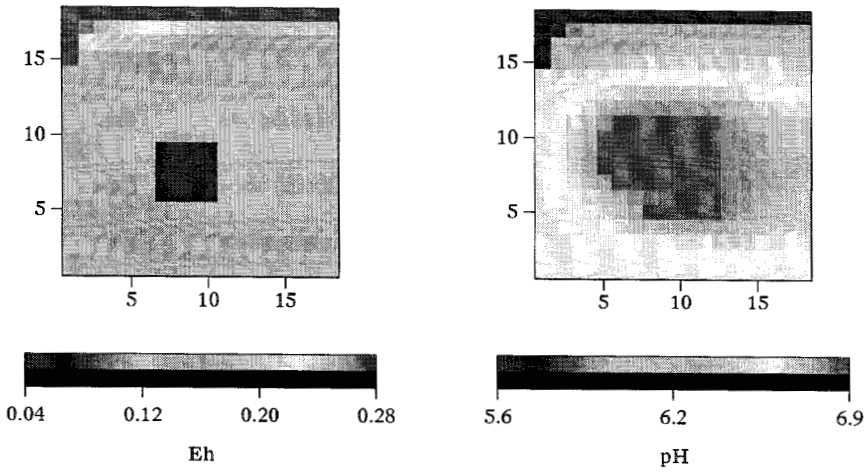

Figure 4 - Evolution of Eh and pH values around the reaction zone (with redox buffer and with precipitation of secondary minerals possible).

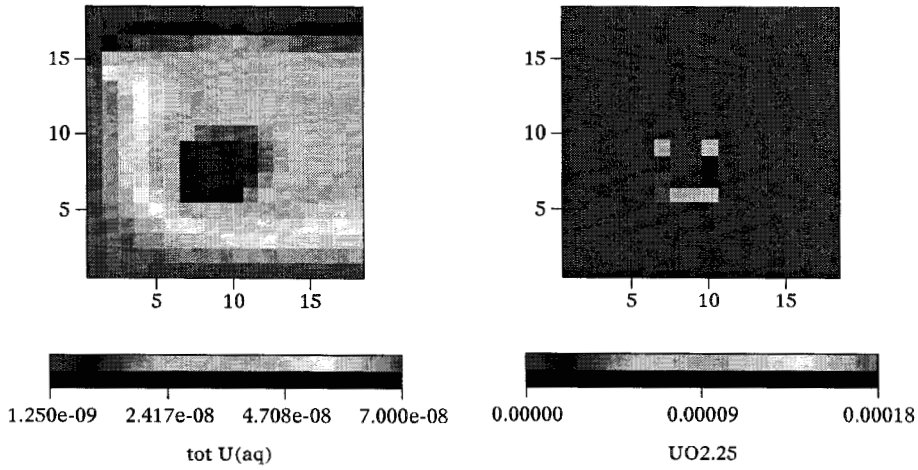

Figure 5 - Evolution of the aqueous uranium concentration around the reaction zone (mol/l). $UO_{2.25}$ concentration (mol /l) in the reaction zone (with precipitation of minerals possible).

In the redox buffer zone, the amount evolution of siderite and ferrihydrite shows a total destruction of siderite ($3x10^{-2}$ mol/l) and a slightly dissolution of ferrihydrite ($4x10^{-5}$ mol/l) under the influence of oxidising water. The Eh and pH evolution show successive redox buffer describes by several "plateau" in the Eh-pH values. After the siderite dissolution, additional Fe^{2+}/Fe^{3+} equilibrium between Magnetite/Nontronite or between Daphnite-14A/Cronstedtite-7A controls the Eh value.

In the reactor, the Eh increases from 26 to 43 mV with a maximum value close to 55 mV. The pH varies from 6.69 to 6.86 due to the HCO_3^- ions coming from the siderite dissolution.

Conclusions

In the case where the precipitation of secondary minerals are permitted, the aqueous distribution of uranium around the reactor zone is similar with or without redox buffer zone taken into account. The concentration of aqueous uranium and Eh is controlled by the equilibrium constraint with respect to $UO_{2.25}$ solid phase. It means that the precipitation of minerals (as uraninite, $UO_{2.25}$...) has a higher impact on the uranium behaviour than the presence or not of the redox buffer zone. The impact of redox buffer zone on the uranium transport has been observed in the field. Downstream the reactor, the Eh describes a reductive plume and a diminution of the uranium transport is shown. The plume of depleted uranium can be explain the anomaly ratio $^{235}U/^{238}U$ characterising an isotopic signature from the reactor zone.
In these simulation tests, the U secondary mineral precipitating ($UO_{2.25}$) is the mixed solid phase U^{IV}-U^{V}. Nevertheless, this phase is not dominant in the reactor zone, but the coexistence between uraninite and coffinite has been observed frequently at Bangombé.

3.4 Precipitation of coffinite in reaction zone

Uraninite-Coffinite stability domains

At Bangombé, the uraninite is omnipresent, excepted in the recovering bed. The weathering of uraninite with the aqueous solution of sandstones rich in silica leads at the coffinite formation following the stoechimetric relation :

$$UO_2 + H_4SiO_4 = USiO_4 + 2\,H_2O$$

In the reactor zone, the coffinite has been observed (Bros *et al.*,1993). The coexistence of uraninite and coffinite is frequently described in the sandstone environments rich in uranium (Hemingway, 1982).
In the HYTEC-2D simulations, the oversaturation with respect to chalcedony is possible allowing to reach the silica activity necessary to the coffinite precipitation in the reactor zone.
In the reaction zone the pH value increases from 6.6 to 6.9 and the Eh remains constant close to 26 mV (Fig. 6). A plume of reducing Eh (from 40 to 60 mV) is simulated behind the reaction zone indicating the oxidising dissolution of reactor.
On the figure 7, we can observe the dissolution of uraninite and the precipitation of coffinite in the reactor (oversaturation with respect to chalcedony). The Eh value in the reactor is close to the initial Eh (26 mV) because, the coffinite is a U^{IV} mineral as the uraninite and its stability is function especially to the silica concentration coming from sandstones (BAX05 borehole).

The presence of coffinite in the reactor zone can be connected with two main physico-chemical parameters :
- the arrival of aqueous solution with an enrichment of silica content (and uranium U^{IV}) ;
- the existence of redox buffer zone controlling the Eh value close to reducing conditions.

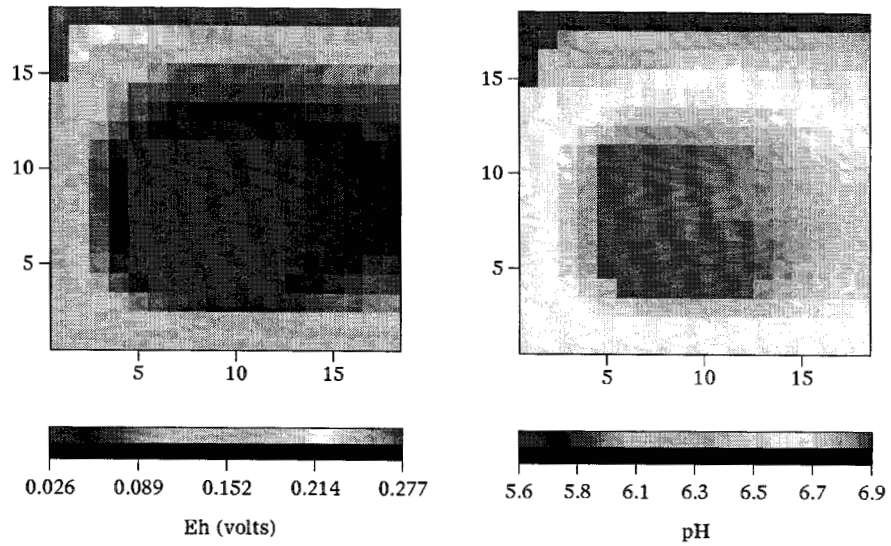

Figure 6 - Evolution of Eh and pH values around the reaction zone with coffinite precipitation (oversaturation of chalcedony).

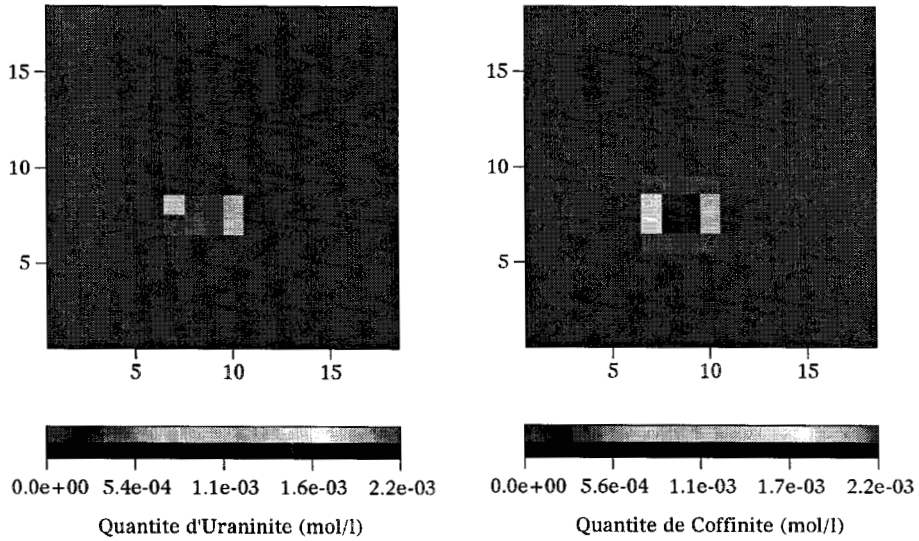

Figure 7 - Evolution of uraninite and coffinite amount (mol/l) in the reaction zone.

After the siderite destruction into the redox buffer zone, the Fe^{2+}/Fe^{3+} equilibrium is controlled by minerals containing ferrous ions as magnetite, daphnite or argile de pile. Frequently, the last redox buffer zone is characterised by the geochemical system ferrihydrite-argile de pile constraining the Eh value close to 80 mV. In this case, the aqueous uranium concentration in the buffer is equal to 3.5×10^{-8} mol/l (U(aq) = 6.8×10^{-8} mol/l in borehole BAX05). Under the oxidising groundwater, the illite de pile is dissolved and the Eh increases to 130 mV. This increasing of Eh produces the oxidation of U^{4+} to U^{6+}. The coffinite precipitation is stopped and the aqueous uranium is controlled by the formation of U^{VI} minerals (Fig. 8) as haiweeite ($Ca(UO_2)_2(Si_2O_5)_3(H_2O)_5$) or uranophane ($Ca(UO_2)_2(SiO_2)_2(OH)_6(H_2O)_2$) observed around the reaction zone at Bangombé. The aqueous uranium concentration calculated is equal to 8.5×10^{-8} mol/l. The dissolution rate of coffinite is 1.31×10^{-6} mol/l/yr and the precipitation rate of haiweeite is 6.38×10^{-7} mol/l/yr ; thus, the near total of uranium is incorporated into a U^{VI} mineral.

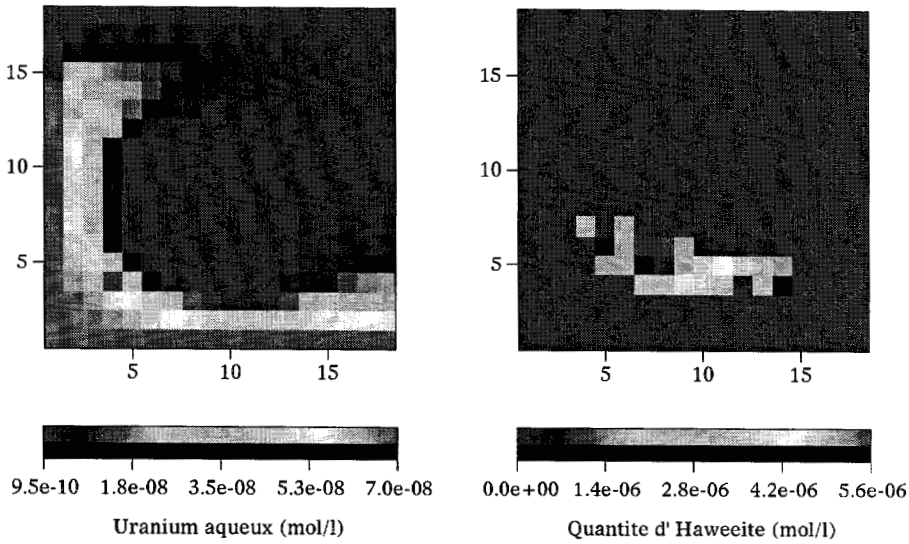

Figure 8 - Aqueous uranium concentration (mol/l) and amount of haiweeite precipitated (mol/l) around the reactor zone.

4. Conclusions

The deterministic approach using the coupled reactive transport code HYTEC-2D has allowed to propose some understanding the hydro-geochemical behaviour of the reaction zone at Bangombé.

The reaction zone is under the influence of oxidising groundwater producing water-rock interactions. A redox buffer zone based on Fe^{II}/Fe^{III} equilibrium which can be characterised by different minerals as siderite/ferrihydrite, daphnite/ferrihydrite, magnetite/nontronite or argile de pile/ferrihydrite allows chemical protection of the reactor zone. However, the oxidising groundwater dissolves the redox buffer zone and this one cannot permanently protect the reactor of oxidation. Thus, a plume of depleted uranium ($^{235}U/^{238}U$ ratio) coming to the dissolution of the uraninite from the reactor can be simulated by the coupled reactive transport codes. The aqueous uranium concentration predicted is in good agreement with the field measurements.
The aqueous uranium concentration is controlled around the reaction zone by uraninite and coffinite (U^{IV} minerals) for Eh value less than 80 mV and by uranophane or haiweeite (U^{VI} minerals) in more oxidising conditions.

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Geochemical environment around Okélobondo reactor zone (Gabon)

R Mathieu and M Cuney
(Regis.Mathieu@g2r.uhp-nancy.fr)
CREGU - UMR G2R 7566 Géologie et Gestion des Ressources Minérales et Energétiques,
Université Henri Poincaré, BP239, 54506 Vandoeuvre-lès-Nancy Cedex, France

For the past twenty-five years, all geochemical and mineralogical studies around Okélobondo reaction zones (Franceville basin, south-eastern part of Gabon) have been mainly focused on (i) the detection of high temperature fluids circulation issued from the functioning of the natural nuclear reactors which have induced strong disturbance in the host sandstones and (ii) associated near-field migration of fissiogenic products such as Nd and Cs (Sère, 1996) or Pu (Bros, 1993). A bibliographical synthesis (Michaud and Mathieu, 1998) on the geological history of the Franceville basin and the nuclear reactor zones has allowed (i) to recognise at least twelve main types of fluid circulation in relation with two main diagenetic phases, four major tectono-metamorphic events, one supergene alteration phase and (ii) to identify four major episodes of elemental migration. Accessory minerals behaviour is useful to better constrain the geochemical mass balance in U, Th, REE migration processes existing in the near-field, related specifically to the reactors functioning and the far-field, related to basin-scale circulation. Fractures filled by minerals offer the opportunity to gain some key answers to problems such as transport of chemical elements and preferential flow pathways, evolution relative to time or scale of migration.

Extreme rare earth element migration processes has been discovered in silicified sandstone of the Lower Proterozoïc series in the Franceville basin (Gabon) and particularly around Okélobondo natural reaction zones. The silicified sandstone present anomalous Th/La ratio (around 1.8) higher than Archean and Proterozoïc metasedimentary rocks (Th/La≈0.25). Anomalous Th/La ratio of silicified sandstone is due to monazite alteration. Three stages of monazite alteration were observed: (1) non-altered monazites, (2) corroded monazites mixed with Th-silicate alteration phases, (3) totally altered monazites, the residual phase corresponding to a microcrystalline Th-silicate. The Th/U ratio increase from monazite (Th/U=20) to the Th-silicate phase (Th/U>50) is interpreted as the effect of an oxidising fluid able to leach U together with LREEs and P. Alteration of the zircon crystals lead to the new-formation of a Zr/LREE-Si/P phase in cracks fillings and/or along growth zones. Galena inclusions are also common in such external growth zones of zircon crystals. The volume of newly formed galena (2 to 14 vol. %) largely exceed the amount of lead (< 0.1 wt.%) which was produced by radioactive decay of U and Th in the accessories. Most of the lead has been introduced during the diagenetic event from external radiogenic ($^{206}Pb/^{204}Pb$ = 7000 for the near-field OK84bis sample) and/or non-radiogenic sources.

Structural and micro-structural data reflect at least three major tectonic phases in agreement with Hassenforder et al. (1994): (1) a first extensive phase related to normal faulting oriented NE-SW,

N-S, E-W and NW-SE, (2) a second extensive phase related to regional flexuration responsible for major N-S faulting associated to NW-SE and NE-SW collapses and (3) a compressive phase related to dextral-inverse N15°, sinistral-inverse N165° strike-slip faults, dextral NW-SE and sinistral NE-SW reactivation. These 3 phases are well correlated to 3 stages of mineral paragenesis. Stage I consists of overgrowths and dissolution around detrital quartz, illitisation and chloritisation of detrital quartz grains, monazite and zircons dissolution, several REE phosphate minerals, mainly florencite, crystallisation in FA sandstone matrix and subvertical fractures fillings with mainly chlorite and quartz and at a lesser extent calcite, barren bitumen and Pb/Fe/Cu sulphides. Stage II consists of mineralised bitumen incorporation and Pb/Fe/Cu sulphides crystallisation in FA sandstone matrix and sub-vertical fractures filled by same minerals than stage I but carbonates, mineralised bitumen and sulphides are the more important phases. Stage 3 presents the fracture filling of stage I plus several oxyhydroxides and sulphates. The transition between stages I and II may correspond to an evolution of fluid geochemistry because of high salinity variation from 0.2-30 wt.%eq. NaCl to more than 30 wt.%eq. $CaCl_2$. Low saline fluids contain only Na and highly saline fluids contain Na with Ca and Li.

This data points out the basin-scale mobility of LREEs and U by phosphate-complexes in an oxidising highly saline fluid. Mineralising fluid have migrate during the second extensive phase, mainly through N-S fractures drains previously initiated by the first extensive phase.

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REACTIVE TRANSPORT MODELLING AROUND THE OKELOBONDO URANIUM DEPOSIT (OKLO, GABON)

J. Salas, C. Ayora
Institut de Ciències de la Terra Jaume Almera, CSIC, Barcelona (Spain)

Abstract

The Okelobondo uraninite massive body is located in the Oklo district at a depth of about 300 m. Groundwater samples from boreholes located at shallower depths (100 to 200 m) show neutral to basic pH and reducing conditions, and they are saturated with respect to uraninite (Type I water). In constrast, deeper samples collected in the vicinity of the ore body are oxidizing (Eh= 320 to 470 mV) and slightly basic (pH= 7 to 8.5) (Type II water). Under these conditions uraninite is subsaturated and dissolves. These oxidizing conditions at depth are unique, and their origin deserves investigation given that they affect the chemical stability of uranium oxide under repository conditions. We analyzed the feasibility of the processes leading to this situation by simulating the water flow and the chemical reactions three 1D columns. Regional lithology is made up of sandstones, pelites and dolomitic pelites arranged subhorizontally.

From the hydrogeological point of view, the Okelobondo deposit is situated in the mixing zone of two topography-driven groundwater flow systems which discharge in to the river Mitembe located above the deposit. Meteoric waters infiltrating through the upper boundary are acidic and dissolve the Fe-bearing silicates (chlorite and illite). As a result, the water samples from the upper part of the system (Type I) show pH-Eh values that decrease along the Fe^{2+}-$FeOH)_3$ equilibrium. This feature is currently observed in many localities.

However, most of the water forming the eastern flow system infiltrates in the Masango plateau, where important Mn deposits (rhodochrosite and manganite) overly the pelites. The meteoric water dissolves the Mn-bearing minerals, yielding Eh-pH values close to the rhodochrosite-manganite equilibrium. On account of the high pH values after the dissolution of the Mn-strata, the water infiltrating into the pelites dissolves a low amount of Fe-silicates before attaining equilibrium. As a result, the Fe content of these waters (Type II) is lower than the Mn content (as observed), and the Mn^{2+}-Mn^{3+} pair controls the pH-Eh evolution of the system (too oxidizing for uraninite to be stable). Therefore, it may be concluded that the abundance of a Mn-carbonate in the recharge area is required to obtain the high Eh-pH found at depth in the Okelobondo mine.

1.-Introduction

The Okelobondo uraninite body is located at a depth of about 300 m, and is affected by oxidation/dissolution processes which lead to high U concentration in water and precipitate UO_2-bearing minerals. The presence of high pH-high pE water at depths similar to those expected for radioactive waste confinement is unusual. Since this depth is similar to radioactive waste repository, it is important to determine whether the processes leading to this situation are site specific or whether they can be found in other places.

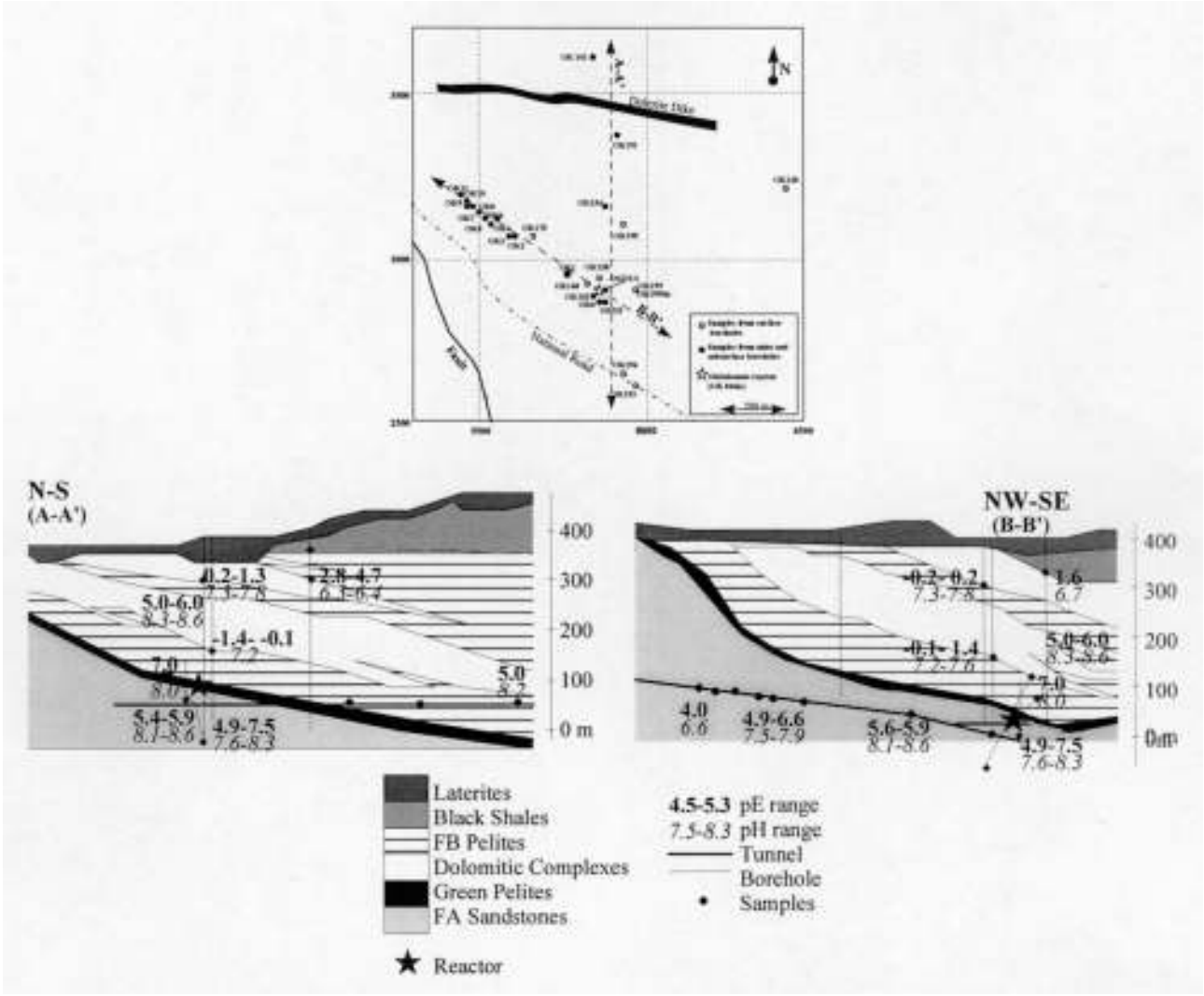


Figure 1: *Map of sample location in Okelobondo area. Geological sections A-A' and B-B', including the pH-pE values of the water samples and the OK84bis uraninite body*

The aim of the study is to test the feasibility of the hypotheses that the high pH-pE values found at depth are due to water-rock reactions along the flow path. To this end, reactive transport modelling is used to test the different hypothetical scenarios of the ground water system around the Okelobondo uranium mine.

2. Geological setting

The Okelobondo uranium deposit is part of the uraniferous system of the basal detrital sediments of the Franceville Basin, in the Republic of Gabon. The domain of the present study is described by two geological sections N-S and WNW-ESE, which include the OK84 reactor (Fig. 1). The higher areas are located in the Massango plateau, in the SE margin of the sections, whereas the natural drainage area is the valley of the Mitembe river, in the central part of the sections.

The sedimentary materials are made up of FA-sandstones and FB-pelites with some interbedded sandy-dolomitic bodies called 'Complexes'. The OK84 uraninite body is located at the top of the

FE sandstones. Economically important manganese-rich pelites overlie the FB-pelites and complexes and outcrop in the plateau. They are made up of a compact layer and a laminated layer (plate level) of rhodochrosite ($MnCO_3$) and manganite (MnOOH), which constitute the main part of the deposit (Bouladon et al., 1965). Finally, a few metres thick lateritic soil is developed.

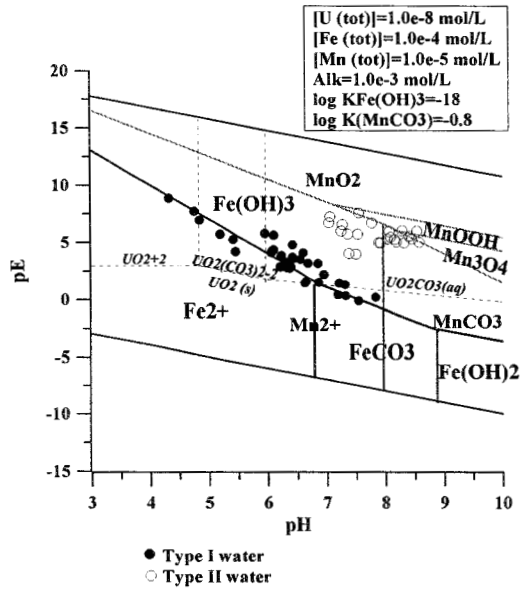
3. Ground water chemistry

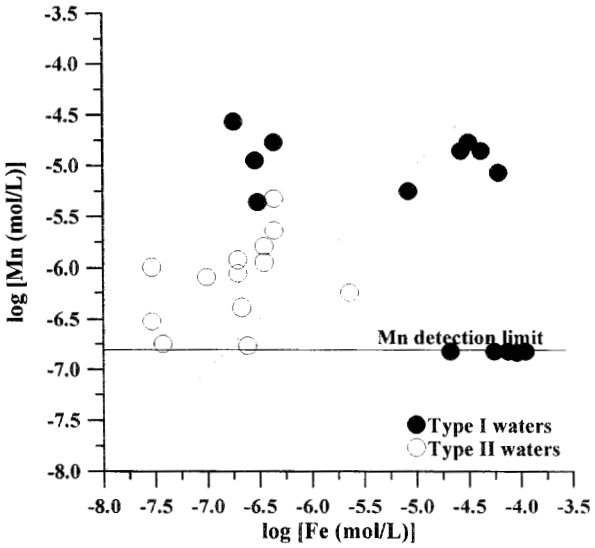
Ground water was collected from several boreholes in the area (Gurban et al., 1996; Bruno et al., 1997). The pH an pE values (obtained from Eh field measurements) are plotted in Figure 1. Two types of ground water are distinguished in a pH-pE diagram (Fig. 2a):

Type I: the pH-pE values are plotted parallel to the Fe^{2+}-$Fe(OH)_3$ equilibrium. This group could be divided into two subgroups. Type I-A showed more oxidizing conditions, neutral to slightly acidic, and subsaturated with respect to uraninite; the samples were from boreholes drilled from galleries in FA-sandstones (to the NW of the BB' section in Fig. 1). Type I-B showed neutral to basic pH and reducing conditions, and were saturated with respect to uraninite; the samples were from boreholes drilled in the Complexes and FB-pelites above the uranium deposits.

Type II: water samples were oxidizing, slightly basic and subsaturated with respect to uraninite. The samples were collected in boreholes drilled from mining galleries around the ore body in the FA-sandstones and at the base of the FB-pelites.

The two water types described above also differed with respect to the Fe/Mn ratio. Type I and II samples showed Fe/Mn ratios higher and lower than 1, respectively (Fig. 2b). The above description (Fig. 2a) suggests that the Fe^{2+}-$Fe(OH)_3$ played an important role in controlling the chemistry of the Type I water. This control has been described commonly in groundwater and especially around the Bangombe uranium deposit, 20 km south in the same lithologies. The relative abundance of Mn with respect to Fe, and the location of the type II water samples close to equilibrium with Mn-minerals (Fig. 2a), suggest that the pair Mn^{2+}/Mn^{3+} could play a significant role in controlling the pH-pE of this type of water.





(a) **(b)**

Figure 2: a) *pH-pE relations of Okelobondo water samples in the system U-Mn-Fe-H_2O at 25°C;* ***b)*** *Fe-Mn plot of water samples from Okelobondo.*

4.- Methodology

4.1.-Okelobondo hydrological model

The hydrogeochemical system is based on a local flux model described in earlier studies (Gurban et al., 1992, 1996). This model describes the existence of two convective cells formed by a topography-driven flow. One cell is located to the W of the river Mitembe, which mainly drains the FA sandstones. The other cell is located to the E of the river, and crosses the FB-pelites, the dolomitic complexes and the FA-sandstones (Fig. 3a-b). The existence of a superficial short path, through the lateritic soil was assumed to be independent of the convective path. The porosity values were estimated to range between 1 and 10% by means of environmental tracers (^{18}O, ^{3}H), confirming that the permeability around the reaction zone is very low. The residence time was calculated as tens of thousands of years (supported by the ^{14}C measurement in well OKH3, which suggests an apparent age for the water of 20,000 years).

We built a model, which was divided into six different lithological domains (Fig. 3b): FB-pelites, dolomitic complexes, Mn-deposits, the uranium body, FA-sandstones and a basement fault area. Three conceptual 1D models were built, in accordance with characteristic flow paths and crossing the different lithologies, in order to identify the main geochemical processes, which control the water composition,

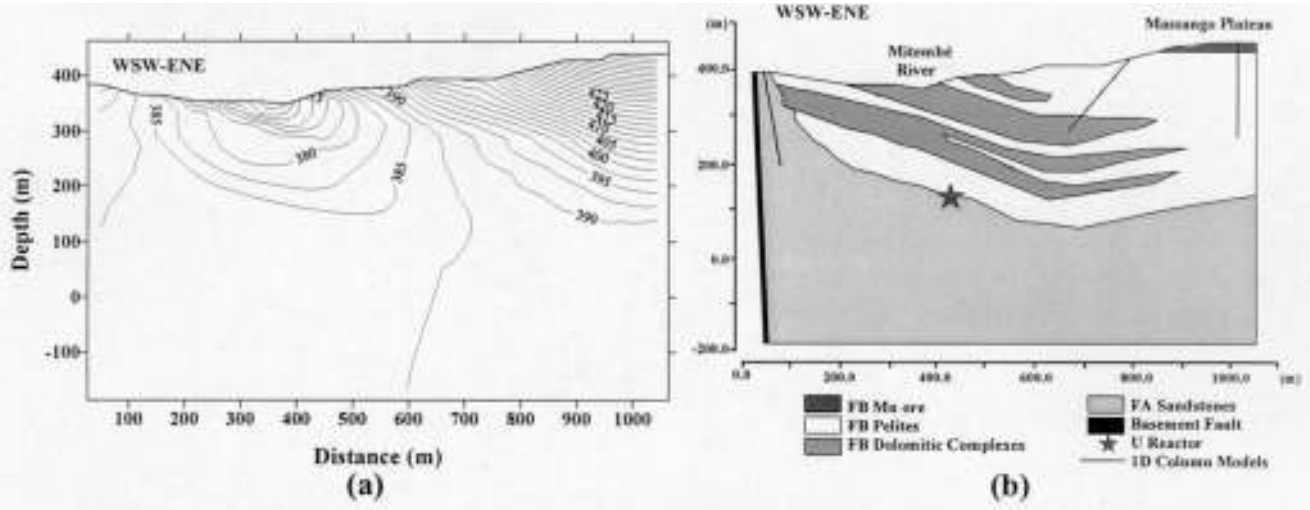


Fig. 3: a) *Potentiometric lines resulting from the hydrogeological properties and boundary conditions described in the text;* ***b)*** *lithologic domains of the Okelobondo system including the flow path considered in the 1D models.*

Primary aqueous species
H_2O, $Al(OH)_4^-$, Na^+, Ca^{+2}, Mg^{+2}, Mn^{+2}, K^+, Fe^{+2}, $SiO_2(aq)$, SO_4^{-2}, $UO_2(CO_3)_3^{-2}$, HCO_3^-, H^+, e^-
Aqueous complexes

OH^-, Al^{+3}, $Al(OH)_3(aq)$, $Al(OH)_2^+$, $AlOH^{2+}$, CO_3^{-2}, $CO_2(aq)$, $O_2(aq)$, $CaCO_3(aq)$, Mn^{+3}, $MnCO_3(aq)$, MnO_4^{2-}, MnO_4^-, $Mn_2(OH)^{3+}$, Fe^{+3}, $Fe(OH)_3(aq)$, $Fe(OH)_2^+$, $FeHCO_3^+$, $Fe(OH)_4^-$, $FeCO_3(aq)$, *HS^-*, *S^{2-}*, *$UO_2(CO_3)^{-4}$*, *UO_2^{+2}*, *$U(OH)_4$ (aq)*, *UO_2CO_3 (aq)*, *UO_2OH^+*, *$UO_2(OH)_2$ (aq)*		
Minerals	**Dissolution rate constant, 25°C**	**Refer.**
Illite	= muscovite	
Chlorite	= muscovite (Fig. 10)	
Muscovite	$(4.2\cdot10^{-12}\cdot a_H^{0.38}) + (1.5\cdot10^{-13}\cdot a_H^{0.09}) + (1.1\cdot10^{-15}\cdot a_H^{-0.22})$	(1)
Kaolinite	$1.7d\text{-}11\ a_H^{0.5} + 2.5d\text{-}17\ a_H^{-0.3}$	(2)
Chalcedony	precipitation in equilibrium	
Pyrolusite	precipitation in equilibrium	
$Fe(OH)_3$	precipitation in equilibrium	
Quartz	$4.1\cdot10^{-14}$	(3)
Uraninite	$(1.4\cdot10^{-8}\cdot a_H^{0.53}) + 10^{-12}$	(4)
Rhodochrosite	= calcite	
Calcite	$4.64\cdot10^{-7}$	(5)
Manganite	10^{-7} (assumed)	
Dolomite	$2.2\cdot10^{-8}$	(6)
Smectite	$[(10^{-9}\cdot a_H^{0.38}) + (10^{-13}\cdot a_H^{-0.22})]\cdot(\Omega^{0.1}-1)^{13}$	(7)
K-Feldspar	$(10^{-10}\cdot a_H^{0.5}) + (2.5\cdot10^{-17}\cdot a_H^{-0.45})$	(8)
Plagioclase	$(7.5\cdot10^{-10}\cdot a_H^{0.5}) + (1.2\cdot10^{-14}\cdot a_H^{-0.30})$	(9)
Pyrite	$[6.4\cdot10^{-9}\cdot(a_{H^+}^{-0.11}\cdot a_{O2(aq)}^{0.5})]$	(10)

Table I: *Geochemical model and kinetic data used in the calculations. Equilibrium constants from EQ3NR datafile (version R10, Wolery, 1992), except for Illite (Gurban et al., 1996). References: (1) Wieland and Stumm, 1992;(2) Ganor et al., 1995; (3) Rimstidt and Barnes,1980; (4) Bruno et al., 1991; (5) Inskeep and Bloom, 1985; (6) Mucci and Morse, 1983; (7) Cama et al., 1995; (8) Schweda, 1989,1990, Blum & Stillings, 1995; (9) Chou & Wollast, 1985, Casey et al., 1991; (10) Nicholson, 1994.*

4.2.-Geochemical model

Fourteen primary species and twenty-eight additional aqueous complexes were selected to describe the pore aqueous solution in the Okelobondo system (Table I). The composition of the aquifer lithologies was described with the following minerals: illite, smectite, chlorite, $Fe(OH)_3$(am), kaolinite, plagioclase, k-feldspar, dolomite, calcite, siderite, rhodochrosite, pyrolusite, manganite, quartz, chalcedony, pyrite and uraninite. The equilibrium constants were included in the EQ3NR datafile (Wolery, 1992).

4.3. Numerical codes

The reactive transport calculations were performed with the computer codes RETRASO, developed by the UPC-CSIC group (Saaltink et al., 1997) under a contract with ENRESA, and HYTEC-1D, developed by the Ecole des Mines de Paris (van der Lee, 1997).

5.- Results: The Pelite-Dolomitic Complex and Sandstone 1D Models

5.1.-The pelite and dolomitic complex system

A heterogeneous column with pelites, in the first 180 metres, and dolomitic complex lithologies, in the following 20 metres was assumed. The pelites are the most representative lithology in the Okelobondo System and infiltration takes place through them (Table II).

Solute	Initial pore water	Recharge Water	Lithology	Minerals	Initial vol. frac. (%)	Reac. Surf. (m^2/m^3)
Fe	4.11d-4	1.00d-8	Pelites	Chlorite	10.00	1.00d-0
Na	2.00d-3	1.00d-4		Illite	40.00	1.00d-1

Ca	9.08d-4	1.00d-6
K	5.00d-5	5.00d-5
Mg	9.63d-4	1.00d-6
Al	1.00d-6 (2)	1.00d-6
HCO_3	5.36d-3 (1)	2.00d-3
Si	4.87d-4	1.65d-4
Mn	3.39d-5	1.00d-8
pH	6.87	4.50
pE	3.00	12.00

	Plagioclase	10.00	1.00d-0
	Dolomite	10.00	1.00d-4
	Quartz	30.00	1.00d-2
	K-Feldspar	5.00	1.00d-2
	Manganite	0.00	1.00d+2
	Rhodochrosite	0.00	1.00d+2
	Smectite	0.00	1.00d+2
	Kaolinite	0.00	1.00d-3
	Pyrolusite	0.00	**
	Chalcedony	0.00	**
	$Fe(OH)_3$	0.00	**
Dolomitic Complexes	Dolomite	25.00	1.00d-1
	Chlorite	3.00	1.00d-0
	Illite	30.00	1.00d-1
	K-Feldspar	5.00	1.00d-2
	Quartz	30.00	1.00d-2
	Smectite	0.00	*1.00d+2
	Rhodochrosite	0.00	*1.00d+2
	Manganite	0.00	*1.00d+2
	Kaolinite	0.00	*1.00d-3
	Pyrolusite	0.00	**
	Chalcedony	0.00	**
	$Fe(OH)_3$	0.00	**

Table II: *Initial and boundary conditions used in the Pelite-Dolomitic Complex 1D model. (1) equilibrium with dolomite ; (2) equilibrium with chlorite, (**) precipitation in equilibrium.*

Chlorite dissolution was the main geochemical mechanism analyzed: it added Fe^{2+} ions to the system, they were subsequently oxidized to Fe^{3+}, and $Fe(OH)_3$(am) precipitated. Water remained subsaturated in chlorite through the column, except in the dolomitic complexes (Fig. 4a). The Fe content in solution attained values of the order of magnitude measured in the type I water samples (10^{-5} mol/L). This concentration decreased slightly in dolomitic complexes because of chlorite precipitation. Other silicates, such as plagioclase and K-feldspar dissolved consuming H^+, which contributed to the pH increase. Kaolinite, illite, and chalcedony precipitated, counteracting the previous effect. Smectite was also precipitated instead of illite in some runs, leading to a similar water composition.

A small amount of dolomite dispersed in pelites was dissolved, increasing the Ca and Mg concentrations. This was the main process responsible for the progressive pH increase. In the dolomitic complexes, dolomite dissolution was only effective in the initial part, attaining equilibrium very fast (Fig. 4a-b). The pH value was controlled by dolomite dissolution/precipitation and to minor extent by silicates. In the pelites, the pH value increased slowly from values close 5 to 6-6.5, attaining values around 8 in the dolomitic complexes.

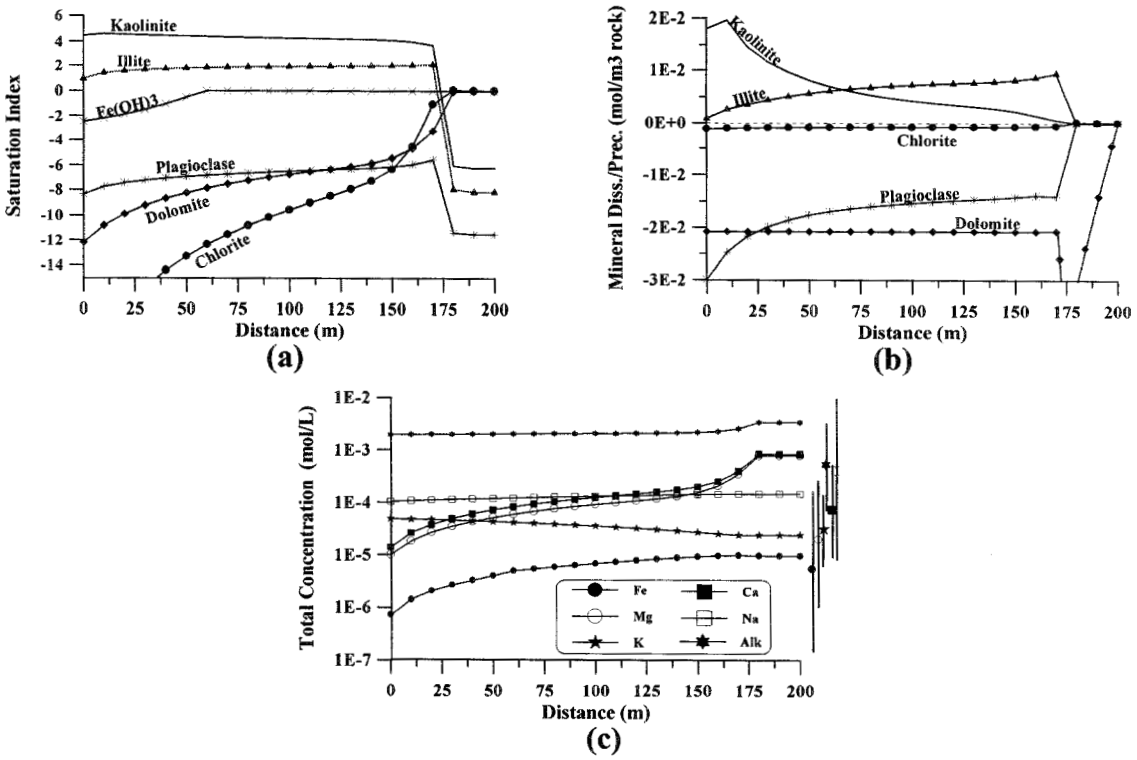


Figure 4: ***a)*** *Saturation index,* ***b)*** *mineral precipitation/dissolution; and* ***c)*** *solute concentration in the Pelite-Dolomitic Complex 1D Model. Analytical data ranges for type I water are included as vertical bars.*

5.2.-The sandstone system

The sandstone lithology was assumed to be homogeneous and was made up of quartz and clayey minerals, such as illite and chlorite. Minor amounts of K-feldspar, plagioclase and dolomite were also included in the model. The geochemical processes assumed were similar to those described for the pelite system, with a lower proportion of reactive minerals. As the Fe concentration is basically controlled by chlorite dissolution, and as this mineral is only present as a minor mineral in the sandstones rocks, the resulting Fe concentration is smaller than in the pelites. As a consequence, the Fe^{2+}-$Fe(OH)_3$ equilibrium line attains to higher pE values (Fig. 5).

5.3.-Sensitivity analysis of the most important parameters

The main parameters controlling the pH-pE distribution in the earlier models were the Fe concentration and the dolomite dissolution. The total Fe concentration controlled the location of the $Fe^{2+}/Fe(OH)_3$ equilibrium, and depended on the chlorite reactive surface, and on the Fe concentration and pE of the recharge. Thus, if chlorite reactive surface decreased, its dissolution would be slower, smaller amounts of Fe^{2+} would be added to the pore solution and the $Fe^{2+}/Fe(OH)_3$ equilibrium would take place at higher pE values (see the sandstone model in Fig. 5).

The alkalinity of the recharge controlled the carbonate saturation and its dissolution. If alkalinity was low, the pH of dolomite equilibrium would be high (8.5 or 9.0). As a result, pE values as low as –3 would be reached following the $Fe^{2+}/Fe(OH)_3$ equilibrium. An alkalinity value of $2 \cdot 10^{-3}$ mol/L

and a pH of 4.5 (pCO_2=1.5) leads to pH values in the dolomitic complexes between 7.5 and 8, in agreement with the analytical data.

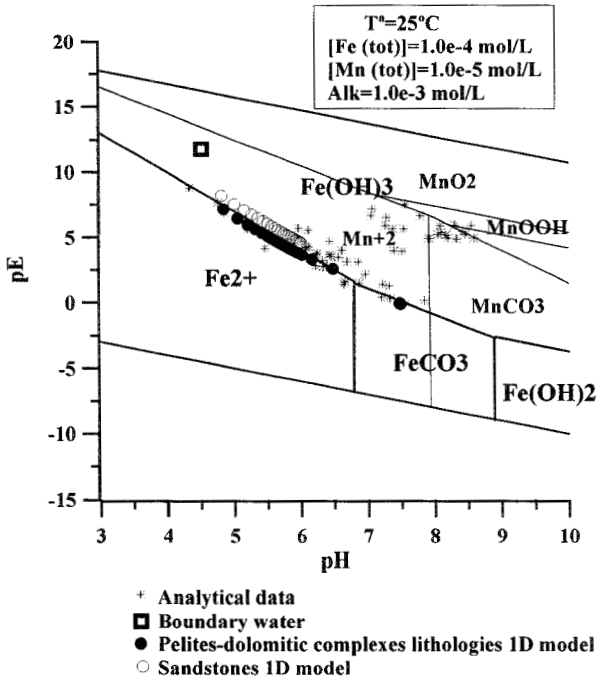


Figure 5: *pH-pE diagram for the Pelite-Dolomitic Complex and Sandstone 1D models.*

6.-Results: The Mn-deposit-Pelite-Dolomitic Complex 1D Model

This model represents a flow path infiltrating through the Massango Plateau, to the E side of the section represented in Figure 3a. Three materials have been included in the model: Mn-deposits, pelites and dolomitic complexes. According to Bouladon et al. (1965), the Mn-deposits are basically constituted by rhodochrosite, manganite, dolomite and silicates, such as illite, chlorite, plagioclase, k-feldspar and quartz, whereas the pelite and dolomitic complex lithologies have been defined as the previous model (Table III).

Solute	Initial pore Waters	Recharge waters	Lithology	Minerals	Initial vol. frac. (%)	Reac. Surf. (m^2/m^3)
Fe	4.11d-4	7.84d-9	Mn-deposit	Rhodochrosite	54.00	1.00d-1
Na	2.00d-3	1.00d-4		Manganite	10.00	1.00d-2
Ca	9.08d-4	1.00d-6		Illite	10.00	1.00d-2
K	1.00d-5	1.00d-5		Chlorite	5.00	1.00d-1
Mg	9.63d-4	1.00d-6		Plagioclase	10.00	1.00d-0
Al	1.00d-6 (2)	1.00d-6		K-Feldspar	5.00	1.00d-2
HCO3	5.36d-3 (1)	1.00d-3		Quartz	10.00	1.00d-2
Si	4.87d-4	1.65d-4		Kaolinite	0.00	1.00d-2
Mn	3.39d-5	1.00d-9		Smectite	0.00	1.00d+2
pH	6.87	5.65		Pyrolusite	0.00	**
pE	3.00	12.00		$Fe(OH)_3$	0.00	**

	Chalcedony	0.00	**
Pelites	Chlorite	10.00	1.00d-1
	Illite	40.00	1.00d-2
	Plagioclase	10.00	1.00d-1
	Dolomite	10.00	5.00d-4
	K-Feldspar	5.00	1.00d-2
	Quartz	30.00	1.00d-2
	Smectite	0.00	1.00d+2
	Manganite	0.00	1.00d+2
	Kaolinite	0.00	1.00d-2
	Rhodochrosite	0.00	1.00d+2
	Pyrolusite	0.00	**
	$Fe(OH)_3$	0.00	**
	Chalcedony	0.00	**
Dolomitic Complexes	Chlorite	3.00	1.00d-1
	Illite	30.00	1.00d-2
	Dolomite	35.00	1.00d-1
	Quartz	30.00	1.00d-2
	K-Feldspar	5.00	1.00d-2
	Smectite	0.00	1.00d+2
	Kaolinite	0.00	1.00d-2
	Rhodochrosite	0.00	1.00d+2
	Manganite	0.00	1.00d+2
	Pyrolusite	0.00	**
	$Fe(OH)_3$	0.00	**
	Chalcedony	0.00	**

Table III: *Initial and boundary conditions used in the Rhodochrosite-Pelite-Dolomite 1D model (1) equilibrium with dolomite; (2) equilibrium with illite, (**) precipitation in equilibrium.*

6.1.-Water-rock reactions

Rhodochrosite, manganite, chlorite and dolomite dissolution/precipitation were the main mechanisms controlling the hydrogeochemistry (Fig. 6a-b). Manganite, dolomite and chlorite were dissolved throughout the Mn-deposits but rhodochrosite only in the first metres. Chlorite reached equilibrium in the pelites, precipitating in small quantities downstream. Alternatively, (Fe,Mg)-smectite precipitated, resulting in a similar pore water composition. The Fe concentration remained practically constant ($2 \cdot 10^{-7}$ mol/L approximately) in agreement with analytical data for type II water (Fig. 6c).

Rhodochrosite dissolved in the first metres, reaching supersaturation due to dolomite dissolution. In the rest of the Mn-deposits and downstream, rhodochrosite precipitated in small quantities. This process was mainly responsible for the decrease of the Mn concentration from $3 \cdot 10^{-4}$ mol/L in the recharge to $6 \cdot 10^{-6}$ mol/L in the dolomitic complex lithologies. The latter value is consistent with the analytical data, whereas no analytical data are available for the first part of the system. Manganite dissolution only took place in the Mn-deposits, attaining equilibrium. Manganite remained subsaturated through the pelites and precipitates in the dolomitic complexes (Fig. 6e) as will be discussed below.

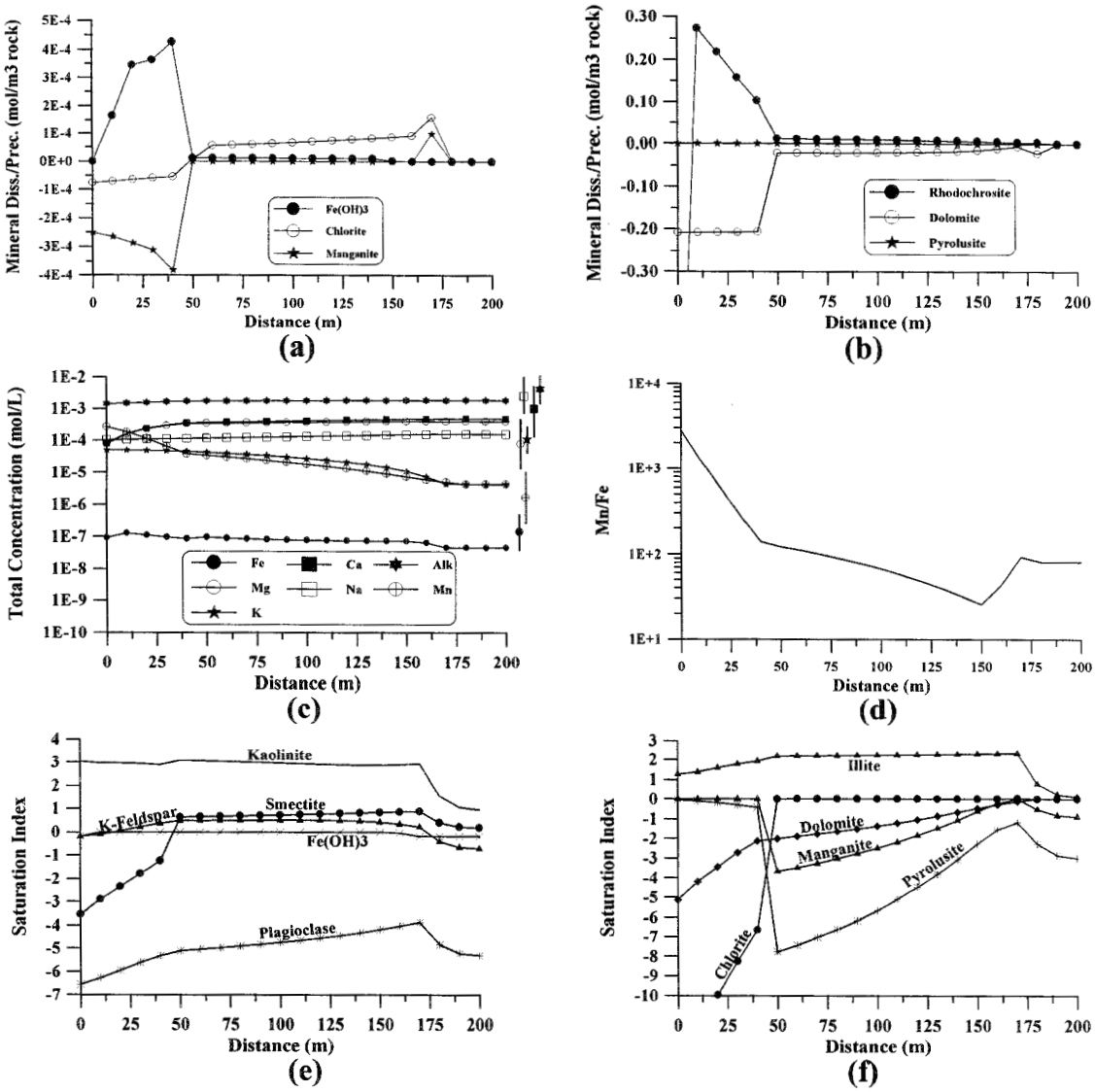


Figure 6: a, b) *Mineral precipitation/dissolution,* ***c)*** *total solute concentrations,* ***d)*** *the Mn/Fe ratio and* ***e,f)*** *saturation index distribution in the Mn-deposits-Pelites-Dolomitic complexes. Analytical data ranges for type II water are included as vertical bars.*

Dolomite dissolved throughout the Mn-deposits and the pelites, attaining equilibrium in the dolomitic complexes (Fig. 6e). Kaolinite, smectite and illite remained supersaturated but only the first two phases were allowed to precipitate (Fig. 6c-d).

The pH evolution rose from 6.5 to 7.1 in Mn-deposits, to values close to 8.0 in the pelites, and remained practically constant in the dolomitic complexes. Dolomite dissolution, ratter than silicate dissolution, was the process which controlled the pH evolution.

6.2. The redox evolution mechanisms

The pE-pH evolution is illustrated in Fig. 7. The recharge water is in the Mn^{2+} stability field. It dissolved rhodochrosite and manganite reaching equilibrium with both minerals. Pyrolusite was also in equilibrium and could precipitate in the first node. As a result of dolomite dissolution

through the Mn-deposits, the pH and alkalinity rose, rhodochrosite precipitated and the Mn concentration decreased. As a consequence, the Mn^{2+}-rhodochrosite boundary moved to higher pH values (around 7.0), and the pE decreased accordingly (from 9.5 to 8.5).

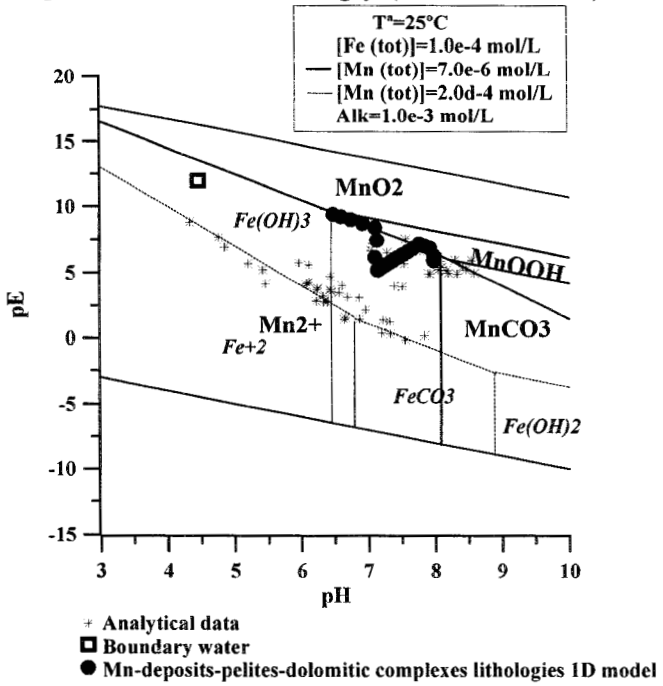


Figure 7: *pH-pE diagram for the Mn-deposit-Pelite-Dolomite Complex model.*

Chlorite dissolved through the Mn-deposits. However, the supply of Fe to the solution was slower than Mn (see the scale of the vertical axes in Fig. 6a and 6b). In the pelites, no Mn minerals was assumed to be present, and chlorite was a main mineral. Therefore, dissolution of chlorite supplied Fe^{2+} to the solution and $Fe(OH)_3$ precipitated. Given the excess of electrons, the pE value dropped (to around 5.0). However, chlorite reached equilibrium and supersaturation owing to the continuous dissolution of dolomite and plagioclase. Both have faster dissolution kinetics. Precipitation of chlorite (or a Fe-Mg-smectite) consumed Fe^{2+} and the pE value increased with pH. As a consequence, manganite reached equilibrium at about 150 m of the system (Fig. 6f). The precipitation of manganite caused the pore water to evolve in accordance with the manganite-rhodochrosite equilibrium. The resulting pE-pH values are close to these of type II water samples.

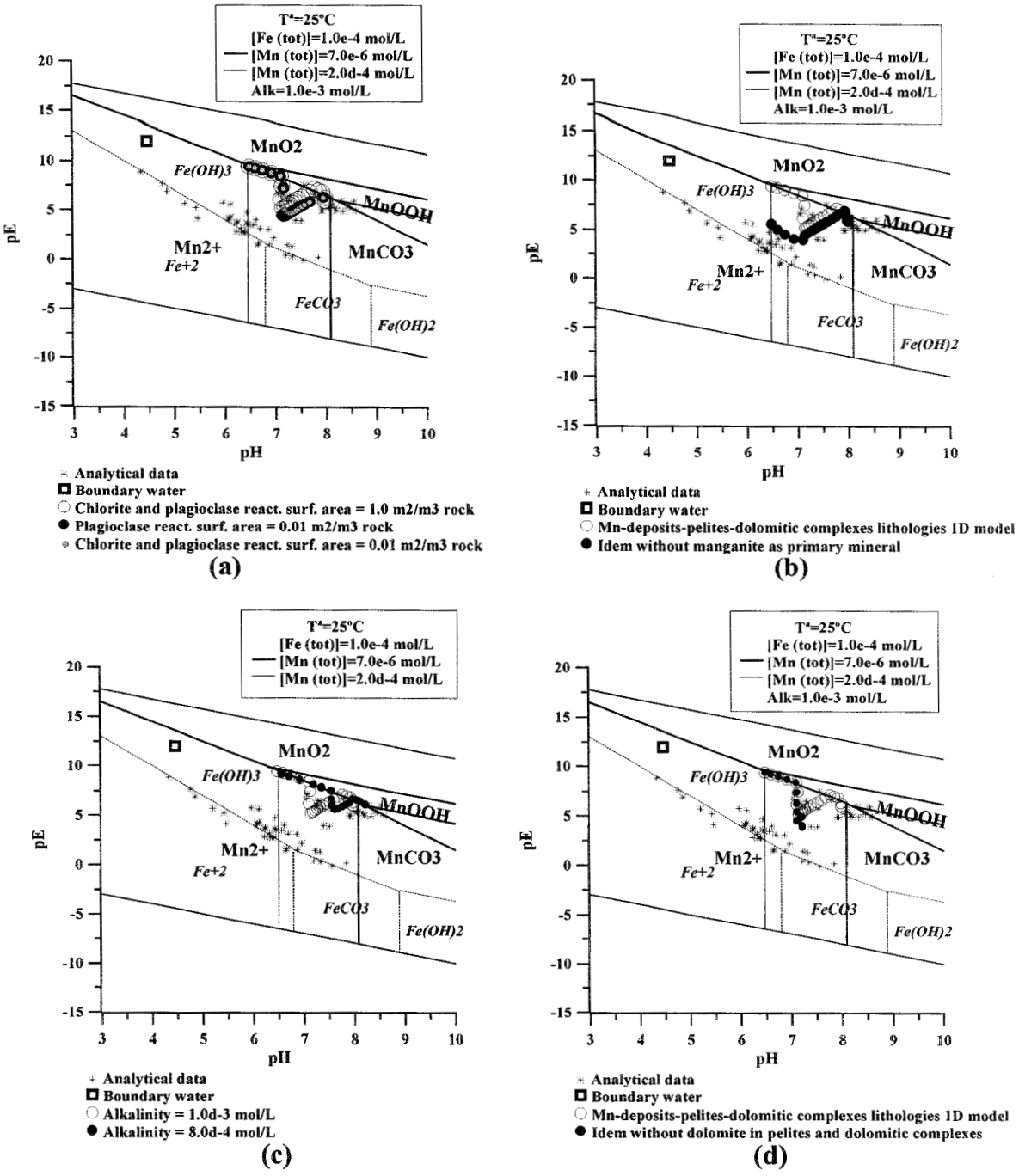


Figure 8: ***a)*** *pH-pE diagram for the Mn-deposit-pelite-complex models with different silicates reactive surfaces,* ***b)*** *with and without manganite as a reactive mineral,* ***c)*** *with different alkalinity values for the recharge, and* ***d)*** *with and without dolomite as a reactive mineral in pelites.*

In the complexes, dolomite dissolves attaining equilibrium, and the pH rose to values around 8.0. Plagioclase was less abundant than in the pelites and the Si and Al supply to the solution decreased. As a result, chlorite saturation decreased and started to dissolve. The amount of dissolution was too small to be evident in Fig. 6a. However, it caused the pE to drop slightly (to 6.7) as shown in Fig. 7.

Owing to the increase in alkalinite, rhodochrosite precipitated in small amounts in the complexes, and the Fe/Mn concentration rate increased (Fig. 6d).

6.3. Sensitivity analysis of the most important parameters

The main parameters controlling the pH-pE evolution are Fe and Mn concentrations and dolomite and silicate dissolution/precipitation. The unknown factor in the dissolution of silicates was the reactive surface assumed in the calculations. Accordingly, we tested the effect of silicate dissolution with a reactive surface of plagioclase that was two orders of magnitude lower. The pH values did not vary significantly, but Al and Si concentrations feel and the saturation of chlorite decreased. As chlorite was close to equilibrium in the pelites, a decrease in saturation enhanced dissolution, and the Fe^{2+} concentration increased. As a consequence, the resulting pE values in pelites were lower (Fig. 8a). In subsequent test, the reactive surface of chlorite was assumed to be two orders of magnitude. In the first metres of the pelites, chlorite dissolution was slower, the Fe^{2+} concentration lower, and the pE values higher than the previous model (Fig. 8a).

Because of the lack of experimental data, manganite dissolution rate was initially assumed to be similar to rhodochrosite. The effect of a much slower manganite kinetics was tested by assuming that manganite was not present in the system. In such a case, no Mn^{3+} ions were incorporated into the pore water and the pH-pE values in the Mn-deposits evolved according to the Fe^{2+}-$Fe(OH)_3$ equilibrium induced by the slight dissolution of chlorite (Fig. 8b). However, the pH-pE path of the rest of system does not depend on the dissolution of manganite, and resembled the main model. No data on the chemistry of the water in the Mn-deposits are available and, therefore, no fixed kinetic can be assigned to the manganite.

The alkalinity of the recharge could significantly affect the dissolution of carbonates. For alkalinitiy values lower than previously assumed, rhodochrosite saturation was reached at a higher pH (around 7.5 in the Mn-deposit). At such high pH values chlorite was closer to equilibrium in contact with the pelites and its dissolution was slower. As a consequence, the drop in pE due to the Fe^{2+} supply was less important and took place at a higher pH (Fig. 8c).

The role of dolomite in the evolution of the system was also tested by assuming that it was absent in the pelites and no dolomitic complexes were reached by the water flow. In such a case the pH increase is due to silicate dissolution (mainly plagioclase) and a maximum value of 7.0 was attained. At such pH values, chlorite or smectite did not precipitate and the lower pE values did not increase towards the manganite equilibrium.

7.-Conclusions

The chemical composition and the pH-pE values of the water sampled in the upper part and in the western margin of the Okelobondo system (type I water) can be explained in terms of the interaction of a meteoric recharge with the pelites, dolomitic complexes and sandstones. The dissolution of silicates and dolomite caused the pH to attain values of 8.0. The dissolution of Fe-silicates and the precipitation of $Fe(OH)_3$ maintained the pE along the Fe^{2+}-$Fe(OH)_3$ equilibrium, reaching values close to 0. The location of this equilibrium depends on the Fe concentration in

solution, which in turn depends on the kinetics of Fe-silicate dissolution. Uraninite does not dissolve at the low pE values obtained,. This could account for the lower U content in the water samples from the pelites and dolomitic complexes above the Okelobondo deposit.

The high Mn/Fe ratio and the high pH and pE values of the water sampled in the lower part of the Okelobondo system (type II water), are attributed to the interaction of the recharge with the Mn-deposits, pelites and complexes. Three key factors are required to obtain the chemistry of type II water: 1) a fast dissolution of a Mn-phase; 2) a slow dissolution of a Fe-phase; 3) a continuous source of alkalinity. Rhodochrosite dissolution supplied Mn to the pore water. The high pH values resulting from dolomite and rhodochrosite dissolution minimize the dissolution of chlorite and the Fe increase in the solution. Thus, the rhodochrosite and manganite dissolution/precipitation is able to control the pE-pH evolution of the system. This result is not dependent on the kinetics of silicate dissolution and variations in the chemistry of the recharge. The dissolution of manganite in the flow path is not required to obtain type II water characteristics at depth (no samples from the Mn-deposits pore water are available). However, the dissolution of dolomite is required for the pH to reach values as high as 8.0.

8.- Aknowledgements

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III.3.3. Peña Blanca Natural Analogue Project

Peña Blanca and Yucca Mountain: An introduction
W M Murphy, CNWRA (USA)

Geologic setting and mineralisation: Sierra Peña Blanca, Chihuahua, Mexico
I A Reyes - Cortés, UACH (MX)

Uranium chemistry and isotopy in waters and rocks at Peña Blanca, Mexico
D A Pickett and W M Murphy, CNWRA (USA)

Uranium decay series mobility at Peña Blanca, Mexico: Implications for nuclear repository stability
M T Murrell, J J Goldstein and P R Dixon, LANL (USA)

Peña Blanca and Yucca Mountain: An Introduction

William M. Murphy
Center for Nuclear Waste Regulatory Analyses
San Antonio, Texas, USA

In 1987 the government of the United States of America selected Yucca Mountain, Nevada, as the sole site to be characterized as a proposed geologic repository for high-level nuclear waste. The site is in silicic tuffs of Miocene age (12.8 million years) in an arid environment such that the proposed emplacement horizon is hundreds of meters above the saturated zone groundwater table and the geochemical environment is oxidizing. The primary waste form proposed for the repository is spent fuel from commercial nuclear power plants consisting predominantly of UO_2 with small quantities of other actinides and fission products and their decay daughters. Extensive site characterization has been conducted for the Yucca Mountain site, and a series of performance assessment exercises has been undertaken by several organizations. A recent summary of site characterization data is presented in the Department of Energy Viability Assessment (DOE, 1998).

Extensive geological studies were conducted in the Peña Blanca uranium district in the Mexican state of Chihuahua by Mexican, French, and American investigators in the context of uranium mineralization, exploration, and exploitation (e.g., Rodriguez et al., 1976; Calas, 1977; Goodell, 1981; George-Aniel et al., 1991). Natural analog studies at Peña Blanca have focused primarily on the uranium deposit at the Nopal I site. Excellent exposure of primary uraninite and its alteration products is provided at this site because of partial mining. The exposure and adits also provide access to water that has reacted in the geochemical environment and to radionuclides that have been transported from the zone of primary mineralization and deposited in surrounding host rocks and fracture fillings.

The close analogy between the geologic, geochemical, climatic, and hydrologic systems at Yucca Mountain and Nopal I enhances the potential utility of analog data from Nopal I in model development and in support of performance assessments for Yucca Mountain. In the Peña Blanca uranium deposits primary uraninite, a chemical and structural analog of spent nuclear fuel, has been almost entirely oxidized to a suite of secondary uranyl minerals (e.g., Pearcy et al., 1994). Uranium and other radionuclides have been transported from areas of primary mineralization at Nopal I into surrounding tuffs and partially redeposited (e.g., Pearcy et al., 1995; Prikryl et al., 1997). Oxidative alteration of uraninite, release of uranium and other species, transport of radionuclides in surrounding tuffs, and redeposition of radionuclides in fractures and rock matrix are

analogous to source term and transport processes anticipated for the proposed Yucca Mountain repository. The correspondence of the paragenetic development of secondary uranyl mineralogy at Nopal I and spent fuel alteration mineralogy observed in laboratory studies has been widely cited to provide long term and short term bounds on repository predictions (e.g., Murphy and Pearcy, 1994). The primary objective of analog studies at Peña Blanca in the context of the proposed repository at Yucca Mountain has been to illuminate source term and radionuclide transport phenomena as implemented in performance assessments for the proposed repository.

On the initial recommendation by Professor Philip C. Goodell of the University of Texas at El Paso and available literature, the Center for Nuclear Waste Regulatory Analyses (CNWRA), supported by the U.S. Nuclear Regulatory Commission (NRC), has conducted extensive studies of the Peña Blanca area as a natural analog with specific relevance to the proposed repository at Yucca Mountain. A poster and paper were contributed by the CNWRA on possible analog studies at Peña Blanca at the Fourth Natural Analogue Working Group (NAWG) Meeting held in 1990 at Pitlochry, Scotland (Murphy et al., 1991), and results of Peña Blanca studies have been presented at subsequent meetings of the NAWG (Murphy and Pearcy, 1994; Murphy et al., 1997; Pickett and Murphy, 1997; this volume), as well as in other publications. Radionuclide transport phenomena at Nopal I were also recognized to be analogous to processes at the proposed repository at Yucca Mountain by Ildefonse et al. (1990). Recently the U.S. Department of Energy (DOE) has initiated studies of the Peña Blanca system as a potential analog site for radionuclide transport studies (Murrell et al. and Simmons et al., this volume), and Peña Blanca data are cited in the recent DOE Total System Performance Assessment-Viability Assessment (TSPA-VA) in the context of waste form alteration chemistry (see Murphy et al., this volume).

The objective of this session at the 8th EC-NAWG Workshop is to summarize and review a selection of natural analog studies at Peña Blanca. Although studies at Peña Blanca have primarily focused on their applicability to the proposed nuclear waste repository at Yucca Mountain, studies of alteration of uraninite, release and transport of radionuclides, and deposition of radionuclides in host geologic media can provide process oriented information relevant and analogous to a variety of waste disposal systems and problems.

The paper in this volume by I. Reyes provides a description of the paragenesis of the host rocks, the evolution of the geologic structure and lithologic fabric, the primary uranium mineralization and alteration in the Peña Blanca district, and the chronology of these events. In addition, the history of mapping, exploration, and mining operations at Peña Blanca offered by Dr. Reyes provides valuable information to point natural analog investigations to specific sites in the Peña Blanca district of particular significance and usefulness.

Ildefonse, Allard, Muller, and Calas in this volume present a study of radiation induced defects in natural kaolinites at Peña Blanca analyzed by electron paramagnetic resonance. Characterization of these defects, and assumptions regarding the timing of migration and the consequences of radioactivity from other nuclides, provides an estimate of the record of the past radiological environment of the minerals. Radiation effects in kaolinite exterior to the primary uranium deposit are interpreted to exceed by orders of magnitude the effects that would result from the present uranium concentrations in the kaolinite environment. Substantial uranium leaching during the late geological history of the site is indicated by these analyses. Studies of mineralogical paleodosimetry at Peña Blanca are an example of the use of Peña Blanca data for process oriented studies that may be applicable to a variety of sites and systems.

Ildefonse, Agrinier, Allard, Muller, and Calas in this volume describe a multidisciplinary petrological, mineralogical, stable isotopic, and geochemical study of alteration and uranium transport at the Nopal I deposit at Peña Blanca. The sequence of oxidative alteration of primary uraninite is characterized. Oxygen isotope data indicate low temperature mineralization. Rare earth element mobilization was observed in these geochemical studies. These data provide evidence that could be used to help predict actinide migration in an analogous nuclear waste repository environment.

Papers in this session by Pickett and Murphy and by Murrell et al. focus on isotope studies of Nopal I rock, fracture mineralization, and water samples. Pickett and Murphy report uranium decay series and uranium-lead data from alpha and gamma spectrometry techniques for the timing of mineralization, oxidation, and uranium mobilization. An extensive set of uranium decay series data is presented for rock samples and fracture filling materials, indicating that uranium series disequilibrium is the general pattern and that open system, episodic radionuclide transport occurred over a period of hundreds of thousands of years. In contrast, Murrell et al. report uranium and thorium isotopic data analyzed using precise thermal ionization mass spectrometry for a limited number of samples of fracture filling materials. These decay series data indicate closed system behavior for uranium and thorium for the samples during the last 380 ka, and relatively recent radium mobility is indicated by low $^{226}Ra/^{230}Th$ activity ratios. Reconciliation of the possibly contradictory evidence reported in this session respectively by Pickett and Murphy and by Murrell et al. for radionuclide mobility on a time scale of a few hundred thousand years provides strong motivation for additional mapping, sampling, and analytical studies at the Nopal I site.

Murphy et al. (this session) conclude with a summary of the use of data from the Peña Blanca site in recent performance assessment models for the proposed nuclear waste repository at Yucca Mountain. Published performance assessments by the DOE, NRC, and the Electric Power Research Institute (EPRI) all cite Peña Blanca data primarily in regard to uraninite and its alteration products as analogs of spent nuclear fuel and

secondary uranyl minerals as radionuclide source term limiting phases. Although extensive studies of radionuclide transport have been conducted at Peña Blanca, the resulting data have been considered only tangentially in formal assessments of the performance of the Yucca Mountain repository.

As placed in evidence by the papers in this session, natural analog studies at Peña Blanca have received broad attention and have provided valuable information regarding the potential performance of the proposed high level nuclear waste repository at Yucca Mountain, Nevada. Furthermore, the value of prior studies at the site, the clear physical and chemical relevance of processes at Peña Blanca to potential repository systems, especially Yucca Mountain, and the manifestation at Peña Blanca of the geochemical behavior of uranium and other radionuclides on a time scale relevant to geologic disposal of nuclear waste should promote future collaborative and international studies at the site.

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Geologic Setting and Mineralisation: Sierra Peña Blanca, Chihuahua, México

Ignacio A. Reyes-Cortés
Facultad de Ingeniería, Universidad Autónoma de Chihuahua,
Chihuahua, Chihuahua, México.

ABSTRACT
The Sierra de Peña Blanca has been endowed with uranium mineralisation, which has attracted many geological studies. The first part of the work includes the idea of a pull apart basin development, which justifies the local great thickness of the Cuervo Formation. Also includes the regional structural framework and the composite stratigraphic column of the Chihuahua Trough and the equivalent Cretaceous Mexican Sea.
The general geologic features of the Sierra de Peña Blanca are described, which include the folded ignimbrites and limestones in that area; the irregular large thickness of the Cuervo Formation; and the western vergence of the main folding within the area. The ignimbrites of the lower member of the Cuervo Formation have an average age date of 53 Ma. In fact samples of the two Cuervo ignimbrites of the lower member were submitted for K-Ar analysis at the University of Arizona age dating laboratory. Sanidine phenocrystals gave ages of 54.2 Ma and 51.8 Ma ± 2.3 Ma. This age indicates a time before the folded structures, which outcrop in the area, and 44 Ma is a date after the Cuervo Formation was folded. The Hidalgoan orogeny cycle affected the rocks between this lapse of time. Since then the area has been partially affected by three tensional overlapped stages, which resulted in the actual Basin and Range physiography. The jarosite related to the tectonic activity mineralisation has been dated by the Ar-Ar method and yields an age of 9.8 Ma. This is the first report of a date of mineralisation timing at Peña Blanca Uranium District in the Sierra del Cuervo.
There are mineralogic determinations of the fracture fill material in the orebody and host rock; detailed mapping of the fractures and surface alterations; and gamma ray grid measurements and electromagnetic soundings. All these studies indicate a support criterion to take the Nopal 1 as a natural analogue of the Yucca Mountain repository. The total evolution of the Nopal 1 orebody is exposed in the walls and floors of the +00 and +10 levels. Which are ready to perform final safety tests in order to compare it with the future Yucca Mountain repository behaviour. The Nopal in orebody has been there for several hundred of thousands and may be millions of years in a natural equilibrium with the surrounding environment.

1. Introduction

The geology of the area includes a sequence from the Lower Cretaceous up to the Tertiary volcanic rocks covered by Quaternary talus and alluvial material. The older rocks consist of reef and neritic limestones of the Glen Rose Formation and a partial outcrop of the Tamaulipas Superior Formation. The transition between the Late Cretaceous and the Early Tertiary tectonic activity was associated with volcanism and by the accumulation of continental conglomerates. After the Hidalgoan Orogeny, which formed the Chihuahua Tectonic Belt between 53 Ma and 44 Ma ago, the area underwent a release of the compressional stress, which then produced tectonic structures such as grabens and volcanic activity. The Pozos Formation represents the molasse sediments with thicknesses greater than 90 m.

2. Stratigraphy

CUERVO FORMATION. The Cuervo Formation was described by Iparrea and Chávez-A (1969) in the western part of the Cuervo Ranch, at the base of the eastern cliff of the Tehua Cuesta, Sierra del Cuervo. Iparrea and Chávez-A described the formation at the type locality as the folded basal conglomerate intercalated with rhyolitic and tuffaceous horizons. The Cuervo Formation consists of two members, the lower member has two ignimbrites separated by a thick conglomerate. The upper member includes a thick sequence of ash and volcaniclastic material. The lower member of the Cuervo Formation starts at its base with a crystal ignimbrite of 55m thickness, which overlies an almost horizontal erosional surface of the underlying Edwards Formation. The crystal ignimbrite of pinkish to reddish colours is constituted of a well-welded member of an ash flow tuff, characterised by the abundant presence of sanidine, 20 % of the whole rock. The ignimbrite thickness is constant along the outcrops. This first crystal ignimbrite is overlain by a calcareous conglomerate with sandy matrix, which is at least 60 m in thickness. It is formed by boulders of 5 to 50 cm in diameter. Conglomerate fragments are more than 90 % limestone, the rest, less than 10%, are fragments of volcanics dominanted by clasts andesitic to basaltic composition. The conglomeratic unit is overlain by a second ignimbrite. The lithic ignimbrite has a compact structure and pyroclastic and eutaxitic texture. This ignimbrite of reddish brown to whitish brown colours is constituted of 2 to 10 cm flattened pumice fragments. The lithic ignimbrite shows a constant thickness of 65 m along the crops out in the study area. It lacks of basal vitrophyre as was observed in the crystal ignimbrite, or, if present, it is not well developed in the outcrop area. The lithic ignimbrite is unconformably overlain by an interbedded sequence of ash and volcaniclastic material designated as the Cuervo Formation upper member.

This upper member of the Cuervo Formation consists of dark violet and purple volcaniclastic material including such components as conglomeratic sand, volcanic ash, volcanic breccias, air fall tuffs, and volcanic conglomerate. All of these components develop sedimentary structures such as graded beds, cross bedding, cut and fill channels, imbrications, casts, and prints. The upper member has complex folded structures, and a thickness of at least 250m. This thickness was calculated from vertical sections. The true thickness is very difficult to measure due to complex changes of strikes and dips. Bedding of the upper member has almost vertical dips near the lithic ignimbrite contact; but 20 m away to the west, beds can dip either toward the northeast or southwest with angles ranging from 30° to 75°. The total composite thickness of the Cuervo Formation calculated from the vertical sections was approximately 530 m.

The upper contact is covered by debris from the overlying formations, but in the field it is determined by a change in slope and lithology from sandy reddish purple volcaniclastic material to a gray calcareous conglomerate sourced from the overlying the Pozos Formation. This change slope is well marked in some places, these where is interpreted. The Cuervo Formation is unconformably overlain by the Pozos Formation.

The Cuervo Formation is younger than the Middle Albian age because of its stratigraphic position, and similarly is older than the Middle Eocene because it underlies the Nopal Formation of 44 Ma (Alba and Chávez, 1974). Samples of the two Cuervo ignimbrites of the lower member were submitted for K-Ar analysis at the University of Arizona Age Dating Laboratory. Sanidine phenocrystals gave ages of 54.2 Ma and 51.8 Ma ± 2.3 Ma. This is the first time these dates have been reported in print. However, there is a suggested age dated for these basal ignimbrites of the Cuervo Formation at 53-54 Ma (Goodell et al, 1988), which is the same age obtained for the Corrales Formation (Alba and Chávez, 1974) in the arroyo de la Parrita, 10 km to the southwest.

CORRALES FORMATION. The Corrales Formation was described by Iparrea and Chávez-A (1969) on the northern side of the arroyo de la Parrita, at the base of the southeastern cliff of the Cerro de la Parrita, Sierra del Cuervo. The name was taken from fences (corrales) built around the Parrita spring to protect it from cattle. Iparrea and Chávez-A (1969) describe the formation at this type locality as the basal tuff of the lower member of the Nopal Formation, which is separated from the other part of the lithologic unit by a horizon of calcareous conglomerate.

In this work the Corrales Formation is designated as a crystal ignimbrite of the lower member of the Cuervo Formation, which crops out extensively on the northeast flank of the Sierra del Cuervo. This formation was described before as the lower member of the Cuervo Formation. Corrales Formation lithology and field relationships caused McAnulty and McAnulty (1977), to think that the Corrales ignimbrite could be included as part of the base of the lower member of the Nopal Formation, now known as the Coloradas Formation. It was also believed by several geologists that the radiometric age obtained by Alba and Chávez (1974) of 54 Ma was in error. This was because of the extreme similarity between the upper member of the Nopal Formation, now known as Nopal Formation, and the proposed Corrales Formation. Nevertheless, the radiometric age of about 54 Ma (Alba and Chávez, 1974) on the samples of the Corrales ignimbrite outcropping in the western side of the Parrita area was the basis for separating the Corrales ignimbrite as an independent formation. Both formations, the upper member of the Cuervo and Pozos, are composed of continental molasse facies separated by a period of quiescence. The period after the eruption of the Cuervo ignimbrites represents a long volcanic quiescent which was also a time of intense tectonic and erosional activity. This is disrupted eventually by volcanism toward the west of the study area. This age is interpreted to be approximately the beginning time of the maximum orogenic folding. Also since the upper member of the Cuervo Formation was not affected by the folding. These conglomerates pinch out toward the west and south of the study area, because of they were deposited as filling material into lower topographic areas during the folding process of a local pull apart basin.

POZOS FORMATION. The Pozos Formation was described by Iparrea and Chávez-A (1969) as the basal Tertiary unit in the Peña Blanca region; it is an epiclastic conglomerate resting unconformably on Cretaceous limestones and makes a marked angular unconformity with the undelying Cuervo Formation. It was first described in the Nopal Cuesta. The Pozos Formation crops out along a linear belt near the base of the eastern-most escarpment of the Sierra del Cuervo at the Peña Blanca area, mostly east and northeast of the Nopal Camp. The Pozos Formation is commonly covered and relatively poorly exposed such as the arroyo de la Escuadra, southwest of the Margaritas. The Pozos is composed of poorly sorted, angular to subangular, pebble to small cobble clasts of limestone and volcanic material. In the Nopal I Mine area there are horizons of the Pozos in which volcanic clasts comprise an estimated 70 % of the coarse-sized clasts. Toward the base of the unit, and to the north of the mine, the amount of limestone clasts increases up to 95 %, and the angularity of clasts also increases to the north. Sandstone forms the matrix of the conglomerate and lenses of sandstone up to several meters thick are present within the conglomerate. Calcite and caliche cement both the conglomerate and the sandstone and result in a well-indurated unit. The Pozos Formation thickness in the study area ranges from a few meters to approximately 120 m.

COLORADAS FORMATION. Iparrea and Chávez-A (1969) described the Coloradas Formation as the basal pyroclastic member of the Nopal Formation, which unconformably overlies the Pozos Formation. The unit is described as a sequence of lithic tuffs, that are poorly to moderately welded. The Coloradas crops out in a narrow strip along the middle upper slope of the eastern cliff edge of the Sierra del Cuervo. The Coloradas formation is

constituted of a vitric-lithic ash flow tuff of reddish brown, pinkish brown to red colour, with large pumice fragments of 3 to 30 cm long. The unit has a porphyritic-eutaxitic texture with a cryptocrystalline matrix. The Coloradas Formation has elongated and flattened fragments of pumice, and deformed fragments of quartz, sanidine, and oligoclase. The majority of the feldspars are kaolinised and, in some locations, replaced by calcite. The lithics are fragments of rhyolitic rock and devitrified vitrophyre ranging from 1 to 20 cm in diameter. Laterally, there is a devitrified vitrophyre, which in some areas is totally altered to a clay at the contact. At the Nopal I deposit the devitrified Nopal vitrophyre marks the Coloradas upper This unit is equivalent to the red platty unit in the Rancho the Papalote area (Capps, 1981), 25 km to the southwest of the studied area.

NOPAL FORMATION. The Nopal Formation, which was described by Iparrea and Chávez-A (1969), is a composite rhyolitic ash flow sequence that contains several eruptive units. From lithic tuffs at the base (now called The Coloradas) to moderately and densely welded crystal tuffs that predominate in the middle third of the Nopal Formation. The uppermost tuffs of the Nopal are crystal-lithic tuffs, moderately welded. The Nopal Formation crops out extensively along the southern part of the Sierra del Cuervo in the Peña Blanca Uranium Dsitrict. It is of purple-brown to dark-pink colour with abundant dots and spots of white- and yellowish- pink colour. Megascopically the rock shows a porphyritic texture with an aphanitic matrix and slightly eutaxitic to eutaxitic structure. It has abundant feldspar casts and voids, quartz phenocrystals, elongated fragments of kaolinised rock, and partial to totally kaolinised feldspars, as well as some voids left from leached feldspars. Oxidation is present in practically all the unit. Microscopically the unit presents a porphyritic and eutaxitic texture with a micro to cryptocrystalline and partially vitreous matrix. It consists of elongated fragments of rhyolite, partially argillitised, anhedral and deformed quartz and sanidine phenocrystals; and some corroded and partially argillitised plagioclases, within a similar composition matrix, which is derived from the devitrification of the original volcanic glass. It also contains slightly kaolinised, perlitic rock fragments, which differentiate the unit from the others. It also has small amounts of hematite alteration, calcite veinlets, altered biotite, and sphene altered to leucoxene. At the Nopal mine conspicuous disseminated pyrite oxidized to hematite is observed. The calculated thickness is approximately 60 m in the Nopal Cuesta, but it has local variations in the study area, because of the intense erosion of the Nopal Formation before the emplacement of the Escuadra Formation. At the Nopal Mine area the vitrophyre is totally argillitised and zeolitised, with some concretions that are not totally altered. There could be interpreted as lithic fragments. To the south west of the Nopal Camp the vitrophyre has a pale green perlitic texture. Microscopically the texture varies from vitrophyric to vitroclastic tending to perlitic and spherulitic, but preserving the eutaxitic texture. This vitrophyre has scarce corroded quartz and sanidine phenocrystals, andesitic to basaltic lithics, and pyroxene phenocrystals with assimilated borders. There also is some biotite and plagioclase. Some samples have limestone and chert fragments as lithics, as well as calcite and thin laminated gypsum veinlets. The thickness of the vitrophyre is very variable due to the degree of masking alteration. It is 10 to 12 m thick in the Nopal mine area. The upper limit is defined by an unconformable contact with the epiclastic Piloncillos Formation. The Nopal Formation has been dated as 44 Ma (Alba and Chávez, 1974). The age of the Nopal Formation defines the time in which the compressional tectonic events were completed and only the volcanic activity occured in the area. The uninterruped continuity with minor thickness variations of the unit in the Sierra del Cuervo, can be interpreted as indicating that the source vent area was relatively far away from the study area (Goodell, 1984). Then the actual presence of the same or quite similar ignimbrite in the surrounding sierras support that idea of the distant source vent.

PILONCILLOS FORMATION. The Piloncillos Formation was described by Iparrea and Chávez-A (1969) as a thin epiclastic conglomerate and sandstone which marks the base of the Escuadra Formation. The unit ranges from 1 to 3 meters thick and is relatively poorly exposed. Volcanic sandstone is the dominant lithology for the basal unit in the south, whereas limestone pebble conglomerates form the basal unit in the northern part of the range. The basal unit is well cemented by calcite. The Piloncillos Formation was originally described as the volcaniclastic lower member of the Escuadra Formation (Reyes-C, M., 1980a), subsequently, has been separated out as the Piloncillos Formation because of its volcaniclastic character. The Piloncillos Formation crops out as a narrow strip between the Nopal and Escuadra formations, it is along the eastern side of the Sierra del Cuervo at the Peña Blanca area. The strip has widths of 10 to 50 m and continuous lengths of up to 10 km. It is made up of a very weathered, thin ash flow tuffs, reworked tuffs, and a thick layer with sedimentary structures of bedded, graded, and cross bedding. Its thickness varies around the repository site from 60 to 90 meters. North of the repository, the unit consists of a very altered air fall tuffs graded to clay minerals and interbedded with volcaniclastics. The high degree of alteration of the tuffaceous horizon in that site resulted in the development of a clay with high purity, which was then analysed for hydrologic properties at the UACH laboratories. The hydraulic conductivity of this clayey material is 7x10-9 cm/sec, which is an extremely low value. The relative stratigraphic position with respect to the Escuadra Formation at 38 Ma, and to the Nopal Formation at 44 Ma (Alba and Chávez, 1974) indicates an age for the Piloncillo Formation that ranges between the 44 and 38 Ma. It was emplaced by a periodic fluvial activity on an irregularly eroded surface of the Nopal Formation.

ESCUADRA FORMATION. Iparrea and Chávez-A (1969) described the Escuadra Formation as being composed primarily of moderately crystal rhyolite tuff. Moderately welded crystal-lithic tuffs and lithic-vitric tuffs present in the lower one-third of the section, which grade upward into crystal tuffs. Milky feldspar phenocrystals, 5% to 10% of the rock, characterise the crystal tuff and make the Escuadra an easily recognisable, distinctive unit in the volcanic sequence. The upper member of the original unit is now taken as the Escuadra Formation, which consists of a dense and compacted part of the crystal ignimbrite, now strongly altered. The crop out distribution of the Escuadra Formation forms a nearly continuous strip 1.6km wide in the northern part of the Sierra de Peña Blanca. North of the study area, the strip narrows and the exposures become restricted to the eastern cliff edge of the Sierra de Peña Blanca. However, on the western side of the sierra, there several broad outcrops are exposed, because of the complex faultings. This crystal ignimbrite has abundant quartz, iridiscent sanidine, biotite and hornblende phenocrysts. The unit is characterised by the devitrification of the glassy matrix to microscopic quartz and feldspar minerals. The epithermal alteration of the formation is controlled and defined by the fracturing intensity. In the study area the Escuadra is exposed with volcanic fragments of large size (up to 1 m in diameter), and the whole formation shows a very persistent alteration. The presence of large lithic fragments within the unit suggests an interpretation of a near source volcanic eruption. No cooling breaks were noted in the formation, which was probably obscured because of alteration degree. The Escuadra is considered to be a multiple flow of a single composite cooling unit. The ground mass of the ignimbrite is totaly devitrified. The Escuadra ranges from 0 to about 100 m thick, in most exposures in the Sierra del Cuervo, at the Peña Blanca area it averages 50 to 60 m in thickness. The thickness of the Escuadra welded zone decreases rapidly toward the north of the study area, where the formation is just 50 m thick. The upper contact of the Escuadra Formation is lithologicaly disconformable and texturally transitional into the Chontes Formation, the volcaniclastic basal member of the Peña Blanca Formation (Reyes-C, M., et al., 1980a). The contact between Escuadra and Chontes is

geomorphologically marked by a slope change, because the latter is more soft and clayey. The age of the Escuadra Formation was made by Alba and Chávez (1974) at 38 Ma. The great variation in the fragment sizes indicates a nearby source vent. This factor also contributes to the variable thickness observed in the unit.

CHONTES FORMATION. The formation is a thick epiclastic conglomerate and sandstone sequence, which was designated as the Chontes Formation by Iparrea and Chávez-A.(1969). They define it as the unit that marks the base of the Peña Blanca Formation, which unconformably overlies the Escuadra Formation. The unit was subdivided into two members: the lower called Chontes Formation and the upper one the Peña Blanca Formation itself. The Chontes Formation is widely exposed in the northern part of the Peña Blanca area as a narrow strip along the middle slope of the eastern cliff. It is located below the white band that characterises the eastern cliff of the sierra. The Chontes Formation has interbedded strata of conglomeratic and volcaniclastic material 0.1 to 3.0 meters in thickness representing an intensely argillitised air fall tuffs. The formation also has conglomeratic members of limestone and volcanic fragments. The conglomerates of the unit have a sandy matrix, which is composed primarily of volcanic origin grains. The thicker parts of the Chontes Formation have sandstone and conglomeratic sandstone beds and lenses, with some tuffaceous strata interbedded with conglomerates. It varies from a few meters up to 200 m in thickness, with very significant local variations. The lower Escuadra Formation contact is marked by cut and fill structures, which give an idea of the irregular contact, whereas the upper limit practically is unknown, because of the debris coverage that hides the contact in the study area. Its age is defined by the stratigraphic position between the Escuadra Formation at 38 Ma and the Mesa Formation at 37 Ma (Alba and Chávez, 1974). There is no known correlative or equivalent unit to the Chontes Formation in the surrounding sierras and the unit is even absent in some places of the Sierra del Cuervo.

3. Structures

The extensively deformed nature of the pre-Pozos formations in the Sierra del Cuervo has been recognised since GEOCA geologists first studied the area in 1967 (Iparrea and Chávez-A, 1969), but, until now, no detailed structural and stratigraphical study of these rocks had been undertaken. Iparrea and Chávez-A (1969), and PEMEX (1988) presented evidence for a pre-Pozos folding event in the lower member of the Cuervo Formation (equivalent to the Corrales Formation), however these geologists did not present any significant faulting and folding of the ignimbrites in the area. Documentation of several anticlinal folds in which deformed ignimbrites of the Cuervo Formation are made. These structures crop out along cuts of the arroyo Peña Blanca. This documentation not only raises questions about the structural relationships between the Cretaceous rocks and the Cuervo Formation, but also about stratigraphic and structural interpretations made by PEMEX (1988) and Iparrea and Chávez-A. (1969). During this study four distinct trends and styles of structures were found. The oldest structures are related to pre-Cretaceous events and are beyond the scope of this work. The most abundant structures in the study area are Eocene folds and associated thrust faults (before Nopal Formation). These structures formed synchronously with deposition of the upper member of the Cuervo Formation. The lower member of the Cuervo Formation participated in the folding with the limestones, but the upper member represents a transition between folded bedding and unfolded beds of the Pozos Formation, and the flat laying ignimbrites of the Coloradas and Nopal formations. Minor folds and faults are locally abundant and provide considerable information about the behaviour of the Cuervo Formation during deformation and the direction of consequent tectonic transport. Unfortunately, the intensity of the deformation and the stratigraphic ambiguity of the upper member of the Cuervo Formation necessitate

leaving some problems unresolved. Superimposed on the pre-Late Eocene structures are normal and listric faults and fractures with variable displacements of the Miocene (Basin and Range) and Plio-Pleistocene (Rio Grande Rift, which give the sierra its elongated shape and N-S orientation) tectonism in the Sierra del Cuervo, and even some reverse faults which characterise the Late Eocene (Hidalgoan) trough. Syntectonic igneous activity was common in the study area and provides useful information about the evolution of the Basin and Range stress field and the timing of the tectonism. The youngest recognizable structures in the Sierra del Cuervo are range bounding listric and normal faults (Río Grande Rift).

4. Mineralisation

The majority of the uraniferous prospects of the State of Chihuahua have been detected within Sierra de Peña Blanca by airborne survey. The primary prospects which have received some study are the Nopal I, The Nopal III, Margaritas, and Puerto III (Altamirano, 1992; Bazán, 1978; González, 1956; Goodell and Waters eds., 1981; Goodell, 1981b; Goodell, 1984; Goodell, 1992; and Reyes-C., M. et al., 1980a and b).

The Nopal I has been developed as an open pit in the crystal ignimbrite of the Nopal Formation. However, mineralisation in lesser amounts and lower grades also is hosted by the Coloradas Formation, which underlies the Nopal and Escuadra formations. URAMEX has reported approximately 200,000 tons of ore with a grade above 0.2 % of U3O8 at the Nopal I deposit. The mineralogy includes a greater variety of minerals than any other ore deposit in the district; there include: uranophane, betauranophane, weeksite, sodyite, boltwoodite, masuyite (Reyes-C, M. et al., 1980a and b; and Pearcy et al., 1993), and minor amounts of uraninite, which are mainly fracture fillings and disseminations. The Margaritas deposit, located in the central part of the Sierra del Cuervo, is hosted in the Coloradas-Nopal-Piloncillos-Escuadra formations. Mineralisation was concentrated within a dissected horst. Ore mineralisation was discovered during prospecting of radiometric anomalies by trenches along the eastern side of the hill. The trench rock display intense fracturing with uranium mineralisation, which occasionally also fills fractures as a stock work. There are approximately 1,250,000 tons of ore with an average grade above 0.1 % of U3O8. The mineralogy of Margaritas is represented by uranophane, beta-uranophane, carnotite, tyuyamonite, meta-auntunite, weeksite, and margaritasite. Molybdenum is present as powellite. The elements molybdenum and uranium are present as fracture fillings and disseminated as feldspar replacements, associated with kaolinite, alunite, hematite, calcite, fluorite, and jarosite (Reyes-C, M. et al., 1980a and b; and Pearcy et al., 1993). The jarosite has been dated by the Ar-Ar method and yields an age of 9.8 Ma. The Margaritas orebody uranium is associated with molybdenum. It has a volume of more than 5,300,000 tons, with an average grade above of 0.15 % of CaMoO4 (powellite); therefore, representing about 8,000 tons of molybdenum. The molybdenum tonnage in other areas outside the Margaritas deposit is expected to involve 4,500,000 tons, with an average grade above 0.1 % of CaMoO4 (powellite). That represents another 3,850 tons of molybdenum. The closure of URAMEX took place in April 1983; as a result of this, the study of the deposit ceased at the evaluation of recovery costs of molybdenum. The Puerto III orebody is located at the western limit of the Margaritas orebody, on the western side of the NW-SE trending graben fault. It is hosted at the Nopal-Escuadra formational contact as well as in the uppermost part of Nopal Formation and the lower part of the devitrified vitrophyre of the Escuadra Formation, which has been altered to montmorillonite, saponite, and nantronite. The mineralisation is located along the contact, forming a sill shaped orebody, which dips eastward. The uranium is in fracture fillings with lesser amounts in disseminations within the devitrified vitrophyre. The identified mineralogy includes uranophane, meta-tyuyamonite, carnotite, and minor quantities of powellite, with a texture similar to that in Margaritas (Reyes-C, M. et al., 1980a and b; and Reyes-C, M., 1985). Reserves are calculated to be approximately 570,000 tons, with an

average grade of 0.12 % of U3O8. At the termination of URAMEX activities, development of the mine was taking place by subsurface works through two inclined adits. The two adits were designed to recover the orebody through two operational fronts. These three important ore bodies have mineralogical similarities such as uranophane, weeksite, soddyte, schoepite, boltwoodite, carnotite, and meta tyuyamonite. However at the Nopal I minor pitchblende or uraninite was found. The more important identified alteration types within the deposits include silicification, argillitisation, and carbonatisation. The composition of the hydrothermal fluids was enriched in CO2, F, S, Si, U, and Mo. The genesis of these uranium deposits is controversial, and is not the topic of the present study.

The Nopal I orebody was formed by hydrothermal solutions that moved through an almost vertical and intensely fractured rock, precipitating uraninite, which was secondarily altered to minerals ranging from the oxyhydroxides to the silicates. These secondary uranium minerals have a very complex distribution in the orebody and the interpretation of their presence could be the result of a combination of factors: such as hydrothermal, supergene, volcanogenic, and weathering processes (George-Aniel et al., 1991; Goodell and Trentham, 1980; Goodell, 1981b and 1985a). Hydrothermal alteration after deposition for example could radically change and redistribute the mineralisation in the fractured zone. Uraninite is a primary uranium mineral deposited along the fractures. It is still preserved because of the strong silicification of the breccia. Uraninite also has been precipitated as pore fillings and replacement of some feldspar and ilmenite phenocrystals as has been described by Leslie et al., 1993b. The majority of the uranium mineralographic studies were made by Leslie et al., 1993b at the SWRI. Uraninite occurs with three diferent textures: a). Granular uraninite is the most abundant morphology observed within the deposit. It is intergrown with euhedral kaolinite when it replaces phenocrystals; uraninite also displays intergrowths with euhedral pyrite (Pearcy et al., 1993). Uraninite has been considered to be a pitchblende analog (George-Aniel et al., 1991; George-Aniel et al., 1985). b). Colloform uraninite growths as radial crystals is observed in open spaces. This type of uraninite does not have kaolinite or pyrite associated with it. It appears to be subsequent to the granular morphology. c). Euhedral uraninite in cubic crystals are associated with and/or intergrown with pyrite. Uraninite even replaces pyrite (Pearcy et al., 1993). These morphologies are protected from weathering by a strongly silicified shell. The first dissolution stage of uraninite produced ianthinite, schoepite, and dehydrated schoepite. Ianthinite (U4+U6++O2)5(OH)1 4-3H2O), forms as strong red to violet acicular crystals filling cavities and fracture spaces. It is unstable in air, and can convert to schoepite. Its presence at the Nopal I mine gives us a concept as to the degree of isolation of the minerals within the orebody. Schoepite (UO3-2H2O) is more abundant than the ianthinite, and it is found filling the open spaces over colloform uraninite. Schoepite is a distinct brown to amber color under crossed nichols. It is followed and even replaced by the uranophane. Other minor recognized minerals includes billietite Ba(UO2)6O4(OH)6-4-8H2O, abernathyite K(UO2)(AsO4)-4H2O, and becquerelite Ca(UO2)O6O4(OH)6-8H2O (Pearcy et al., 1993). The main associated secondary minerals are kaolinite Al2Si2O5(OH)4, hematite Fe2O3, and goethite alpha-FeO-OH. The uranium silicates occur either as pseudomorphs on pre-existing minerals or as euhedral forms in open spaces. The uraninite alters to uranium oxyhydrates, which alters again to silicate form. Silicates are better preserved and more resistant to weathering. The soddyite (UO2)2SiO4-2H2O is present within the more strongly oxidised zone. It is in euhedral, rhombic, yellow-orange, bipyramidal crystals, which are intergrown with uranophane, weeksite, and boltwoodite. Uranophane Ca(UO2)2Si2O7-6H2O is much more abundant around peryphery of the orebody. Uranophane and beta uranophane coexist within the centre of the orebody, but peripheral to the orebody, uranophane is the common species of mineral. Uranophane fills the open spaces with fine, equidimensional yellow to yellowish green crystals, whereas the yellow alpha uranophane forms in clusters of acicular crystals. The beta

uranophane is deposited as yellow-orange prismatic crystal masses. Weeksite K2(UO2)2Si6O15-4H2O and boltwoodite HK(UO2)SiO4-1.5H2O occurs as fine-grained-equigranular-anhedral, yellowish, and acicular-radiating crystal masses. Euhedral and granular uraninite are intergrown with kaolinite and pyrite, but not in the colloform morphology. One concept is that the colloform uraninite was dissolved by acid sulfate solution and transported for short distances to reprecipitate at the actual orebody within the breccia. This particular process leachs Ca, Na, Pb and other cations from the original uraninite precipitation. According to this interpretation the colloform uraninite has no nonradiogenic lead, and the average age of the colloform uraninite is 7.9 + 5.2 Ma (Leslie 1993a and b). Other age dating of the euhedral uraninite give results of 27.52 + 0.07 and 60.68 + 0.34 Ma (Leslie et al., 1993b). Early dissolution and uraninite reprecipitation has produced strong alteration at the Nopal I deposit. The centre of the deposit is a depleted cylinder of uranium minerals and is enriched in K-Fe sulfate minerals such as jarosite and alunite. This removal and redeposition of minerals can be generated by oxidation of the primary pyrite within the orebody. Oxidising fluids provide the mechanism to generate alunite and at the same time produce the conditions of uranium removability, which could generate the depleated uranium zone at the center of the orebody. The primary ore mineral association was uraninite + kaolinite + pyrite + quartz. The sequence of ore deposit alteration goes from oxides to oxyhydrates to silicates, which represents uraninite to ianthinite and schoepite and these minerals to uranophane, weeksite, and boltwoodite. The majority of the silicates are recorded as intergrown crystal masses. The alteration of the primary uraninite may be produced as the product of the episodic infiltration of meteoric waters, the hydrothermal fluids immediately after the deposition, the heated fluids from later volcanic activity passing through the ore deposit, or some combination of these processes. Actual alteration of the deposit is the result of more than a single event and can be processing for hundreds of thousands to millions of years. Obviously the fluids causing alterations must contain some of the impurities that were leached from the host rock such as silica, calcium, and potassium. The last alteration system would seem to be related to weathering as a consequence of the deposit being uplifted with the Nopal Cuesta. This tensional stresses uplift and exposes the deposit to meteoric waters. The 13.5m N fracture is one of most recent of the fractures (E-W subsystem). It crosses and cuts the orebody itself indicating that the fracture is younger than the deposit. In conclusion the 13.5m N fracture is a natural pathway to remove uranium away from the deposit. Also the jarosite content in the fracture filling material decreases with distance from the orebody, this suggests that the deposit itself was the source for uranium (weeksite and uranophane) and sulfur (jarosite). The Rio Grande Rift tectonism during which the Nopal Cuesta was formed, possibly this tectonic process has exposed the orebody to direct weathering processes. The caliche shells from filled fractures have partial uranium mineralisation in the immediate surroundings of the orebody. This caliche shell has been dated at 53.6 + 0.8 by 103 a (Leslie et al., 1993b). The presence of caliche at this height suggests the climatic dominance and alteration processes that were generated on the exposed orebody.

Alteration defined in the study area is separated by the altered type material, to be analysed by fluorescence and X-ray diffraction. The identified alteration types are: argillitization, silicification, oxidation, carbonatation and fluoritisation, pyritization, and leaching (Goodell and Trentham, 1980; Goodell, 1981b; Goodell, 1983; and Reyes-C, M. et al., 1980a). Argillitisation: This is the strongest alteration within the Sierra del Cuervo and it is divided into two types: feldspars and rock fragments kaolinisation with products such as kaolinite, dikite, and alunite derived from the supergenic alteration with acid solutions. The Nopal Formation is the most kaolinised formation in which uranium mineralisation is concentrated within the district. Alunite is associated with uranium silicates, and both are substituting and filling phenocrystals of leached feldspars. The second type is related to the clay minerals of the

montmorillonite group: nontronite, saponite, and montmorillonite. The majority of the altered vitrophyre horizons correspond to this second type. The kaolin is the result of the feldspar alteration and montmorillonite in the result of vitrophyre alteration. Silicification: Silicification is abundant within the area, quartz forms veins, and veinlets, and, eventually, substitutes for feldspar phenocrystals. Sometimes quartz has uraninite inclusions, uranium silicates, hematite, and unidentified fluids. It also is present in an opaline form in veinlets of void fillings of leached feldspars and rock fragments. Silica forms in botryoid clusters covering and protecting other uranium silicates. Silicification is abundant within the Nopal I and Margaritas orebodies, but within the Puerto III, it is negligible. Oxidation: This type of alteration affects most of the ignimbrites; however, it is not present in some parts of the ore deposit because of the extreme kaolinisation. Hematite is found concentrated along the fault walls and fracture fillings. Oxidation also replaces feldspar phenocrystals that are disseminated within the devitrified glass of the ignimbrite. The hematite could also be associated with leucoxene. Carbonatisation and fluoritisation: this type of alteration is scarce or absent within the upper formations (Escuadra, Peña Blanca, Mesa), but are common within the Nopal and Coloradas formations. Calcite is observed in thin veinlets, which increase in number and thickness as one goes deeper, closer to the underlying limestone contact. Near the contact veinlets are abundant and also calcite replaces feldspars and portions of the glass of the ignimbrite matrix. Black calcite is abundant and fluorite is scarce in the study area. Calcite also is present at the contact between the Nopal and Escuadra formations. The argillitised vitrophyre of the Escuadra Formation apparently blocked the development of fluorine fluids. Pyritization: this type of alteration can not be taken as general alteration feature. It has a very restricted at the Nopal I and Margarites. However, most of the pyrite is oxidized to hematite and cubic hematite pseudomorphs of the pyrite. Leaching: The feldspar casts are voids produced by the feldspar argillitisation and later leaching. This argillitisation and leaching alterations are common in the Chontes, Escuadra, and Piloncillos formations; however, they are more abundant in parts of the Nopal Formation. Leaching has restricted extent at the Nopal I orebody, but in the Margaritas and Puerto II, it is very significant to assume that supergenic solutions had different effectiveness in their degrees to dissolve, leach, or precipitate.

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Uranium Chemistry and Isotopy in Waters and Rocks at Peña Blanca, Mexico

David A. Pickett and William M. Murphy
Center for Nuclear Waste Regulatory Analyses
Southwest Research Institute
6220 Culebra Rd.
San Antonio, TX 78238 USA

Abstract

A geochemical chronology of uranium (U) behavior is described for the Nopal I natural analogue, which is hosted in 44 Ma tuffs. Available evidence points to primary U mineralization at around 8 Ma, followed by oxidative alteration as recent as 3 Ma. The past few million to several hundred thousand years were marked by open-system U mobilization, with episodes of U release and deposition at around 400 and 54 ka. This timing information has implications for attempts to model release and transport processes in nuclear waste repositories.

1. Introduction

The geologic history of U at the Nopal I U deposit, Peña Blanca, Mexico, is useful for understanding processes of U solid phase evolution and radionuclide transport (RT) in nuclear waste disposal analog studies. The purpose of this paper is to outline the Nopal geochemical chronology, drawing on data presented in Murphy and Pearcy (1992), Leslie et al. (1993), Pearcy et al. (1994), Pearcy et al. (1995), Pickett and Murphy (1997), Prikryl et al. (1997), Pickett and Murphy (1999), Pickett et al. (1999), and Murrell et al. (this volume). As background to this summary, this volume includes an introductory paper by Murphy and a geologic overview by Reyes. In addition, Murphy et al. (this volume) present applications of Nopal results in performance assessment (PA) analyses and process model sensitivity analyses.

2. Primary Mineralization

The first U mineral to be deposited at Nopal was uraninite with formulae between UO_2 and $UO_{2.33}$ (Pearcy et al., 1994). Associated primary minerals were pyrite, kaolinite, and quartz. The preferred model for ore formation (Pearcy et al., 1994) involves reduction of dissolved U(VI) by fluid interaction and deposition of the sparingly soluble U(IV) as uraninite. The thermal regime of this presumably hydrothermal mineralization is not well constrained; limited stable isotope data suggest temperatures as low as 50–75 °C (Idlefonse, Agrinier, Allard, Muller, and Calas, this volume). Textural and mineralogical chemical evidence suggests limited mobilization and recrystallization of U, possibly related to acid sulfate fluids generated by pyrite oxidation. This event did not produce uranyl minerals. The latest stage uraninite tended to contain low concentrations of cation impurities and elevated sulfur, consistent with the presence of acidic fluids. Electron microprobe data on U and Pb concentrations in the late, cation-poor uraninites yield a chemical U-Pb age of 8±5 Ma (Table 1). Only small quantities of uraninite are preserved at Nopal, shielded from oxidative alteration by surrounding silicic material.

Table 1. Nopal I uranium chronology

Time	Process or event	Data	Reference
44 Ma	age of host rocks	K-Ar age of Nopal Fm	Alba and Chavez (1974)
8±5 Ma	uraninite formation	U-Pb chemical age of latest stage, during limited remobilization	Pearcy et al. (1994)
3 Ma	oxidative alteration	U-Pb isotopic ages of late-stage uranophane	Pickett and Murphy (1997)
3(?)-0.2 Ma	ongoing U mobilization and deposition outside primary deposit	U-series disequilibrium systematics of fracture fill and bulk tuff	Pickett et al. (1999)
400 ka	U mobilization episode	U-Th ages on fracture fill	Murrell et al. (this volume)
200 ka to present	ongoing mobilization marked by partial release from U-enriched rocks	U-series disequilibrium systematics of fracture fill and bulk tuff	Pickett et al. (1999)
54 ka	U mobilization episode	U-Th ages on U-rich caliche and opal	Leslie and Pearcy, 1993

3. Secondary Mineralization

Present U mineralogy at Nopal is dominated by uranyl phases resulting from oxidative alteration of uraninite (Pearcy et al., 1994). The general alteration progression was uranyl oxide hydrates—chiefly schoepite ($UO_3 \cdot 2H_2O$), but including the mixed-valence phase ianthinite $[U^{4+}(U^{6+}O_2)_5(OH)_{14} \cdot 3H_2O]$—then uranyl silicates—dominantly uranophane $[Ca(UO_2)_2Si_2O_7 \cdot 6H_2O]$ and soddyite $[(UO_2)_2SiO_4 \cdot 2H_2O]$. Alteration was caused by reaction with oxidizing groundwaters. This alteration period may have been contemporaneous with (i) redistribution of U to the outer annulus of the deposit (Pearcy et al., 1995) and (ii) initial mobilization of U out of the primary deposit. Likely contemporaneous oxidized minerals include early iron oxides and oxyhydroxides and sulfate minerals jarosite and alunite.

With regard to age constraints on secondary U mineralization, U-Pb isotopic data on three samples of late-stage uranophane were presented in an earlier Natural Analogue Working Group volume (Pickett and Murphy, 1997). Five fractions from one sample yielded ^{238}U-^{206}Pb and ^{235}U-^{207}Pb ages of 3.4 and 3.2 Ma, respectively, and the two other samples plotted on the same isochron. These data indicate a U phase oxidation event at around 3 Ma (Table 1). Given the uncertainty on the uraninite age discussed above, it is possible that oxidation followed relatively soon after primary U mineralization.

4. Mobilization

Mobilization of U out of the area of visible U mineralization characterized uranium evolution subsequent to oxidation. Detailed observations of transported U have been carried out primarily in the horizontal dimension, and information on the vertical component of transport is limited.

Contact gamma dosimetry and rock concentration data show that U has been mobilized and transported outside the zone of visible U mineralization (Leslie et al., 1993; Pearcy et al., 1995; Prikryl et al., 1997; Pickett et al., 1999). These data indicate that transport was enhanced along fractures; in generally fractured tuff, transport was greatest in the downslope direction. Traverses across fracture boundaries suggest that matrix diffusion of U was limited (Pearcy et al., 1995). Microprobe data show that U was incorporated in iron oxide/oxyhydroxide fracture filling minerals at concentrations of up to thousands of ppm (Prikryl et al., 1997). Sequential extraction experiments confirm that U is concentrated strongly in these phases—both amorphous and crystalline—and that lesser but substantial amounts of U reside in adsorption sites (Pickett et al., 1999).

Uranium-series disequilibrium data on bulk rocks and fracture filling materials outside of the primary ore deposit indicate a recent, complex history of U mobilization (Pickett and Murphy, 1997; Pickett et al., 1999). Non-unity $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ activity ratios demonstrate that U has been mobile during the past several hundred thousand years, and relationships between the $^{230}Th/^{238}U$ and $^{234}U/^{238}U$ ratios require that U transport has not followed a single-stage evolution. Data suggest initial U deposition exterior to the primary deposit took place several hundred thousand years ago (and perhaps earlier, if deposition was more continuous) and that more recently, U was partially remobilized and removed. Furthermore, coeval ages of 54 ka for U-rich opal and caliche adjacent to the U deposit indicate that recent mobilization has been episodic in nature. Other U-series data on three samples of fracture fillings (Murrell et al., this volume) are consistent with an episode of U deposition around 400 ka, followed by maintenance of a closed system with respect to U and Th; unlike the data in Pickett et al. (1999), the ^{230}Th–^{234}U–^{238}U systematics of the Murrell et al. data do not require multistage evolution. Taken together, these data show, for the last 10^5 to 10^6 yr, an open-system U history marked by episodes of more pervasive mobilization, both into and out of fracture filling materials outside the ore deposit. Recent partial U removal from host rocks is consistent with interpretations of radiation-induced damage in kaolinite (Allard and Muller, 1998; Ildefonse et al., this volume).

5. Current Mobilization

Information on current U mobilization is limited because of the scarcity of water data from this arid site in the unsaturated zone (UZ). Perched and seep waters from Nopal are dominated by calcium bicarbonate, and geochemical modeling indicates that aqueous U is in the form of uranyl carbonate complexes (Pickett and Murphy, 1999). The U contents of these waters—which, based on the locations from which they were collected, have not apparently interacted with U minerals—are below uranyl mineral solubility limits. Elevated Si contents of most waters lead to low calculated solubility limits on dissolved U, with haiweeite and soddyite being the least undersaturated uranyl phases (based on limited thermodynamic data on these phases). In this system, therefore, secondary uranyl silicates would be predicted to suppress dissolved U concentrations. Uranium-series activity ratio data on these waters display a linear correlation between $^{234}U/^{238}U$ and the reciprocal of U concentration, consistent with progressively higher degrees of U leaching in the perched waters relative to the seep waters. This contrast is likely due to longer contact times for the perched waters (Pickett and Murphy, 1999).

Evidence of current radium mobilization is found in plants growing on piles of Nopal ore (Leslie et al., 1999). Plant leaves contain unusually high concentrations of Ra. The high rate of Ra enrichment relative to U suggests that daughter radionuclide release from U minerals in some cases may exceed U release.

6. Summary

The history of U at the Nopal I natural analogue is complex. Following primary uraninite mineralization at approximately 8 Ma, oxidizing conditions led to secondary uranyl mineral formation (and perhaps initial U mobilization outside the deposit) by around 3 Ma. Open-system mobilization continued to the present, marked by episodes of more extensive U release recorded by U-series mineral age data at around 400,000 and 54,000 yr before present. It is likely that other episodes occurred, but data are limited. Recent history is also marked by partial U remobilization out of U-enriched host rocks and fracture fill. Present-day UZ waters are capable of only limited U transport according to thermodynamic modeling, but isotopic data show progressive leaching in waters with prolonged contact with U-enriched rocks. Radium is apparently capable of significant release in the present environment.

The relevance of Nopal geochemical processes to nuclear waste disposal studies in general, and the proposed U.S. repository at Yucca Mountain in particular, are well established (Murphy, this volume). Applications of these results to nuclear waste repository PA are discussed by Murphy et al. (this volume). The most important Nopal observation applicable to PA is the correspondence between Nopal uranyl mineral paragenesis and laboratory studies of alteration of spent fuel and waste form analogues. With respect to RT issues in this analogue setting, the Nopal results point to the importance of fracture transport as well as sequestration on minor fracture phases such as iron oxides/oxyhydroxides, the limited significance of matrix diffusion, and the episodic nature of U mobilization and transport.

Geochronologic data on U mobilization events and processes at Nopal are sparse. Useful information on the rates of pertinent processes may be gained from more dating of U-rich caliches, U-rich opals, uraninite, and uranyl phases. More information on transport processes requires additional rock sampling in the vertical direction and analyses of UZ waters that have traversed U mineral-bearing rock.

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Uranium Decay Series Mobility at Peña Blanca, Mexico: Implications for Nuclear Repository Stability

M T Murrell, S J Goldstein and P R Dixon
Los Alamos National Laboratory
MS 1663
Los Alamos, NM 87545

Abstract
Studies of U-series disequilibria near uranium ore deposits can provide valuable information on the mobility of uranium and its daughters over the range of timescales needed to assess the stability of proposed waste repositories. We have applied TIMS methods to obtain ^{238}U-^{234}U-^{230}Th-^{226}Ra and ^{235}U-^{231}Pa data for whole rock samples within a ~30 m long fracture emanating into surrounding tuff from the Nopal 1 uranium ore deposit at Peña Blanca, Mexico. Most of the primary uranium ore (uraninite/pyrite) at this site has been altered to uranium- and iron- hydroxides, oxides, and silicates. Solutes were transported short distances away from the main mineralised area along fractures and faults. Since all of the fracture minerals were deposited by aqueous solutions, the ages of the mineral phases are related to the timing of the primary fluid flow(s). Subsequent alteration of these secondary mineral phases during more recent fluid movement can also be evaluated using measurements of uranium-series disequilibria.

The ^{238}U-^{234}U-^{230}Th data we obtained using thermal ionisation mass spectrometry lie on a whole-rock isochron that requires closed-system behaviour for the last 400ka. The ^{231}Pa-^{235}U data also indicate closed system behaviour for at least the last 100ka. In contrast, $^{226}Ra/^{230}Th$ activity ratios range from 0.76-0.99, which suggests more recent Ra mobility within the fracture, most likely due to surface water infiltration. Our results require uranium, thorium and protactinium immobility within the fracture over at least the past 100ka. This geochemical stability has apparently survived the more recent hydrologic disturbances that have mobilised radium. These results provide important constraints on repository stability over ~100ka timescales.

Introduction
The Nopal 1 uranium ore deposit in the Peña Blanca district, Chihuahua, Mexico, has been extensively studied as a natural analog for actinide transport from the proposed high level nuclear waste repository at Yucca Mountain, Nevada (e.g. Pickett et al., 1996; Wong et al., 1996; Pearcy et al., 1995; Prikryl et al. 1995, Pearcy et al., 1994; Murphy and Pearcy, 1993; Murphy and Kovach, 1993; Pearcy and Murphy, 1990). Studies of U-series disequilibrium within and around uranium deposits can provide valuable information on the timing of actinide mobility and hence the stability of any proposed repository over the geologic time

scales associated with the required lifetime of the facility (Wong et al., 1996; Pearcy et al., 1995; Cramer and Smellie, 1994; McKinley and Alexander, 1993; Scott et al., 1992; Petit, 1990; IAEA, 1989). We have applied precise thermal ionisation mass spectrometric (TIMS) methods to obtain ^{234}U-^{230}Th dates as well as ^{231}Pa and ^{226}Ra concentrations for three samples from a ~30 m long uranium mineralised fracture emanating into surrounding silicic tuff from the Nopal 1 uranium deposit.

Geologic Setting

The geologic setting of the Nopal 1 uranium deposit is analogous in many respects to the proposed high-level waste repository at Yucca Mountain (Pearcy et al., 1994; Murphy and Pearcy, 1993; Pearcy and Murphy, 1990). Both Yucca Mountain and Nopal 1 are located in semi-arid environments in Tertiary rhyolitic tuffs that are underlain by carbonate sedimentary rocks. Furthermore, both the proposed repository horizon and Nopal 1 are in unsaturated welded tuffs well above the present day water table.

Most of the primary uranium ore (uraninite/pyrite) at Nopal 1 has been altered in the recent past to uranium and iron hydroxides, oxides, and silicates. Solutes were transported short distances away from the main mineralised area along fractures and faults (Pearcy, et al., 1995; Pearcy et al., 1994). All of the fracture minerals were deposited by aqueous solutions. Thus, the ages of the mineral phases are related to the timing of fluid flow that deposited the minerals in the fractures. Furthermore, any subsequent alteration of these secondary mineral phases during recent fluid movement will be detectable by uranium series disequilibria measurements.

Analytical Methods

Three whole rock samples were obtained from a major east-west trending fracture set of the Nopal 1 uranium deposit. The fracture is located at 13.5 m north on the reference grid employed by Pearcy et al. (1995). One sample is from within the zone of visible mineralisation and the other two are from ~10 m and ~26 m outside of this zone. For each sample, approximately 100 grams of each sample was subdivided into tuff and fracture filling mineral fractions of <1 cm size with a chisel. The fracture filling mineral fractions of 5-10 g were then homogenised and powdered with a mortar and pestle, and aliquots of 0.5 g were taken for U-series analysis. A sample replicate, standard reference ore BL-4 supplied by the Canadian Certified Reference Material Program, and blanks were also analyzed.

The aliquots were dissolved in Teflon vials with hydrochloric, hydrofluoric, nitric, and perchloric acids. After treating insoluble fluorides with boric acid, samples were re-dissolved in 1M nitric acid and centrifuged. Samples were then quantitatively transferred, and 1M nitric acid stock solutions were prepared in 1-L polyethylene bottles. For measurement of ^{238}U, a small (0.1% of the total dissolved sample volume) aliquot was spiked with ^{233}U tracer and the U was separated by standard anion exchange methods, loaded onto a single Re filament coated with graphite, and analysed in a VG Sector 54-30 thermal ionisation mass spectrometer. For measurement of $^{234}U/^{238}U$, ^{230}Th, and ^{232}Th, a larger (20%) aliquot was spiked with ^{229}Th tracer and the U and Th were isolated by co-precipitation with ferric hydroxide and standard anion exchange methods and separately loaded onto a Re triple filament assembly for Th and a Re-Ta-Ta filament assembly for U. For measurement of ^{226}Ra and ^{231}Pa an aliquot equal in size to the Th aliquot was taken and spiked with ^{228}Ra tracer and ^{233}Pa tracer. The Ra and Pa were isolated by co-precipitation with ferric hydroxide, organic extraction, and standard anion exchange methods and separately loaded onto a Re filament

assembly with graphite for Pa and on a Pt filament assembly with silica gel for Ra. Radium and Pa were analysed using an NBS 12-90 thermal ionisation mass spectrometer.

Replicate analyses generally show agreement to better than 0.2% for all parameters, demonstrating acceptable reproducibility. Results for the uranium ore standard BL-4 and TML (Table Mt. Latite) are within error limits of the expected values of secular equilibrium, which are indicative of analytical accuracy. Analysed values for process blanks are 40 pg for U, 100 pg for Th, 0.2 fg for Ra and 0.5 fg for Pa and are negligible in comparison with the amounts of these elements in the samples analysed.

Uranium and Thorium Isotopic Results

Uranium concentrations for the samples decrease from ~5500 ppm at the outer margin of the deposit to ~300 ppm at the far end of the fracture, in general agreement with prior studies (Pearcy et al., 1995; Wong et al., 1996). $^{234}U/^{238}U$ activity ratios for the three samples range from ~1.14 to 1.22 and show no systematic spatial trend within the fracture. These results are also similar to values reported by Pearcy et al. (1995) and Pickett et al. (1996). The $^{234}U/^{238}U$ results are generally consistent with an old (~100-1000 ka; calculated model ^{234}U ages from Ivanovich and Harmon, 1992) ^{234}U enrichment produced during dissolution processes and preserved in precipitated minerals.

$^{230}Th/^{234}U$ activity ratios range from 1.026 to 1.044 for the three samples and sample ratios are only resolvable from secular equilibrium and each other using precise methods such as TIMS. In comparison, results from Pickett et al. (1996) show much higher $^{230}Th/^{234}U$ ratios, with values ranging up to 1.39. Model ^{230}Th-^{234}U ages for the three samples range from 380 to 480 ka and appear to be related to the Th/U of the sample, with highest ages for samples with the lowest authigenic component and greatest Th/U. Since the ages appear to be affected by the relative abundance of authigenic and non-authigenic components in the samples, a correction is needed to obtain an age for only the authigenic component (Ivanovich and Harmon, 1992; Scott et al., 1992). Hence, we use the measured Th/U ratios to correct the measured $^{230}Th/^{234}U$ and $^{234}U/^{238}U$ ratios for the non-authigenic component within these samples. This is accomplished by plotting the data in two diagrams (Fig. 1): one with $^{234}U/^{232}Th$ vs. $^{238}U/^{232}Th$ and another with $^{230}Th/^{232}Th$ vs. $^{234}U/^{232}Th$. If the samples are isochronous and derived as mixtures of two components, then these plots will yield a linear trend or isochron. The slopes of the whole-rock isochron correspond to the $^{230}Th/^{234}U$ and $^{234}U/^{238}U$ ratios in the authigenic components of the samples. As is shown in Fig. 1, the data lie on a whole-rock isochron with slopes corresponding to $^{230}Th/^{234}U= 1.039$ and $^{234}U/^{238}U= 1.210$. Based on these ratios, the calculated age for the authigenic component is 408±16 ka. This age is in excellent agreement with uncorrected data from NOPI-418, the sample with the highest U concentration. Based on this age, initial $^{234}U/^{238}U$ activity ratios are ~2, in reasonable agreement with typical values for modern water samples near other uranium ore deposits (Cramer and Smellie, 1994).

Radium and Protactinium Isotopic Results

Radium concentrations for the samples decrease from ~2255 pg/g at the outer margin of the deposit to ~98 pg/g at the far end of the fracture, and protactinium concentrations decreased from ~ 1787 pg/g to ~100 pg/g over the same interval.

$^{226}Ra/^{230}Th$ activity ratios for the three samples range from 0.9871 to 0.7638 and show no systematic spatial trend within the fracture. These results are similar to values reported by Wong et al. (1996) and Pickett et al. (1996) for other parts of the deposit. The $^{226}Ra/^{230}Th$

results are consistent with open system behaviour and radium loss. In contrast, the $^{231}Pa/^{235}U$ activity ratios are all very close to secular equilibrium for the three samples and the standard, which indicates closed system behaviour over the last 100ka.

Discussion and Conclusions

In contrast to the closed system evolution described above, Pickett et al. (1996), Wong et al. (1996), and Pickett and Murphy (1999, these proceedings) and have concluded on the basis of their alpha spectrometric measurements that multiple U mobilisation events involving both U enrichment and removal are required over the past few hundred thousand years to explain their data. This is a consequence of their higher $^{230}Th/^{234}U$ and variable $^{226}Ra/^{230}Th$ measurements, which cannot be explained by a simple model of closed system evolution.

In contrast, our results indicate that the uranium, thorium and protactinium in the fracture filling minerals in this fracture have remained in a closed system for the past 400 ka. Hence, the secondary fracture minerals have been stable with respect to uranium, thorium, and protactinium mobility over this time period. This stability has apparently survived even recent hydrologic disturbances due to surface water infiltration of the fracture due to mining activities, as well as the infiltration of rain water since the fractured rock was uplifted above the water table (Pickett et al., 1996; Pearcy et al., 1994). The radium disequilibria data suggest that this hydrologic disturbance occurred in the past 2000 years. Hence, it appears that uranium, thorium, and protactinium in secondary fracture materials appears to be unaffected by surface water infiltration and perhaps saturated ground-water flow over ~100 ka time scales. This research provides one important indication of the probable immobility of radionuclides in a high-level nuclear waste repository over its required lifetime. By analogy with our results, the tuffs at Yucca Mountain should have similar retentive properties to impede oxidised uranium mobility. The accumulation of natural analogue data from Peña Blanca and similar sites would be of particular importance if it demonstrates the general validity of low actinide mobility in unsaturated siliceous tuffs under semi-arid climate conditions.

Ongoing Research at Peña Blanca

To help better understand the discrepancies between the Pickett et al. (1996) data and model with ours, we will analyse samples from the SWRI study that show large excesses and/or depletions in the $^{230}Th/^{234}U$ data. This exercise will hopefully lead to a better understanding of the mobility of radionuclides at Peña Blanca.

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Figure Captions

Figure 1. Whole rock isochron for the Peña Blanca samples, with $^{234}U/^{232}Th$ vs $^{238}U/^{232}Th$ and $^{230}Th/^{232}Th$ vs. $^{234}U/^{232}Th$ plots. The dashed lines corresponding to secular equilibrium is shown for reference and errors are smaller than the size of the symbols. The solid line or isochron represents the best-fit least squares linear regression for the data. The slopes of the whole-rock isochron correspond to the $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ and ratios in the authigenic component of the sample, which are 1.210 and 1.039, respectively. These ratios are used to calculate an age for the authigenic component of 408 +/- 16 ka. Uranium concentrations are shown as labels for each of the samples.

Figure 2. $^{231}Pa/^{235}U$ activity ratios for the three Pena Blanca samples as a function of distance from the zone of uranium mineralisation as well as data for two reference samples (TML and BL-4). All data is at or very near to secular equilibrium values which requires closed system behaviour for these sample.

Figure 3. $^{226}Ra/^{230}Th$ activity ratios for the three Pena Blanca samples as a function of distance from the zone of uranium mineralisation as well as data for one reference sample (BL-4). The results for the two samples outside the zone of uranium mineralisation indicate loss of radium within the last 2 ka.

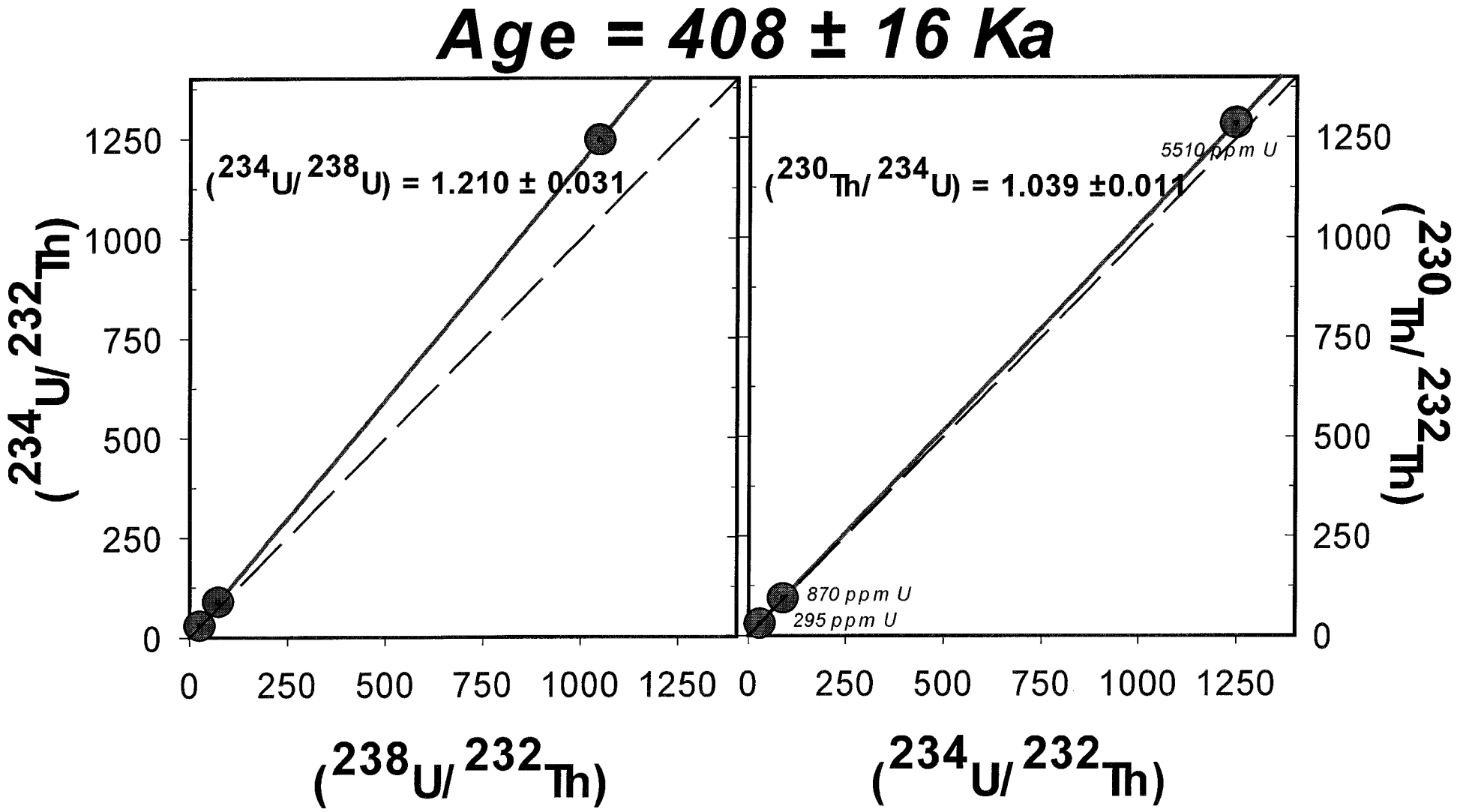
Age = 408 ± 16 Ka
(234U/238U) = 1.210 ± 0.031
(230Th/234U) = 1.039 ±0.011
5510 ppm U
870 ppm U
295 ppm U
(234U/232Th)
(230Th/232Th)
(238U/232Th)
(234U/232Th)
0
250
500
750
1000
1250

Figure 1

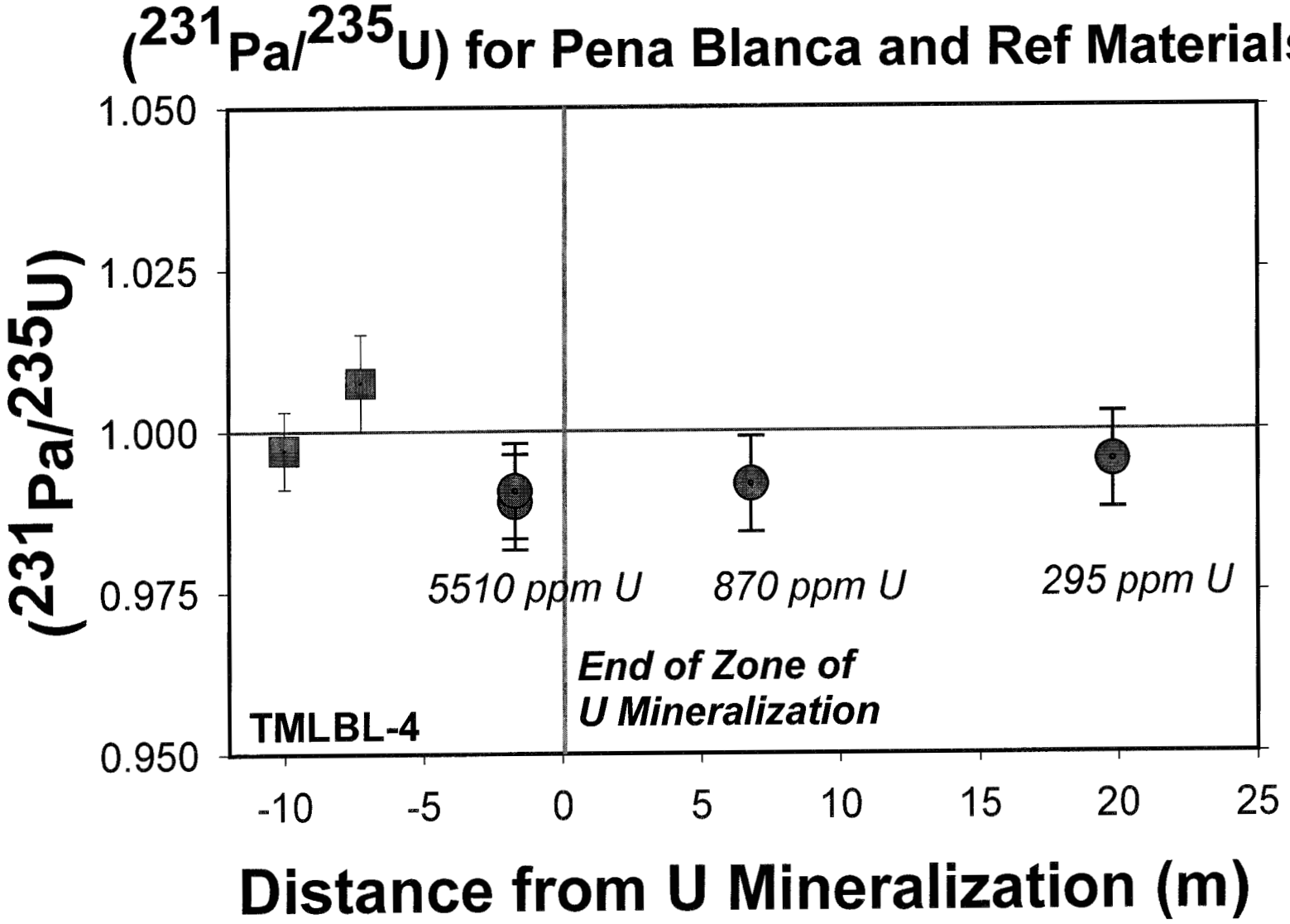
(231Pa/235U) for Pena Blanca and Ref Materials
1.050
1.025
1.000
0.975
0.950
(231Pa/235U)
5510 ppm U
870 ppm U
295 ppm U
End of Zone of
U Mineralization
TMLBL-4
-10
-5
0
5
10
15
20
25
Distance from U Mineralization (m)

Figure 2

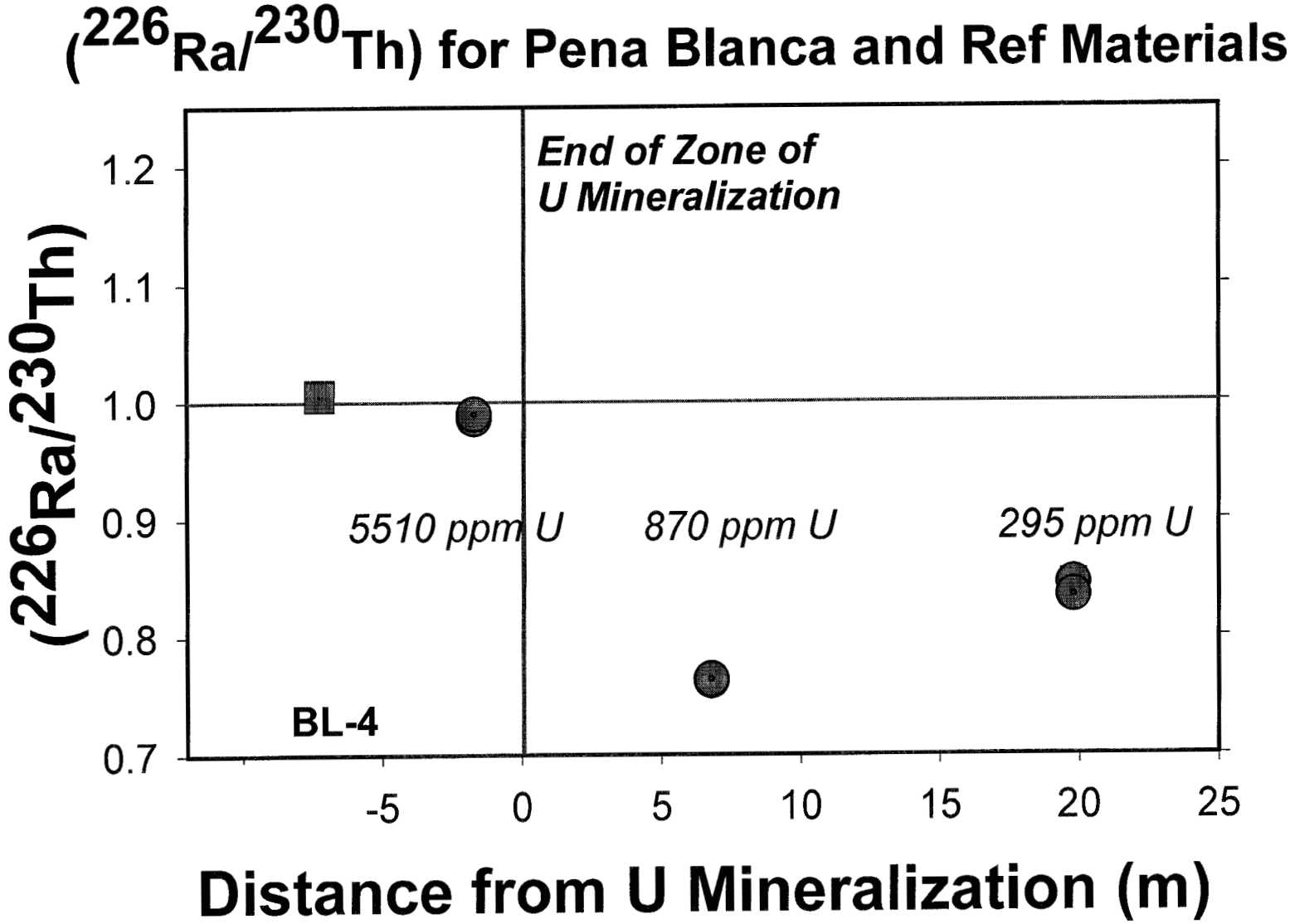
(226Ra/230Th) for Pena Blanca and Ref Materials
End of Zone of
U Mineralization
5510 ppm U
870 ppm U
295 ppm U
BL-4
(226Ra/230Th)
1.2
1.1
1.0
0.9
0.8
0.7
-5
0
5
10
15
20
25
Distance from U Mineralization (m)

Figure 3

IV LESSONS LEARNED FROM THE THREE INTERNATIONAL NATURAL ANALOGUE PROJECTS : PALMOTTU - OKLO - PEÑA BLANCA

Important lessons for PA: A first summing up from Palmottu

B. Grundfelt
Kemakta Konsult AB, Sweden

Introduction

An important part of the Palmottu project is the close integration of the natural analogue study with repository performance assessment (PA). The Palmottu project is one of the few natural analogue projects in which PA has been integrated into the project from the very beginning. This PA work has been arranged as a separate workpackage: WP 5: Conclusions relevant to repository performance assessment (PA). The objective of WP5 is to highlight those conclusions from the Palmottu project that are of particular importance to PA. The tool to be used for meeting this objective is to produce a report that will discuss, from a PA perspective, those tasks within the project that are of particular relevance and the findings from these tasks.

The main areas of interaction between natural analogues in general and PA are the following (Brandberg *et al.*, 1993):

1. Development of scenarios. Studies of natural geological, hydrological and hydrogeochemical systems provide essential evidence of the effects of many scenarios that could be of importance to analyse in repository performance assessments. For slowly evolving scenarios, *e.g.* climatic changes, studies of natural systems probably are the only way to collect evidence of their impacts.
2. Process identification. Interpretations of observations in natural systems are useful in identifying processes that are potentially important for the long-term behaviour of repositories.
3. Testing of models for processes. In the quantitative interpretation of observations from natural analogue studies, simulation models need to be used; this automatically provides a means of testing the models. In addition, specific model tests could be designed based on data from natural analogues. Model testing using natural analogues, in common with any site characterisation, is constrained by lack of knowledge of initial conditions and historical development of the boundary conditions as mentioned above.
4. Cross-checking of data consistency with natural systems. Natural analogues have proven to be valuable for checking that data determined in the laboratory are consistent with observations in nature and vice-versa.
5. Data collection. Some observations made in natural analogue studies can be directly utilised for determining reasonable parameter values for models used in PA. Such data may be of particular value if they represent processes that have been going on in the natural system without or with only insignificant interference from human activities.

The main contributions of the Palmottu project are within the areas 1-3, and this is probably a situation that is common to many studies of natural analogues. Next, examples of PA applications will be shortly discussed.

Development of scenarios

With respect to scenario development the main contribution from the Palmottu project will be in increasing the knowledge of effects of glaciations on the geochemistry of the system. The Palmottu study will help to predict and establish processes within future glacial events. There is significant evidence that glacial melt water intrusion in the vicinity of the ice margin and/or long-term permafrost during glacial times may have influenced the palaeoevolution at Palmottu at considerably depths (Smellie *et al.*, in this volume). Studies on oxygen isotopes show that groundwaters with glacial melt water signatures have been found at depths from 300 to 350 m at Palmottu (Blomqvist *et al.*, 1998, Pitkänen *et al.*, in this volume), and this may suggest that the system has been open to the penetration of oxidising waters. This is not desirable from PA perspective. However, it is highly unlikely that the glacial melt waters would retain their oxidation capacity to any great depth because of the buffering capacity of first the overburden and then the bedrock itself; this is supported by mineralogical evidence (Smellie *et al.*, in this volume). Moreover, the measured present-day redox conditions are reducing below the upper hydraulically active zone (*i.e.* below approx. 150 m). This further demonstrates the rock's capability to re-establish reducing conditions after penetration of oxidising groundwater during past glaciations.

Based on young calcite and uranophane, a continuous alteration and oxygenating process is proceeding at Palmottu (Ruskeeniemi *et al.*, in this volume). This process is also manifested by high concentrations of dissolved uranium in the aqueous phase of the bicarbonate groundwaters (Suksi *et al.*, 1999; Kaija and Blomqvist, 1999). However, with respect to the site-scale uranium balance, the dominant part of the uranium has remained in the ancient U(IV) phases, uraninite and coffinite, throughout its geological history for 1.7-1.8 Ga, despite the fact that the mineralisation has been subject to supergene processes for long times. In conclusion, the dispersion of U has been very limited over millions of years. This increases the confidence in the safety of spent fuel disposal in crystalline rocks.

Process identification

In the area of process identification the Palmottu project will give several important outputs. One such output is the identification of those geochemical reactions and mixing processes governing the evolution of the composition of infiltrating water (*c.f.* Gimeno and Peña, 1999, Laaksoharju *et al.*, 1999, Pitkänen *et al.*, in this volume). In order to test the proposed hypothesis of groundwater evolution, the data have been described and modelled using several standard geochemical tools including principal component analysis (Laaksoharju *et al.*, 1999, Gimeno and Peña, 1999) and both inverse and forward geochemical modelling approaches (Gimeno *et al.*, in this volume). The modelling results received are in good accordance with the identified evolutionary processes of hydrogeochemistry at Palmottu.

Uranium minerals at Palmottu were studied and the processes that have affected the alteration of the uranium mineralogy were discussed, both with respect to ancient and present-day alteration (Ruskeeniemi *et al.*, in this volume). The U(IV) minerals, uraninite and coffinite, show dates of 1.7 to 1.8 Ga and these minerals incorporate the overwhelmingly dominant part of uranium of the mineralisation. Uranophane is the only identified U(VI) mineral and it has been recorded close to ground surface (down

to depths of 30 m) of the uranium-rich Eastern Granite. U-series dating indicate that uranophane is young, from 90 to 240 ka. During a field experiment, performed in a short borehole of the Eastern Granite where uranophane occurs as fracture infilling (Kaija and Blomqvist, 1999), a rapid increase of dissolved uranium concentrations of the recharge water was observed within a short time (a few weeks) following *heavier* precipitation (and lower pH values). Due to the absence of other U(VI) phases, the pH dependent dissolution of uranophane was concluded as the most likely source for increased uranium concentrations. This conclusion was supported by modelling calculations of uranophane solubility and reaction kinetics (Bruno *et al.*, 1999a).

A third output is the identification of redox processes affecting at Palmottu (Bruno *et* al., 1998, Cera *et al.*, in this volume. Thermodynamic modelling performed at Palmottu indicates two zones with different redox controls: the Western Granite where the sulphide minerals seem to control the redox potential, and the Eastern Granite where the uranium minerals could play an important role as a redox buffer in the reduced area, while the most common redox pair $Fe^{2+}/Fe(OH)_3(s)$ appears to control the redox behaviour in the most oxidised surface zones of the same area (Cera *et al.*, in this volume).

Testing of models for processes

Testing of models in different levels is a part of the scientific process of understanding what is going on in the system. The first phase of the project involved integration of geochemical and hydrogeological models for describing the groundwater flow situation of the site. Independent chemical and hydrogeological observations were used to support the interpretations made (Blomqvist *et al.*, 1998).

A well-characterised sub-system of the Palmottu site was selected for testing different types of transport models for describing the behavior of uranium along a selected flow path: The Eastern Flow System. The flow system starts with precipitation under strongly oxidative conditions and continues until reaching 100 m depth, where a relatively mature bicarbonate groundwater and redox values around 0 mV prevail (Read *et al.*, 1999). The target of the modelling exercise was to assess and compare diverse modelling approaches for simulating the migration-fixation of U at the site, and to test alternative hypotheses of U behaviour as a means towards constructing a defensible, conceptual model of site evolution (*c.f.* Read *et al.*, in this volume).

In the modelling work the following processes were considered when attempting to explain the means by which U concentrations in Palmottu groundwater are gained:

- diffusion from the rock matrix
- adsorption/desorption onto/from Fe oxyhydroxides
- dissolution of primary U(IV) minerals
- dissolution of readily mobilised U associated with fracture calcites
- mixing of water bodies
- dissolution of secondary U(VI) minerals.

The final modelling work is not yet completed, but part of the hypothesis testing has already been preliminary reported. Matrix diffusion from the intact rock to the flowing water in fractures appears reasonable in general, but the idea incorporates unrealistically high uranium concentrations for the intact rock in order to create sufficiently large concentration gradients (Nordman and Rasilainen, 1999). Also, the

uranium levels in groundwater would not show a rapid response to seasonal changes of precipitation. Desorption from Fe oxyhydroxides would give realistic concentrations of dissolved uranium, however, most of the sorbed uranium would be removed after ten years, unless substituted from another source (Salas and Ayora, 1999). Dissolution of uraninite, the primary U(IV) mineral, could only produce concentrations that are three orders of magnitude lower than those actually measured in the upper part of the recharge system (Salas and Ayora, 1999), and the authors propose the presence of an eventual additional uranium source, which later was discovered (uranophane, U(VI)-silicate). The ongoing final refinement of the model exercise is now proceeding and taking in account the presence of uranophane in the upper part of the flow system (Read *et al.*, in this volume).

At Palmottu, neighboring drill holes are much closer than would be expected at a potential repository site, allowing a good possibility for quantitative comparison of modelled and measured data. This has provided a valuable test of the applicability of diverse modelling approaches to a real and complex site (Read *et al.*, in this volume).

Another modelling exercises, *e.g.* blind predictive modelling (Bruno *et al.*, 1999b), was set up to test the capability of PA supporting codes and databases to reproduce the behaviour of trace metals in Palmottu groundwaters. In case of uranium, the aqueous speciation is dominated by carbonate U(VI) complexes in the shallow and oxidising groundwaters, and by $U(OH)_4(aq)$ in the deepest, more reducing groundwaters. The results are in good agreement with the conclusions obtained from the solubility calculations: coffinite [$USiO_4(s)$] or U_4O_9 seem to control the solubility of U in the deepest groundwaters, while in the oxidising area, either U(VI) silicates, such as uranophane of soddyite, or a mixed U-Ca carbonate phase could be solubility limiting phases (Fig. 1).

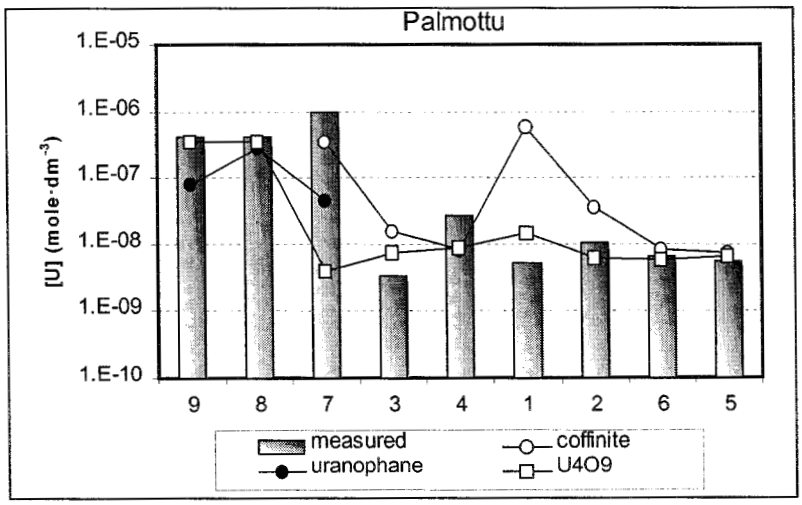

Figure 1. Comparison between the measured and calculated solubility of uranium (Bruno *et al.*, 1999b).

Forthcoming activity

The final evaluation of PA applications of the Palmottu project will be done only after having access to complete reports of individual workpackages. The present paper

presented a short evaluation of PA applications based on three years follow-up of the project.

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Oklo Natural Analogue Project, Phase II

Project Overview and Performance Assessment Applications

V. M. Oversby
VMO Konsult
Stockholm, Sweden

1. Introduction

1.1 Background

Evidence for sustained nuclear fission reactions in a natural uranium ore deposit in Oklo, Gabon, was discovered in 1972. During the following few years, an intense international study of the "Oklo Phenomenon" was undertaken and the results documented in the proceedings of two international symposia. The most important questions for the early investigations centered around the physics of sustaining nuclear reactions in a geologic setting, the response of the host rock to the nuclear events, and the retention or dispersion of the actinides and fission products related to the "natural reactors".

While some reference was made in the early studies to the possibility to use results from investigations of the Oklo Phenomenon to draw conclusions relevant to radioactive waste disposal, there was little attention paid to the Oklo natural reactors during the 1980s. This oversight was corrected in 1991, when a French CEA project with support from the EU was begun. The project title was "Oklo, Natural Analogue for a Radioactive Waste Repository". Participants from other countries - notably Sweden, Japan, and the USA - also participated in the project with associated independently-financed studies. This project, now referred to as the Oklo Phase I Project, concentrated on the new reactor zones discovered after the 1970s work had been finished, with particular attention to reactor zones 10 and 13, which were located near an intrusion, and the Bangombé deposit, which is located to the south of Oklo in a near-surface setting. Bangombé was considered to be particularly useful for studying the effects of oxidative dissolution on the uranium ore and for developing and evaluating hydrochemical modelling codes.

1.2 The Oklo Phase II Project

At the end of the Oklo Phase I project, a group of organizations responsible for waste management activities and research in France, Spain, and Sweden decided to propose a continuation of studies with the objective of undertaking a quantitative assessment of processes of radionuclide migration/retention within the Oklo region, and to relate these processes to analogous parts of a deep repository system for high level radioactive waste. This project, which we refer to as the Oklo Phase II Project was proposed to the EU and accepted for a three year work period beginning in June 1996. The main focus of activities was the Bangombé site, with a minor focus on Okélobondo. The project was organized into four working areas involving

the sampling and characterization of drill core and water samples, detailed assessment of the location of fission products within the samples and in the surrounding geologic environment, refinement of hydrochemical models to describe the transport of uranium at Bangombé and Okélobondo, and modeling of the geochemical processes associated with the ores and weathering at Bangombé.

The project began with a sampling mission to Bangombé in 1996. There was a great sense of urgency concerning sampling, both at Bangombé and from the core storage area at Okélobondo, because the mining company (COMUF) had decided to shut down mining operations by the end of 1996. Eight boreholes were drilled at Bangombé in October, 1996, and drill cores were recovered for shipment to Strasbourg. In early 1997, a meeting was held in Strasbourg of project participants to examine the new material and set priorities for sample distribution and work efforts. During 1997 and 1998, work on Bangombé core samples has investigated the timing of weathering processes using uranium series disequilibrium studies, the geochemistry of the weathering process using characterization of alteration of uraninite, formation of secondary phases, characterization of the mineralogy and chemistry of fracture-coating materials, and analysis and modeling of the water chemistry from the boreholes. Studies have also been undertaken using Bangombé materials to evaluate the potential for retardation of radionuclide transport via sorption of dissolved species onto solids. Other laboratory studies have investigated the dissolution behavior of noble metal alloys, which host Tc in spent fuel, the dissolution of ores samples from Oklo reactor zones, and the control of redox chemistry through mineral/water interactions.

1.3 Project Performance Assessment Activities

The Oklo Phase II Project included as one of its activities an effort to integrate the field and laboratory studies and the project modelling efforts with the Performance Assessment needs of the project supporters' organizations. This was done through the Performance Assessment Interface Group, which had three meetings during the course of the project. At the first meeting, held in conjunction with the first annual project meeting, the Technical Committee and a performance assessment representative from ENRESA discussed ways in which the project information might be better structured to communicate with PA workers. In December 1997, a second meeting of the PA Interface Group discussed three specific focus areas: spent fuel stability, radionuclide behavior at the near-field to far-field interface, and radionuclide retardation mechanisms through sorption and secondary mineral formation.

The most recent meeting of the PA Interface Group was held in Helsinki in conjunction with the 2nd annual Oklo Project meeting and included a wider group of participants, including interested parties who were from countries not participating actively in the Oklo Project. These meetings have opened a dialog between the project participants and those involved in the work of long term assessment of the behavior of a geologic repository. They have increased the understanding between the two groups of workers, but a great deal remains to be done before results from the Oklo Project can be included quantitatively in PA analyses.

2. Potential for use of Results from Oklo in Performance Assessment of Radioactive Waste Repositories

2.1 Uses and Limitations of Natural Analogues

Research and development activities related to nuclear waste repositories have benefited from pre-existing knowledge in the fields of geology, geochemistry, and engineering. Geology and geochemistry were used to evaluate rock types for general suitability as repository host rocks, especially with respect to the interaction of ground water with the rock. The response of different rock types to heat and fluid circulation was known through studies of burial of sediments, diagenesis, regional metamorphism, and local thermal events such as volcanic intrusions. Mining engineering contributed information concerning the response of rock bodies to excavation. In this sense, the evaluation of natural geologic systems represented the start of "performance assessments" for waste repositories. We should, therefore, not be too surprised if further studies of geologic occurrences of specific minerals or ores fail to produce startling revelations.

Laboratory studies of potential waste products, container materials, and other engineered components that might be used in a radioactive waste repository form the framework of studies that will enable us to evaluate the potential future behavior of a waste disposal system. Even these studies have limitations, since we have to predict the future based on our understanding of past behavior of materials under conditions that only approximate those that will pertain in the repository. Our extrapolations are based on our understanding of the equilibrium chemical and physical behavior of the materials and on the kinetic restraints that may prevent equilibrium from being achieved.

In the laboratory, we can control the physical and chemical conditions of experiments rather well. In a natural setting, especially where we are using existing geologic evidence as our area of investigation, we have considerable uncertainties about fundamental parameters. We can, sometimes with difficulty, establish the present temperature, chemical compositions of solids and liquids, and flow rates - if any - of fluids in the system. But we are always left with the problem of trying to "read the record" and estimate how long the present conditions have been constant, and whether conditions in the past have been radically different. The older the natural material that we investigate is, the more uncertain we are concerning the integrated chemical/physical conditions to which it has been exposed. It is precisely these uncertainties that make it difficult, if not impossible, to provide quantitative information from geologic studies that can be used in waste repository performance assessment. This is without considering the even larger problem of finding a natural occurrence that is truly analogous to a waste disposal system or subsystem.

With all of these difficulties, why do we try to study "natural analogues" for waste disposal systems? There are two main reasons. First, we want to convince ourselves, as well as others, that we have not overlooked an important process that will affect the ability of our waste disposal system to function as designed. By studying as many natural systems as possible, we gain confidence that we have not overlooked some essential process. The

particular area where natural systems provide extremely useful information is that of kinetics of slow processes with low activation energies. In the laboratory, we try to speed up processes by increasing the temperature. This may move us into a regime that has a different equilibrium chemical assemblage, but we can usually discover this and not be misled. A more difficult problem occurs when there is a process that has a very low activation energy. In this case, over thousands of years the low activation energy process will dominate, but we will only see high activation energy processes in our laboratory "accelerated" experiments. The second area where natural analogues are particularly helpful is with communication to non-specialists, both the general public and scientists whose area of expertise is somewhat to very far from those of the repository developer and performance assessor. Seeing a "natural analogue" of a waste form that is more than some tens to hundreds of millions of years old gives one a comfortable feeling that the earth in the regions within a few kilometers of the surface is not such an aggressive environment after all.

2.2 Performance Assessment Needs

The structure of a performance assessment analysis or a safety assessment of a nuclear waste repository will depend on the local geologic conditions, the particular engineered barriers selected for the repository, the choice of scenarios for analysis, and the particular regulatory framework in which repository licensing will occur. Despite these potential differences, most repository performance assessment calculations will use quantitative information concerning the behavior of the waste products and their interaction with water. If we break down the types of quantitative information that are likely to be used, we find (for repositories designed for spent nuclear fuel disposal)

Rate of dissolution of spent fuel matrix

Rate of release of fission products and actinides from spent fuel matrix

Rate of transport of radioactive materials after release from the matrix

Effect of processes that can trap or retard transport of radioactive materials.

Depending on the repository design and on the analysis tactics chosen, the importance of each of these types of information will vary. For example, it is possible to imagine a case based only on transport of material after release from the matrix. For that analysis case, the first two types of rate information would not be needed.

2.3 Spent Fuel Matrix Dissolution Rates

Many laboratory studies attempt to measure parameters that can be used to determine the rate of dissolution of spent fuel under repository disposal conditions. These studies use either spent fuel itself, uranium dioxide as an "analogue" for spent fuel, or uraninite as a "natural analogue". Some studies have also been done on a synthetic material, SIMFUEL, that attempts to duplicate the chemical and physical condition of spent fuel without using

radioactive materials. In all cases, the data from these experiments must be extrapolated from the conditions used in the laboratory to the conditions expected in the repository. The key extrapolations include estimates of water chemistry under repository conditions, water flow rate, geometry of water-waste form contact, and redox conditions.

There are four basic sets of conditions for water-waste form interaction. They are oxidizing conditions with stagnant water, oxidizing conditions with flowing water, reducing conditions with stagnant water, and reducing conditions with flowing water. The complexity of the situation becomes apparent when one realizes that there is a continuous gradient in oxygen fugacity between the extremes of "oxidizing" and "reducing" conditions, and a continuous range in flow rates for water between the extremes of zero (stagnant water) and unrestricted flow. Laboratory studies, and field studies of natural analogues of waste forms, must first be located within the two continua of oxygen fugacity and water flow rate, and then the data must be extrapolated from the conditions of measurement to those expected in the repository. An additional level of uncertainty is introduced, of course, because the actual conditions in the repository cannot be precisely defined.

Depending on the location of experimental or field conditions in the continuum of flow rate, one may measure the initial rate of dissolution at infinite dilution (very large flow rate), a dissolution rate that is much slower because the species of interest is present in solution in considerable abundance (low flow rate), or the solubility of the material itself or of some secondary alteration product of the material being examined. When one is dealing with uraninites, both in the laboratory and in natural settings, one must also be aware that the presence of minor phases and of substantial amounts of lead formed as the long-term decay product of uranium, must also be taken into account.

It is also tempting to try to estimate spent fuel dissolution rates using the release of highly soluble materials such as Cs, I, or Tc under oxidizing conditions. There are two additional considerations if this type of analysis is attempted. First, the material analyzed may not be homogeneously distributed in the fuel matrix - e.g., Tc. Second, even at equilibrium, where no net dissolution of the fuel matrix would occur, there will be a dynamic process of dissolution and reprecipitation at the fuel surface, which may release materials that are present in solid solution in the matrix. Once these materials are released, if they have a solubility higher than the fuel matrix, they will not reprecipitate. Use of the change in concentration of such an element in solution to infer the matrix dissolution rate would lead to an erroneous overestimate of the matrix dissolution rate.

2.4 Oklo as an Analogue for Spent Nuclear Reactor Fuel

The reactor zones at Oklo, Okélobondo, and Bangombé are the only places where nuclear chain reactions have been identified as occurring in natural uranium ore deposits. The reactor zones are similar to spent commercial reactor fuels in that the amount of ^{235}U at the time of reactor operation was about 3.5%, which is similar to the enrichment of ^{235}U in commercial reactor fuel. The reactor zone uraninites contain as solid solutions in the uraninite matrix many of the original fission products or the isotopes produced after decay of

the original fission products. In all cases except for the current near-surface environment of the Bangombé reactor zone, the redox conditions have been such that UO_2 remained stable.

Despite the similarities between Oklo reactor zones and spent commercial reactor fuels, there are important differences between these materials that may lead to differences in their long-term behavior under geologic conditions. The first difference is that the Oklo reactor zones "burned" very slowly over periods of hundreds of thousands of years, with the ores most likely passing into and out of the critical state many times. This would lead to lower average temperatures for the Oklo materials than for the commercial fuels that are burned out over a period of 3 to 4 years. The Oklo uraninites contain Pb, produced as the long-term decay product of both ^{235}U and ^{238}U. Almost all Oklo uraninites have experienced Pb-loss during their long geologic history on at least one occasion. The Pb may now be present in galena (PbS) crystals near and within uraninite grains, or may have completely escaped from the vicinity of its parent U. The presence of large amounts of radiogenic lead - up to 20% by wt. - within the uraninite will affect its chemical stability in a different way than would the presence of a few % of fission products in solid solution in spent commercial reactor fuel. A final complication at Oklo is the presence of large amounts of organic matter in the near vicinity or intimately mixed with uraninite. This organic matter is likely to influence the chemical behavior, especially the redox stability, of the uraninite.

Because of the important differences between the uraninite at Oklo and commercial nuclear reactor fuels, the reactor zones at Oklo should not be considered as a natural example of a spent fuel repository. In addition, there are other features of a repository that are missing at Oklo, such as the canister into which spent fuel assemblies will be placed and the cladding that surrounds fuel pellets in the commercial reactor fuels. We will learn most from Oklo if we consider it as a location to examine processes that might take place after disposal of spent fuel in a geologic setting rather than as a direct material analogue for spent fuel after disposal. In this way, we can avoid the pitfalls of trying to stretch the analogy beyond its limits and, thereby running the risk of losing credibility for the concept of "natural analogues".

The most important feature at Oklo that can help us understand possible events in a repository comes from the fact that portions of the ore deposit sustained nuclear fission reactions while nearby regions of rich ore did not. This allows one to determine the necessary and sufficient conditions for criticality to occur and be sustained in a geologic environment. The behavior of the Oklo uraninites after the nuclear reactions can be compared with that of nearby uranium dioxide that did not have fission reactions. Through such comparisons we can conclude that the portions of the ore that were once reactor zones did not behave significantly differently from other parts of the ore body once the fission reactions were finished. Indeed, this is probably the reason that the discovery of the reactor zones occurred through isotopic analysis of the ore rather than through examination of the ore during prospecting and mining operations.

If we examine the evidence from reactor zone 2, we find that the original rock material, which was approximately 70% quartz, 20% uranium dioxide, and 10% clay, now consists only of uraninite and clay. During the course of the

nuclear reactions, water dissolved the quartz and subsequently transported it out of the reactor zone to nearby locations, where the quartz reprecipitated. During this dissolution and transport, little of the U was removed, indicating that the redox conditions remained within the stability field of U(IV) rather than the more soluble U(VI) species. The local environment was able to counteract the effects of radiolysis arising during and after the nuclear fission reactions and prevent significant oxidative dissolution and transport of U from the system after the reactions had proceeded to the extent that rare earth element fission products were present in moderate amounts.

Another important conclusion that can be drawn from the Oklo reactor zones is that criticality in a natural setting is difficult to achieve and, if it occurs at all, it is a self-limiting process. This is an important point that is very relevant to performance assessment in geologic repositories, especially if waste forms rich in fissile isotopes are to be included in the inventory.

Finally, we find that reactor zone 2 seems to have been preserved for nearly 2 billion years, despite a period of tectonic activity at about 900 million years ago, as evidenced by numerous dikes in the Oklo vicinity. The thermal pulse accompanying the dyke intrusions and the fluid circulations that are evidenced by trapped fluid inclusions in secondary mineral phases, were not sufficiently powerful to homogenize the uraninites on the scale of a few centimeters, let alone dissolve and transport away significant amounts of the uranium and fission product relicts. While this does not give us quantitative data for use in performance assessment calculations, it does provide excellent qualitative information to support the expected stability of UO_2 in environments that maintain redox potentials that are within the U(IV) stability region.

While acknowledging the important positive evidence that can be obtained from reactor zone 2, we should be careful to remember that there are some things we cannot learn from studies at Oklo. Most importantly, we cannot determine the rate of dissolution of uraninite in reactor zone 2 conditions. We do not know how much water has flowed through the ore after reactions stopped, nor at what temperatures water may have contacted the ore and for how long. We also cannot determine unambiguously whether it is the organic matter, the ferrous iron in clay minerals, or the uraninite itself that controls the local redox potential.

3. Discussion and conclusions

In addition to the use of Oklo reactor zones as an analogue for spent commercial reactor fuel, we may use other aspects of the Oklo deposits to learn about processes that may be important for nuclear waste disposal. In addition to the information obtained concerning criticality in a natural environment, we can learn about the effects of radiation-induced radiolysis on materials by examining minerals from reactor zones and from nearby ore samples that did not sustain reactions. We can study the effects of different materials, such as organic matter, on the preservation of the ore, and at Bangombé, we can examine the effects of near-surface weathering in a tropical climate on the dissolution behavior of uraninite.

Through the presence of excess ^{99}Ru, we have evidence for retention of ^{99}Tc even when there was still significant fluid circulation occurring that removed Mo and other soluble fission products from the reactor zones. This suggests that Tc may be stabilized in the metal alloys formed by fission products and may not be as easily oxidized to a soluble form as has been assumed in many performance assessment calculations.

Studies of secondary minerals at Oklo have shown incorporation of fission products and Pu, which is evidenced by small excesses of ^{235}U in some apatite and clay samples. These minerals formed before the decay of ^{239}Pu occurred, and thus at rather high temperatures (several hundred degrees C), so they cannot be used to infer trapping of fission products and actinides under conditions expected for long-term behavior of a waste repository. Sorption studies using materials from Oklo can, however, be used to understand the importance of sorption for retardation during recent fluid circulation, especially in the active weathering environment at Bangombé.

Finally, while we cannot extract quantitative information concerning uraninite dissolution rates and fission product transport rates at Oklo and Bangombé, we have learned something very important. We have seen no evidence for processes occurring in the reactor zones after the reactions were finished and the ore returned to ambient (albeit rather high) temperatures that are different from processes that have been seen in other U ore bodies that have not undergone sustained nuclear chain reactions. That means that any uranium occurrence in a natural setting would be an equally good analogue for spent fuel disposal. This allows us to examine U deposits, or even small occurrences of U in rocks that are similar to the intended host rock for the repository of interest and not have to worry about whether the absence of fission reactions in the materials might make the analogy less valid than the Oklo reactor zone analogues.

Peña Blanca Natural Analog Data in Recent Performance Assessment Models for the Proposed Geologic Repository at Yucca Mountain, Nevada

William M. Murphy, David A. Pickett, and English C. Pearcy
Center for Nuclear Waste Regulatory Analyses
San Antonio, Texas, USA

1. Introduction

Studies at Peña Blanca have provided valuable natural analog information in recent performance assessments for the proposed geologic repository site at Yucca Mountain, Nevada. Since 1987 the U.S. government program to provide a permanent geologic repository for high-level nuclear waste has focused solely on the site at Yucca Mountain, Nevada. Studies in the Peña Blanca uranium district near Chihuahua, Mexico, as a natural analog system to the proposed repository at Yucca Mountain, commenced about the same time. These studies were motivated by the recognition in scientific literature and in high-level waste regulations of the important role of natural analog studies to support long term predictive performance assessment modeling. The Peña Blanca site has received particular interest and investigation because of the remarkable geologic, climatic, hydrologic, and geochemical similarities between the environments at Peña Blanca and at Yucca Mountain (see article by Murphy in this volume). Several performance assessments for the proposed repository at Yucca Mountain have been conducted as dates approach for submission by the U.S. Department of Energy (DOE) of a site suitability recommendation to the President of the United States and of a license application to the U.S. Nuclear Regulatory Commission (NRC). The latest in these series of performance assessments by DOE, NRC, and the Electric Power Research Institute (EPRI) (DOE, 1998; TRW, 1998; NRC, 1998, 1999a,b; EPRI, 1998) all refer to natural analog studies at Peña Blanca. The purpose of this article is to summarize and critique the actual use of Peña Blanca data in these recent performance assessment models for the proposed repository at Yucca Mountain.

2. Department of Energy Total System Performance Assessment - Viability Assessment

The DOE Total System Performance Assessment - Viability Assessment (TSPA-VA) (DOE, 1998, chapter 3) and its supporting technical documents (TRW, 1998, chapters 4 and 6) make qualitative reference to the occurrence of uranyl (oxidized uranium) minerals as the dominant form of uranium at Peña Blanca in support of repository performance modeling. The observation of uranium mineralogy is used primarily to

sustain the relevance of experimental studies of spent fuel dissolution, designed in part to mimic conditions at the proposed repository, in which similar uranyl minerals are produced, which are similar to those observed at Peña Blanca. The role of the properties of secondary minerals in repository performance is particularly noted in the TSPA-VA because crystallographic theory and experimental data indicate that neptunium may be incorporated in the structures of these relatively stable minerals (Burns et al., 1997; Buck et al., 1998). Neptunium is consistently a major contributor to predicted radioactive releases at long times in DOE performance assessments for the proposed Yucca Mountain repository (Wilson et al., 1994; TRW, 1995; DOE, 1998).

A description of the recognition and use of data from Peña Blanca is described in the Technical Basis Document (TBD) for the DOE TSPA-VA (TRW, 1998, Chapters 4 and 6). The paragenetic development of secondary phases at Peña Blanca has been compared to that observed in experimental studies of synthetic UO_2 and spent fuel. Similarity of secondary mineral development between the laboratory and natural field occurrences led to the conclusion that "conditions in the experimental tests have replicated an environment that may be representative of that occurring during uraninite alteration in natural oxidized systems." It was concluded that "These comparisons provide confidence that the degradation of these waste forms over time is well represented by the models, and that the long-term prediction of alteration rates is reasonably realistic" (TRW, 1998, Chapter 6). The conclusion regarding alteration rates appears to be unsupported by applications of measurements of rates of alteration of natural uranium deposits in performance assessment models or by comparisons to laboratory based rates reported in the TSPA-VA or its associated technical basis document. However, based in part on observations of secondary mineralogy at Peña Blanca, the secondary uranyl minerals schoepite, soddyite, uranophane, and Na-boltwoodite are included in reactive transport simulations for TSPA-VA to predict the evolution of the chemistry of water resulting from geochemical interactions in emplacement drifts (TRW, 1998, Chapter 6). Also, a degree of confidence is provided for use of release rates adopted in reactive transport models for radionuclide release that are based in part on the aqueous solubility and kinetic properties of secondary uranyl minerals observed to occur in analogous natural settings such as Peña Blanca (TRW, 1998, Chapter 6).

Generally the DOE TSPA-VA recognizes the Peña Blanca site as a significant analog to the proposed geologic repository at Yucca Mountain. Applications in performance assessments are qualitative and provide support or confidence in the credibility of conceptual and numerical models. In the TSPA-VA TBD the use of Peña Blanca data in reactive transport modeling of radionuclide release is summarized in the statement that "The good match in paragenetic sequence between simulation results and laboratory and field observations suggests that the model qualitatively reproduce [sic] the replacement relations among uranyl minerals. It suggests the thermochemical and kinetic data used in the model can correctly reflect the phase relations, at least qualitatively" (TRW, 1998,

Chapter 6). Applications of Peña Blanca data in the DOE TSPA-VA focus on source term issues of waste form alteration and the formation and performance of secondary oxidation products of spent nuclear fuel. Although it is suggested in the TSPA-VA that information from Peña Blanca may bear on radionuclide transport issues, there is no apparent use of Peña Blanca data in the DOE TSPA-VA for this purpose.

Peña Blanca analog studies used in support of the TSPA-VA are derived primarily from work conducted by the CNWRA. Primary literature on Peña Blanca research cited in the TSPA-VA and TBD include Leslie et al., 1993; Pearcy et al., 1994; Murphy, 1995; Murphy, 1997; and Murphy et al., 1997.

3. Electric Power Research Institute Yucca Mountain Performance Assessment, Phase 4

The recent EPRI performance assessment (EPRI, 1998) notes that dissolution of nuclear waste forms in the Yucca Mountain environment will lead to precipitation of more stable secondary uranyl minerals, citing Peña Blanca data reported by Leslie et al. (1993) as an example. Stability of these minerals was used as an argument in the performance assessment to propose lower source term concentrations of released radionuclides than provided by experimental solubility studies.

4. Nuclear Regulatory Commission Total-System Performance Assessment, Version 3.X

In the latest version of the NRC performance assessment for the proposed repository at Yucca Mountain (NRC, 1998, 1999a,b) several alternate source term models are provided. Two models are based on an interpretation by NRC (NRC source term model 2; Mohanty et al., 1997) and a regression by Gray and Wilson (1995, adopted for NRC source term model 1) of laboratory data for spent fuel dissolution reported by Gray (1992), Gray et al. (1992), and Gray and Wilson (1995). Source term model 2 was adopted as the NRC base case model (NRC, 1998, 1999a,b). The other two (models 3 and 4) are based in part on natural analog studies. Model 3 permits use of a constant release rate of matrix components from the primary spent fuel waste form. This rate may be specified on the basis of constraints such as those derived from natural analog data. Model 4 is based on the assumption that radionuclides from the spent fuel matrix become incorporated in the oxidized secondary uranium mineral schoepite. Radionuclide releases then occur in proportion to the solubility limited dissolution of schoepite. Schoepite solubility is calculated in the model as a function of temperature, pH, and aqueous carbonate and uranyl speciation. The selection of secondary schoepite as a likely source term controlling phase is justified in part by its common occurrence in natural geologic settings analogous to the Yucca Mountain site such as Peña Blanca.

Murphy and Codell (1999) present Yucca Mountain performance assessment calculations using the NRC TPA version 3.2 code to test the sensitivity of performance results to the two alternate NRC source term models 3 and 4. For source term model 3, the release rate of matrix components from spent nuclear fuel is assumed to be limited by the maximum average oxidation rate of uraninite (a spent fuel analog) estimated for the Nopal I uranium deposit at Peña Blanca and scaled to the proposed repository inventory. Radionuclide releases based on the maximum average oxidation rate of uraninite are assumed to place a conservative upper limit on the average release rate of matrix components from the waste form because sequestration of radionuclides in secondary, relatively stable uranyl minerals is disregarded in this model. The maximum average oxidation rate of uraninite at Peña Blanca is estimated based on reported measurements of the mass of oxidized uranium remaining at the site, the minimum period of oxidation based on geochronological dating of late forming oxidized uranium minerals, and a maximum estimate of the amount of uranium that has been oxidized and subsequently removed from the uranium deposit by aqueous transport (Murphy and Pearcy, 1992; Murphy et al., 1997).

For the alternate NRC TPA version 3.2 source term models 3 and 4, doses (with associated probabilities) were calculated for a critical group located 20 km from the waste emplacement site at 10,000 and 50,000 years after repository closure (Murphy and Codell, 1999). All other aspects of the performance calculations were modeled in a fashion equivalent to that of the NRC base case source term model. Alternate source term models based on the Peña Blanca oxidation rate model and the schoepite solubility model yield lower doses than the base case model (model 2) in the NRC TPA version 3.2 analyses. Comparisons are made of performance assessment results using the natural analog oxidation rate model (implemented with the TPA 3.1.3 code) to results computed using several other alternate conceptual models in the recent report on NRC performance assessment sensitivity and uncertainty analyses (NRC, 1999b). These comparisons showed generally that the natural analog oxidation rate model leads to predictions of dose effects that are low relative to most alternate models considered, and concluded that "taking credit for phenomena such as ... lower release rates based on observations of natural analogs could result in considerably smaller doses" (NRC, 1999b).

5. Caveats

Despite the remarkable similarities in geology, hydrology, climate, and waste analog material between the Peña Blanca analog and the proposed Yucca Mountain repository, and the value of investigating processes that occur on a geologic time scale, there are important differences between the natural and repository systems and substantial uncertainties remain concerning the evolution of the Peña Blanca system. Indications of paleotemperatures during uranium mineralization and alteration at Nopal I (see Ildefonse, Agrinier, Allard, Muller, and Calas, this volume) suggest that they were similar to those

projected for the proposed repository (e.g., DOE, 1998). Peña Blanca uranium deposits probably had a water saturated episode of ore genesis, sulfide was an important component during and after the period of primary mineralization at Nopal I, and aqueous conditions became acidic due to pyrite oxidation (see Reyes in this volume). Such conditions are unlikely to develop in the unsaturated and sulfide poor environment of the proposed repository. In contrast to the Peña Blanca system, the proposed repository will have engineered containment facilities and strong radiation effects, which will affect the chemical environment, including radiolytic production of oxidizing species, and the properties of the waste forms. In contrast, remaining old (e.g., 8±5 million years) uraninite persists at Nopal I probably because of its physical isolation from the oxidizing environment by natural silica cementation. In addition, minor and trace components in spent fuel are dissimilar to those in primary uraninite from Peña Blanca.

In contrast to performance models for the evolution of the proposed repository at Yucca Mountain, the evolution of the Peña Blanca system was apparently characterized by episodic hydrogeochemical events. Primary uraninite deposition occurred at approximately 8 Ma (Pearcy et al., 1994); an oxidation event is indicated by dates on uranophane at 3 Ma (Pickett and Murphy, 1997; Pickett and Murphy, this volume); data presented by Murrell (this volume) suggest a transport event occurring at approximately 400 ka; stages of mobilization, precipitation, and remobilization over the past hundreds of thousands of years are indicated by uranium decay series data from Pickett and Murphy (1997) and Pickett et al. (1999); and a late stage mobilization of uranium and precipitation of secondary calcite and opal is indicated by dating of these phases at approximately 50 ka (Pearcy et al., 1994). Performance assessment models and interpretations of natural analog data that neglect the episodic nature of geochemical processes can lead to estimates of average rates and average doses far below maximum rates and doses.

Episodic, possibly rapid periods of oxidation and potential radionuclide release at Nopal I were not treated explicitly in the calculation by Murphy and Codell (1999) of the maximum average oxidation rate for uranium at the Nopal I deposit. Consequently, the NRC alternate source term model 3 suffers from this potential lack of conservatism. Although tied to observed mineral paragenesis at Nopal I, the schoepite solubility model of Murphy and Codell (1999) cannot be considered to be conservative either, particularly because of provisional assumptions in the model regarding distribution of radionuclides between secondary schoepite and other phases.

6. Tangential Contributions of Natural Analog Data to Yucca Mountain Performance Assessments

The importance of flow and radionuclide transport in fractures is receiving increasing recognition for performance of the proposed Yucca Mountain system (e.g., TRW, 1998,

Chapter 7; NRC, 1998) and is strongly supported by the distribution of uranium surrounding the Nopal I deposit at Peña Blanca (Pearcy et al., 1995; Prikryl et al., 1997). In the NRC review (Baca and Jarzemba, 1997) of the DOE TSPA-1995 (TRW, 1995), the distribution of uranium in and around fractures at Nopal I, as described in Pearcy et al. (1995) was used, along with other arguments, to question the effectiveness of matrix diffusion as a retardation mechanism invoked in performance modeling of radionuclide transport.

Observations made at Peña Blanca have contributed to improved understanding and conceptual models of matrix diffusion and its significance for repository performance. At Nopal I, whereas a minor proportion of uranium is retained in the matrix (i.e., tuff that is homogeneous at optical microscopy scales), a significant fraction of uranium is retained in networks of microfractures (i.e., fractures with apertures of tens to hundreds of microns and trace lengths of centimeters) (Pearcy et al., 1995). In contrast, PA geosphere transport models typically are represented on scales of tens to hundreds of meters. Generalizations required in performance assessment calculations are such that networks of fractures too small to be treated explicitly in flow and transport calculations have been typically considered to be "matrix" and the processes by which radionuclides become partitioned into those networks are deemed "matrix diffusion." Consequently, geochemical transport models and total system performance assessment models have sometimes suffered a mismatch in conceptualizations of "matrix diffusion." Although small scale heterogeneities are generally neglected in PA geosphere transport modeling, this approach is assumed to be appropriate for evaluations of overall repository behavior (NRC, 1999a). Uranium partitioning at Nopal I has provided a useful data set for clarifying these alternative conceptualizations regarding radionuclide transport at different spatial scales (e.g., NRC, 1994, 1997).

Sorption/coprecipitation on minor phases such as transition metal oxides is receiving increasing recognition in performance modeling for the Yucca Mountain system (e.g., Hardin, 1998) and is strongly supported by the Peña Blanca data. The strong association of uranium with fracture filling iron oxyhydroxides at Peña Blanca (Prikryl et al., 1997; Pickett et al., 1999) supports experimental evidence of sorption on oxyhydroxides (Hsi and Langmuir, 1985; Hardin, 1998), and strengthens arguments for the importance of sorption on oxide mineralization in fractures as a retardation mechanism for radionuclide transport.

7. General Observations

Natural analog studies at Peña Blanca are widely recognized and used in recent performance assessments for the proposed repository at Yucca Mountain. Applications have been primarily qualitative, providing support for conceptual models, and justification for the relevance of experimental studies. Quantitative applications of Peña

Blanca data to Yucca Mountain performance assessments have been attempted (e.g., Murphy and Codell, 1999). Although they are based on quantifiable geologic and geochemical data they are attended by approximations and uncertainties associated with understanding natural system evolution over long periods of time. Approximations and uncertainties are characteristic of performance assessments in general. The general correspondence in the chemical behavior of spent nuclear fuel in laboratory studies and of uraninite in the Peña Blanca system has provide the strongest contributions of Peña Blanca analog data to Yucca Mountain performance assessments to date. Radionuclide transport at Peña Blanca has received extensive study and is recognized to be analogous to potential radionuclide transport in the Yucca Mountain system (e.g., Ildefonse et al., 1990; Leslie et al., 1993; Pearcy et al., 1995; Prikryl et al., 1997; Pickett et al., 1999). These studies have contributed to conceptual modeling related to performance assessments for Yucca Mountain. However, direct implementations of radionuclide transport data from the Peña Blanca analog system in performance assessments are absent at present.

Uncertainties and assumptions in interpretations of analog data must be recognized, and no system is perfectly analogous to a geologic repository. Transfer of information from analogs to performance assessment models is challenging. Similarly, extrapolations of laboratory studies and theoretical predictions have inherent uncertainties and limitations. Nevertheless, the large uncertainties associated with long term prediction of geologic repository performance compel examination and comparison of alternate approaches to performance assessment modeling. Confidence in predictive models and in evaluations of the safety of geologic disposal of nuclear waste should be enhanced through multiple lines of investigation, including studies of natural analogs.

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PANEL DISCUSSION

Ardyth Simmons, LBNL, U.S.A.,

facilitated the discussion on the lessons learned from Palmottu, Oklo and Pena Blanca by putting the following questions to the panellists:

1. What are the main contributions of the three projects (Palmottu, Oklo, and Pena Blanca)?
2. More generally, what have been the contributions of natural analogues to national programmes?
3. What issues for radioactive waste management remain to be addressed by analogues?
4. What pointers or guidance can be given to countries beginning analogue studies?
5. What should be the future direction of analogue work and of NAWG?

Runar Blomqvist (Palmottu),
François Gauthier-Lafaye (Oklo), and
William Murphy (Peña Blanca). (Names abbreviated below).

Question 1:
WM: Peña Blanca is a site-specific analogue to a repository site. From this we can tell source term phases and what phases will control U transport. It is also an analogue for unsaturated zone transport of radionuclides.

RB: We have obtained confidence in modelling processes at Palmottu and in making predictions. It is good to look at different sites, because surprises come up, e.g., the different groundwater chemistry that was not expected at Palmottu. Also Palmottu demonstrated the movement of U along a redox front (with the caveat that all of the data have not been reviewed).

FG: With Oklo, the direct relevance to a repository is less evident, but it was important that Oklo showed the role of the complexity of the geologic system in U migration and stability. Also radiolysis effects (e.g., α-radiolysis in clays) and criticality were very clearly shown at Oklo. He noted that the question of stability of uraninite may be different at Oklo than at Peña Blanca.

Question 2:
WM: Peña Blanca was recognised in all three PAs for Yucca Mountain and could be extended to other sites as well for other PAs. The main use of Peña Blanca data in PAs has been to identify stable uranium minerals. Peña Blanca data have demonstrated the long-term (geologic) stability of uranium minerals in an environment analogous to Yucca Mountain. A goal of analogue studies would be to demonstrate viability of geologic disposal.

RB: He noted that analogues have shown the importance of the effects of glaciation on a site; e.g., the role of old groundwater in a closed system. Also they have contributed to the understanding of U speciation in groundwater, and to the role of fracture flow in U transport.

FG: He cited the significance of the phosphate matrix at Oklo as an analogue for sequestering radionuclides.

Question 3:
RB: Analogues can contribute in a major way to scenario development and the processes that need to be considered in a safety assessment. They can also contribute to a better understanding of uranium redox issues.

WM: Analogues can contribute to understanding other radionuclides besides U, and other systems besides U-systems. The source term for other radionuclides can be addressed through analogues. In addition, the analogue community can make a judgement in other PA's by finding assumptions that can be tested by natural analogues.

Question 4:
RB: He noted the necessity for setting up a study very well at the beginning and then characterising the site very well from the start. He recommended allowing at least three to five years for the analogue study, followed by a period of more focused study.

WM: Don't oversell the analogue programme as doing more than it really can.

FG: Plan for an adequate length of research time for analogue programs, at least ten years. As the work progresses, more questions will arise that need to be settled.

Question 5:
WM: NAWG could provide a stronger role in co-ordinating and influencing the study of specific processes to address issues in nuclear waste disposal.

RB: A joint discussion with regulators would be helpful. It is not sufficient to provide the information on analogues; a strong interaction with decision-makers and regulators is needed.

After the panellists addressed the five questions above, the rest of the audience was allowed to comment on the five questions or on other relevant points.

Virginia Oversby noted the need for information on long-term dissolution of spent fuel and the need to invest significant time and resources into the search for a "perfect" analogue site that would allow collection of this long-term information.

Jordi Bruno reiterated the utility of exploring scenarios in PA using information from natural analogues. For example, Peña Blanca did not evolve in a linear mode, but showed pulses of oxidation; this can be used in development of a scenario for U alteration. Regarding Oklo and Palmottu, one needs to ask whether the models reproduce the U mineral compositions at Oklo and the redox conditions at Palmottu; the models need to do this. With respect to the public, we have missed the crucial link of communicating with our scientific peers; we must be able to reach them and convince them first, because they will be our judges and will check the validity of our work.

Susan Duerden emphasised the manner in which information is communicated is very important and should vary according to the audience. She noted that it is far more important to find ways of transferring the existing analogue information, which in very many cases provides confidence for a safety case, than it is to initiate new analogue studies.

Philippe Ildefonse stated that the key was to identify common, fundamental processes for waste repositories, and cautioned that we should not "miss the forest for the trees". A better understanding of processes is needed, e.g., redox, and the role of colloids in radionuclide transport. Daughter elements can be understood through analogues to uranium.

Rod Ewing commented that the U.S. PA Peer Review could not grapple with various levels of uncertainty in PA. It is worth considering how natural analogues could contribute to uncertainty reduction or analyses. He endorsed a process understanding related analogue rather than additional large-scale projects as the wave of the future for natural analogue studies. He also added that we are beyond use of the label "natural analogue"; it is outdated – we are studying natural processes in natural systems. How about renaming NAWG?

Bill Miller noted that "natural analogue" was coined to use the term for PA, but other sites have useful information that can apply to process understanding. These should not be called natural analogues, however.

Jan Cramer had made a table showing components of a repository system (see foreword), and where those aspects could be understood with fair confidence through natural analogue information, as well as areas where additional insights are needed. As a group, many in the audience thought this concept was a useful way of displaying how analogues have contributed to understanding. Russell Alexander said that the table would be added to the NAWG web page, if NAWG approved, and that others would be allowed to add to it before it was finalised. This concluded the open discussion following the panel.

Wrap-Up

W R Alexander, NAGRA (CH) and H von Maravić, EC-Research (B)

Russell Alexander, NAWG Chairman, provided the wrap-up of the workshop. He stated that NAWG had "broadened the gene pool" by including representatives from many more national programmes (now 22) when compared to the original, smaller NAWG (8 programmes). The intention behind this expansion was to develop further the original aims of NAWG, namely to encourage the appropriate applications of Natural Analogues in waste programmes worldwide. In addition, NAWG was continuing, albeit slowly, along the path of encouraging the use of Natural Analogues in chemotoxic waste disposal and in communication with the public (see Foreword of these proceedings).

Naturally, these changes were not easy to implement but, with the support of the NAWG members, the Steering Committee hoped to see them through. On a more negative point, he noted that, despite the ongoing changes within NAWG, the same topics of discussion are going around as were ten years ago, especially the never-ending angst about the application of natural analogues to performance assessment (see Foreword of these proceedings).

He mentioned the NAWG web page is currently under development and it will be opened up later to all interested parties. The assembled group was enthusiastic about broadening the use of the web site. He noted that the format of this meeting was something between the workshop style of the 1994 meeting in Santa Fe, New Mexico (EUR 16761) and the review of projects that took place in Toledo, Spain at the 1992 meeting (EUR 15176). The next meeting will probably return to a workshop format. He stated that in 18-24 months he hoped that a position paper would be drafted that will document the lessons learned from natural analogues from NAWG. In the future, NAWG hope to strengthen their connections to the natural analogue programmes of the IAEA and OECD/NEA.

Henning von Maravić, secretary of NAWG, reminded the participants that the European Commission 5th EURATOM Framework programme (1998-2002) in the area 'waste and spent fuel management and disposal' includes research activities on Natural Analogues and that proposals in this respect can be submitted to the open call in October 1999. He indicated that the next NAWG meeting is scheduled for April 2001, and many participants have expressed interest in an associated field trip. The location of the meeting has not yet been decided.

He closed the meeting by thanking all of the speakers, session chairs, and participants for a worthwhile meeting.

APPENDIX 1 : LIST OF PARTICIPANTS

Mr Lasse AHONEN
Geological Survey of Finland (GTK)
Betonimiehenkuja 4
P.O. Box : 96
FI - 02151 ESPOO

Phone:+358.205.502.522
Fax: +358.205.50.12

Email: lasse.ahonen@gsf.fi

Mr Peter AIREY
ANSTO-Lucas Heights Research Lab.
Private Mail Bag 1
Sutherland
AU - NSW 2234 MENAI

Phone:+61.2.9717.3272
Fax: +61.2.9717.9293

Email: pla@ansto.gov.au

Mr Russell ALEXANDER
NAGRA
Hardstrasse 73
CH - 5430 WETTINGEN

Phone:+41.56.4371.320
Fax: +41.56.4371.317

Email: russell.alexander@nagra.ch

Mr Thierry ALLARD
Universités Paris 6 - 7, UMR CNRS 7590
Laboratoire de Minéralogie - Cristallographie
4, place Jussieu, case 115
FR - 75252 PARIS Cedex : 05

Phone:+33.1.44.27.74.52
Fax: +33.1.44.27.37.85

Email: allard@lmcp.jussieu.fr

Mr David ARCOS
QuantiSci S.L.
Parc Tecnològic del Vallès
ES - 08290 CERDANYOLA

Phone:+34.93.582.44.10
Fax: +34.93.582.44.12

Email: darcos@quantisci.es

Mr Carlos AYORA
Institut de Ciencies de la Terra, CSIC
Lluis Solé y Sabaris s/n
ES - 08028 BARCELONA

Phone:+34.93.409.54.10
Fax: +34.93.411.00.12

Email: ayora@ija.csic.es

Mr W BERNOTAT
FZK/INE
Weberstraße 5 (P.F. 3640)
DE - 76021 KARLSRUHE

Phone:+49.7247.824.728
Fax: +49.7247.823.927

Email: bernotat@ine.fzk.de

Mr Runar BLOMQVIST
Geological Survey of Finland (GSF)
Betonimiehenkuja 4 (P.O. Box 96)
FI - 02151 ESPOO

Phone:+358.205.50.24.69
Fax: +358.205.50.12

Email: runar.blomqvist@gsf.fi

Mr Jean-Yves BOISSON
CEA/IPSN/DPRE-SERGD - CEN-FAR
60-68, avenue du Général Leclerc - PB 6
FR - 92265 FONTENAY-aux-ROSES

Phone:+33.1.46.54.80.73
Fax: +33.1.47.35.14.23

Email: jean-yves.boisson@ipsn.fr

Mr Alain BOUCHET
Etudes Recherches Matériaux, ERM
40, avenue du Recteur Pineau
Bât. G.O.N. sous-sol
FR - 86000 POITIERS

Phone:+33.5.49.46.18.11
Fax: +33.5.49.45.40.26

Email: etremat@wanadoo.fr

Mr Guido BRACKE
Depl.-Chem. Guido Bracke, CNRS
Centre de Géochimie de la Surface
1, rue de Blessig
FR - 67084 STRASBOURG

Phone:+33.3.88.35.86.88
Fax: +33.3.88.36.72.35

Email: bracke@illite.u-strasbg.fr

Mr Thomas BRASSER
GRS-Geochemistry Department
Theodor-Heuss-Straße 4
DE - 38122 BRAUNSCHWEIG

Phone:+49.531.80.12.238
Fax: +49.531.80.12.200

Email: bra@grs.de

Mr Jordi BRUNO
QuantiSci S.L.
Avda. Universitat Autonoma 3
Parc Tecnològic del Vallès
ES - 08290 CERDANYOLA

Phone:+34.93.582.44.10
Fax: +34.93.582.44.12

Email: jbruno@quantisci.es

Mr Georges CALAS
Universités Paris 6 - 7, Laboratoire de Minéralogie - Cristallographie
4, place Jussieu, case 115
FR - 75252 PARIS Cedex 05

Phone:+33.1.44.27.52.33
Fax: +33.1.44.27.37.85

Email: calas@lmcp.jussieu.fr

Mr Bernard CÔME
ANTEA (BRGM group)
Avenue Claude Guillemin (B.P. 6119)
FR - 45061 ORLÉANS Cedex 2

Phone:+33.2.38.64.35.34
Fax: +33.2.38.64.33.90

Email: b.come@antea.brgm.fr

Mr Jan CRAMER
Norges Geologiske Undersøkelse (NGU)
Leiv Eirukssons vei 39
NO - 7491 TRONDHEIM

Phone:+47.73.90.4310
Fax: +47.73.92.1620

Email: jan.cramer@ngu.no

Mr Michel CUNEY
UMRGCR-7566 - CREGU
3, rue du Bois de la Champelle (B.P. 23)
FR - 54500 VANDOEUVRE-les-NANCY

Phone:+33.3.83.91.38.22/79
Fax: +33.3.83.91.38.01

Email: michel.cuney@gzr.u-nancy.fr

Mr Christophe DAVIES
EUROPEAN COMMISSION
DG RTD/J/4
Rue de la Loi 200 (Office MO75 5/42)
BE - 1049 BRUSSELS

Phone:+32.2.296.16.70
Fax: +32.2.295.49.91

Email: christophe.davies@cec.eu.int

Mrs Mireille DEL NERO
Institut de Recherches Subatomiques - CNRS/IN2P3
Laboratoire de Chimie Nucléaire
23, rue de Loess
FR - 67037 STRASBOURG

Phone:+33.3.88.106.408
Fax: +33.3.88.106.431

Email: mireille.delnero@ires.in2p3.fr

Mrs Dominique DELLEUZE
SCK.CEN
Boeretang 200
BE - 2400 MOL

Phone:+32.14.33.32.74
Fax: +32.14.32.35.53

Email: ddelleuz@sckcen.be

Mrs Susan DUERDEN
Environment Agency of England and Wales, UKEA
Radioactive Waste Disposal Assessment
Steel House - 11, Tothill Street
UK - LONDON SW1H 9NF

Phone:+44.171.664.6813
Fax: +44.171.664.6836

Email: susan.duerden@environment-agency.co.uk

Mr Rod EWING
Nuclear Engineering and Radiological Sciences
The University of Michigan
2355 Bonisteel Boulevard
US - ANN ARBOR, Michigan 48109-2104

Phone:+1.313.647.85.29
Fax: +1.313.647.85.31

Email: rodewing@umich.edu

Mr Erik FRANK
Swiss Federal Nuclear Safety Insp., HSK
CH - 5232 VILLIGEN

Phone:+41.56.310.39.45
Fax: +41.56.310.39.07
Email: frank@hsk.psi.ch

Mr François GAUTHIER-LAFAYE
CNRS/CGS
1, rue de Blessig
FR - 67084 STRASBOURG

Phone:+33.3.88.35.85.62
Fax: +33.3.88.36.72.35

Email: gauthier@illite.u-strasbg.fr

Miss Maria José GIMENO
CIEMAT
Avenida Complutense 22
ES - 28040 MADRID

Phone:+34.91.346.61.58
Fax: +34.91.346.62.69

Email: mariajo@crayb.ciemat.es

Mr Bertil GRUNDFELT
KEMAKTA Konsult AB
Pipersgatan 27 (P.O. Box 12655)
SE – 112 93 STOCKHOLM

Phone:+46.8.617.67.00
Fax: +46.8.652.16.07

Email: bertil@kemakta.se

Mr Pil-Soo HAHN
Korea Atomic Energy Research Institute (KAERI)
P.O. Box 105, Yuseong
KR - TAEJON, 305-600 (Rep. of Korea)

Phone:+82.42.868.2332
Fax: +82.42.868.8850

Email: pshahn@nanum.kaeri.re.kr

Mrs Vaclava HAVLOVA
Nuclear Research Institute
Dept. of Waste Disposal
CZ - 250 68 REŽ (Czech Republic)

Phone:+420.266.173.619
Fax: +420.220.941.153

Email: bun@nri.cz

Mr Karl-Heinz HELLMUTH
Radiation and Nuclear Safety Authority (STUK)
Laippatie 4 (P.O. Box 14)
FI - 00881 HELSINKI

Phone:+358.9.759.88.307
Fax: +358.9.759.88.670
Email: karl-heinz.hellmuth@stuk.fi

Mr Pedro HERNAN
ENRESA
Calle E. Vargas 7
ES - 28043 MADRID

Phone:+34.91.566.81.92
Fax: +34.91.566.81.65
Email: pher@enresa.es

Mr Philippe ILDEFONSE
Universités Paris 6 - 7, Laboratoire de Minéralogie - Cristallographie
4, place Jussieu, case 115
FR - 75252 PARIS Cedex 05

Phone:+33.1.44.27.50.63
Fax: +33.1.44.27.37.85
Email: ildefons@lmcp.jussieu.fr

Mr Kai Olof JAKOBSSON
Radiation and Nuclear Safety Authority (STUK)
Laippatie 4 (P.O. Box 14)
FI - 00881 HELSINKI

Phone:+358.9.7598.8308
Fax: +358.9.7598.8670
Email: kai.jakobsson@stuk.fi

Mr Neil JARVIS
Atomic Energy Corporation of South Africa Limited
Building 1600 (P.O. Box 582)
ZA - 0001 PRETORIA (South Africa)

Phone:+27.12.316.52.46
Fax: +27.12.316.59.44
Email: nvjarvis@aec.co.za

Mr Gerard KLAVER
NITG-TNO
Richard Holkade 10 (P.O. Box 157)
NL - 2000 AD HAARLEM

Phone:+31.23.530.03.82
Fax: +31.23.540.17.54
Email: g.klaver@nitg.tno.nl

Mr Milos KOVACIK
Geological Survey of the Slovak Republic
Dept. Engineering Geology
Mlynska, dolina 1
SK - 84104 BRATISLAVA (Slovak Republic)

Phone:+421.7.59375.415
Fax: +421.7.54771.940
Email: mkovacik@gssr.sk

Mr Emmanuel LEDOUX
ARMINES, Ecole des Mines de Paris
35, rue Saint-Honoré
FR - 77305 FONTAINEBLEAU

Phone:+33.1.64.69.47.02
Fax: +33.1.64.69.47.03

Email: ledoux@cig.ensmp.fr

Mr Pierre MANFROY
ONDRAF/NIRAS
Avenue des Arts 14
BE - 1210 BRUSSELS

Phone:+32.2.212.10.43
Fax: +32.2.218.51.65

Email: p.manfroy@nirond.be

Mr Régis MATHIEU
URM-GZR -7566 CREGU
Géologie et Gestion des Ressources Minerales et Energétiques
3, rue du Bois de la Champelle
FR - 54500 VANDOEUVRE-lez-NANCY

Phone:+33.3.83.91.38.41
Fax: +33.3.83.91.38.01

Email: regis.mathieu@gzr.u-nancy.fr

Mr William MILLER
QuantiSci Limited, Geosciences Group
47, Burton Street
Melton
UK – MOWBRAY, Leicest. LE13 1AF

Phone:+44.1664.411.445
Fax: +44.1664.411.402

Email: wmiller@quantisci.co.uk

Mr Antoni Edward MILODOWSKI
British Geological Survey, BGS
Kingsley Dunham Centre
Nicker Hill
UK - KEYWORTH, Nottinghamsh. NG12 5GG

Phone:+44.1159.363.548
Fax: +44.1159.363.352

Email: a.milodowski@bgs.ac.uk

Mr William MURPHY
Center for Nuclear Waste Regulatory Analyses
Southwest Research Institute
6220 Culebra Rd.
US - SAN ANTONIO, TX 78238

Phone:+1.210.522.52.63
Fax: +1.210.522.51.55

Email: wmurphy@swri.edu

Mr Michael MURRELL
Los Alamos National Laboratory (LANL)
MS J514
US - LOS ALAMOS, NM 87545

Phone:+1.505.667.4845
Fax: +1.505.665.4855

Email: mmurrell@lanl.gov

Mr Ulrich NOSECK
GRS, Gesellschaft für Anlagen-und Reaktorsicherheit
Theodor-Heuss-Strasse 4
DE - 38122 BRAUNSCHWEIG

Phone:+49.531.8012.247
Fax: +49.531.8012.200

Email: nos@grs.de

Mrs Virginia OVERSBY
VMO Konsult
Karlavägen 70
SE – 114 59 STOCKHOLM

Phone:+46.8.667.26.45
Fax: (c/o SKB) +46.8.661.57.19

Email: virginia.oversby@stockholm.mail.telia.com

Mr Jean-Claude PARNEIX
ERM, Etudes-Recherches-Matériaux
Espace 10 - Z.I. République II
Rue Albin Haller
FR - 86000 POITIERS

Phone:+33.5.49.46.18.11
Fax: +33.5.49.45.40.26

Email: etremat@wanadoo.fr

Mrs Rita PELLEGRINI
ISMES S.p.A.
Structural Engineering Dept.
Via Pastrengo 9
IT - 24068 SERIATE, BG

Phone:+39.035.307.656 (direct)
Fax: +39.035.302.999

Email: rpellegrini@ismes.it

Mr Luis PEREZ DEL VILLAR
CIEMAT
Av. Complutense 22
ES - 28040 MADRID

Phone:+34.91.346.63.89
Fax: +34.91.346.65.42

Email: lpvillar@ciemat.es

Mr David PICKETT
Center for Nuclear Waste Regulatory Analyses
Southwest Research Institute
6220 Culebra Rd. (Post Officer Drawer 28510)
US - SAN ANTONIO, TX 78238

Phone:+1.210.522.55.82
Fax: +1.210.522.51.55

Email: dpickett@swri.edu

Mr Petteri PITKÄNEN
VTT/Communities and Infrastructure
Betonimiehenkuja 1 (P.O. Box 19041)
FI - 02044 VTT ESPOO

Phone:+358.9.456.48.54
Fax: +358.9.46.79.27

Email: petteri.pitkanen@vtt.fi

Mr Laurent POURCELOT
CNRS/CGS
1, rue de Blessig
FR - 67084 STRASBOURG

Phone: +33.3.88.35.85.92
Fax: +33.3.88.36.72.35

Email: pourcelo@illite.u-strasbg.fr

Mr Kari Olavi RASILAINEN
VTT Energy, Nuclear Energy
Tekniikantie 4 C (P.O. Box 1604)
FI - 02044 VTT, ESPOO

Phone:+358.9.456.5060
Fax: +358.9.456.5000

Email: kari.rasilainen@vtt.fi

Mr Michel RAYNAL
IAEA, Waste Technology
Wagramer Strasse 5 (P.O. Box 100)
AT - 1400 VIENNA

Phone:+43.1.(2600).22673/26108
Fax: +43.1.26007

Email: m.raynal@iaea.org

Mr David READ
ENTERPRIS
University of Reading
Whiteknights, Philip Lyle Building
UK - READING RG6 6BX

Phone:+44.1189.868.250
Phone:+44.1372.451.520
Fax: +44.1189.861.894
Email: - enterpri@readinguni.u-net.com
- ullaread@compuserve.com

Mr Ignacio-Alfonso REYES
Universidad Autónoma de Chihuahua
Tehueque 6722, Karike, Chihuahua
CP 31160
MX - CHIHUAHUA, Chih. - Mexico

Phone:+52.1417.1203/52.1413.6715
Fax: +52.1413.5055

Email: ireyes@seidel.fing.uach.mx

Mr Chris ROCHELLE
British Geological Survey, BGS
UK – KEYWORTH, Nottinghamsh. NG12 5GG

Phone:+44.1159.363.259
Fax: +44.1159.363.261
Email: c.rochelle@bgs.ac.uk

Mr Timo RUSKEENIEMI
Geological Survey of Finland
Betonimiehenkuja 4 (P.B. 96)
FI - 02151 ESPOO

Phone:+358.205.50.23.29
Fax: +358.205.50.12

Email: timo.ruskeeniemi@gsf.fi

Mrs Sonia SALAH
CNRS/CGS
1, rue de Blessig
FR - 67084 STRASBOURG

Phone: +33.3.88.35.85.92
Fax: +33.3.88.36.72.35

Email: salah@illite.u-strasbg.fr

Miss Ardyth SIMMONS
Lawrence Berkeley National Laboratory
MS 90-1116
1 Cyclotron Rd.
US - BERKELEY, CA 94720

Phone:+1.510.486.7106
Fax: +1.510.486.6115

Email: asimmons@lbl.gov

Mr John SMELLIE
CONTERRA AB
Fridhemsgatan 66B
SE – 112 46 STOCKHOLM

Phone:+46.18.123.241
Fax: +46.18.123.262

Email: john.smellie@conterra.se

Mr Walter STEININGER
Forschungszentrum Karlsruhe
Projektträger des BMBF und BMWI für Entsorgung (PTE)
Weberstraße 5 (P.F. 3640)
DE - 76021 KARLSRUHE

Phone:+49.7247.82.5788
Fax: +49.7247.82.5796

Email: walter.steininger@pte.fzk.de

Mr Laurent TROTIGNON
CEA/DESD/SESD
CE Cadarache
Bât. 307
FR - 13108 St. PAUL-lez-DURANCE

Phone:+33.4.42.25.26.78
Fax: +33.4.42.25.62.72

Email: laurent.trotignon@cea.fr

Mr Shih-Chin TSAI
Energy and Resources Laboratories (ERL)
Industrial Technology Research Institute (ITRI)
Bldg. 24, 195-6 Sec.4, Chung Hsing Rd.
Chutung, Hsinchu
CNTW - Taiwan 310 (Republic of China)

Phone:+886.3.591.4293
Fax: +886.3.582.0017

Email: f840237@erl.itri.org.tw

Mr Henning von MARAVIĆ
EUROPEAN COMMISSION
DG RTD/J/4
Rue de la Loi 200 (Office MO75 5/50)
BE – 1049 Brussels

Phone:+32.2.296.52.73
Fax: +32.2.295.49.91

Email: henning.ritter-von-maravic@cec.eu.int

Mr Hidekazu YOSHIDA
Japan Nuclear Cycle
Development Institute (JNC)
Tono Geoscience Center
959-31, Jyorinji, Izumi, TOKI CITY
Gifu Pref. (Japan)

Phone:+81.572.53.0211
Fax: +81.572.55.0180

Email: yoshida@tono.jnc.go.jp

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