

Technical Report

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**The applicability and limitations
of the geochemical models and
tools used in simulating radionuclide
behaviour in natural waters**

**Lessons learned from the Blind Predictive
Modelling exercises performed in conjunction
with Natural Analogue studies**

Jordi Bruno, Lara Duro, Mireia Grivé

QuantiSci S L Parc Tecnològic del Vallès, Spain

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Svensk Kärnbränslehantering AB

Swedish Nuclear Fuel
and Waste Management Co
Box 5864

SE-102 40 Stockholm Sweden

Tel 08-459 84 00

+46 8 459 84 00

Fax 08-661 57 19

+46 8 661 57 19



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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the author(s) and do not necessarily coincide with those of the client.

Abstract

One of the key applications of Natural Analogue studies to the Performance Assessment (PA) of nuclear waste disposal has been the possibility to test the geochemical models and tools to be used in describing the migration of radionuclides in a future radioactive waste repository system. To this end, several geochemical modelling testing exercises (commonly denoted as Blind Predictive Modelling), have formed an integral part of Natural Analogue Studies over the last decade. Consequently, we thought that this is a timely occasion to make an evaluation of the experience gained and lessons learnt.

We have reviewed, discussed and compared the results obtained from the Blind Prediction Modelling (BPM) exercises carried out within 7 Natural Analogue Studies: Oman, Poços de Caldas, Cigar Lake, Maqarin, El Berrocal, Oklo and Palmottu.

To make this comparison meaningful, we present the main geochemical characteristics of each site in order to highlight the most relevant mineralogical and hydrochemical differences.

From the complete list of elements studied at all the investigated sites we have made a selection based on the relevance of a given element from a PA viewpoint and on the frequency this element has been included in the BPM exercises. The elements selected for discussion are: Sr, Ba, Sn, Pb, Se, Ni, Zn, REEs, Th and U. We have based our discussion on the results obtained from the speciation as well as solubility calculations.

From the comparison of the results it is concluded that we can differentiate between three element categories:

1. Elements whose geochemical behaviour can be fairly well described by assuming solubility control exerted by pure solid phases of the given element (i.e. Th, U under reducing conditions and U in some sites under oxidising conditions);
2. Elements for which the association to major geochemical components of the system must be considered in order to explain their concentrations in groundwaters (i.e. Sr, Ba, Zn, Se, REEs and U under certain oxidising conditions), and
3. Elements for which no conclusions can be drawn and, therefore, should be subject of a more extensive study (i.e. Sn, Pb and Ni).

Additionally, we discuss the main improvements made to the thermodynamic databases and the geochemical calculation methodologies due to the BPM. Furthermore, the most important characterisation geochemical data needed to carry out predictive solubility and speciation calculations are identified.

Finally, the most important contributions of the BPM to Performance Assessment exercises are indicated.

Sammanfattning

Naturliga analogier studeras för att ge underlag till säkerhetsanalyser av förvar för radioaktivt avfall. En av nyckelanvändningarna av resultaten från studierna är tester av geokemiska modeller. Dessa modeller används bland annat för att beräkna spridning av radionuklider från ett förvar av radioaktivt avfall. Av den anledningen har geokemiska beräkningsövningar av typen "Blind Prediktiv Modellering" ofta funnits med som en del av analogistudierna de senaste tio åren. Vi ansåg att tiden nu var mogen att samla erfarenheterna från dessa övningar och sammanfatta vad vi har lärt oss.

Vi har granskat, diskuterat och jämfört resultaten från Blind Prediktive Modellering (BPM) som utförts inom 7 olika analogistudier: Oman, Poços de Caldas, Cigar Lake, Maqarin, El Berrocal, Oklo och Palmottu.

För att göra jämförelsen meningsfull, presenterar vi de viktigaste geokemiska förhållandena på varje plats för att belysa de mest relevanta mineralogiska och hydrokemiska skillnaderna.

Vi har gjort ett urval från den fullständiga listan av element, som studerats på de olika platserna, baserat på betydelsen i säkerhetsanalysen och hur ofta elementet inkluderats i BPM-övningar. De utvalda elementen är: Sr, Ba, Sn, Pb, Se, Ni, Zn, REE (sällsynta jordartsmetaller), Th och U. Vi har utgått från resultat av beräkningar av såväl speciering som löslighet.

Av jämförelsen drar vi slutsatsen att vi kan urskilja tre kategorier av element:

1. Element vars geokemiska egenskaper kan beskrivas tämligen väl genom att anta att lösligheten kontrolleras av rena fasta faser av det givna element (t ex Th, U under reducerande förhållanden och U på en del platser under oxiderande förhållanden);
2. Element för vilka man måste ta hänsyn till kopplingen med geokemiska huvudkomponenter i systemet för att kunna förklara elementens koncentration i grundvattnet (t ex Sr, Ba, Zn, Se, REE och U under vissa oxiderande förhållanden);
3. Element för vilka inga slutsatser kan dras och därför bör studeras ytterligare (t ex Sn, Pb och Ni).

Dessutom diskuterar vi de viktigaste förbättringar som gjorts av de termodynamiska databaserna och de geokemiska beräkningsmetoderna till följd av BPM. Vidare identifieras de viktigaste geokemiska data som behövs för att prediktivt beräkna löslighet och speciering.

Slutligen anges de viktigaste bidragen från BPM till säkerhetsanalysen.

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1 Background and Objectives

Natural Analogue studies have become an integral part in the Performance Assessment (PA) of nuclear waste repositories, although in many occasions the use of analogue data tends to be qualitative and therefore restricted mainly to define and exemplify the major Features and Events and Processes to be considered. However, one of the most tangible (i.e. quantitative) outcomes of Natural Analogue studies has been the possibility to test our conceptual geochemical models, the associated thermodynamic databases and required numerical codes to describe radionuclide migration under repository conditions. Consequently, these exercises are directed to test the predictive capabilities of thermodynamic models to describe the geochemical variability in sufficiently well characterised natural systems. Since they have been performed as blind predictive modelling exercises, they are commonly denoted as BPM exercises.

BPM exercises are designed to compare the model calculations results obtained by different groups of modellers, using different geochemical codes, thermodynamic databases and modelling approaches, in predicting the expected behaviour of trace metals in natural environments. The results obtained from these tests have helped not only to identify the main mathematical limitations of available geochemical tools but, more importantly, mainly to highlight new processes controlling radionuclide solubility and the necessary thermodynamic data or mathematical models to represent them.

BPM exercises have been undertaken in the following systems:

- Oman, a system of hyperalkaline springs generated by low temperature serpentinisation reactions.
- Poços de Caldas (Brazil), a Mesozoic volcanic ring-structure hosting a U-Th mineralisation.
- Cigar Lake (Canada), a 1.3 billion year old U deposit located in a water saturated sandstone where the ore is surrounded by a clay-rich halo.
- Maqarin (Jordan), spontaneous combustion of bituminous-rich marl has produced natural cements which, through interaction with normal pH groundwater, has produced hyperalkaline waters similar to those expected within a cementitious radioactive waste repository.
- El Berrocal (Spain), a granitic Hercinian massif intercepted by a quartz vein with associated primary U mineralisations.
- Oklo (Gabon), a fossil natural nuclear reactor systems located in a Precambrian sedimentary basin.
- Palmottu (Finland), a U deposit located within Precambrian metamorphosed supracrustal and sedimentary rocks in SW Finland.

Although a substantial effort has been dedicated within each of the individual projects to the BPM exercises, no overall summary and synthesis of the results obtained has been carried out to date. For example, the studies at Oklo and Palmottu were completed only during 1999. Consequently, there is now sufficient information to produce a summary

and comparison of the main results obtained from BPM exercises and to draw several conclusions concerning the PA implications for each of the elements studied under different geochemical conditions from the study areas.

The main objective of the work presented is to identify the strengths and weaknesses of the geochemical modelling of the trace metals of interest for PA. This will be done by comparing the results obtained from the BPM exercises undertaken within the different natural analogue projects up until December 1999.

The result of this review is not a list of definitive conclusions, but rather an indication of the state of the art of radionuclide geochemical modelling. In addition to the analysis of the results so far obtained, we aim to suggest some strategies to be followed in the future development of our understanding radionuclide migration and our capabilities to predict it. We have identified the investigated trace elements for which we have a good geochemical understanding and, consequently, reasonable predictive capabilities. We will also indicate for which elements we require an improved conceptual, numerical and/or experimental approach.

This report is structured as follows. First, we will start by briefly reviewing the general methodology used in the BPM exercises. An introduction to the sites studied in the BPM exercises, giving a short overview of their mineralogical and hydrochemical characteristics follows in section 3. In section 4 we discuss, on an element by element basis, the results obtained for all the investigated sites in order to obtain a general state of the art picture of present knowledge of every element included in the BPM exercises. In section 5 we highlight the main needs of the geochemical modelling identified in the BPM exercises and review the inconsistencies or the reasons for the lack of agreement between measurements and predictions. Finally, a short review is given of the integration of results from the BPM into PA exercises.

2 Brief review of the methodology used in the BPM exercises

The objective of a BPM exercise is twofold: (1) to compare the thermodynamic databases (TDB) used by different geochemical modelling groups, and (2) to test the ability of the geochemical modellers to predict the concentrations of trace metals of interest in a set of selected groundwater samples. The name of the Blind Predictive Modelling exercises is self-explanatory: they are blind, in the sense that the modellers do not have access to the actual data that they are expected to predict and model. As it is stated in /Pate et al, 1993/ “The aspect of blind testing is particularly important as, in many cases, the manner in which the simulation is carried out can be very objective and, if the answer is known, can be biased either consciously or subconsciously. The difference between blind testing of model predictions and testing if a model can simulate particular observations is fundamental, although often not evident from the literature”.

The methodology followed by the BPM modellers from the Oman and Poços de Caldas to the Oklo and Palmottu projects has not varied significantly. The modellers are provided with the main chemical analyses of a set of selected groundwaters sampled in the study site in terms of pH, Eh, temperature and major ion concentration, and they are asked to calculate the speciation and the solubility of a set of trace elements in these samples.

Many different modelling groups and organisations have participated in the various BPM exercises included in this revision:

- *Oman: EIR (Switzerland), BGS (UK), IH (UK) and Nagra (Switzerland).*
- *Poços de Caldas: SKB (Sweden), KTH (Sweden), PSI (Switzerland), Harwell (UK) and Atkins (UK).*
- *Cigar Lake: MBT (Spain).*
- *Maqarin: AEA (UK), Chalmers University (Sweden), MBT (Spain), Nagra (Switzerland) and SKB (Sweden).*
- *El Berrocal: AEA (UK), Ciemat (Spain), CSIC (Spain) and MBT/QuantiSci (Spain).*
- *Oklo: CEA (France), Ciemat (Spain), CNRS (France), CSIC (Spain), EMP (France) and QuantiSci (Spain).*
- *Palmottu: Ciemat (Spain), GTK-VTT (Finland) and QuantiSci (Spain).*

Each group used a geochemical code and database of its choice, leading in some cases to rather complex but always fruitful comparisons among the results obtained.

A BPM exercise is usually divided into two main stages:

Stage 1: In the first stage of the exercise, the participants are asked to calculate the speciation of the chosen trace metals in the selected groundwaters. They are also requested to propose the solid phase most likely to control the solubility of the different trace metals and to calculate the concentrations of the trace metals resulting from the control of the solubility by the selected phase. To perform these calculations, the information supplied to the modellers is the major component composition of the groundwaters, and the master variable values, pH and Eh. This information helps the modellers to obtain a basic understanding of the system under study in terms of which are the main processes governing the major chemistry of the waters and which are the main processes that can potentially affect the behaviour of the elements they are asked to predict.

Stage 2: In the second stage, the mineralogical information gathered from the natural analogue site is released to the participants. With this additional information the modellers re-calculate the solubilities of trace metals by assuming equilibrium with the solid phases characterised at the site. In addition, the association of the trace metals considered with major minerals observed in the zone is reported, and the participants are asked to take into account mixed solid phases to calculate the solubilities. Values for the molar fractions of trace metals in major minerals are also given in case they are present.

The results obtained by each participant are compared with the aim to detect possible discrepancies in the databases, either due to erroneous data input or to up-dating failures. Also, the different calculation algorithms contained in the codes may lead to different predictions. Another important point affecting the predictions can be the differences in the calculation methodologies followed by the different participants.

Finally, the calculated solubilities are compared with field measurements in order to check the outcome of the predictive exercise.

In more detail, the modellers are asked:

a) To calculate the speciation of the trace metals of interest in the selected samples.

For this purpose they assume that the trace element is present in the groundwater at a trace concentration, usually ranging between 1 ppm to 1 ppb. In some of the exercises, the speciation was calculated after equilibrating the groundwater with the solid that the modellers selected as more likely to control the solubility in the site. Nevertheless, we must consider that the main objective of this initial calculation is to compare the different TDBs. Therefore, given that in some cases the aqueous speciation depends upon the total metal concentration, the comparison of the TDBs from the results obtained by equilibrating with a solid phase is more complex. For this reason, and for the sake of simplifying comparison among different TDBs, it is advisable that all groups calculate the aqueous speciation of the metal by working with the same total trace concentration of the element in solution.

b) To select the mineral(s) controlling the solubility of the trace metals in the selected samples.

For this purpose, the modellers add between 1 ppm and 1 ppb of the trace metal to the solution and calculate which are the most supersaturated solid phases. These will be, in principle, the most thermodynamically stable solids and, therefore, the a priori solids thought to control the solubility of the given metal under the given chemical conditions.

In the first stage of the BPM exercises, the modellers do not have any information on the possible mineral sources and sinks for the metals of interest. Therefore, the only criterion for the selection of a given mineral is its saturation index.

c) To calculate the solubility of the trace metal of interest given by equilibrium with the solid phase(s) selected in point b).

At this stage, an intercomparison among the results obtained by the modelling groups is made and the main discrepancies among the different TDBs and calculation methodologies are identified.

A second comparison, in this case with the actual trace element concentration data, leads to a preliminary choice of the minerals more likely to control the solubility of the elements of interest.

In the second stage of the BPM exercises, the modellers are provided with mineralogical information on the possible mineral sources and sinks for the metals studied. This is, when available, complemented by information on the mineralogical associations identified in the site between trace and major elements. With this new information, the modellers are able to eliminate those minerals selected as likely to control the solubility of the metals during the 1st Stage, but that have not been identified by mineralogical analyses. In this way the modellers obtain more realistic and sensible predictions of the solubility of the metals in question.

Besides, when mineralogical information on the associations between trace and major elements is available, the modellers are in some cases able to make use of alternative modelling approaches to quantify these interactions. This is explained below.

2.1 Dealing with the association of trace metals with major geochemical components

All the BPM exercises have been mainly based on the assumption of thermodynamic equilibrium between the groundwater and the contacting minerals. With the aim to describe (or predict) the geochemical behaviour of the trace elements investigated, in most of the BPM tests the modellers have made use of individual solid phases of the trace metals in question. This leads in many cases to sizeable overestimations of the actual measurements. In the light of these results, during the Poços de Caldas and Cigar Lake studies, the conclusion was that the only way to describe the behaviour of some of the trace metals was to consider their association to the major mineralogical components of the system. In other cases, such as in Maqarin, the coupling between major and trace components was considered but due to the lack of data available this alternative was not implemented.

An attempt to model the U/Fe association was done in Poços de Caldas, by assuming the co-precipitation of U_3O_8 with $Fe(OH)_3$ /Bruno et al., 1992/. This followed the work previously done to explain the variability of U with redox potentials in deep-sea sediments in the Abyssal plain /Santschi et al., 1988/. However, no predictive modelling of this association was performed due to the lack of simple models. It was not until the revision of the Poços de Caldas data /Bruno et al., 1998/ and the final stages of the El Berrocal project that these associations were quantitatively considered. Two different approaches were used to quantify these processes, referred to as *Coprecipitation* and *Codissolution models* within the framework of the El Berrocal, Oklo and Palmottu BPM exercises (see below).

The basis of these two approaches are described below:

2.1.1 Coprecipitation approach

This model, also known as the conditional solubility product approach, is based on the thermodynamics of ideal solid solutions /Bruno et al., 1998/. Let us assume the coprecipitation of a trace element, T, with a major metal such as Ca, forming a mixed solid phase $T_xCa_{(1-x)}CO_3(s)$.

If the trace metal T were forming a pure carbonate phase, $TCO_3(s)$, its solubility equilibrium would be given by:



with a solubility constant defined by:

$$K_s = \frac{a_{T^{2+}} \cdot a_{CO_3^{2-}}}{a_{TCO_3(s)}} = ([T^{2+}] \gamma_T \cdot [CO_3^{2-}] \gamma_{CO_3}) / a_{TCO_3(s)} \quad (\text{eq. 2})$$

where g_T and g_{CO_3} , stand for the activity coefficients for species T^{2+} and CO_3^{2-} respectively. If the dissolution of a minor amount of $TCO_3(s)$ in the host carbonate phase, $CaCO_3(s)$, can be considered ideal, its thermodynamic activity, $a_{TCO_3(s)}$, may be equated to its molar fraction, $c_{TCO_3(s)}$, for percentages of $TCO_3(s)$ less than 5%. Therefore, we can define a conditional solubility product, K_{so}^* , as:

$$K_{so}^* = K_{so} \cdot c_{TCO_3(s)} = [T^{2+}] \gamma_T \cdot [CO_3^{2-}] \gamma_{CO_3} \quad (\text{eq. 3})$$

Where (eq. 3) is the expression used in the co-precipitation approach adopted in this work.

In this approach we are assuming that the activity coefficient of the trace component of the solid solution is 1 and, strictly speaking, it should be calculated for each composition of a solid solution by using the excess-free-energy of mixing /Glynn et al., 1990/. However, for cases in which $c_{TCO_3(s)} < 0.05$ it is reasonable to assume that $g_{TCO_3(s)} \approx 1$.

This is a very simple model that can be used to calculate the aqueous concentration of a trace metal, T, which can be solubility controlled by a mixed $T_xCa_{(1-x)}CO_3(s)$ phase. Furthermore, it is simple to integrate this approach in the traditional codes used to perform geochemical calculations. It just requires the multiplication of the solubility constant of the trace solid phase, $TCO_3(s)$, by its molar fraction in the bulk solid.

2.1.2 Codissolution approach

This model is based on the stoichiometric saturation concept that was formally defined by /Thorstenson and Plummer, 1977/. According to these authors, the composition of a solid solution may remain invariant during the dissolution of a solid phase due to kinetic restrictions. This is a model intended to explain the concentrations of trace metals in non-equilibrium systems. It assumes that an ideally mixed solid, such as the one proposed

in the previous section, $T_xCa_{(1-x)}CO_3(s)$, will dissolve in a congruent fashion. This implies that for each $1-x$ moles of Ca dissolved, x moles of T will be released to the aqueous phase. In other words, the dissolution process will be given by the following equation:



Note that in contrast to (eq. 1), where an equilibrium process was formulated, in (eq. 4), we have used an uni-directional arrow to express that the solid is effectively dissolving in the system.

If this assumption is valid, the aqueous concentration of T can be calculated very simply once the aqueous concentration of Ca is known:

$$[T^{2+}] = x/(1-x) [Ca^{2+}] \quad (\text{eq. 5})$$

This provides a useful way to estimate [T] in environments where the association of T with Ca or another major cation is documented.

As we have seen, these two models are based on the application of ideal solid solution thermodynamics. The fact that this approach was simple and applicable to elements with quite a different charge to ionic radius ratio (Fe^{3+} vs. UO_2^{2+}) caused some initial reaction from the geochemical community /Nordstrom, 1996/. Some of the arguments adduced in this regard are the lack of information on the amount of trace element in the ideal solid solution considered to govern its behaviour, i.e., the uncertainty in the molar fraction used in the calculation. A closer study of the natural systems we are dealing with permits us to identify that the extent of the substitution of a major cation by a trace metal is, normally, between very well defined ranges. Therefore, it is very sensible to use an average molar fraction in the calculations indicated above. As an example, we can see that the ratio between the aqueous concentrations of Sr and Ca in all the studied sites is in the order of 0.0035, the miscibility limit of Sr with Calcite (see Figure 2-1).

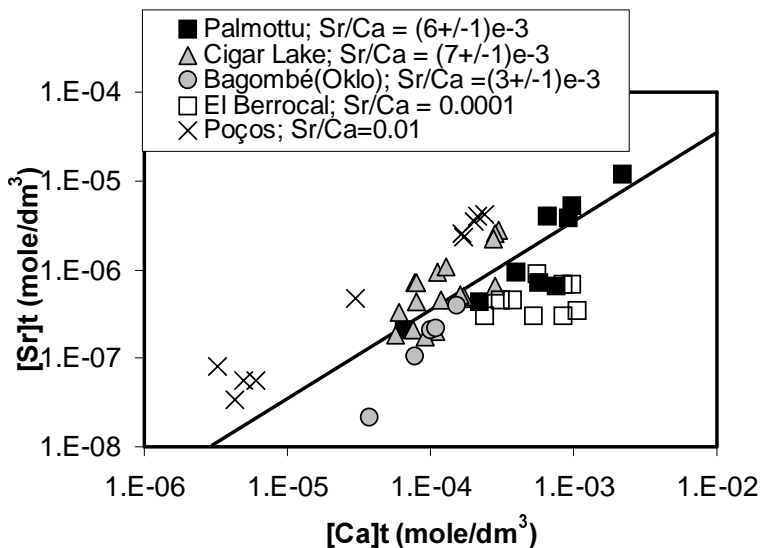


Figure 2-1. Aqueous Sr versus aqueous Ca concentrations in the studied systems. Solid line indicates the miscibility limit for Sr in calcite according to Tesoriero and Pankow (1996).

Another argument that has been used against the applicability of the simple models detailed above is that different cations in terms of charge and radius do not form ideal solid solutions and the calculation of the solubility of the mixed solid must be undertaken by using excess free energy of mixing parameters /see Glynn, 1990/. Some tests conducted by using non-ideal solid solution approaches do not provide any substantial improvement in describing the behaviour of those trace metals associated to major components, as it was already evidenced in /Bruno et al., 1998/. Besides, the obtention of these mixing parameters is never an easy process and strongly depends on the methodology used for their determination or for their estimation /Glynn, 1990/.

Experimental evidence of the formation of mixed solids was gathered from laboratory experiments /Bruno et al., 1995/ and integrated with the classical body of the underlying solid solution theory. Additionally, testing the applicability of these approaches to field data provided sufficient scientific integrity such that nowadays they form part of the routine models that should be included in any prediction of the concentration of trace elements in natural environments.

3 Description of the studied environments

The natural systems that have been used to conduct BPM exercises can be classified according to their dominant lithology and geochemistry. This classification will facilitate analysis of the results obtained that will hopefully be translated in a simpler understanding of the conclusions extracted from this work.

The different geochemical environments considered can be classified into four groups:

- *Crystalline media, in analogy to the far-field of a repository located in granite:*
El Berrocal (Spain) and Palmottu (Finland)
- *Sandstone-Clay media in analogy to the buffer material in the repository:*
Oklo (Gabon) and Cigar Lake (Canada)
- *Alkaline volcanic media, in analogy to the near-field of a repository:*
Poços de Caldas (Brazil)
- *Hyperalkaline media in analogy to the cementitious barrier of a repository:*
Maqarin (Jordan) and Oman.

The main characteristics of these 7 sites according to the mineralogy and to the composition of fracture filling material are summarised below. Also some indications on the hydrochemistry are given.

3.1 Crystalline media

Two of the studied sites, El Berrocal (Spain) and Palmottu (Finland), are located in a granite and gneiss/granite crystalline environment respectively.

3.1.1 El Berrocal (Spain)

The site is located around 100 km SW of Madrid. The granite hosts two U ore bodies, mined during several years but now abandoned. The El Berrocal granite pluton is near the central part of the Iberian Zone of the Hesperian Massif and in the SW part of the Spanish Central Massif.

/Pérez del Villar et al., 1996/ distinguish five different geological entities at the site:

- a) The reference granite which is rich in alkaline feldspars. The volume percentage of muscovite exceeds that of biotite and the U and Th accessory minerals are uraninite, thorite, monazite, anatase, apatite and zircon.
- b) The hydrothermally altered granite, where most of the U is in the form of autunite.
- c) The U Quartz Vein (UQV), formed of quartz associated with sulphide minerals, mainly pyrite, galena and sphalerite. The primary U minerals are pitchblende and coffinite. Fe(III) oxides, gummite and uranyl phosphates are the main secondary minerals.

- d) The weathered granite, characterised by the presence of oxidised phases resulting from the weathering of the primary minerals. Fe-Mn oxyhydroxides and uranyl phases such as phosphates are common.
- e) The fracture filling material, characterised mainly by quartz, K-feldspars, albite, phyllosilicates and carbonates. Fe-Mn oxyhydroxides are ubiquitously distributed from the shallowest to the relatively deep fractured zones.

According to the hydrochemical investigations conducted at the site /Gómez et al., 1996/ the groundwater sampled can be classified into two main groups. The Ca-SO₄ type waters in the vicinity of the UQV, due to the process of pyrite oxidation, and Ca-HCO₃ type waters in the boreholes located farther from the UQV, which have greater alkalinity. The role of the UQV in modifying the chemistry of the waters is clearly depicted in Figure 3-1, where the Stiff diagrams of the samples used in the BPM exercise are superimposed on a cross section of the site. The water flow lines go from north to south, and we can see that in the samples located downstream the concentration of sulphate is greater relative to the waters sampled upstream.

The pH of the samples ranged from acidic in the vicinity of the UQV to values around 7 in the deepest samples of boreholes S14 and S11. The redox potential is oxidising in the more shallow waters, achieving reducing values in the deepest samples.

A complete description of the El Berrocal project can be found in /Enresa, 1996/. The results of the BPM exercise undertaken in El Berrocal and discussed here correspond to the data published by /Bruno et al., 1996b/.

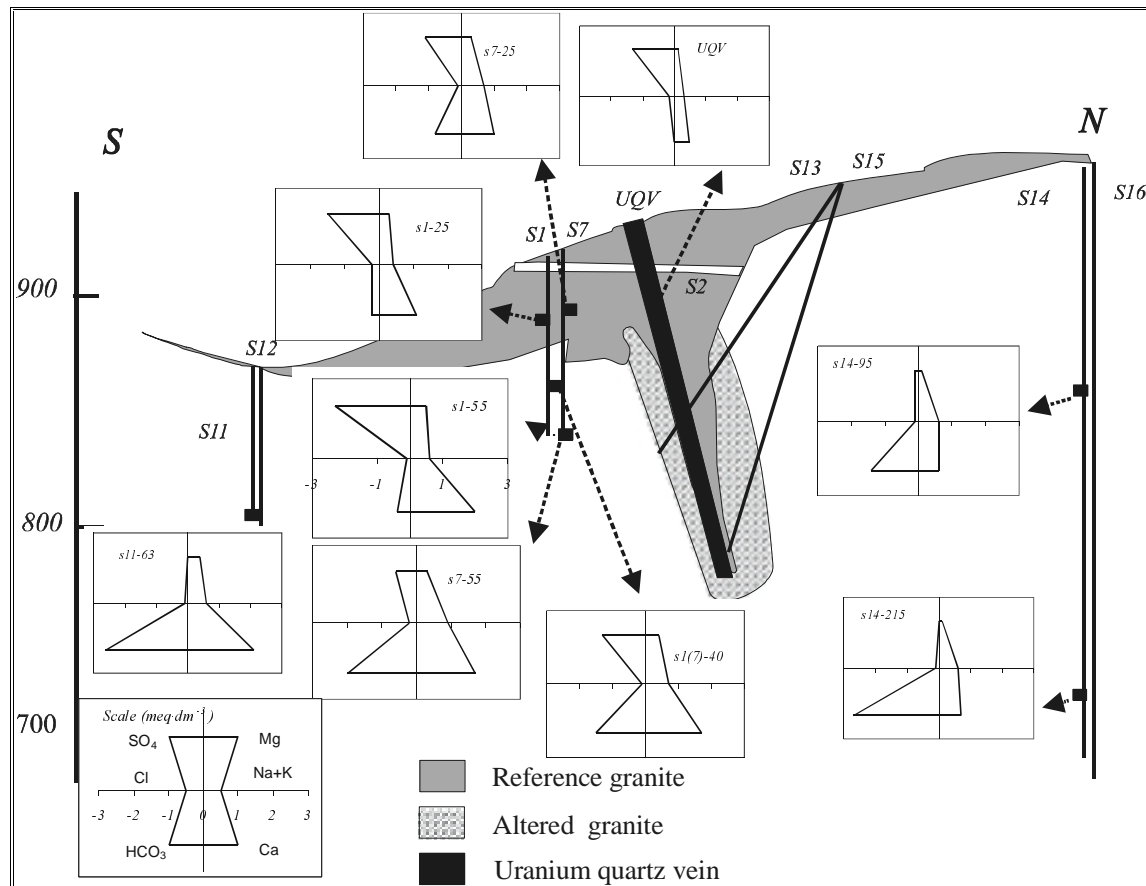


Figure 3-1. Cross section of the El Berrocal zone showing the Stiff diagrams of samples selected for the BPM exercise. (Adapted from Bruno et al. (1996b)).

3.1.2 Palmottu (Finland)

The Palmottu study area occurs within a zone of Precambrian gisses and granites in SW Finland. An U-Th mineralisation type characterises the site forming discrete lenses and dispersions over an area which varies up to 15 metres in width with a total length of about 400 m. The U occurs mainly as disseminated uraninite in microcline granite dykes. This uraninite has been altered along grain boundaries producing rims comprising mainly coffinite.

According to the groundwater geochemical modelling in the Palmottu site performed by /Gimeno and Peña, 1999/, the composition of the water sampled in the site changes from Ca-HCO₃-type near the surface to Na-HCO₃-type at intermediate depths. At greater depths, the waters are of Na-SO₄-Cl type with the Na-SO₄ groundwater is apparently confined to the mineralised area. In general, an increase in total dissolved solids and a decrease in the redox potential is observed with depth. The pH values of the groundwater samples used in the Palmottu BPM exercise range from 7.5 to 9.3. The measured Eh values are normally reducing, in the range -12 to -360 mV, except for the shallowest sample, which gave a redox potential of 414 mV. In Figure 3-2, the Palmottu study site is illustrated with the Stiff diagrams superimposed.

A complete description of the Palmottu Natural Analogue study can be found in /Blomqvist et al., 2000/. The results of the BPM exercise in Palmottu discussed here correspond to the 2nd. Phase of the Palmottu Natural Analogue Project and are published as a Technical Report /Bruno et al., 1999/.

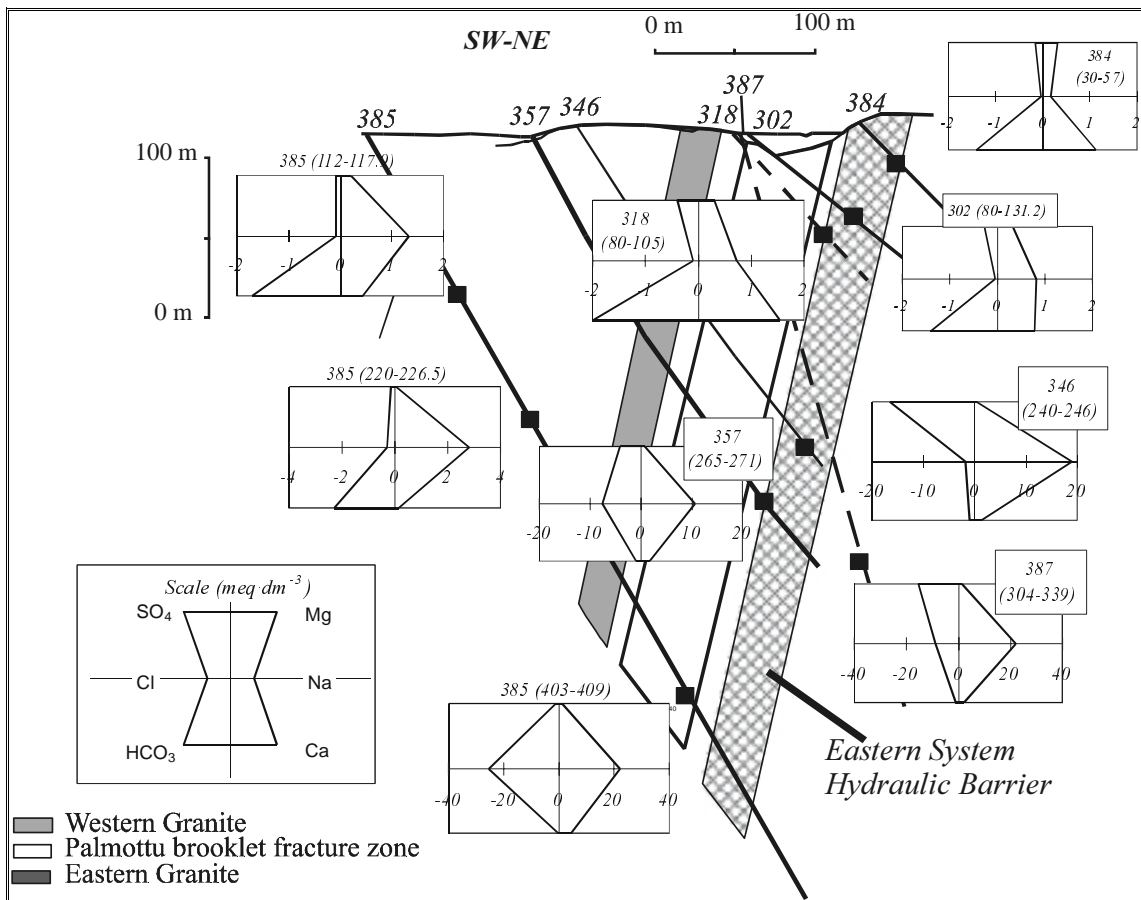


Figure 3-2. Cross section of the Palmottu site showing the Stiff diagrams of samples selected for the BPM exercise. (Adapted from Bruno et al. (1999)).

3.2 Sandstone-Clay media

The geology of two of the studied sites reflect a sandstone-clay media: Oklo (Gabon) and Cigar Lake (Canada).

3.2.1 Oklo (Gabon)

The Oklo region in Gabon, West Africa, presents a regional U mineralisation confined to the basal sandstone layers of an intracratonic sedimentary basin (the Franceville Basin). The Franceville Basin consists of a massive thickness of bedded sediments comprising five different formations; FA to FE. The FA formation is a sandstone-conglomerate deposit; the FB formation is mainly pelitic in its lower part and evolves to sandstones at shallower zones; formations FC, FD and FE are mainly volcanic-sedimentary with intrusions of dolomitic zones. All the U mineralisations identified in the Franceville basin are located in the FA formation. Some 15 different natural nuclear reactors are known in the Oklo/Okélobondo area and 9 of them were mined out between 1974 and 1980. Within the last phase (Phase II) of the Oklo project, reactor OK84 located at Okélobondo and the reactor at Bagombé have been studied. Bagombé is of particular interest since it is located at very shallow depths (~ 12 m), while all the others are at depths between 200 and 400 m.

In the Okélobondo area quartz, calcite, chlorite and illite mainly compose the host rock, while the fracture fillings contain quartz, calcite, pyrite, chlorite, Fe oxy-hydroxides and illite. Near the OK84 reactor the fracture fillings are mainly composed of quartz, chlorite, illite, kaolinite, pyrite, chalcopryrite, galena, Fe oxy-hydroxides, organic matter, zircon and gypsum. The variability of the groundwater samples used in the BPM exercise conducted at Okélobondo is shown in the Stiff diagrams superimposed on a cross section of the area (Figure 3-3). According to the geochemical modelling reported in /Peña et al., 2000/, the groundwater samples can be classified into 4 different groups:

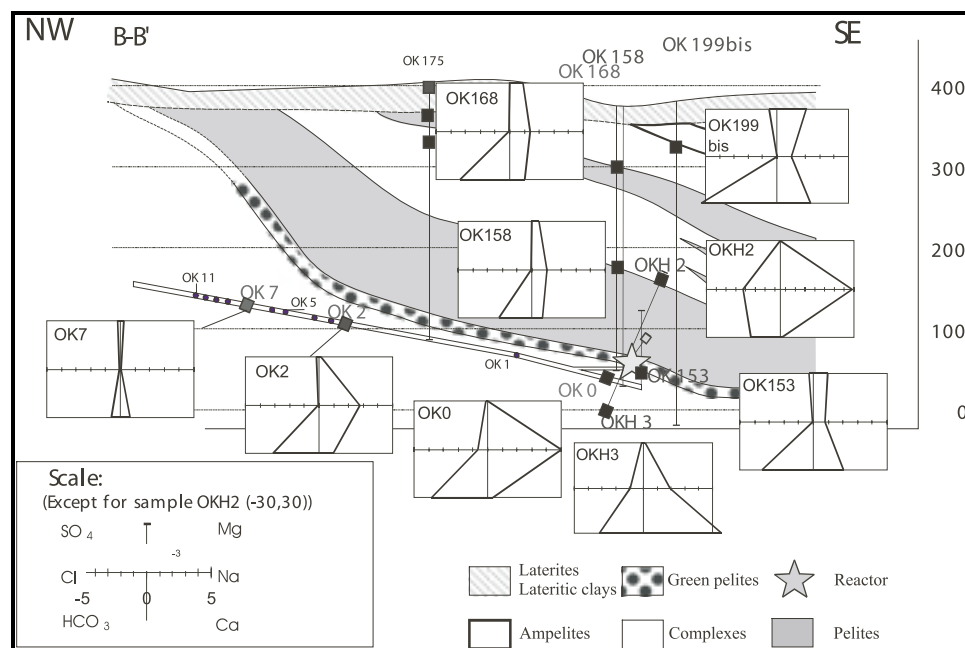


Figure 3-3. Cross section of the OK84 Okélobondo area showing the Stiff diagrams of samples selected for the BPM exercise. From Duro et al. (2000a).

- 1) Samples of the west gallery (Okélo C), representing low mineralisation, slightly acidic to neutral pH values and oxidising conditions.
- 2) Samples from boreholes drilled from the surface, sampled in the Complexes Formation, presenting neutral pH and reducing Eh values.
- 3) Samples close to the reactor (Okélo E), corresponding to groundwaters which have interacted with pelites, representing alkaline pH and oxidising Eh values.
- 4) Surface waters, representing acidic pH values and oxidising redox conditions.

In the Bagombé area quartz, chlorite goethite and clay minerals mainly compose the host rock, while the fracture fillings contain quartz, carbonates, sulphides (pyrite), chlorite, Fe oxy-hydroxides and illite. Near the reactor quartz, chlorite, illite, kaolinite, pyrite, Fe oxy-hydroxides, and organic matter mainly compose the fracture fillings. The Stiff diagrams of the groundwater samples used in the BPM are shown in Figure 3-4 superimposed on a cross section of the area. It is possible to see that all samples are of Ca-HCO₃ type. These groundwaters moderately acidic to neutral pH values (from 4 to 7). The redox potentials are discussed in /Louvat et al., 2000/.

A complete description of the Oklo Natural Analogue study can be found in /Louvat et al., 2000/. The results of the BPM exercise in Oklo discussed in this report correspond to the 2nd. Phase of the Oklo Natural Analogue Project and are published within a series of EUR reports /Duro and Bruno, 1998/, /Duro et al., 2000a/ and /Duro et al., 2000b/.

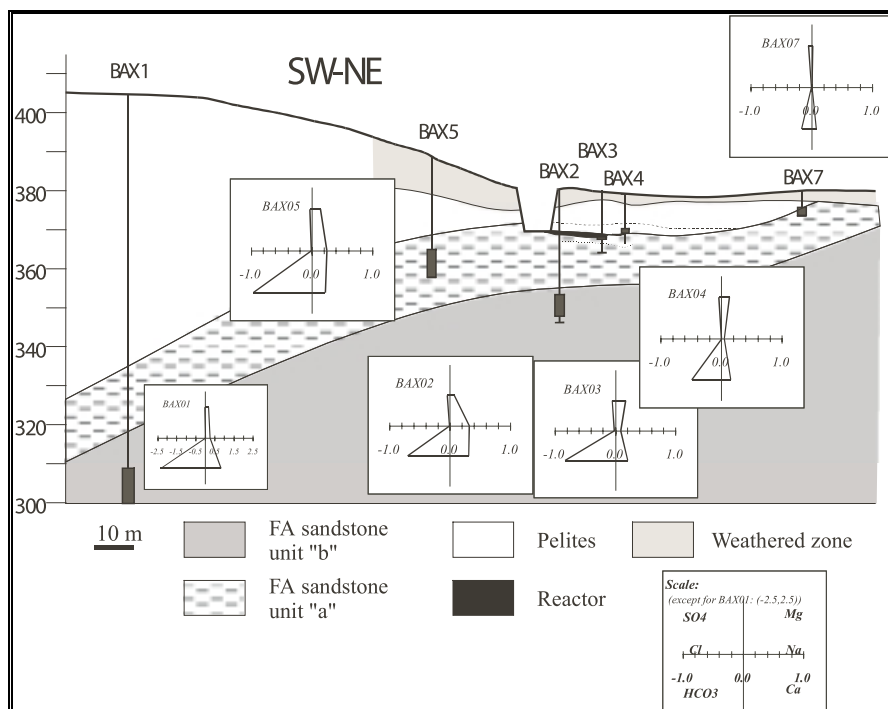


Figure 3-4. Cross section of the Bagombé showing the Stiff diagrams of the samples selected for the BPM exercise. From Duro et al. (2000b).

3.2.2 Cigar Lake (Canada)

The U deposit at Cigar Lake is located in northern Saskatchewan, Canada. The U mineralisation, located at 450 m depth, is mostly surrounded by a clay-rich zone resulting from the localised hydrothermal alteration of the host sandstone close to the contact between the sandstone and the underlying Archean basement rocks /Cramer and Smellie, 1994/. This site presents some features analogous to aspects considered in the PA for the disposal of high-level radioactive waste (HLW) in crystalline rocks. For example, the geometric arrangement of the deposit is generally similar to the concept of a deep HLW repository, i.e. U matrix surrounded by a clay zone and buffered by several hundred metres of host rock. Furthermore, despite the fact that Cigar Lake represents the world's second largest U deposit, there is no surface expression of its existence. The deposit has remained relatively intact during at least the last 10^4 years.

The U mineralisation is comprised mainly of uraninite and pitchblende and has an average U content of 8% wt. with local enriched zones containing up to a 60% wt. Illite and chlorite mainly form the clay matrix surrounding the U mineralisation. This zone has played an important role in preserving the ore due to its low permeability that contrasts with the highly permeable host sandstones. In addition, the relatively large Fe(II) sulphide content of the clay halo has probably contributed to the redox stability of the orebody. A general view of the geometry of the Cigar Lake deposit is illustrated in Figure 3-5.

The groundwaters at depth are weakly mineralised and highly reducing, with an ionic strength in the range 10^{-4} to $5 \cdot 10^{-3}$ and Eh values ranging from -0.3 to 0.1 V /Cramer et al., 1994/. From the study of the groundwater evolution at the site /Cramer and Nesbitt, 1994/, it appears that the bulk composition of the groundwater is controlled by interactions with clay minerals, mainly illite-kaolinite, and that the redox geochemistry is controlled by the iron and sulphur redox couples.

A complete description of the Cigar Lake Analogue study can be found in /Cramer and Smellie, 1994/. The results of the BPM exercise discussed in this report correspond to those published in the same report /chapter by Bruno and Casas, 1994/ and in /Casas and Bruno, 1994/.

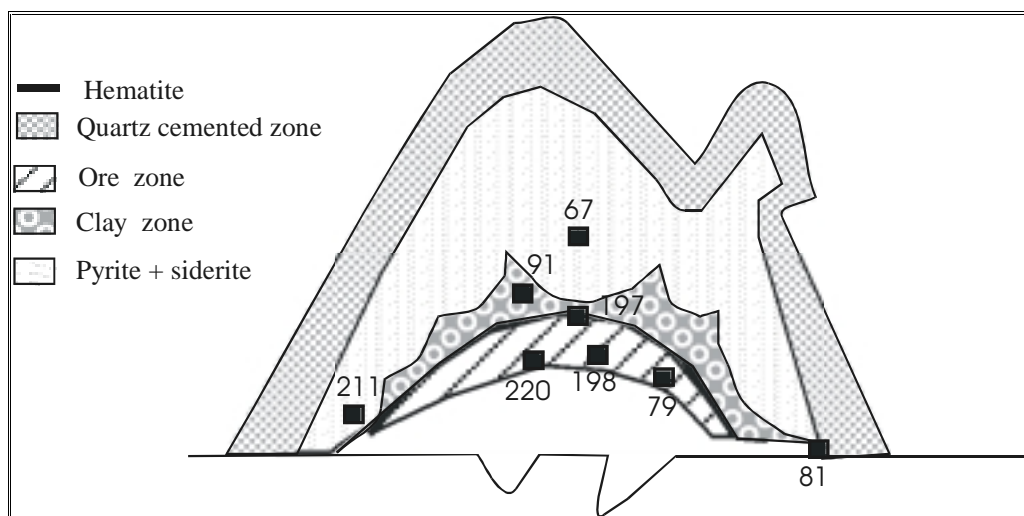


Figure 3-5. The Cigar Lake U mineralisation showing the hematite marginal to the orebody and the clay halo which acts as a hydraulic barrier to water circulation (Adapted from Cramer and Smellie, 1994).

3.3 Alkaline volcanic media: Poços de Caldas (Brazil)

The Poços de Caldas alkaline complex is one of the Mesozoic alkaline occurrences of south-eastern Brazil that developed from the Upper Jurassic onwards during continental break-up and drift. It comprises a suite of alkaline volcanic and plutonic rocks (mainly phonolites and nepheline syenites) with normal background amounts of U, Th and REEs. Hydrothermal fluid rock interactions of local extent led to pyritization, strong potassium enrichment and the formation of several important radioactive anomalies. Two of these anomalies, the Osamu Utsumi U deposit and the Morro do Ferro Th and REE deposit were studied within the Poços de Caldas Analogue Project /Chapman et al., 1993/. The predominant rock types at the Osamu Utsumi mine are phonolites and nepheline syenites and Morro do Ferro represents a highly weathered carbonatite complex. The major mineralogical components of the former are alkali feldspars, illite, kaolinite and subordinated zeolites, minor amounts of pyrite and sphalerite, barite and cryptocrystalline U-phases as trace components. The Morro do Ferro deposit is traversed by magnetite veins; the major mineralogical components of the host rock are illite and kaolinite, minor amounts of hematite, goethite and hydrous ferric oxides, and trace quantities of different Th and REE-bearing minerals, such as florencite, bastnaesite, and monazite.

The Poços de Caldas sites are very interesting from a PA viewpoint since Morro do Ferro was identified as the most naturally radioactive places in the surface of the Earth. Furthermore, the redox front displayed in the vicinity of the Osamu Utsumi mine made this site very useful to study the redox fronts likely to occur from radiolysis reactions around HLW containers of certain designs.

The groundwaters at the Osamu Utsumi mine are of K-Fe-SO₄ type, with F much more important than Cl. This groundwater composition is very unusual and is due to the weathering of the hydrothermally altered complex of volcanic and plutonic phonolites. K is in higher concentration than Na and other common cations in most groundwaters. For example, Ca and Mg are commonly below 1 mg/dm³, comparable in concentration to Sr and Ba. At the Morro do Ferro site, the groundwaters sampled show very low mineralisation in the shallow boreholes; increased values of the main components are observed in borehole MF12 since it corresponds to a discharge zone.

These characteristics are illustrated in Figures 3-6 and 3-7 where cross sections of the two sites with the superimposed modified Stiff diagrams are shown. In general, the groundwaters are highly oxidising in the recharge areas whereas deeper groundwaters are mildly reducing. The pH values are mildly acidic, between 5 and 6.5, with high concentrations of dissolved silica.

A complete description of the Poços de Caldas Natural Analogue study can be found in /Chapman et al., 1993/. The results of the BPM exercise discussed here correspond to those published by /Bruno et al., 1992 and 1996/.

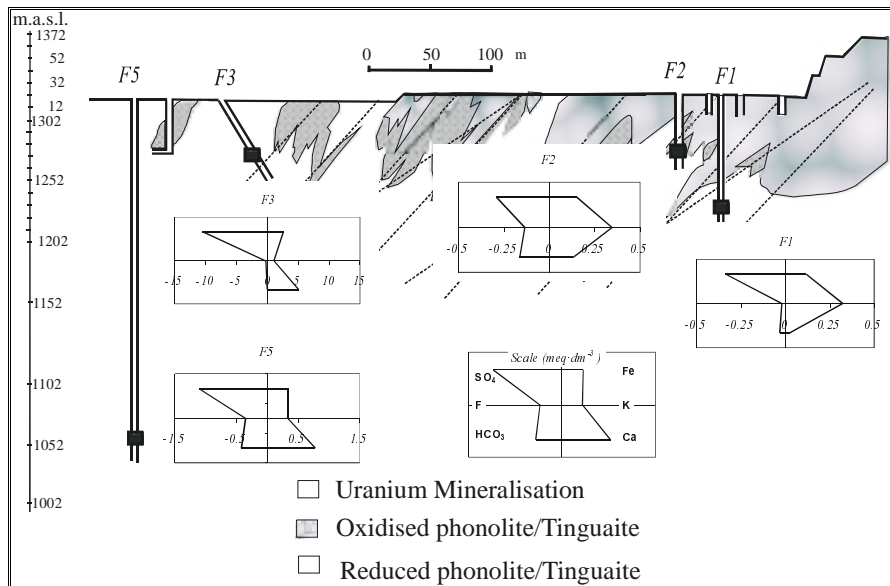


Figure 3-6. Cross section of the Osamu Utsumi mine showing the modified Stiff diagrams of groundwaters sampled at the site. (Adapted from /Nordstrom et al., 1990/.)

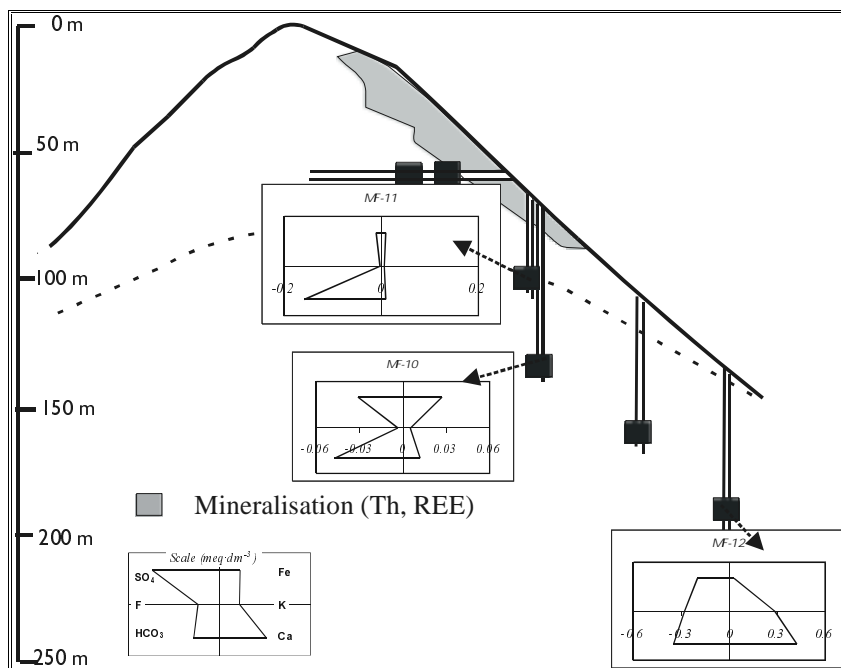


Figure 3-7. Cross-section of the Morro do Ferro site showing the modified Stiff diagrams of groundwaters sampled the site. (Adapted from /Nordstrom et al., 1990/.)

3.4 Hyperalkaline media

3.4.1 Maqarin (Jordan)

Spontaneous combustion of bituminous-rich marl has produced natural cements which, through interaction with normal pH groundwater, has produced hyperalkaline waters and the formation of hydrated CSH (Calcium-sulphate-hydrates) phases similar to those expected within a cementitious radioactive repository.

Three seepage water samples were selected for the Maqarin BPM exercise; two of them from the Eastern springs (M1 and M3) and one from the Western springs (M5). These waters present pH values between 12.3 and 12.9, and redox potentials in the range 150 to 300 mV. The main cations are Ca, K and Na and the major anions are SO_4 , Cl and NO_3 (see Figure 3-8).

A complete description of the Maqarin site can be found in /Smellie, 1998/. The results of the Maqarin BPM exercise discussed here correspond to the 1st and 2nd Phases of the Maqarin Natural Analogue Project and are published in /Alexander, 1994/, /Alexander et al., 1992, 1998/ and /Linklater et al., 1996/.

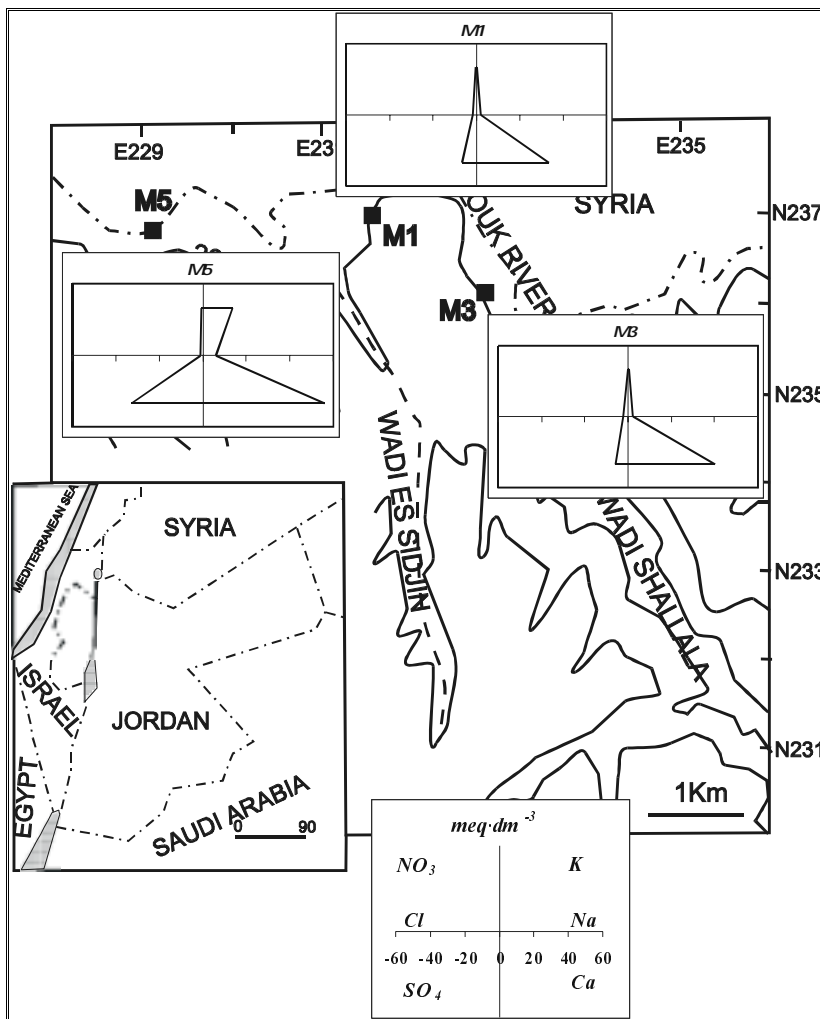


Figure 3-8. Maqarin study site. Location of the samples studied in the BPM exercise with modified Stiff diagrams superimposed. (Adapted from /Linklater et al., 1996/.)

3.4.2 Oman

The springs system from the Semail Ophiolite Nappe in Northern Oman were used as analogue of aged cement porewater. These springs are natural Ca-OH-type groundwaters with pH values higher than 11 and very reducing, even with evolution of free hydrogen gas. Such waters were generated by low temperature serpentinisation reactions /McKinley et al., 1988/. The typical Oman water presented redox potential between -100 and -600 mV a pH of 11.5 and temperature of 34°C.

4 Results of elemental comparison from each site

In order to present a summary of the results obtained in the different BPM exercises performed up to date, we have selected a series of elements for discussion. This means that we will not discuss the results obtained for all the elements studied at all the sites. The criteria followed to make the element selection is based on the frequency that a particular element has been included in a BPM exercise and on its relevance from a PA point of view. This selection is described in the following sub-section.

Comparison of the results obtained has been based on: (1) aqueous speciation, and (2) solubility results. From the initial discussion on the aqueous speciation obtained for each selected element under different geochemical environments, we will identify the main aqueous species to consider and the main counter-ions affecting the behaviour of each element, thus indicating critical factors for its behaviour. We will also identify gaps or discrepancies in the geochemical databases used in the BPM exercises which has led to the improvement of these crucial tools for geochemical modellers.

The discussion on the solubility results will help us to identify the main solids responsible for the control of the concentrations of a given radioelement under different geochemical conditions. It will allow us to determine which experimental or theoretical studies should be carried out in order to improve our understanding of the radionuclide geochemistry of interest.

Finally we present a summary of the conclusions obtained from the discussion.

4.1 Selected elements

The elements studied at each one of the sites are shown in Table 4-1. If a given element has been studied at one site, it is represented by a cross. The selected elements are in bold and indicated by a cross in the last column, "Selected".

As explained previously, the selection is based on the frequency an element has been studied and on its relevance from a PA point of view. The selection of Sr, Pb, Ni, Zn, REEs, Th and U is straightforward since they are relevant for PA and they have been studied in, at least, two of the sites included in this analysis.

In spite of the fact that Ba is not included in the list of the PA relevant elements, its chemical analogy to Ra and the fact that Ra has been studied only in the hyperalkaline environment of Maqarin, has led us to select Ba for discussion in this present report.

Although Mn has been studied in 3 of the 7 sites, we have not selected it for the present work due to the fact that it is not relevant to the PA of nuclear waste repositories. Nevertheless, Mn is a useful element to describe the redox geochemistry of some of the sites.

Table 4-1. Elements studied from each site and elements selected for discussion

El./Site	El Berrocal	Palmottu	Oklo	Cigar Lake	Poços	Oman	Maqarin	Selected
Li			x					
Sr	x	x		x	x			X
Ba	x		x	x				X
Ra							x	
Al			x					
Sn						x	x	X
Pb	x			x	x		x	X
As				x				
Se						x	x	X
V					x			
Zr						x		
Cr				x				
Mo				x				
Mn	x	x	x					
Tc				x				
Ni	x	x	x	x	x	x	x	X
Pd						x		
Cu	x			x				
Zn	x		x	x	x			X
REE		x	x					X
Th	x	x		x	x	x	x	X
Pu				x				
U	x	x	x	x	x	x	x	X

The remaining elements have been studied at only one or two of the sites. Among them, Sn and Se have been selected due to the following reasons: a) they represent a quite different behaviour from the rest of the studied elements, b) they are of interest from a PA perspective, and c) they are considered worthy to discuss hyperalkaline environments such as Maqarin and Oman.

4.2 Results

In this section, the aqueous speciation and the solubility calculations performed for each of the selected elements from the studied sites is presented. We will systematically address the list in Table 4-1 in order to make discussion of the results as logical as possible.

4.2.1 Strontium

Sr has been studied in four of the studied sites: two crystalline media (El Berrocal and Palmottu), one clay medium (Cigar Lake) and one alkaline volcanic medium (Poços de Caldas).

The concentrations of Sr in the El Berrocal groundwaters were very close to the analytical detection limit, in the order of 10^{-6} mole/dm³. Very similar or slightly higher concentrations were measured at Palmottu, as expected due to the similar geochemical environment of these two sites. The concentration of this metal measured at Poços de Caldas presents a lower range, from 10^{-8} to 10^{-5} mole/dm³, reflecting the exceptional differences in the geochemistry of this site. At Cigar Lake, concentrations of Sr in the range 10^{-6} to 10^{-7} mole/dm³ were measured (see Figure 4-1).

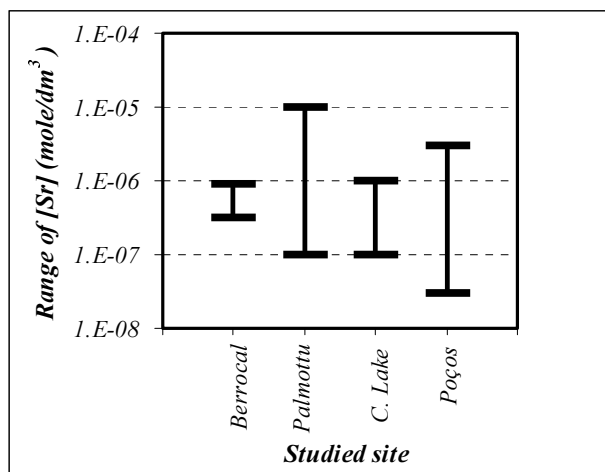


Figure 4-1. Range of concentrations of Sr measured at the different sites.

The main species accounting for the aqueous speciation of Sr at El Berrocal is Sr^{2+} , with minor amounts of $\text{SrSO}_4(\text{aq})$ in those samples of lower pH values and higher sulphate concentrations (as a result of the weathering of the pyrite present in the quartz vein). The same speciation is obtained from Palmottu, reflecting again the similarity between the groundwater composition of these two sites and the influence of the sulphur cycling on the geochemical behaviour of Sr.

At Poços de Caldas and Cigar Lake, Sr^{2+} was the main species calculated by the modellers as dominating the Sr aqueous speciation in all waters.

The assumption of pure Sr solid phases controlling the concentrations of Sr in solution resulted, at all sites, in a general overestimation of the actual concentration of this metal in groundwater. For this reason, the modellers tested alternative approaches. In general, they tested models based on the association of Sr with the major minerals comprising fracture fillings at the sites or those minerals readily available for water-rock interaction processes.

An *a priori* analysis of the mineralogical data of El Berrocal indicated that Sr was associated with solid carbonates, mainly calcites, in a ratio close to 0.001 moles of Sr per mole of Ca in calcite. On the other hand, the main source of Ca in this site is the dissolution of calcite. After testing this association, it was proven that the process best suited to reproducing the concentration of Sr was the congruent dissolution of a Sr-substituted calcite. The evidence found in the literature /Tesoriero and Pankow, 1996/ and references therein concerning the formation of solid solutions between strontianite (SrCO_3) and calcite (CaCO_3) up to a miscibility limit of 0.0035 supported this approach.

The same process, i.e. congruent dissolution of a Sr-substituted calcite, was able to explain also the behaviour of Sr at the Palmottu site. In this case, though, the average Sr content in calcite was lower than the content needed to reproduce the data. The explanation given was that the Palmottu calcites did not present a homogeneous distribution of Sr, i.e. the content of Sr in the calcite surface available for the present water-rock interaction processes is larger than in the bulk of the calcite chemically analysed. In fact, the best predictions were accomplished by assuming a content of Sr in calcite given by their miscibility limit (Sr molar fraction = 0.0035).

At Cigar Lake, /Casas and Bruno, 1994/ indicated the possibility of a Sr-bearing Ca carbonate controlling the solubility of this element in groundwaters and an ideal solid solution model using the miscibility limit gave a good match with the measured results.

At Poços de Caldas, /Nordstrom et al., 1992/ indicated that the good correlation between the Sr and P concentrations in the sampled groundwaters might indicate that minerals like goyazite (a Sr phosphate identified in the site) could control Sr solubility. Nevertheless, the lack of thermodynamic data on this mineral in the TDBs so far available made it very difficult, if not impossible, to test this possibility. The results from the blind test of Sr in Poços de Caldas indicated that the assumption of equilibrium with any of the pure Sr solid phases tested (strontianite and SrHPO_4) resulted in important overestimations of the actual concentrations. Therefore, as at the other sites, its association with major components of the system was considered. The aqueous Sr concentration is also very well correlated with that of Ca, indicating the possibility of these two elements being derived from the same source in the system. Both calcite and fluorite are able to host Sr in their crystalline structures. However, the low alkalinity of the Poços de Caldas groundwaters indicate that calcite is not a major mineral at this site and fluorite seems to be the solid controlling the solubility of Ca. According to /Nordstrom et al., 1992/ the dissolution of fluorite is one of the main driving forces acting in the system due to the general undersaturation of all groundwaters with regards to this phase. In order to explain the actual concentrations of Sr in Poços de Caldas by assuming a congruent dissolution of a Sr-bearing fluorite, the contents of Sr in the solid should be around 1%. /Nordstrom et al., 1992/ argued that the maximum amount of Sr that fluorite can host is 0.5% and, therefore, this process cannot account for the observed Sr concentration in water. In a later revision of the Poços de Caldas data, /Bruno et al., 1996/ provide some references where the maximum amount of Sr in fluorite is increased up to a 1%; according to this, the hypothesis of congruent dissolution of a 1%-Sr-bearing fluorite should not be disregarded.

The correlations between the concentration of Sr and Ca in the three sites where it has been studied can be observed in Figure 4-2. We can see that the correlation is, generally, fairly good and that the molar ratio Sr:Ca ranges from 10^{-2} to 10^{-4} .

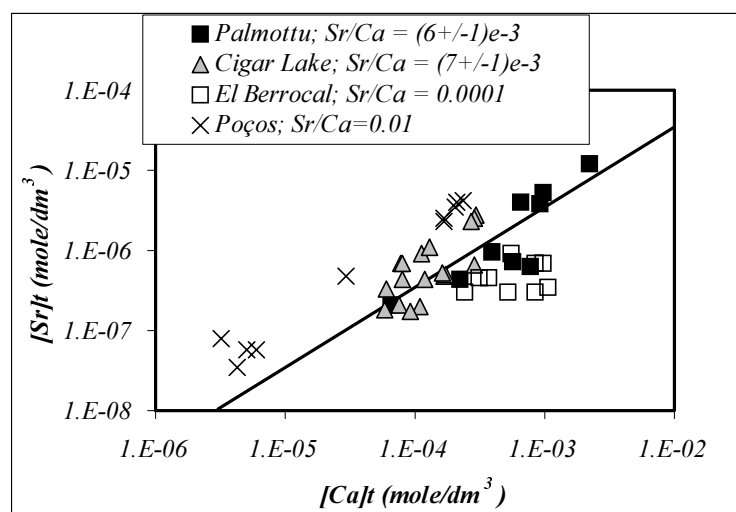


Figure 4-2. Sr:Ca correlation in groundwater samples from El Berrocal, Palmottu, Cigar Lake and Poços de Caldas. The solid line stands for the Sr miscibility limit in calcite (0.0035).

The main conclusion is that, in general, the behaviour of Sr in groundwaters is intimately linked to Ca. Therefore, the more convenient way of dealing with further predictions of the aqueous concentrations of Sr is to look for the mineral acting as the main Ca source and test the possibility of this phase to host Sr in its structure. In both crystalline media studied, the main Ca source is attributed to calcite, while in the alkaline-volcanic complex of Poços de Caldas, fluorite seems to be the main mineral releasing Ca to groundwater. Therefore, despite the general dissimilarity existing between the two types of environments studied, the behaviour of Sr can be interpreted on the same basis.

4.2.2 Barium

Ba has been studied at three of the five sites included in this analysis: a granitic crystalline environment (El Berrocal) and two sandstone-clay media (Oklo and Cigar Lake). As already discussed, the chemical analogy of Ba and its association with Ra makes it interesting from a PA point of view.

The aqueous concentration of Ba at all three sites is at the level of 10^{-7} to 10^{-6} mole/dm³ (see Figure 4-3). In all cases, too, the aqueous speciation of this element is governed by the free cation Ba²⁺.

The most common phases tested in the solubility predictions of Ba in these groundwaters were barite (BaSO₄) and witherite (BaCO₃). These solids readily precipitate from a supersaturated solution and their solubility is in agreement with the observations within ± 1 order of magnitude in most of the El Berrocal, Oklo and Cigar Lake groundwaters.

At El Berrocal, the difference between the control exerted by barite or witherite is clearly given by the sulphate content in groundwaters. Those waters of low alkalinity and high sulphate concentrations seem to be close to equilibrium with barite, while those of greater alkalinity and lower sulphate content are better described by assuming equilibrium with witherite.

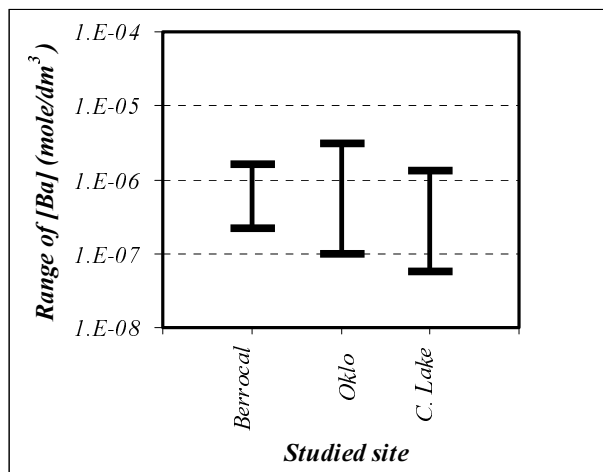


Figure 4-3. Range of concentrations of Ba measured at the different sites.

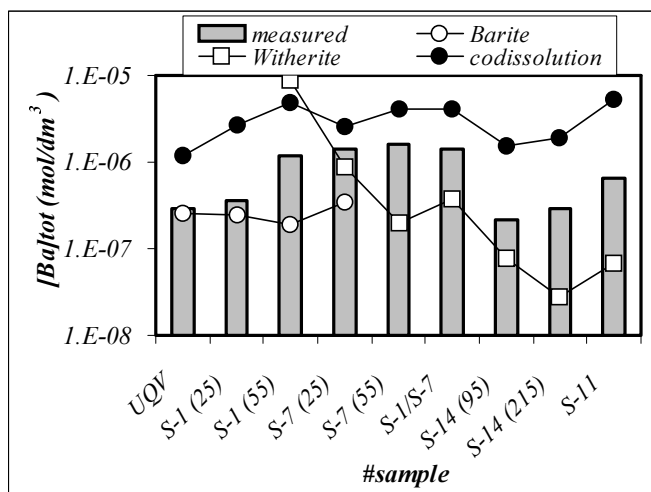


Figure 4-4. Ba(II) in El Berrocal groundwaters. Predictions compared with actual measurements.

The modellers used the reported association between Ba and Ca in El Berrocal to estimate the concentrations of Ba given by a congruent dissolution of a Ba-bearing Ca phase, mainly calcite. This was the approach that best reproduced the observed concentration of Ba in El Berrocal groundwaters, providing also the most conservative predictions (see Figure 4-4).

At Bagombé (Oklo), equilibrium with witherite overestimates the actual Ba concentrations and the best agreement is achieved when the congruent co-dissolution of a Ba-rich Ca solid phase is assumed (see Figure 4-5).

In the light of these results we can conclude that the concentration of Ba in these groundwaters can be fairly well predicted by considering its association to Ca, as was the case of Sr, and this is to be expected from the similar behaviour that these alkaline-earth elements exhibit.

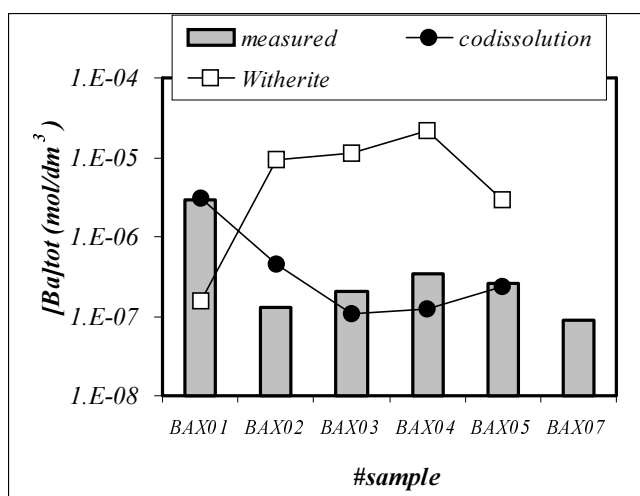


Figure 4-5. Ba(II) in Bagombé (Oklo) groundwaters. Predictions compared with actual measurements.

4.2.3 Tin

Sn has been only studied at two of the sites included in this revision; the bituminous limestone and marl site at Maqarin in Jordan and in Oman. The concentrations of this element in the Maqarin groundwaters are in the order of 10^{-9} mol/dm³, while in Oman, the concentrations measured are below $2 \cdot 10^{-9}$ mol/dm³.

In Oman, the predicted aqueous speciation changed from cationic Sn(OH)⁺ to anionic Sn(OH)₃⁻ in more reducing waters /McKinley et al., 1988/. According to results obtained /Alexander, 1994/, /Alexander et al., 1998/, the speciation of Sn in Maqarin is dominated by hydroxo species, as would be expected from the high pH value of these groundwaters. The suggestion is also made to include the Sn(IV) hydrolysis products in the thermodynamic databases due to the influence they have on the solubility of Sn solids at high pH.

The calculated solubility of Sn in Oman was extremely low, due to the assumption of equilibrium with SnO₂(s). The lack of appropriate thermodynamic data on Sn in the calculations made difficult any interpretation of the results obtained. No agreement was reached on the solubility-limiting phase of Sn in Maqarin, mainly due to the differences existing among different databases. As it is stated in /Linklater et al., 1998/ one of the limitations associated to the understanding of the behaviour of Sn is the inadequacy of the TDB regarding to the inclusion of relevant solid phases. Cassiterite, which is the most common mineral used to conduct this type of calculations is normally a high-T phase and therefore it is not expected to be of relevance for PA purposes. For this reason, it was suggested to expand Sn databases by taking into account the phases more relevant at low temperatures..

This reasoning together with the fact that the mineralogical data in Maqarin and in Oman did not indicate the presence of discrete Sn in any of the solids analysed /Alexander, 1994/ made difficult the understanding of the behaviour of Sn. In conclusion, we can say that the problem of Sn remains still open. It has not been studied at a sufficiently large number of sites to draw a general picture about its likely behaviour in groundwater.

4.2.4 Lead

Pb has been studied at four different sites: El Berrocal, Cigar Lake, Maqarin and Poços de Caldas.

The concentrations of Pb in El Berrocal groundwaters could not be quantified because they were below the analytical detection limit, $2.5 \cdot 10^{-7}$ mole/dm³. At Poços de Caldas, the concentration of Pb in the samples included in the BPM exercise was in the range 10^{-9} to 10^{-7} mole/dm³, and at Maqarin values of around 10^{-9} mole/dm³ were measured (see Figure 4-6). In groundwaters sampled at Cigar Lake, only 2 analytical data are available (around 10^{-8} mole/dm³), while the concentration of Pb in all other samples is below the detection limit ($5 \cdot 10^{-9}$ mole/dm³).

In El Berrocal groundwaters, the calculations indicated that the dominant Pb species were the free cation Pb²⁺ in the acidic waters, and the neutral carbonate in the more alkaline waters. The omission of PbCO₃(aq) in the databases causes the erroneous predominance of the free cation. Subsequently this led to the inclusion of PbCO₃(aq) in the TDB used. At Poços de Caldas, the same results were obtained: if no PbCO₃(aq) was included in the database, the calculations indicated that the dominant aqueous species was Pb²⁺. The picture at Maqarin is totally different due to the high pH measured. At this site, which is to be expected, the hydroxo Pb(OH)₃⁻ species dominate the aqueous

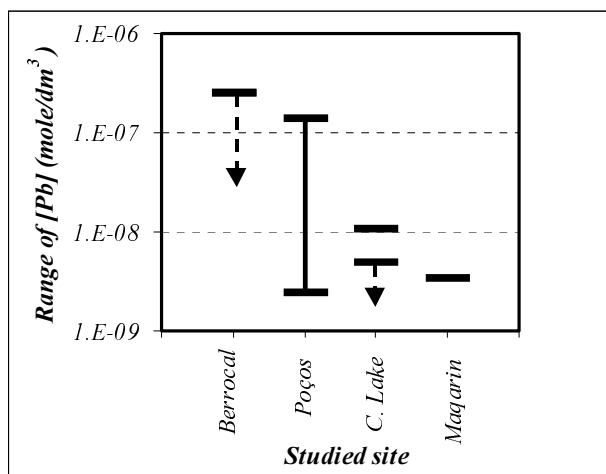


Figure 4-6. Range of concentrations of Pb measured at the different sites. At El Berrocal and Cigar Lake the arrows indicate that values below the indicated analytical detection limit were obtained.

Pb speciation, unless hydroxo Pb complexes are not included in the database, in which case $\text{PbCO}_3(\text{aq})$ is calculated to dominate. At Cigar Lake Pb^{2+} , PbOH^+ or $\text{PbCO}_3(\text{aq})$ dominated the speciation, depending on the pH of the sample.

Initial calculations at El Berrocal were conducted by assuming that the solubility of Pb could be limited by Galena (PbS), cerussite ($\text{PbCO}_3(\text{s})$) or anglesite ($\text{PbSO}_4(\text{s})$). However, most of them produced concentrations of Pb in solution greater than the analytical detection limit, below which were the actual Pb concentrations. Therefore, it was concluded that this metal could be source-limited at the site. The same phases (cerussite and anglesite) were also proposed at Poços de Caldas with similar results, i.e. strong overestimation of the actual aqueous Pb concentrations. Here it was concluded that Pb was associated with colloidal particulates. The good correlation between Pb and P_2O_5 Morro do Ferro indicated the possibility of Pb-phosphates controlling its solubility, but the lack of analytical phosphate data prevented testing this hypothesis.

At Maqarin, gross overestimations of the actual Pb concentrations were obtained also, evident by the very negative saturation indexes of the most common Pb minerals present in the databases (cerussite and $\text{Pb}(\text{OH})_2(\text{s})$). Comparison with the mineralogy showed that the solid phases present in the databases were not present at the site and vice versa, indicating the limitations of the databases. Finally, at Cigar Lake, the scarcity of the data does not allow any conclusion, although according to /Casas and Bruno, 1994/ galena can be the solubility limiting solid phase in the most reducing samples.

Summarising, we can state that no conclusions for Pb can be drawn from any of the studied sites, except on the limitations of the existing TDB. Therefore, the geochemistry of this element in low temperature waters remains an open question and an important effort concerning the updating of TDB should be undertaken.

4.2.5 Selenium

In common with Sn, Se has been studied only at the hyperalkaline environments of Maqarin and Oman. The aqueous concentration of Se in the Maqarin groundwaters is in the range 10^{-6} - 10^{-5} mole/dm³, while in Oman the concentrations were always below $3 \cdot 10^{-9}$

mole/dm³ All Se was observed to be in anionic form in the Maqarin waters, since its speciation is dominated by selenate (SeO₄²⁻).

According to /Linklater et al., 1996/, the mineralogical data indicate the presence of Ca-selenate and elemental Se in the Maqarin rocks. However, both solids present solubilities far above the observed Se concentrations, which in the case of elemental Se is mainly due to the oxidising redox potentials measured at Maqarin.

A likely explanation to the behaviour of Se in this environment is, as noted in /Linklater et al., 1994/ and in /McKinley et al., 1988/, that its chemistry is closely linked to the S system and Se is incorporated into sulphate minerals, but this is a phenomenon not easy to quantify and to make predictions upon. The same authors comment on the few quality Se data available in the literature. Recent determinations of the stability of metallic Se and on several aqueous species are found in the literature /Séby et al., 2001/ would allow certain updating of the existing databases. Besides the limitation of the Se TDB available up to date, we must also bear in mind the possible redox disequilibria existing in the Se system /McKinley et al., 1988/ as it has been many times manifested in the case of sulphur, and which is related to the existence of bacterial activity. However, no clear conclusions can be drawn in this case and the prediction of the solubility of Se in natural groundwaters remains an open question.

4.2.6 Nickel

Ni is a very interesting element for the purpose of this review since it has been included in all the referenced BPM exercises.

The concentration of Ni measured in the groundwaters of El Berrocal is around 10⁻⁶ mole/dm³, while at Palmottu it is two orders of magnitude lower, around 10⁻⁸ mole/dm³. In the Oklo environment, these concentrations are similar to those measured in El Berrocal. In Poços de Caldas the concentrations are similar to the ones of Palmottu, around 10⁻⁷ mole/dm³. In Maqarin, the levels are of the same order of magnitude. In Oman values in the order of 3·10⁻⁹ mole/dm³ and below are measured, and in the Cigar Lake groundwaters only 2 analytical data (around 10⁻⁷ mole/dm³) are available; the other samples contain Ni concentrations below the limit of analytical detection (see Figure 4-7).

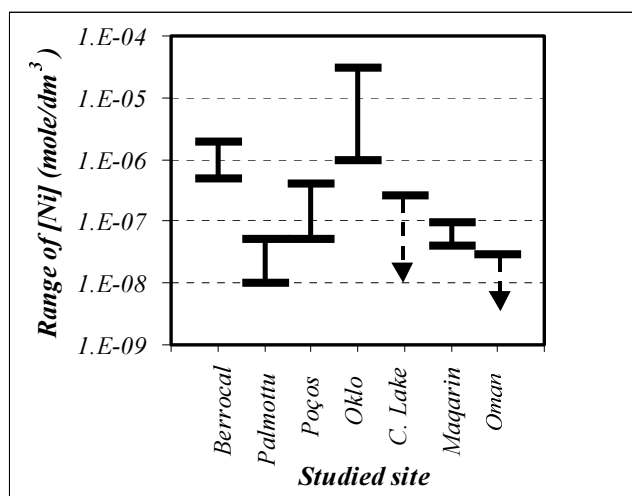


Figure 4-7. Range of concentrations of Ni measured at the different sites. The arrows denoting Cigar Lake and Oman indicate values below the analytical detection limit.

In general, at all the sites studied it is observed that the aqueous speciation of Ni is dominated by the free cation Ni^{2+} in the most acidic waters and by carbonato-complexes in alkaline samples. The exceptions to this rule are the cases of Oman and Maqarin, where hydroxo-complexes were calculated to dominate the speciation of this metal. Comparison of the calculations performed by different modelling groups using different thermodynamic databases, highlighted the lack of data for carbonato-complexes in some of the original databases used. Therefore, one of the conclusions is that before performing any speciation or solubility calculation of Ni one must ensure that the aqueous Ni-carbonato species are included in the thermodynamic database.

With respect to the solid phases potentially controlling the concentrations of Ni in the groundwaters of the different sites studied, *a priori* the modellers proposed Ni oxides and hydroxides apart from silicates, sulphides and trevorite (NiFe_2O_4).

In all cases, equilibrium with trevorite produced concentrations far below the actual ones. As discussed in /Bruno et al., 1992/, that type of solid solutions are not formed at low temperatures, despite of the evidence of formation of low-T spinels already pointed in /Linklater et al., 1998/. This clearly indicates that before proposing a solid acting as a sink for a given trace element, we must think of the normal conditions under which such a solid is formed.

In general, equilibration of the groundwaters with pure Ni oxides or hydroxides produced concentrations far above the actual measurements. This is normal if we consider that the hydrolysis of Ni is very low up to a pH close to 10, which is only achieved in the case of the hyperalkaline media of Oman and Maqarin (see Figure 4-8).

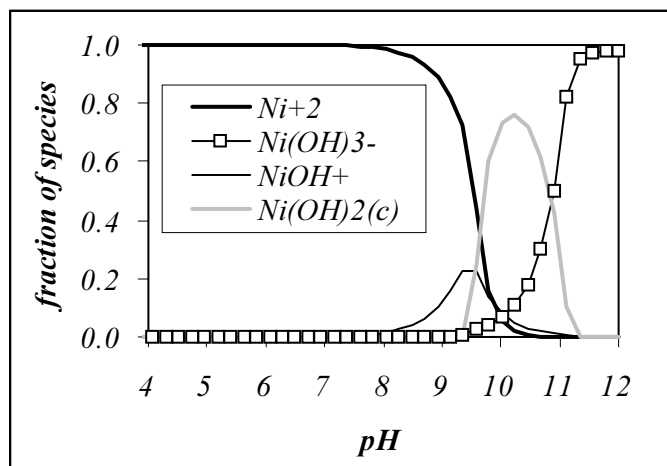


Figure 4-8. Fractional diagram of Ni at a total $[\text{Ni}] = 10^{-8}$ mole/ dm^3 .

The assumption of Ni sulphides controlling the concentrations of Ni was tested in two of the 5 investigated sites: El Berrocal and Palmottu. Neither produced results which were satisfactory. In a recent publication by /Thoenen, 1999/, the solubility of Ni in sulphidic groundwaters is reviewed. According to the author, most of the solubility calculations on Ni sulphides are incorrect due to several reasons, including:

- 1) The thermodynamic databases do not contain aqueous Ni-sulphide complexes, which may give rise to underestimations of the actual solubility of the solid sulphides.
- 2) Most of the Ni sulphides are high-temperature phases, with the only exception of millerite (NiS).
- 3) In most cases, Ni is present in solid sulphides as a trace component, i.e., it is frequently co-precipitated with pyrite, but not separately as Ni-sulphide.

All these arguments are extensively discussed in the referred work and provide a reasonable explanation why these type of solid phases usually fail in explaining the behaviour of Ni at the sites reviewed in this work.

The last hypothesis tested in the BPM exercises is to consider the association of Ni to major components of the systems. Normally, Ni is found associated with Fe(III)-oxyhydroxides. However, the assumption of the formation of mixed Ni-Fe solid phases has not rendered satisfactory results where it has been considered. For this reason, alternative explanations to explain the behaviour of Ni in low temperature environments must be sought in relation with source-term limitation, short residence times of groundwater or sorption phenomena.

Among these plausible explanations, the short residence times of groundwater may explain the disequilibrium existing among the minerals and the groundwaters in contact with them. This would cause the actual concentrations of Ni to be lower than that calculated by assuming equilibrium with a given solid phase. Although this is a possibility that we cannot disregard *a priori*, the disagreement between the calculations and the observations obtained at those sites with greater groundwater residence indicate that this is not the full explanation for the observed phenomenon.

Source-term limitation would indicate that there is not enough Ni in the minerals present at the site to achieve the concentrations needed for the precipitation of solid phases of this element. This has not occurred at all of the sites investigated despite the fact that it is the fourth most abundant element on Earth.

Finally, the most plausible explanation is that sorption processes control the concentration of Ni in groundwater. However, this possibility is very difficult to test due to the lack of simple sorption models to apply to natural systems. Besides, under slow water flow-rates it would be expected that the initially weak surface interaction would evolve towards the formation of stronger bonds between the surface of the minerals and the sorbed Ni.

In summary, we can say that we have not achieved a full understanding of the processes governing the behaviour of Ni in groundwaters to predict realistic solubility limits for this element. Therefore, some additional effort should be focussed to understand which processes are responsible for its behaviour and to develop geochemical models able to quantitatively describe those processes.

4.2.7 Zinc

Zn has been studied in the BPM exercises performed at El Berrocal, Poços de Caldas, Cigar Lake and Oklo.

The aqueous concentrations of Zn at El Berrocal is in the range 10^{-6} to 10^{-4} mole/dm³; in Poços de Caldas values of 10^{-6} to 10^{-5} mole/dm³ are present. This is also the case at Oklo, while at Cigar Lake the values are in the range 10^{-8} to $5 \cdot 10^{-7}$ mole/dm³ (see Figure 4-9).

At all the investigated sites the free cation Zn^{2+} dominates the aqueous speciation of this element in the groundwater samples.

The solid phases proposed *a priori* as likely to control the solubility of Zn are smithsonite ($ZnCO_3$), $ZnFe_2O_4$ (analogous to trevorite in the case of Ni, $Zn_3(PO_4)_2$) and sphalerite (ZnS).

As in the case of Ni, the assumption of $ZnFe_2O_4$ controlling the concentrations of Zn in groundwaters produces levels of aqueous Zn that are too low, except in some of the more reduced samples at Cigar Lake. This indicates that although the association of Zn with Fe is documented in most of the studied sites, this does not imply the formation of ferrite-type solid solutions. Again, the selection of solid controlling phases must be carefully considered in relation to the low temperature environments we are dealing with.

Among the pure Zn solid phases proposed, equilibrium with smithsonite was the one which best reproduced the trend of data in the El Berrocal groundwaters, despite the general 2 orders of magnitude (or larger) overestimation obtained using this assumption. In this case, when comparing the results obtained among the different groups, it is evident that although all of them used the same thermodynamic database, the difference in the way of introducing the alkalinity in the simulations caused important discrepancies in the results obtained among different groups. As an alternative, the modellers assumed that Zn was present in the calcites. This indicated that a congruent dissolution of this Zn-bearing calcite produced a better agreement with the measured data than any other of the phases tested. Nevertheless, no conclusions could be drawn due to the lack of data on the mineralogical association between Zn and calcite at the studied sites.

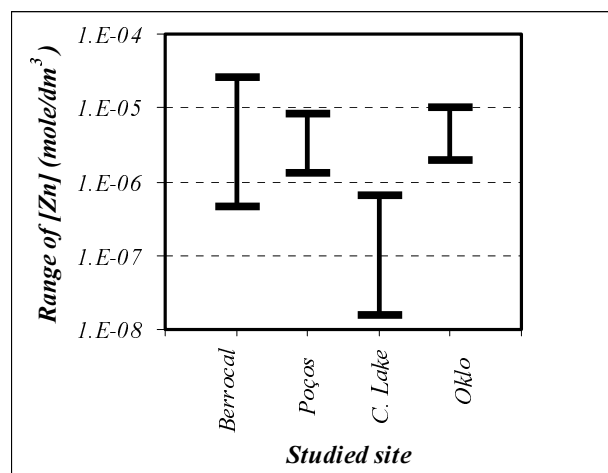


Figure 4-9. Range of concentrations of Zn measured at the different sites.

At Poços de Caldas the results were very similar to those of El Berrocal. The assumption of Zn controlled by the solubility of smithsonite or Zn phosphate produced an over-estimation with respect to the analytical data. When considering the Zn and Fe content in the host rock, and assuming the formation of a mixed Zn-Fe oxide controlling the solubility of Zn, the results substantially improved and were fairly similar to the actual measurements.

At Oklo, the best agreement between the predictions and the measurements was obtained by assuming the congruent dissolution of a Zn-bearing Ca phase, such as calcite; this was also the case at El Berrocal.

Summarising, we can say that Zn does not seem to be controlled by any of the pure Zn minerals known and that the best predictions should be carried out based on the association of Zn with other major minerals present at the site. Among these minerals we should focus on Ca-containing minerals, mainly calcite and Fe(III) oxy-hydroxides.

4.2.8 REEs

In spite of their intrinsic PA relevance, rare-earth elements (REEs) have only been lately included in the BPM exercises performed at Palmottu and Oklo. The range of aqueous concentrations measured is shown in Figure 4-10. In all cases, the light REEs are present in larger concentrations than the heavy REEs.

At Palmottu and Oklo the REE speciation is dominated by carbonato-complexes. This is more evident for the light REEs since the stability of the REE-CO₃ complexes increases with decreasing atomic number. This observation is illustrated by the results shown in Figure 4-11, where the increase in the percentage of the carbonate species with increasing the REE atomic number in sample BAX-05 from Oklo is plotted.

At Poços de Caldas the REEs were not included in the BPM exercise. However, the large amount of analytical data reported by /Miekeley et al., 1992/ showed that the increase in the concentration of REEs was associated with an equivalent increase of the concentrations of the main complexing ligands in that site, i.e., sulphates. Therefore, REE-sulphate complexes should be included in the thermodynamic databases in order to describe their behaviour in moderately acid waters.

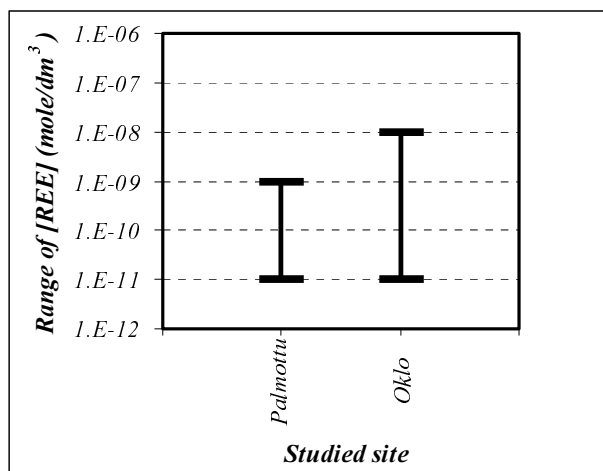


Figure 4-10. Range of concentrations of REEs measured at the different sites

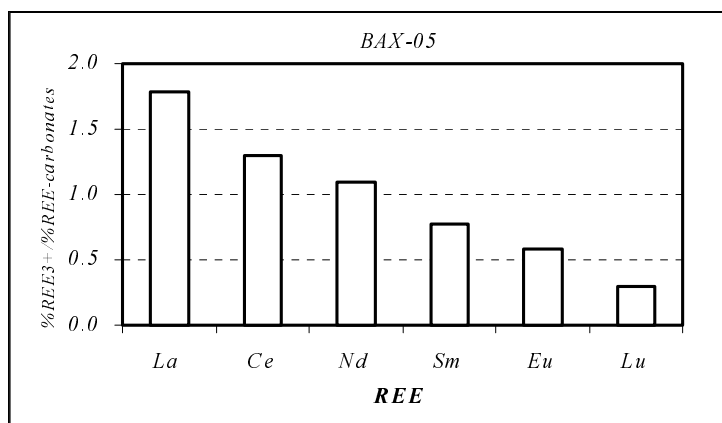


Figure 4-11. Increase in the percentage of carbonate species when increasing the REE atomic weight in BAX-05.

For the solubility limiting solid phases of the REEs at Oklo and Palmottu, the modellers proposed hydroxides, carbonates and phosphates. The concentrations of REEs calculated from equilibrating the groundwaters with solid hydroxides of carbonates were several orders of magnitude larger than the actual measurements. This, in spite of being conservative from a PA viewpoint, was not a satisfactory result from a geochemical perspective. As an alternate approach, the modellers equilibrated the groundwaters with solid REE phosphate phases.

The result of equilibrating the groundwater compositions with solid REE phosphates produced a certain overestimation of the actual REE concentrations at Bagombé (Oklo), which increased with increasing atomic weight. The presence of major phosphate minerals at this site, such as apatite, and the fact that the replacement of Ca by REEs in the apatite lattice is documented in the literature /Jones et al., 1996/, suggested that the concentration of REEs at Oklo could be explained by co-precipitation with apatite /Duro et al., 2000b/. According to /Jones et al., 1996/, the incorporation of the lighter REEs in the apatite cell is favoured over the incorporation of the heavier REEs. This is in agreement with the increase in the overestimation of the actual REE concentrations when increasing the atomic weight.

The difference between the measured REE concentration and the $\text{REEPO}_4 \cdot 10\text{H}_2\text{O}$ calculated solubility for the REEs included in the Oklo BPM, is shown in Figure 4-12, which illustrates the foregone discussion.

Similar behaviour is observed in the groundwaters of Palmottu, i.e., the difference between the measured REE concentration and the solubility of the pure REE phosphate phase increases when increasing the atomic weight, but even negative differences are obtained in this case (see Figure 4-13).

The interpretation of these results is hampered by the lack of analytical data on phosphate concentration at Palmottu. The negative values for the parameter $\log[\text{REE}]/\text{S REEPO}_4$ is mainly due to the fact that the modellers assumed a phosphate concentration in solution resulting from equilibration with hydroxilapatite, which rendered phosphate

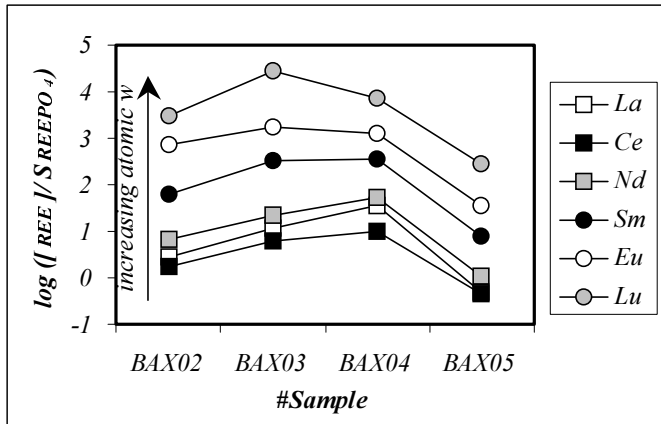


Figure 4-12. Difference between the measured REE concentrations and the concentrations calculated by equilibrating the Bagombé (Oklo) groundwaters with pure $\text{REEPO}_4 \cdot 10\text{H}_2\text{O}$. (From Duro et al., 2000b).

concentrations fairly large (from 10^{-5} to 10^{-7} mole/dm³). Thus, we can conclude that co-precipitation with apatite is able to explain the behaviour of REEs at both the Oklo and Palmottu sites.

Summarising, we can say that a complete analysis of the main components in groundwater is essential for any prediction of the concentration of REEs and any other trace metal in groundwaters.

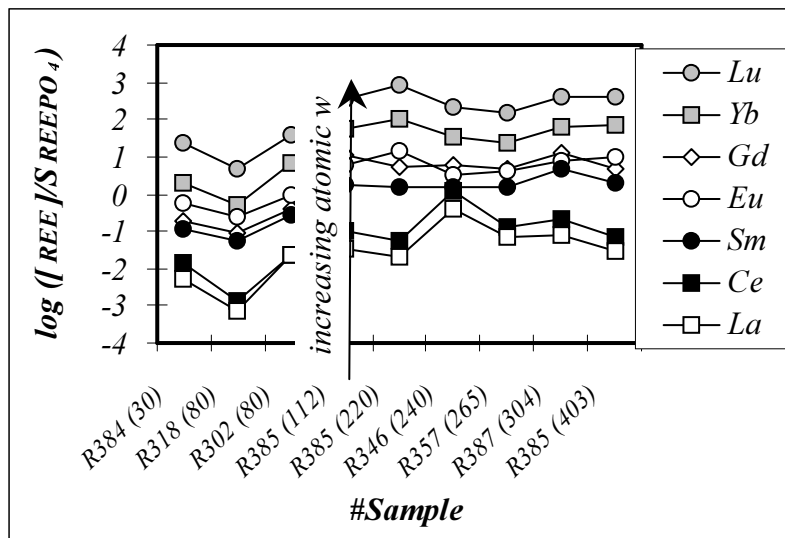


Figure 4-13. Difference between the measured REE concentrations and those calculated by equilibrating the Palmottu groundwaters with pure $\text{REEPO}_4 \cdot 10\text{H}_2\text{O}$. (From Bruno et al., 1999).

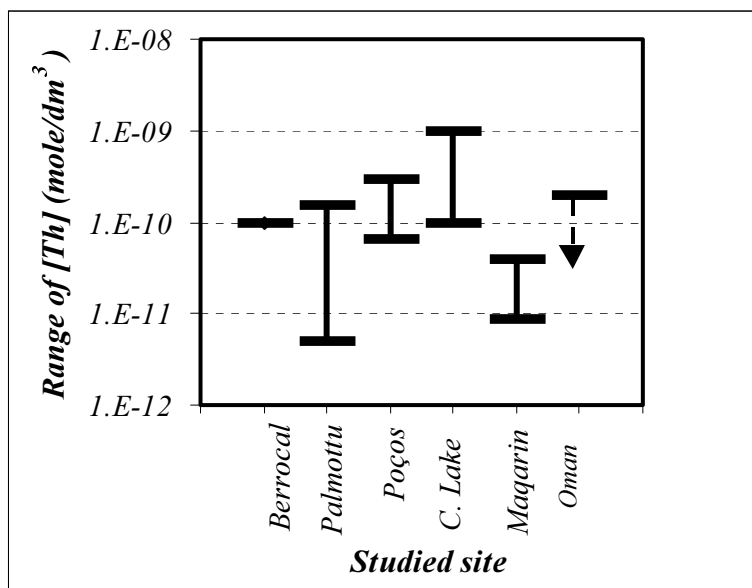


Figure 4-14. Range of concentrations of Th measured at the different sites.

4.2.9 Thorium

Th has been studied in the BPM exercises at El Berrocal, Palmottu, Poços de Caldas, Cigar Lake and Maqarin.

The concentrations of this element are in the range 10^{-9} - 10^{-11} mole/dm³ (see Figure 4-14).

The speciation calculated in the El Berrocal groundwaters is dominated by the neutral complex $\text{Th}(\text{OH})_4(\text{aq})$, with a predominance of the sulphate complex ThSO_4^{2+} in the sulphate waters sampled in the uraniferous quartz vein (UQV).

There seems to be a problem concerning the selection of the $\text{Th}(\text{OH})_4(\text{s})$ solubility constant, together with the stability of the mixed hydroxo-carbonato complex $\text{Th}(\text{OH})_3\text{CO}_3^-$ /Östhols et al., 1994/. If the selection of these two data is not consistently done, an overestimation of the actual Th(IV) concentrations may arise. This was indicated in some of the calculations performed at Palmottu.

At Poços de Caldas, the speciation calculated by the modellers is dominated by the neutral species $\text{Th}(\text{OH})_4(\text{aq})$, fluoride complexes, and the phosphate species when included. The inclusion of Th(IV) phosphate complexes in the calculations gave solubility values above the measured data. This is a well-established problem arising from the data selected by /Moskvin et al., 1967/.

The solubility of Th oxides or hydroxides is in agreement with the Th concentrations measured at El Berrocal, Palmottu, Poços de Caldas, Cigar Lake, Maqarin and with the upper value given in Oman. However, one of the problems associated with the calculation of the concentration of Th deals with the solubility constant used for the Th(IV) oxide solid phase equilibrated with the groundwater. Indeed, Th oxides may present very different crystallinities, which is translated into a large range of solubility constants. In Table 4-2 we show the different solubility constants found in the literature for the Th oxides and hydroxides.

Table 4-2: Solubility constants of Th oxides and hydroxides found in the literature.

Solid	Log Ks	Source	Solubility reaction
Th(OH) ₄ (am)	10.50	Felmy et al., (1991)	Th(OH) ₄ (c) + 4H ⁺ = Th ⁴⁺ + 4H ₂ O
ThO ₂ (act)	6.30	Baes & Mesmer, (1976)	ThO ₂ (am) + 4H ⁺ = Th ⁴⁺ + 2H ₂ O
	7.31	Östhols et al., (1994)	
	7.60	Thomason et al., (1992)	
ThO ₂ (c)	1.80	Langmuir & Herman, (1980)	ThO ₂ (c) + 4H ⁺ = Th ⁴⁺ + 2H ₂ O

As we can see from the previous table, the solubility constants range from 1.8 for the crystalline phase to 10.5 for the amorphous one. However, the best agreement with the data collected from the different sites studied is obtained when the solubility constant of Th(OH)₄(s) reported by /Baes and Mesmer, 1976/ (logKs = 6.3) is used in the thermodynamic databases, and not the aqueous phosphates at Poços de Caldas or Th(OH)₃CO₃⁻ at Palmottu.

However, this is not consistent with the experimental solubility data for Th(IV) determined by /Östhols, 1994/, indicating that there is a need to derive a consistent data base for this element that conciles the observations from natural systems together with the experimental data derived in carefully conducted solubility experiments.

4.2.10 Uranium

Because of its obvious importance to PA, U has been studied in all the BPM exercises performed on the sites. The concentrations measured in groundwaters are shown in Figure 4-15 for each of the investigated environments.

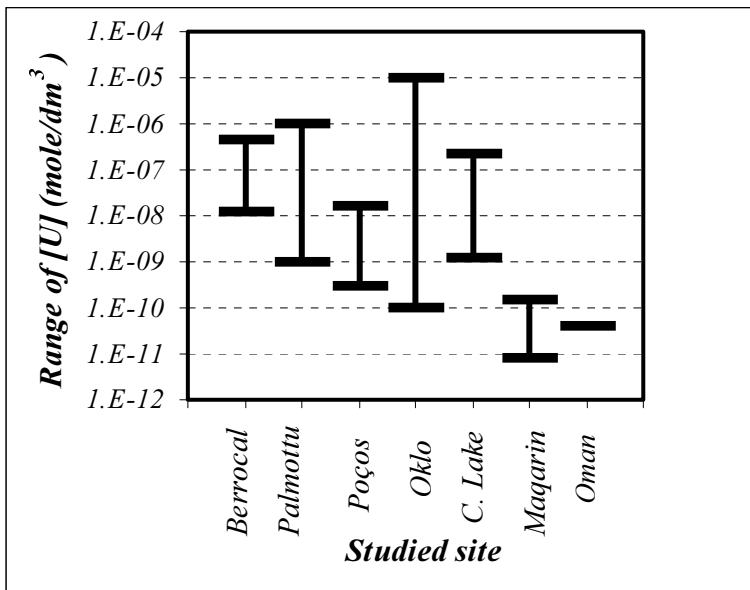


Figure 4-15. Range of concentrations of U measured at the different sites investigated.

As we can observe from Figure 4-15, a wider concentration range is measured at Oklo, due to the very different Eh values measured in the reaction zones of Okélobondo and Bagombé.

The concentrations measured at El Berrocal and Palmottu are rather close, as would be expected from the geochemical similarities between these two sites. The range of concentrations measured at Poços de Caldas is fairly narrow, in the order of 10^{-9} mole/dm³, and the concentrations measured at Maqarin are below the ranges measured at all the other sites. This fact is an indication that increased alkalinity decreases the expected U concentrations in groundwaters.

Because of the rather complex chemistry of U, it is difficult to make similar generalisations as we have previously done for other elements with a simpler chemistry. Consequently, the geochemical behaviour of U will be discussed on a site by site basis.

At El Berrocal the speciation of U is dominated by carbonato complexes, except for the groundwater sampled in the UQV. This is expected due to the alkalinity of the sampled groundwaters and to the large stability of the U(VI)-carbonato species. Only for one reduced sample is the predominance of U(OH)₄(aq) reported. One of the agreements reached during the El Berrocal BPM exercise was to eliminate the U(V) hydroxo species from the databases, since they may induce erroneous calculations under reducing conditions.

In spite of the similarities between El Berrocal and Palmottu, we can find a very important difference that changes totally the calculated speciation of U: the redox potential. U is very sensitive to the redox state of the system and the groundwater samples from Palmottu used in the BPM exercise are mainly reducing. This is the reason why in most of the samples studied the calculated speciation is dominated by the neutral U(IV) complex U(OH)₄(aq).

The groundwaters sampled at Poços de Caldas are mostly oxidising and the main complexes accounting for the aqueous U speciation are U(VI) fluorides, carbonates and hydroxides. Some of the modellers included uranyl phosphates in their databases and calculated a significant amount of these species in the samples. Nevertheless, as indicated in /Bruno et al., 1992/ the existence of UO₂(HPO₄)(aq) is rather questionable.

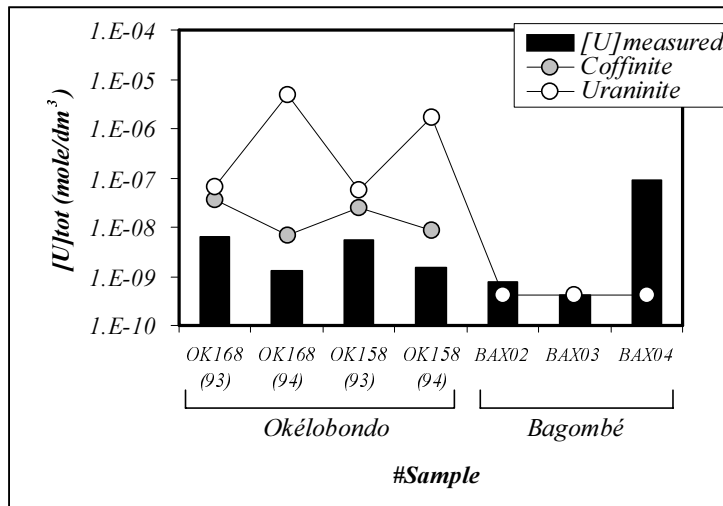
The Oklo samples are rather heterogeneous in terms of the large range of U concentrations measured (see Figure 4-15). Nevertheless, due to the alkalinity of the samples, in most of them the U speciation is dominated by U(VI) carbonato complexes. During the last sampling campaign undertaken in 1998 at Bagombé, a new methodology was used to measure the value of the redox potential that resulted in very different Eh values. Whereas oxidising values had been obtained in all the previous campaigns, the 1998 values measured were much more reducing. This caused the calculated speciation of U in solution to change dramatically from U(VI) carbonato complexes to the neutral U(OH)₄(aq) species. The fact that this does not only affect the calculated speciation, but also the predicted U solubility, highlights the importance of the quality of the analytical data used on any attempt to predict the solubility of metals in groundwaters. Another point worth to highlight here is the convenience of developing sensitive in situ speciation analytical techniques. These techniques were used in Maqarin, but no conclusions for U could be obtained due to the fact that the concentrations were below the detection limit of the technique.

In the Cigar Lake U deposit, the calculated speciation is dominated by U(VI) carbonato complexes, as reported in /Bruno and Casas, 1994/. These authors compared the speciation obtained by assuming the presence or otherwise of the phosphato species

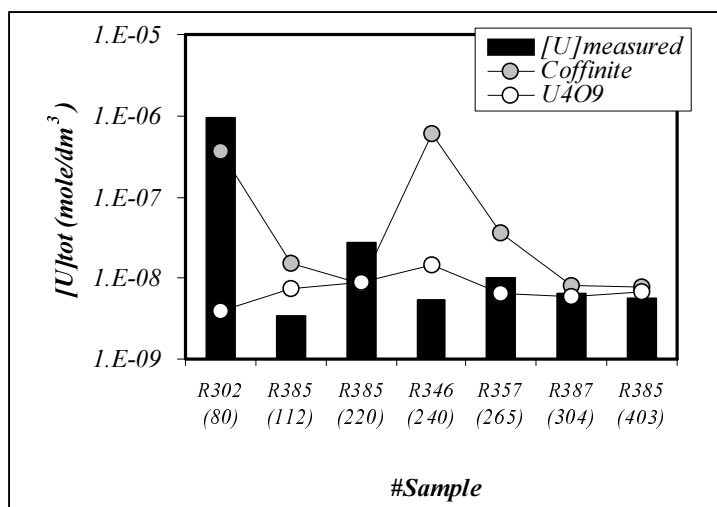
$\text{UO}_2(\text{HPO}_4)_2^{2-}$ and observed a totally different speciation dominated by this species. $\text{UO}_2(\text{HPO}_4)_2^{2-}$ was subsequently included in the thermodynamic database. However, due to experimental evidence on the overestimation of the stability of this complex, and the inability of the calculations to reproduce the solubility of U at Cigar Lake if this species is included in the database, it was advised not to consider it for later exercises.

The picture of the U speciation in the hyperalkaline groundwaters sampled at Maqarin is totally different from the other sites. The high pH of these samples causes the predominance of hydroxocomplexes such as $\text{UO}_2(\text{OH})_4^{2-}$ and/or $\text{UO}_2(\text{OH})_3^-$ in most groundwaters. In the case of Oman, in some of the databases used the species $\text{U}(\text{OH})_5^-$ was included. Despite that this species is rather suspicious, during the Oman exercise its existence was considered as ensuring the conservatism of the predictions.

Under reducing conditions different uraninites, of general stoichiometry UO_{2+x} , with x varying from 0 to 0.33, are the phases that better reproduce the measured aqueous U concentrations at all sites. In some cases, for reducing groundwaters, also coffinite, USiO_4 , has been reported as a solubility-controlling phase. This can be observed in Figure 4-16, where the actual U concentrations in the reducing samples of Oklo and Palmottu are compared with the calculated uraninite and coffinite solubility.



a) Oklo samples



b) Palmottu samples

Figure 4-16. Comparison between the actual U concentrations measured in the reduced groundwater samples of Oklo and Palmottu and the calculated solubility for uraninite and coffinite.

In the oxidising samples, the modellers tested the possibility of several other U solids controlling the solubility.

In those samples from El Berrocal where a U-phosphate association was mineralogically reported, equilibrium with autunite provided satisfactory results. However, this conclusion is hampered by the lack of good analytical data on aqueous phosphate. For the rest of the samples, U(VI) silicates such as soddyite, haiweeite and uranophane were, *a priori*, suggested as likely to control the concentration of U in solution. Nevertheless the results did not agree with the observations. Due to the association of U with Fe(III) oxy-hydroxides, the possibility of co-precipitation of these metals was tested, and the results were much closer to the measured values. Therefore, the conclusion was that U(VI)-bearing Fe(III) oxy-hydroxides were controlling the U concentrations in these groundwaters.

The same conclusion was valid for Poços de Caldas. When assuming U_3O_8 as the solubility-limiting phase, the calculations overpredicted the measurements by several orders of magnitude. However, when the association of U to Fe(III) oxy-hydroxides was considered, the calculated concentrations were in close agreement with the measurements (see Figure 4-17).

In the oxidising samples of Oklo many different U(VI) solid samples were tested as to their potential role in controlling the U solubility. Within this BPM exercise a large effort was made to include in the thermodynamic databases those phases identified at the site by mineralogical analyses. In most cases, the thermodynamic data for these phases are not well established, perhaps due to a scarcity of data or some other reason, as is the case of Na-zippeite ($Na_4(UO_2)_6(SO_4)_3(OH)_{10} \cdot 4H_2O$), swartzite ($CaMgUO_2(CO_3)_3 \cdot 12H_2O$) or liebigite ($Ca_2UO_2(CO_3)_3 \cdot 10H_2O$). Nevertheless, the assumption of the solubility control of U exerted by Na-zippeite in some of the groundwater samples studied has been confirmed by the identification of this solid /see Mathieu and Cuney, 1997/ and /Jensen 1998/ and the modelling results have been rendered fairly satisfactory.

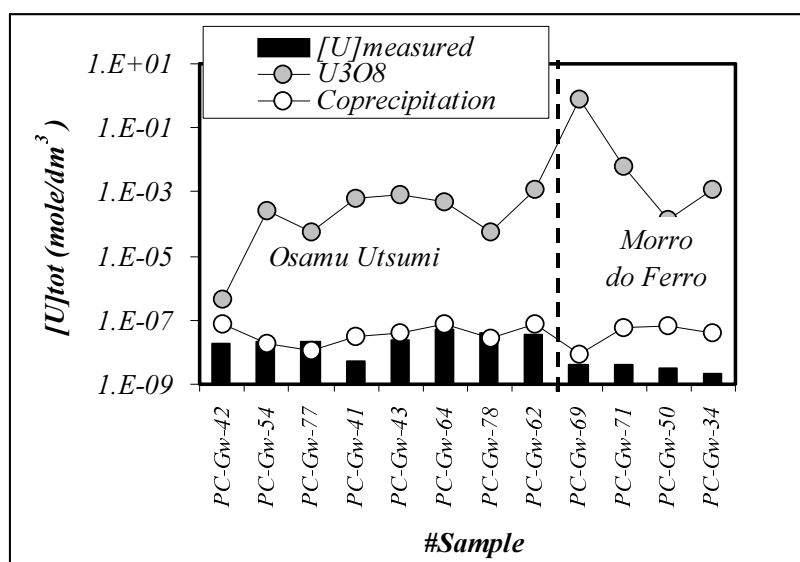


Figure 4-17. Comparison of the agreement reached between the actual U concentrations measured in the groundwater samples of Poços de Caldas, the calculated solubility for U_3O_8 and the solubility of U calculated by assuming the coprecipitation of U(VI) with Fe(III) oxy-hydroxides.

In general, though, it seems that the precipitation of U(VI) silicates, such as uranophane and haiweeite, account for the U concentrations observed in the more oxidised samples at Oklo. On the other hand, the association of U with Fe(III) oxy-hydroxides is able to represent fairly well the concentration of U measured in the surface acidic waters of Okélobondo, which was tested by applying a co-precipitation model to a U-bearing Fe(III) oxy-hydroxide (see Figure 4-18).

In Oman, concentrations several orders of magnitude above the measurements were calculated, even by assuming the presence of some speculative minerals Ca-U minerals /see McKinley et al., 1988/. Finally, in the hyperalkaline groundwaters of Maqarin, the assumption of U(VI) oxides and hydroxides as solubility controlling phases resulted in overestimations of the actual measurements. The modellers selected the solid phase CaUO_4 as likely to control the solubility of U at the site. However, the solubility constant for this solid included in the most common thermodynamic databases corresponds to a crystalline solid and, consequently, very low U concentrations were calculated. As highlighted in /Alexander et al., 1998/ an effort should be made to include more amorphous Ca uranates in the databases in order to constrain the solubility of U under cementitious environments.

The main conclusions can be summarised as:

- Under reducing conditions the solid phases controlling the solubility of U are U(IV) oxides or silicates, i.e., uraninite with different oxidation degrees (UO_{2+x} with x varying from 0 to 0.33) and coffinite.
- Under oxidising conditions, U(VI) silicates and/or U(VI)-bearing Fe(III) oxy-hydroxides are responsible for the aqueous U concentrations measured in groundwaters.

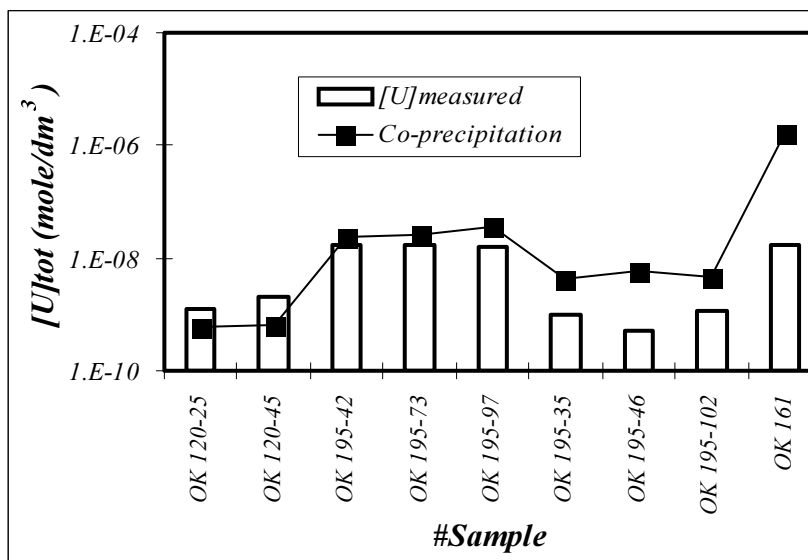


Figure 4-18. Comparison between the actual U concentrations measured in the surface oxidising groundwater samples of Okélobondo (Oklo) and the concentrations calculated by assuming the coprecipitation of U(VI) with Fe(III) oxy-hydroxides.

4.3 Summary

In general, we can see that the main aqueous ligands affecting the speciation of the studied metals in solution are carbonates and, therefore, they must be included in the TDBs. Nevertheless, the lack of *in-situ* speciation data in most of the studied environments renders the comparison between the predicted and the actual speciation quite difficult.

In the Table 4-3 we have summarised the results of the solubility calculations in terms of the degree of agreement between measurements and predictions, as well as the geochemical needs detected for each metal, which are more extensively discussed in the next section.

Table 4-3: Degree of agreement between measurements and predictions.

Elem.(N)*	Degree of agreement		Geochemical needs
	Pure phases	Mixed phases	
Sr (4)	Poor Overestimation	Good Linked to Ca	Mineralogical evidence of the association
Ba (3)	Poor except in sulphate rich samples (Barite)	Good Linked to Ca	
Sn (2)	Poor	Not tested	TDB improvements
Pb (4)	Poor Overestimation	Not tested	Good PO ₄ data. Mineralogical evidence of association to major components
Se (2)	Poor Overestimation	Not tested	Good Eh measurements;TDB improvements. Investigation of the role of bacteria on the Se system
Ni (7)	Poor Overestimation	Poor Possibility of sorption or source limitation?	Development of alternative models to account for association to major components Additional species possible
Zn (4)	Poor Overestimation	Medium Linked mainly to Ca sometimes to Fe(III)	Development of alternative models to account for association to major components
REE (2)	Poor Overestimation	Fair Linked to PO ₄ .	Good PO ₄ data.
Th (6)	Fair	Not tested	TDB improvement. Internal consistency of aqueous and solid data required.
U reducing	Fair	Not tested	Good Eh measurements
U oxidising	Fair	Fair Linked to Fe(III)	TDB expansion

N* number of sites where the element has been investigated.

In summary, according to their solubility control we can see that the elements reviewed can be classified into three different groups:

- Elements whose solubility control seems to be exerted by *individual solid phases*:
Th: apparently controlled by the solubility of $\text{Th}(\text{OH})_4(\text{am})$ at all the sites investigated.
U under reducing conditions: controlled by the solubility of uraninite with varying oxidation degrees (UO_{2+x}) or by coffinite (USiO_4).
U under oxidising conditions: partially controlled by the solubility of U(VI) silicates.
- Those elements whose *behaviour seems to be linked to the major components of the system*:
Sr, Ba and Zn: controlled by mixed Ca-Sr, Ca-Ba or Ca-Zn/Fe(III)-Zn solid phases
Se: possibility of control by S(II)-Se(II) mixed solid phases and bacterial action
REEs: controlled by incorporation with solid phosphates (apatite)
U under oxidising conditions: partially controlled by its association with Fe(III) oxyhydroxides.
- Those elements for which *no definitive conclusions* can be drawn:
Sn, Pb and Ni.

5 Needs for geochemical modelling development

From the comparison of the results obtained during the BPM exercises, the modellers have reached different consensus about several important aspects of the geochemical modelling:

- a) The species that should be present or eliminated from the TDB in order to model low temperature systems
- b) The limitations of the various geochemical codes used
- c) The main analytical and mineralogical characterisation data required to predict radionuclide mobility.
- d) The alternative conceptual approaches that can be used to model the behaviour of the relevant trace elements in groundwater.

Obviously, all these aspects are interrelated but we will try to discuss them separately in this section to highlight the areas of main consensus reached during the BPM exercises.

5.1 Thermodynamic databases

One of the added values of the BPM exercises is to allow the comparison among different thermodynamic databases used by the various geochemical modelling groups. Within the BPM exercises undertaken in El Berrocal, Palmottu, Oklo, Cigar Lake, Poços de Caldas and Maqarin, the following TDBs were used:

WATEQ4F /Ball and Nordstrom, 1991/; SKB TR 95-35 /Spahiu and Bruno, 1995/; NEA-U /Grenthe et al., 1992/; NAGRA 91-18 /Pearson and Berner, 1991; Pearson et al., 1991/; Gembochs-LLNL DATA0.COM.R10 /Johnson and Lundeen, 1994/; SKBU/HATCHES 2.0, 3.0 and 5.0 /Puigdomènech and Bruno, 1989; Cross and Ewart, 1991/; CHEMVAL /Falck et al., 1996/, /SKB, 1993/. NEWTHERM /Yusaf and Hamilton, 1990/, MINEQL /Schweingruber, 1982/, and MINTEQA1 /Peterson et al., 1987/.

In spite of the fact that most have the same origin, there are important differences that contributed to the different values in terms of speciation and solubility calculations obtained by the modelling groups.

Nevertheless, we must bear in mind that the agreement among groups may imply that all databases used in the modelling consistently show the same gaps or errors (10 fools do not make up for a clever person). For this reason, when no-agreement with the measured data could be reached by any of the modelling groups, an effort was made in order to analyse whether the error might be hidden behind an incorrect TDB and/or an erroneous conceptual assumption.

It is not the aim of this work to conduct a thorough comparison of the available databases, however we want to highlight the main improvements made to the TDBs as a result of the BPM exercises. For this purpose, and as in the previous section, we will proceed element by element indicating the modifications that the various modelling groups agreed upon to include in the databases.

- **Sr and Ba:** No important disagreements among groups were observed, neither in the aqueous speciation nor in the solubility of the solid phases tested in the analyses. The only modification suggested was the inclusion of appropriate thermodynamic data, such as goyazite, in the databases /Bruno et al., 1992/.
- **Sn:** This element was only studied at Maqarin and at Oman. From the comparison among groups it was decided to include the Sn(IV) hydrolysis products in all the TDBs. It was also suggested to expand the Sn solids present in the TDBs in order to account for the phases more relevant at low temperatures and high pH values. These inconsistencies in the Sn(IV) hydrolysis scheme, particularly at moderate temperatures, became evident in the latest solubility calculations performed within the SR 97' PA exercise /SKB, 1999/.
- **Pb:** From the BPM exercises performed at El Berrocal and Poços de Caldas, the need to *include the carbonato species $PbCO_3(aq)$* in the TDBs was agreed among the modellers. In the case of Maqarin the need to *include hydroxo Pb complexes* was highlighted for such high pH environments.
- **Ni:** As in the case of Pb, the *inclusion of Ni-carbonato aqueous species* in all TDBs was agreed by the modellers. In Maqarin *the lack of quality data for aqueous Ni hydroxides* and the need of further work were identified. Also the *exclusion of high temperature phases*, such as $NiFe_2O_4$, from the TDBs used for calculations in low temperature environments has been recurrently suggested.
- **Zn:** As in the case of Ni, the *exclusion of high temperature ferrite solid phases* was suggested.
- **REEs:** From the results obtained at Poços de Caldas, it was clear that *REE-SO₄ complexes must be included in the TDBs*.
- **Th:** The need to *work with a consistent aqueous and solid phase TDB* was highlighted from the Palmottu BPM results. This has not been undertaken yet, but it is necessary to carry out in order to calculate realistic solubility limits for Th. From the results obtained from Poços de Caldas, it was suggested that *the stability of the REE-phosphate complexes was overestimated in the TDBs used*. This should also be reappraised. On the other hand, it was suggested to consider in the TDBs only the solid Th hydroxide which is able to reproduce the concentrations of Th measured in groundwaters, i.e. the *Th(OH)₄(s)* reported by /Baes and Mesmer, 1976/, with $\log K_s = 6.3$. The inclusion of the other Th oxides and hydroxides rendered unsatisfactory results at all the sites tested.
- **U:** Once the NEA TDB for U /Grenthe et al., 1992/ became available, calculations for U became more consistent. However, from the BPM exercise performed prior to the publication of this TDB it was agreed to *question the existence of the complex $UO_2(HPO_4)_2^{2-}$* and to *eliminate the U(V) hydroxo species from the TDBs*. Even after the publication of the NEA TDB it was clear that the limiting value for the stability constant of the species $UO_2(OH)_2(aq)$ was slightly overestimated in the mentioned reference, and that the *use of the value suggested in the SKBU-TDB* /Puigdomènech and Bruno, 1989/ produced more realistic calculations of the solubility of U. The stability for this species was revisited by the NEA and a value more similar to the SKBU-TDB was recommended /Silva et al., 1995/. With regard to the solid phases, it was agreed that *uncommon solid phases identified in the site by means of mineralogical analyses should be included in the TDBs, in spite of the lack of good quality data for their solubility equilibria*. This can help the modellers to improve the TDB step by step, by firstly including the solid and later on suggesting experimental work to assess a more realistic solubility constant for such phase. From the Maqarin BPM it was suggested that the TDBs used

for predictive calculations should contain amorphous uranate solid phases, given that the crystalline solids included do usually predict solubilities lower than the measurements, due to the fact that the phases actually precipitating in the system are normally amorphous. The role and stability of U(IV) silicates, particularly coffinite, has been identified also in the later exercises, where the evidence of the existence of low temperature coffinite indicates that this phase should be taken into consideration in silicate rich waters under reducing conditions. So far, only estimates of the stability of this phase are available. Amazingly enough, these estimates have been used to select the value for the stability constant for coffinite in the U-TDB, NEA selection /Grenthe et al., 1992/.

5.2 Geochemical codes used

Although most of the geochemical codes used in the BPM exercises were very similar in terms of computational procedures, some differences produced variations in the results obtained by groups. In some cases it was not an inherent fault with the code which produced the observed differences, but rather the modellers approach to any given problem. In this section we will indicate the main differences identified, resulting either from the codes used or the model procedures employed, that resulted in the discrepancies among groups.

Within the BPM exercises reviewed here, the following geochemical codes were used:

PHREEQE /Parkhurst et al., 1980/; EQ3NR /Wolery, 1992/; ; MINEQL /Westall et al., 1976/; HARPHRQ /Brown et al., 1991/; RIPP2 and RIPP2S /Yusaf and Hamilton, 1990/; PHREEQC /Parkhurst, 1995/; MINTEQ /Felmy et al., 1984/; CHESS /Van der Lee, 1998/; KINDIS modified at CNRS /Del Nero et al., 1998/.

As was the case with the TDBs, it is not our intention to compare the performance of these geochemical codes. The use of one or other code must be based on the modeller's knowledge of the code and the associated applications. However, we want to highlight some of the differences that gave rise to discrepancies in the results among groups.

- The *impossibility of fixing the pH* throughout a calculation produced in some cases important variations in the results obtained by the earlier versions of PHREEQE with regard to the other geochemical codes. The latter versions of the program, such as HARPHRQ and PHREEQC, solved this problem, providing a much better description of the real systems.
- The *impossibility of working with a charge imbalance* may cause differences in some of the main cations or anions. This can affect the results obtained from speciation and solubility calculations. Although it is true that a charge imbalance is chemically not possible to achieve, the code should not be allowed to modify the concentrations of the charged species so as to eliminate the initial charge imbalance. What is clear from this fact is the importance of the quality of the analytical data, since this subject will not arise if the charge imbalance of the solution entered in the input of the code is neglectable.
- The *method of treating the alkalinity* may have important implications in the calculations involving aqueous or solid carbonates. For this reason, it is important to know which data comprise the analytical results, i.e., does the laboratory provide alkalinity, total carbonate or free bicarbonate? Most of the codes allow entering data input in all different forms, but the modeller must be sure of which data are available from the analysis.

- The way of calculating the concentration of a metal in equilibrium with a given solid phase by maintaining the rest of the chemical composition of the groundwater invariable. This is a problem for the modeller and not of the code. During some of the BPM exercises different groups obtained different solubility results by using the same TDB and the same geochemical code. We devoted some time to solve this potential paradox. The outcome of this analysis indicated that introducing a certain trace metal into the system by equilibrating with a certain solid resulted in introducing the counterion of the metal we are interested in, thus disturbing the chemical composition of the water. For a detailed example of this type of problem, the reader is referred to discussions in /Bruno et al., 1999b/.

5.3 Analytical data

The quality of the analytical data is of crucial importance for any predictive calculation and by extension to any potential PA analysis of a repository system. As already pointed out by Jim Drever /pers. comm., 1998/, the conceptual and numerical tools are further ahead than the actual analytical data used to describe and predict trace element mobility in subsurface environments. In this sense, we can highlight the shortcomings of the analytical data that have represented an important handicap in the BPM exercises performed up to now:

Redox potential. The lack of good redox potential measurements or the lack of well-determined values for this parameter has very important implications on the results obtained. One example of this can be seen in the redox potentials measured in the Bagombé (Oklo) groundwaters. During all the initial sampling campaigns held in the previous stages of the Oklo Natural Analogue project the potentials measured in Bagombé were around 200 mV. However, the final measurements performed during February 1998 using downhole techniques indicated values around -100 mV, i.e., reducing Eh measurements were obtained in this case. This difference, whether instrumental or due to lithological heterogeneities, had important implications for the solubility of U and other redox sensitive elements. In Duro et al. (2000b) the comparison of the solubility of uraninite with the actual U measurements is carried out by assuming both redox potentials measured in the water sampled in the vicinity of reactor BAX03 at Bagombé. The results indicated that when using the oxidising redox potentials the calculations overestimated the measurements by more than three orders of magnitude, in contrast with calculations performed by assuming the reducing Eh values, which were in close agreement with the measurements. A very detailed examination of the method of measuring and interpreting redox potentials in groundwaters has been undertaken within Phase II of the Palmottu Natural Analogue Project /see Bruno et al., 1999b/ which has rendered this issue a lesser problem.

Phosphate concentration. The lack of data on phosphate concentrations in groundwaters is an important drawback in the prediction of the solubility of some elements of PA relevance, mainly for REEs. This has been highlighted in the BPM exercises performed at Oklo and Palmottu. During the Oklo project, good quality phosphate data were collected; however no data on the concentration of phosphate in the Palmottu groundwaters were available. From the discussion in section 4 we can see that the results obtained in the case of Oklo for the REE solubility may be explained by a coprecipitation of these elements with apatite /Duro et al., 2000b/. This is suggested in the light of the overprediction of the actual REE concentrations that is achieved when assuming that the concentration of REEs is given by equilibrium with the pure REE-phosphate phase. However, at Palmottu, in some cases, the assumption of equilibrium with pure REE phosphates results in underpredicting with regard to the actual REE measurements.

Therefore, we suggested that, in some cases, coprecipitation with apatite could explain the REE behaviour, but that this will not be the case in all the samples. This is due to the fact that the application of a coprecipitation approach produces a decrease in the calculated concentration of the trace metal /Bruno et al., 1999/. If we analyse these results we can see that, in the case of Palmottu, this conclusion is rather speculative since the modellers assumed a given concentration of phosphate in the groundwaters, but no actual measurements were available. Therefore, it could well be that the explanation to REE behaviour at Oklo could also explain the situation at Palmottu. However, this cannot be tested in the absence of appropriate analytical data. The lack of analytical phosphate data represents also a limitation to explain the concentration of Pb in Poços de Caldas, since this metal is correlated to P_2O_5 in the rock at the Morro do Ferro site.

In general, the lack of reliable phosphate data in groundwater systems is a limiting factor for the geochemical characterisation of some sites. This highlights that this type of exercises can guide field work to take samples and analyse parameters needed for further understanding of the system.

Mineralogical association. Adequate data on mineralogical association is always desirable but seldom available. This should be one of the key priorities in any geochemical characterisation of a potential site, particularly the preferential associations of relevant and chemically analogous trace elements (i.e. PA relevant) to the mineral coatings along flow paths.

One of the findings of the BPM exercises is evidence that the behaviour of the trace metals can be explained in terms of their linking to the major chemical components of the system. The approaches that have been used to deal with this association are simple coprecipitation and codissolution models, as explained in previous sections. The appropriateness of these models has been tested where adequate mineralogical information was available, but in some other cases it has only been a rather speculative exercise due to the lack of data on mineralogical associations. In spite of this important limitation, the modellers have been able to provide enough tests of the applicability of these models as to obtain a general picture of the most important associations to consider in each case, as outlined it in section 4.

5.4 Alternative conceptual model approaches to describe the association of trace components to major elements

The preceding sections have described two alternative model approaches used by the modellers to account for the observed associations between trace metals and major minerals present in the system: coprecipitation and codissolution models. We have also observed that these models were able to describe the behaviour of some of the trace metals, such as Sr, Ba, Zn, REEs and U under oxidising conditions. However they have failed in interpreting the behaviour of Ni, for example, when we would expect this metal to be fairly well described by coprecipitation with Fe(III) oxy-hydroxides.

These observations highlight the fact that we need additional modelling approaches to tackle this problem. The conservatism of a prediction is not always desirable, not even from a PA view. It may imply to implement too strict security measures not really necessary and may also introduce a too high risk-preception that neither benefits the waste managers nor the general public. As we mentioned previously, during the three earlier BPM exercises reviewed in this report (Poços de Caldas, Cigar Lake and Maqarin) the need of models able to quantify the mentioned trace-major element associations was debated, but no calculations were made. We are now faced with a similar challenge, in

spite of the fact that our understanding of some trace metals has largely improved from the initial exercises. We still need to go one step further and suggest additional models to describe the behaviour of these complex elements. It is likely that the first thing to do is to gather experimental knowledge about these processes. Perhaps this should go through a simpler description of sorption processes, sufficiently simple to facilitate their inclusion in *predictive geochemical modelling tests*. It is rather likely that this will not be an easy way to go, but any advance in this respect will represent an important step forward to a better understanding of the geochemistry of trace elements and, therefore, to the assessment of the risk associated to a HLW repository.

Summarising, we can say that some of the problems mentioned in this section are avoidable. The proper calculation of a problem does not require more than a *correct interpretation of good quality analytical data* and a *deep understanding of the processes we are considering and the associated tools necessary*. This is required to construct robust but simple models that capture the complexity of the natural systems we are dealing with, but still are able to discriminate between relevant information and the associated noise.

6 Integration of the BPM results in PA exercises

The objective of the Safety Assessment performed by /SKB, SR 97/ has been to undertake a complete analysis of the long-term safety of the KBS-3 system for deep disposal of spent nuclear fuel. For this purpose, the methodology used was /SKB, 1999/:

- To carry out a systematic handling of all the internal processes and external conditions that can cause long-term changes in the repository. and
- to carry out a systematic handling of the different types of uncertainties that always surround the background data for an analysis.

Among other purposes, Performance Assessment exercises shall serve as a basis for specifying the factors for the selection of areas for site investigations and deriving which parameters need to be determined and which other criteria ought to be carried out during a site investigation. For this reason it is said in the mentioned SR97 report that "...it is particularly important to assure the quality of the radionuclide transport calculations".

The input data for radionuclide transport calculations include the concentrations of these radionuclides in the geosphere. That is, the identification of which solids and/or processes control their solubility as well as a quantification of the aqueous concentrations of the radionuclides under the different geochemical conditions expected to occur in the near- and far-field environs of the repository. This is where the information derived from the BPM exercises becomes extremely relevant.

Actually, the results of the BPM exercises have fed some of the safety assessment exercises performed by the various agencies in European countries, such as Sweden /SR 97/ Finland, /TILA-99; Ollila and Ahonen, 1999/ and Switzerland /Kristallin-I; Berner, 1994, Nagra,1994/. Indeed, during 1997, /Bruno et al., 1997/ performed an extensive number of calculations to determine the chemical speciation and solubility of radionuclides to be used in SR97 and undertook an evaluation of the uncertainties associated with the calculated solubilities. In the mentioned work, experience extracted from trace element geochemical investigations and modelling of various natural analogue sites, such as Poços de Caldas, Cigar Lake and El Berrocal, were used to assess realistic solubility limits. For some minor elements the conditional solubility approach (co-precipitation and codissolution) developed and applied during the BPM exercises was incorporated.

The main inputs of the BPM exercises to PA are as follows:

- a) Identification of the main chemical characteristics of groundwaters that affect the speciation of the radioelements.

The speciation of a chemical element is directly related to its mobility. In this sense, the identification of the main parameters increasing or decreasing the mobility of a given nuclide is of crucial interest when selecting a site for further investigations. The groundwater composition of the site must be critically evaluated in order to minimise the risk of enhanced mobility.

- b) Identification of the main geochemical data of importance for the assessment of the speciation and solubility of the radioelements.

In this sense, the BPM exercises have contributed to highlight the need to improve the analytical methods for the determination of phosphate and redox potential in groundwaters. This is a crucial issue when assessing the mobility of radionuclides and important analytical efforts should be devoted to fill these gaps. The solution to these analytical problems will minimise the uncertainty of the solubility and speciation calculated for and used in PA exercises. The lack of these parameters in any evaluation of the safety assessment of a potential site for a repository may induce important overestimations of the actual solubility and mobility of the radionuclides at the site; this has an important impact on the associated risk.

- c) Elimination from the TDB of potential solubility controlling phases not likely to act as radionuclide sinks under repository conditions.

The elimination of “aberrant” solid phases is of major relevance. On one hand, the stability of crystalline solid phases enables their thermodynamic properties to be more easily determined from lab experiments. This is one of the reasons why there is a much wider extent of solubility parameters determined for crystalline than for amorphous solid phases. Nevertheless, according to the Ostwald rule, the most favoured phase to precipitate is the most amorphous one and this will be the one more likely to act as an element sink and, therefore, the most likely to control its solubility. Neglecting this important issue may cause critical underestimations of the actual concentrations of the radionuclides at a given groundwater composition.

- d) Consideration of the mineralogical associations likely to affect radioelement mobility.

In contrast to the previous case, where the error was associated with an underestimation of the actual concentrations of a given radioelement, neglecting the mineralogical associations affecting its mobility may give rise to important overestimates of the actual concentration of an element in groundwater.

Indeed, we have seen in the previous sections that in many cases the assumption of pure phases of the element as solubility controlling solids produces too large concentrations when compared to the measurements. In spite of this approach being conservative from a PA point of view, it does not provide confidence on the correctness of the geochemical concepts considered. By introducing the associations of trace components to major solid phases, the observed trace metal concentrations are better reproduced. This brings more confidence to the predictive capabilities of the model.

In this sense, the BPM exercises have provided a unique test for the application of models able to deal with the linking between trace and major geochemical components of a given system.

- d) Assessment of the best methodologies used in the geochemical calculations.

The quality of the input data to PA exercises must be the best possible. In this respect, it is of prime importance to ensure that the primary data used in any geochemical calculation, as well as the calculation methodology used, are sufficiently tested and contrasted. As we have seen, thanks to the BPM exercises, some of the incorrect calculation methodologies used by geochemical modellers have been identified and rectified, ensuring the generation of improved data for inclusion in PA exercises.

All the reasoning above suggests that BPM-type exercises should form an integral part of all geochemical studies that provide input data to PA exercises. Therefore, we strongly recommend performing this type of testing of databases, codes and models in any further project linked to the characterisation of a potential site.

7 Conclusions

After a full decade of trace element predictive model testing in connection with Natural Analogue studies we can conclude that they have provided a valuable quantitative input to repository performance assessment. The geochemical concepts, associated databases and calculational methodologies to describe radionuclide solubility and speciation, have been largely improved through these reality checks.

One of the main advances in this regard concerns to the acknowledgement of the fact that the behaviour of the trace metals is going to be governed by the major geochemical driving forces in the system, i.e., by the major components systems. This statement is not new, and is not only a direct consequence of the BPM exercises. What these type of predictive modelling has indeed evidenced is the applicability of some simple “ideal solid solution” models to tackle with this issue. During the last BPM conducted at El Berrocal, Oklo and Palmottu, the initial hints on the need of such models highlighted in the former BPM of Oman, Maqarin, Poços and Cigar Lake have crystallized in the form of simple numerical models. The implementation of these models has proven to be useful at predicting and explaining the concentrations of quite an amazing number of the studied trace elements.

The use of ideal solid solution models have been included in the Solubility calculations for SKB SR 97 and Enresa-2000 Performance Assessment exercises /Enresa, 2001/. On the other hand, independent SKI reviews conducted on the SR 97 exercise strongly recommend the inclusion of this type of models in the solubility limits assessment. Besides, within the framework of the NEA-TDB and GEOTRAP working groups the need of the development of solid-solutions models to deal with these interactions is currently gaining acceptance and it is recommended their consideration in further stages of these projects /Bruno et al., 2001/.

Some of the main achievements have been:

1. To improve our conceptual and numerical models to describe the association of relevant radionuclides to the dynamic major component phases (Fe(III) oxihydroxides and carbonates, /Bruno, 1997/. In particular for U, Sr, Ba(Ra), and REE's (Am(III), Pu(III)).
2. To build up a consensus about the most appropriated methodology to tackle “solubility limit calculations”. This agreed methodology is now showing in the current performance assessment exercises /SR 97, Enresa 2000/.
3. To identify and sometimes clarify some of the remaining critical problems in the radionuclide databases.
4. To identify the main requirements for improved site characterisation data to describe radionuclide mobility. These are, for groundwaters: precise redox measurements and phosphate determinations. In terms of the mineralogical characterisation, there is a need to determine the association of relevant trace and PA analogous elements to the actual water flowing fracture fillings at the site.

In the light of this experience, we strongly recommend to incorporate blind predictive trace element modelling as an essential part of any potential site investigation programme to effectively identify the relevant geochemical fluxes in the site critical to radionuclide mobility from the repository.

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