The applicability and limitations of thermodynamic geochemical models to simulate trace element behaviour in natural waters. Lessons learned from natural analogue studies

Jordi Bruno [a,b,*], Lara Duro [a], Mireia Grivé [a]

[a]*QuantiSci S.L., Parc Tecnològic del Vallès, E-08290 Cerdanyola del Vallès, Spain*
[b]*Environmental Science and Waste Management (UPC), Jordi Girona 1-3 Campus Nord, Edifici C2, E-08034 Barcelona, Spain*

Abstract

Natural analogue investigations aim to understand key phenomena and processes in natural systems related to those expected to occur in radioactive waste repositories. One of the key applications of natural analogue studies has been the possibility to test the geochemical models to be used to describe 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, BPM) have formed an integral part of these studies over the last decade.

We have reviewed, discussed and compared the results obtained from geochemical modelling BPM exercises carried out within six natural analogue studies: 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. 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 calculated aqueous speciation as well as by comparing solubility calculations with the actually observed concentrations.

Results can be differentiated into two categories of elemental behaviour:

1. those elements like Th and U under reducing conditions that can be fairly well described by assuming solubility control exerted by pure solid phases as their oxyhydroxides;
2. elements such as Sr, Zn, REEs and U under oxidising conditions for which the association to major geochemical components of the system must be considered in order to explain their concentrations in groundwaters.

Additionally, we discuss the main improvements made to the thermodynamic databases and the geochemical calculation methodologies due to the BPM exercises. Furthermore, the most important characterisation geochemical data needed to complete predictive solubility and speciation calculations are identified.
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* Corresponding author. QuantiSci S.L., Parc Tecnològic del Vallès, E-08290 Cerdanyola del Vallès, Barcelona, Spain. Tel.: +349-35-824-410; fax: +349-35-824-412.

E-mail address: jbruno@quantisci.es (J. Bruno).

1. Background and objectives

Natural analogue studies have become an integral part of the Safety Assessment of nuclear waste repo-

sitories (see for a discussion Miller et al., 2000). The generally accepted definition of a natural analogue (Côme and Chapman, 1986) is "an occurrence of materials and processes which resemble those encountered in a proposed geological repository". However, 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 in the evolution of a repository. However, one of the most tangible (i.e. quantitative) outcomes of natural analogue studies has been the possibility to test the conceptual geochemical models, the associated thermodynamic databases and required numerical codes to describe radionuclide migration under repository conditions. Consequently, these exercises are directed at testing the predictive capabilities of thermodynamic models to describe the geochemical variability in sufficiently well-characterised natural systems. They have been performed as blind predictive modelling (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, 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:

- Poços de Caldas (Brazil), a Mesozoic volcanic ring-structure hosting a U–Th mineralisation (Chapman et al., 1993);
- Cigar Lake (Canada), a 1.3-billion-year-old uranium deposit located in a water saturated sandstone where the ore is surrounded by a clay-rich halo (Cramer and Smellie, 1994);
- 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 (Smellie, 1998);

- El Berrocal (Spain), a granitic Hercinian massif intercepted by a quartz vein with associated primary uranium mineralisations (Enresa, 1996);
- Oklo (Gabon), a fossil natural nuclear reactor systems located in a Precambrian sedimentary basin (Louvat et al., 1998); and
- Palmottu (Finland), a uranium deposit located within Precambrian metamorphosed supracrustal and sedimentary rocks in SW Finland (Blomqvist et al., 2000).

A description of these investigations may be found out in Miller et al. (1994).

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 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 the safety assessment of nuclear waste repositories.

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. As a consequence, these exercises have helped to establish some of the uncertainties associated to radionuclide solubility calculations in waste repository systems.

2. Methodology

The methodology of the BPM exercises, from the 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:

- *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.

The thermodynamic databases used in these exercises were: WATEQ4F (Ball and Nordstrom, 1991), Uranium NEA-TDB (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 (Puigdoménech and Bruno, 1989); SKB 93 (SKB, 1993); SKB-TR 95-35 (Spahiu and Bruno, 1995)., Hatches (Cross and Ewart, 1991); Chemval (Falck et al., 1996); Newtherm (Yusaf and Hamilton, 1990); MINEQL (Schweingruber, 1982); and MINTEQA1 (Peterson et al., 1987).

The geochemical codes used were: PHREEQE (Parkhurst et al., 1980); EQ3NR (Wolery, 1992); MINEQL (Westall et al., 1976); HARPHREQ (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).

A BPM exercise is usually divided into two main stages.

Stage 1: 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 helped to the modellers to get a feel for the geochemical system, prior to the complete mineralogical characterisation.

Stage 2: The mineralogical information gathered from the natural analogue site is released to the participants. With this additional information, the modellers recalculate the solubilities of trace metals by assuming equilibrium with the solid phases identified 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 for the cases for which are known.

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 failures in considering relevant aqueous and/or solid species and their associated thermodynamic data. Also, the different calculation algorithms contained in the codes may lead to different results. Another important point affecting the predictions can be the differences in the calculation methodologies followed by the different participants.

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

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

All the BPM exercises have been based on the assumption of local thermodynamic equilibrium between the groundwater and the contacting minerals. The assumption of local equilibrium is based on the

fact that for most deep groundwater systems like the ones considered in this exercise, the residence times of groundwaters are larger than the characteristic reaction times of the dissolution/precipitation reactions considered. Residence times of groundwaters are in the order of 1000 to 100,000 years, while the low-temperature characteristic reaction times for the precipitation and dissolution of oxyhydroxides and carbonates (the main solubility controlling phases considered in these exercises) are in the range of a few days to hundred years. Hence, it is reasonable to assume that most of these reactions are in equilibrium. The assumption of local equilibrium for other phases like aluminium silicates is far more challenging because of the longer characteristic times of their dissolution–precipitation reactions (10,000 to 1,000,000 years' range). A more detailed discussion on these matters is found in Bruno (1997).

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 range of 3 up to 10 logarithmic units in the concentration scale). This fact leads to the conclusion 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; something well known to field mineralogists, but not represented in the geochemical models at use.

The only attempt to model the U/Fe association was done in Poç os de Caldas by assuming the coprecipitation 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).

The trace elemental association models (coprecipitation and codissolution) are based on the application of ideal solid solution thermodynamics. Nevertheless, experimental evidence was gathered from laboratory experiments (Bruno et al., 1995) and integrated with the classical body of the underlying solid solution theory (Thorstenson and Plummer, 1977). Two different approaches were used to quantify these processes, referred to as *coprecipitation* and *codissolution models.* They basically assume that the trace element T is

ideally mixed within the main component oxide or carbonate solid phase $M_2O_x/M_2(CO_3)_x$ and that the activity of the trace element in the solid phase can be approached by its molar fraction χ_T. This allows to represent the thermodynamic properties of the trace component as a function of the thermodynamic properties of the main component solid phase. In this context, it is fundamental to ascertain which are the key solid phases which are precipitating and dissolving in the system and how is the trace metal related to them. This is achieved by a combination of careful mineralogical characterisation together with some geochemical model calculations. The basis of these two approaches is described elsewhere (Bruno et al., 1998).

3. Description of the geochemistry of the sites investigated

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

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

- *Granitic media*: El Berrocal (Spain) and Palmottu (Finland);
- *Sandstone–clay media*: Oklo (Gabon) and Cigar Lake (Canada);
- *Alkaline volcanic media*: Poços de Caldas (Brazil); and
- *Hyperalkaline media*: Maqarin (Jordan).

The main characteristics of these 6 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. Granitic 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 uranium 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 rich in alkaline feldspars. The volume percentage of muscovite exceeds that of biotite and the U and Th accessory minerals are uraninite, thorite, monazite, apatite and zircon.
(b) The hydrothermally altered granite, where most of the uranium is in the form of autunite.
(c) The Uranium Quartz Vein (UQV), formed of quartz associated with sulphide minerals, mainly pyrite, galena and sphalerite. The primary uranium minerals are uraninite in the form of pitchblende and coffinite. Iron(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 $Ca-SO_4$-type waters in the vicinity of the UQV due to pyrite oxidation, and $Ca-HCO_3$-type waters in the boreholes located farther from the UQV that have greater alkalinity. The role of the UQV in modifying the chemistry of the waters is clearly depicted in Fig. 1a, 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 down-

stream the concentration of sulphate increases (1.6×10^{-3} mol/dm^3 downstream, compared to 4×10^{-5} mol/dm^3 upstream of the mineralised quartz vein). The pH of the samples ranged from acidic (pH: $3-5$) 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).

3.1.2. Palmottu (Finland)

The Palmottu study area occurs within a zone of Precambrian gneisses and granites in SW Finland. A $U-Th$ mineralisation characterises the site forming discrete lenses and dispersions over an area that varies up to 15 m in width with a total length of about 400 m. The uranium 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 $Ca-HCO_3$-type near the surface to $Na-HCO_3$-type at intermediate depths. At greater depths, the waters are of $Na-SO_4-Cl$ type with the $Na-SO_4$ groundwater apparently confined to the mineralised area. In general, an increase in total dissolved solids and a decrease in the redox potential are 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 Fig. 1b, 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 second. Phase of the Palmottu natural analogue project (Bruno et al., 1999a,b).
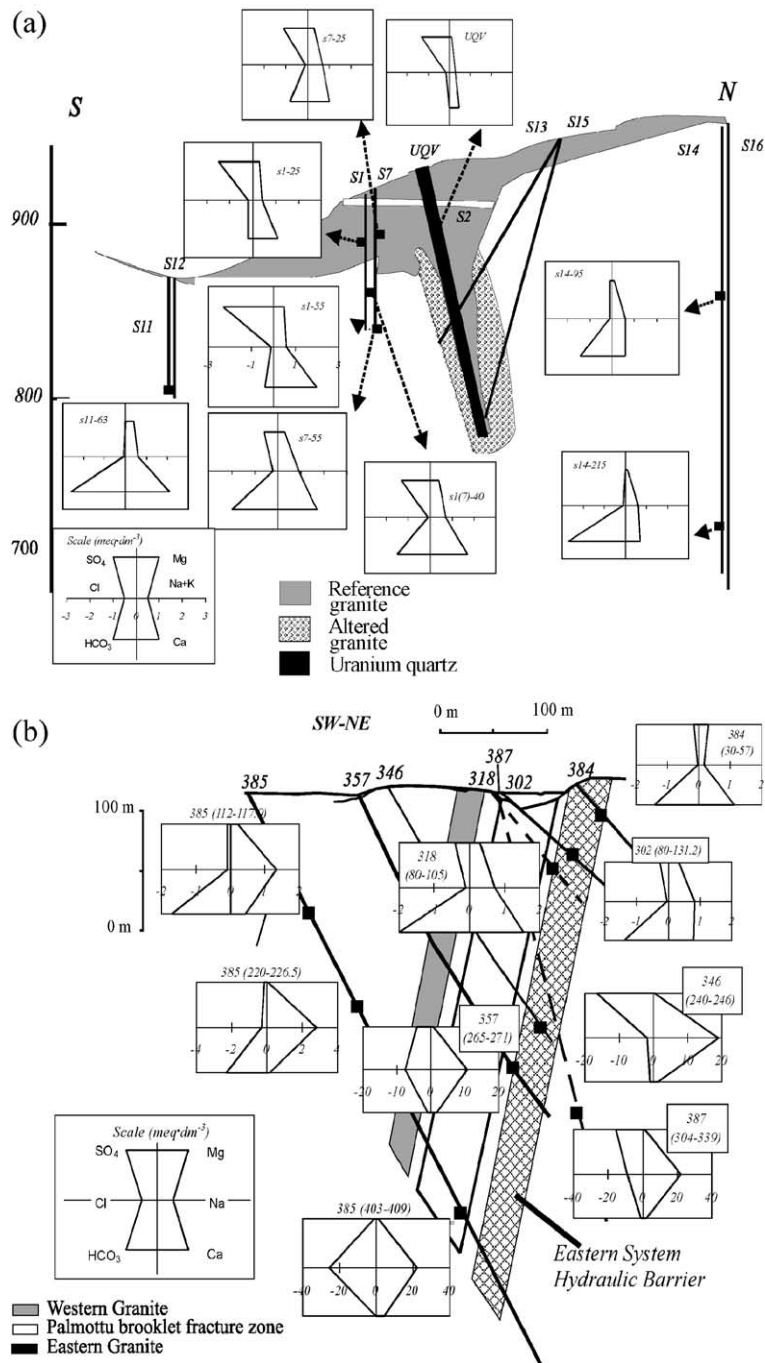
Fig. 1. (a) Cross-section of the El Berrocal zone showing the Stiff diagrams of samples selected for the BPM exercise. (Adapted from Bruno et al., 1996a,b). (b) Cross-section of the Palmottu site showing the Stiff diagrams of samples selected for the BPM exercise. (Adapted from Bruno et al., 1999a,b).

3.2. Sandstone–clay

3.2.1. Oklo (Gabon)

The Oklo region in Gabon, West Africa, presents a regional uranium 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 dolomitic zones. All the uranium mineralisations identified in the Franceville basin are located in the FA formation. Some 20 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 shallow depths (∼ 12 m), while all the others are at depths between 200 and 400 m.

In Okélobondo (see Jensen and Ewing, 2001), quartz, calcite, chlorite and illite mainly compose the host rock, while the fracture fillings contain quartz, calcite, pyrite, chlorite, Fe oxyhydroxides and illite. Near the OK84 reactor, the fracture fillings are mainly composed of quartz, chlorite, illite, kaolinite, pyrite, chalcopyrite, galena, Fe oxyhydroxides, 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 (Fig. 2a). According to the geochemical modelling reported in Peña et al. (2000), the groundwater samples can be classified into four different groups: (1) Samples of the west gallery (Okélo C) that present low mineralisation, slightly acidic to neutral pH values and oxidising conditions; (2) Samples from boreholes drilled from the surface, sampled in the Complexes Formation with neutral pH and reducing Eh values; (3) Samples close to the reactor (Okélo E), corresponding to groundwaters which have interacted with pelites with alkaline pH and oxidising Eh values; (4) Surface waters with 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 oxyhydroxides and illite. Near the reactor, quartz, chlorite, illite, kaolinite, pyrite, Fe oxyhydroxides, and organic matter mainly compose the fracture fillings. The Stiff diagrams of the groundwater samples used in the BPM are shown in Fig. 2b superimposed on a cross-section of the area. All the samples are of Ca–HCO$_3$ type. These groundwaters are moderately acidic to neutral (pH values from 4 to 7). The redox potentials are discussed in Louvat et al. (2000), they range between 100 and 400 mV.

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 paper correspond to the second. Phase of the Oklo natural analogue project and are published within a series of EUR reports (Duro and Bruno, 1998; Duro et al., 2000a,b).

3.2.2. Cigar lake (Canada)

The uranium deposit at Cigar Lake is located in northern Saskatchewan, Canada. The uranium 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). The mineralisation is shaped like an irregular lens approximately 2000 m long, 20 to 100 m wide and 1 to 20 m thick. This site presents some features analogous to aspects considered in 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. uranium 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 uranium deposit, there is no surface expression of its existence. The deposit has remained relatively intact during at least the last 10^4 years.

The uranium mineralisation is comprised mainly of uraninite with an average uranium content of 8% wt. with local enriched zones containing up to a 60% wt. Illite and chlorite mainly form the clay matrix surrounding the uranium mineralisation. This

Fig. 2. (a) Cross-section of the OK84 Okélobondo area showing the Stiff diagrams of samples selected for the BPM exercise. (From Duro et al., 2000a)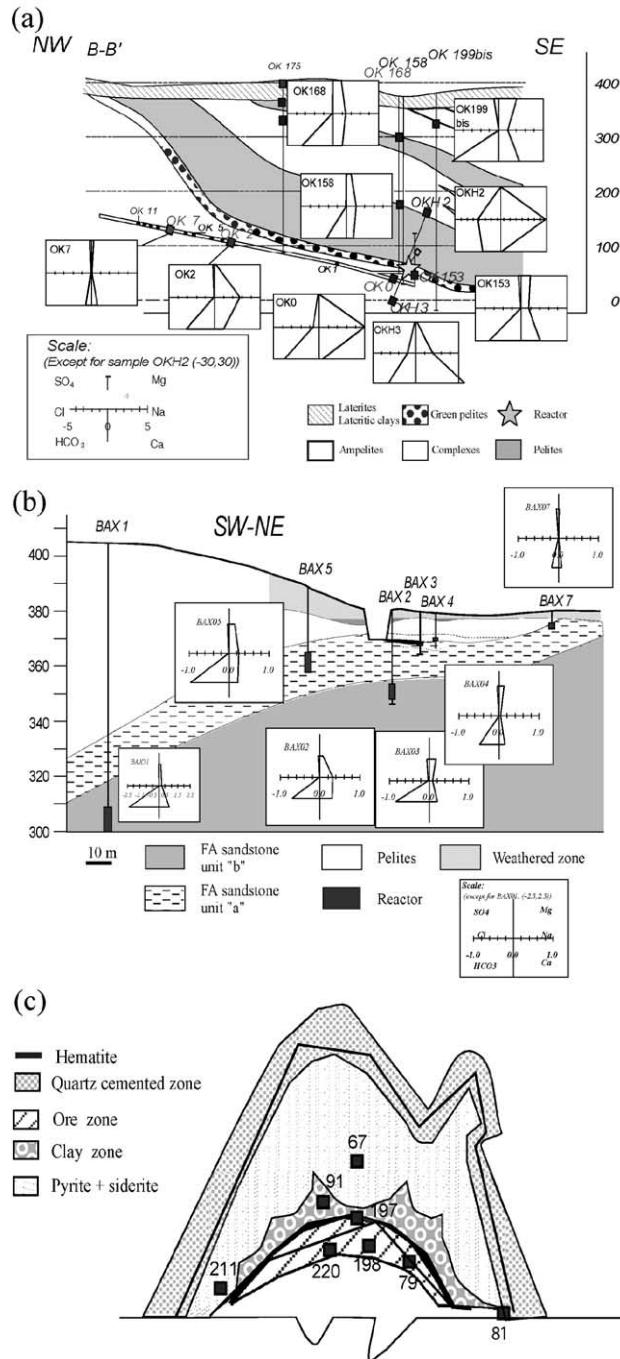. (b) Cross-section of the Bagombé showing the Stiff diagrams of the samples selected for the BPM exercise. (From Duro et al., 2000b). (c) The Cigar Lake uranium mineralisation showing the hematite marginal to the orebody and the clay halo which acts as a hydraulic barrier to water circulation (Adapted from Cramer and Smellie, 1994).

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 iron(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 Fig. 2c.

The groundwaters at depth are weakly mineralised and highly reducing with an ionic strength in the range 10^{-4} to 5×10^{-3} and low Eh (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 (Bruno and Casas, 1994; Casas and Bruno, 1994).

3.3. Alkaline volcanic rocks

3.3.1. Poços de Caldas (Brazil)

The Poços de Caldas alkaline complex is one of the Mesozoic alkaline occurrences of southeastern Brazil that developed from the Upper Jurassic onwards during continental breakup 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 pyritisation, strong potassium enrichment and the formation of several important radioactive anomalies. Two of these anomalies, the Osamu Utsumi uranium deposit and the Morro do Ferro thorium 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 de 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 interesting from a safety assessment viewpoint since Morro do Ferro was identified amongst the most naturally radioactive place in the surface of the Earth (7000 mrem/year, Cullen and Penna Franca, 1977). Furthermore, the redox front displayed in the vicinity of the Osamu Utsumi mine made this site useful in the study the redox fronts likely to occur from corrosion reactions on iron and steel canisters.

The groundwaters at the Osamu Utsumi mine are of $K–Fe–SO_4$ type with F much more important than Cl. This groundwater composition is unusual and is due to the weathering of the hydrothermally altered complex of intrusive 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/dm^3, comparable in concentration to Sr and Ba. At the Morro do Ferro site, the groundwaters sampled show minor mineralisation in the shallow boreholes; increased values of the salinity is observed in borehole MF12 since it corresponds to a discharge zone. These characteristics are illustrated in Fig. 3a and b where cross-sections of the two sites with the superimposed modified Stiff diagrams. In general, the groundwaters are highly oxidising in the recharge areas, whereas deeper groundwaters are mildly reducing. The pH values are slightly 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, 1996a).

3.4. Bituminous limestone and biomicritic limestone

3.4.1. Maqarin (Jordan)

Spontaneous combustion of bituminous-rich marl has produced natural cements which, through inter-
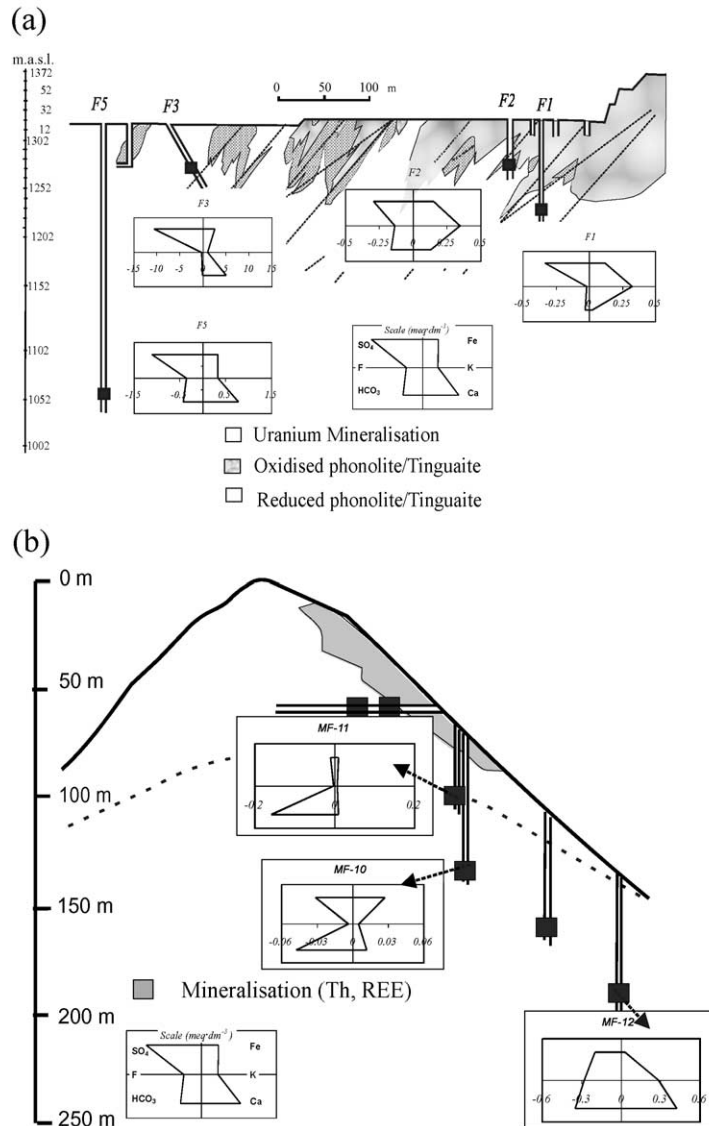
Fig. 3. (a) Cross-section of the Osamu Utsumi mine showing the modified Stiff diagrams of groundwaters sampled at the site. (Adapted from Nordstrom et al., 1990). (b) Cross-section of the Morro do Ferro site showing the modified Stiff diagrams of groundwaters sampled the site. (Adapted from Nordstrom et al., 1990).

action with normal pH groundwater, has produced hyperalkaline waters and hydrated CSH phases similar to those expected within a cementitious nuclear waste 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 have 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 Fig. 4).

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 first and second. Phases of the Maqarin natural analogue
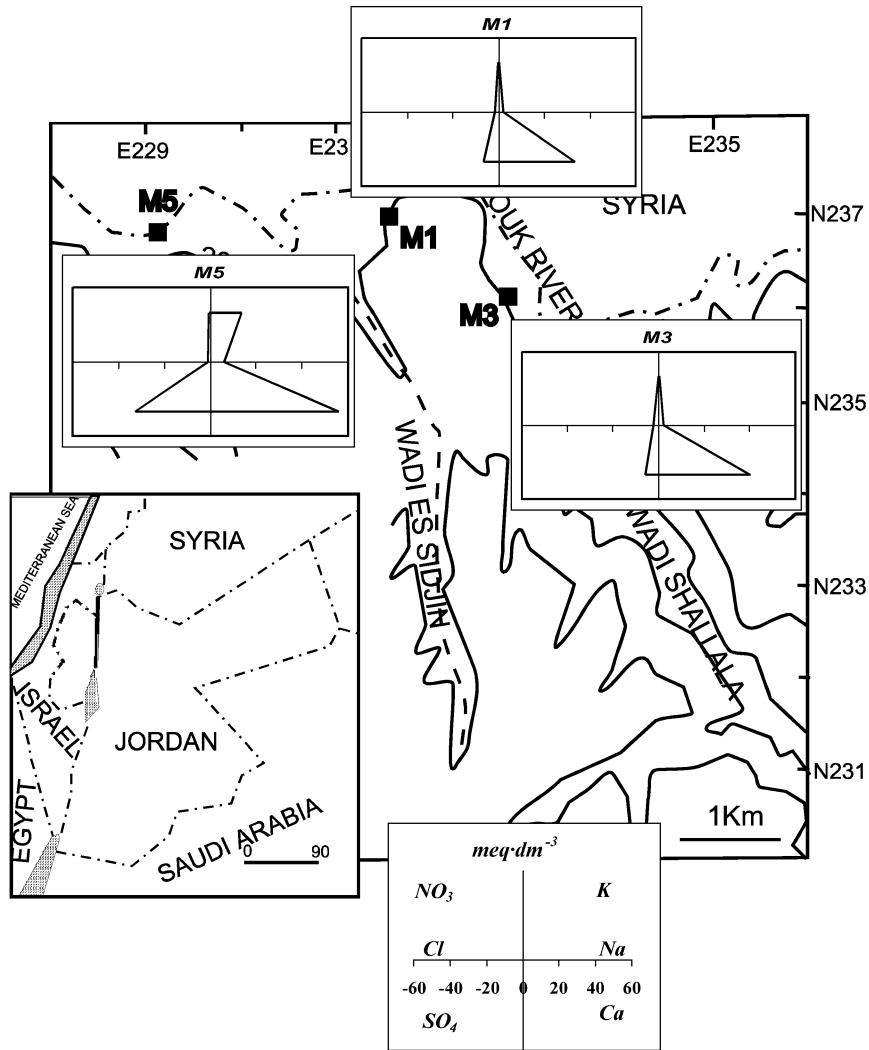
Fig. 4. Maqarin study site. Location of the samples studied in the BPM exercise with modified Stiff diagrams superimposed. (Adapted from Linklater et al., 1996).

project (Alexander, 1994; Alexander et al., 1992, 1998; Linklater et al., 1996).

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 performance assessment (PA) point of view. This selection is described in the following subsection.

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, the main aqueous species

and the main counter ions affecting the behaviour of each element were identified, thus indicating critical factors for its behaviour. Gaps and/or discrepancies in the geochemical databases used in the BPM exercises were also highlighted and this led to the improvement of these crucial tools for geochemical modellers.

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

The elements studied at each one of the sites are shown in Table 1. When 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 previously explained, the selection is based on the frequency an element has been studied and on its relevance from a geochemical point of view. The selection of Sr, Ni, Zn, REEs, Th and U is straightforward since they are relevant for the safety assessment of waste reposito-

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

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

ries and they have been studied in at least two of the sites included in this analysis.

4.1. Results

4.1.1. Strontium

Sr was investigated in four of the studied sites El Berrocal, Palmottu, Cigar Lake and Poços de Caldas. The concentrations of Sr in the El Berrocal groundwaters were close to the analytical detection limit, in the order of 10^{-6} mol/dm^3. Similar or slightly higher concentrations were measured at Palmottu, as expected due to the similar geochemical environment. The Sr concentration measured at Poços de Caldas shows a larger range from 10^{-8} to 10^{-5} mol/dm^3, reflecting the exceptional differences in the geochemistry of this site in terms of pH and fluoride concentration.

According to the equilibrium calculations, the main species accounting for the aqueous speciation of Sr at El Berrocal is Sr^{2+} with minor amounts of $SrSO_4$(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 calculated for the Palmottu groundwaters, 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, mainly strontianite ($SrCO_3$(s)) and celestite ($SrSO_4$(s)), controlling the concentrations of Sr in solution resulted at all sites in a general overestimation (two to three orders of magnitude) 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 readily available for water–rock interaction process, mainly carbonates. However, in Poços de Caldas, the association to phosphates was positively checked.

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. This process not only reproduced the observed concentrations within 0.2 logarithmic units, but it was also able to reproduce the observed trends in Sr concentration as a function of the chemistry of the sampled waters. The evidence that was 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 moles of Sr per mole of calcite supported this approach.

The same process, i.e. congruent dissolution of a Sr-substituted calcite, explained also the behaviour of Sr at the Palmottu site. In this case, however, the average Sr content in calcite was lower than the content needed to reproduce the data. A possible explanation could be 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 would be 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 = 0.035).

At Cigar Lake, Casas and Bruno (1994) indicated the possibility of a Sr-bearing calcium carbonate controlling the solubility of Sr in groundwaters. An ideal solid solution model using the miscibility limit gives a good match (within 0.5 log units) with the measured results.

At Poç os de Caldas, Nordstrom et al. (1992) concluded 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 available made it difficult, if not impossible, to test this hypothesis. 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 (three orders of magnitude) 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 well correlated with that of calcium, indicating the possibility of these two elements deriving 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 calcium. 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 fluorite. 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 Poç os de Caldas data, Bruno et al. (1996a) found some evidence that fluorite could host over 1% Sr (Deer et al., 1985). According to this, the hypothesis of congruent dissolution of a 1% Sr-bearing fluorite cannot be totally disregarded.

The observed correlations between the concentration of Sr and Ca in the three sites where it has been studied can be seen in Fig. 5. As expected, the cor-
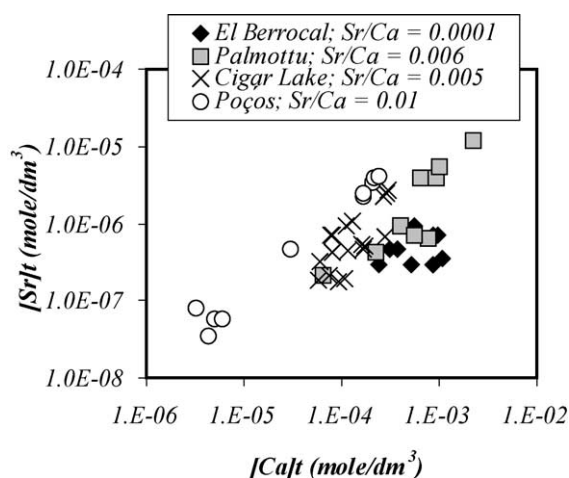

Fig. 5. Sr:Ca correlation in groundwater samples from El Berrocal, Palmottu, Cigar Lake and Poços de Caldas.

relation is, generally, fairly good and the molar ratio Sr/Ca ranges from 10^{-2} to 10^{-4}.

The main conclusion is that, in general, the behaviour of Sr in groundwaters is intimately linked to calcium. 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 basis of the same processes.

4.1.2. Nickel

Nickel is an interesting element for the purpose of this review because it has been included in all the BPM exercises.

The concentration of Ni measured in the groundwaters of El Berrocal is 10^{-6} mol/dm^3, while at Palmottu, it is two orders of magnitude lower, 10^{-8} mol/dm^3. In the Oklo environment, these concentrations are similar to those measured in El Berrocal. In Poços de Caldas, the concentrations are similar to those at Palmottu, 10^{-7} mol/dm^3. In Maqarin, the levels are of the same order of magnitude and in the Cigar Lake groundwaters, only two determinations are available (10^{-7} mol/dm^3).

In general, at all the sites studied, the calculated aqueous speciation of nickel is dominated by the free cation Ni^{2+} in the most acidic waters and by carbonato-complexes in alkaline samples. The exception to this rule is the case of Maqarin, where hydroxo-complexes were calculated to dominate the speciation. 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 nickel one must ensure that the aqueous nickel-carbonate species are included in the thermodynamic database. With respect to the solid phases potentially controlling the concentrations of nickel in the groundwaters of the different sites studied, a priori the modellers proposed nickel oxides and hydroxides apart from silicates, sulphides and trevorite (NiFe$_2$O$_4$). In all cases, equilibrium with trevorite produced concentrations that were five orders of magnitude

lower than the actual ones. As discussed in Bruno et al. (1992), Ni-ferrites are the result of homogeneous solid solution between NiO and Fe$_2$O$_3$ and they are not formed at low temperatures.

In general, equilibration of the groundwaters with pure nickel oxides or hydroxides produced concentrations far above the actual measurements, in the range of five to eight orders of magnitude. This is to be expected if we take into consideration that Ni(II) only builds hydrolysis complexes at pH close to 10.

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

1. The thermodynamic databases do not contain aqueous nickel 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 exception of millerite (NiS);
3. In most cases, Ni is present in solid sulphides as a trace component, i.e. it is frequently coprecipitated with pyrite, but not separately as a 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 to explain 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 associated with iron(III)-oxyhydroxides. However, the assumption of the formation of mixed Ni–Fe solid phases has not rendered satisfactory results when considered. For this reason, alternative explanations to the behaviour of nickel in low-temperature environments must be sought in relation with source-term limitation, short residence times of groundwater or sorption phenomena. If the residence times of groundwater would be short, this could 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. However, as initially discussed the long residence times of groundwater in the systems investigated discard this hypothesis.

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 could be a possible explanation in some of the systems studied. Although Ni is the second most abundant metal in Earth, this is not readily accessible to dissolution in low-temperature groundwater systems.

Finally, another plausible explanation is that sorption processes control the concentration of Ni in groundwater. However, this possibility is difficult to test due to the lack of simple sorption models to apply to complex natural systems. Besides, under slow water flow rates, it could 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 nickel.

4.1.3. Zinc

Zinc 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 are in the range 10^{-6} to 10^{-4} mol/dm^3; in Poços de Caldas values of 10^{-6} to 10^{-5} mol/dm^3 are present. This is also the case at Oklo, while at Cigar Lake the values are in the range 10^{-8} to 5×10^{-7} mol/dm^3. At all the investigated sites, the free cation Zn^{2+} dominates the calculated 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 ($ZnCO_3$), $ZnFe_2O_4$ (a Zn-ferrite analogous to trevorite in the case of nickel, $Zn_3(PO_4)_2$) and sphalerite (ZnS).As in the case of nickel, the assumption of $ZnFe_2O_4$ controlling the concentrations of Zn in groundwaters produces levels of aqueous Zn that are five to eight orders of magnitude lower than the observed concentrations. The exception is 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. 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 two 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. As an alternative, the modellers assumed that Zn was present in calcite. 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.

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 a two to three orders of magnitude overestimation 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, in the range of 10^{-5} mol/dm^3.

At Oklo, the best agreement between the predictions and the measurements was obtained by assuming the congruent dissolution of a Zn-bearing calcium 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 calcium-containing minerals, mainly calcite, and on iron(III) oxyhydroxides.

4.1.4. REEs

In spite of their intrinsic 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 between 10^{-8} and 10^{-11} mol/dm^3. In all cases, light REEs are present in larger concentrations than the heavy ones. At Palmottu and Oklo, the calculated REE speciation is dominated by carbonato-complexes. This is more evident for the light REEs because the stability of the REE–CO_3 complexes
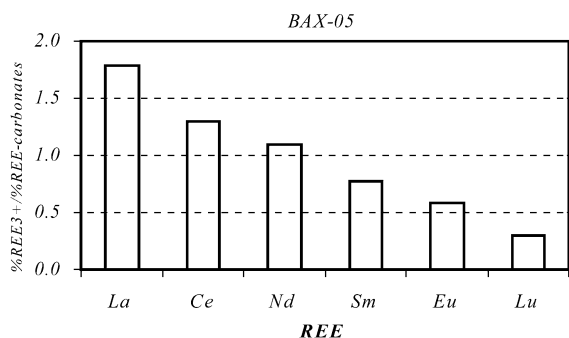
Fig. 6. Increase in the percentage of carbonate species when increasing the REE atomic weight in BAX-05 from Oklo.

increases with decreasing atomic number. This observation is illustrated by the results shown in Fig. 6, where the increase in the percentage of the carbonate species with increasing the REE atomic number in sample BAX-05 from Oklo is shown.

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 at that site, i.e. sulphates.

For the solubility-limiting solid phases of the REEs at Oklo and Palmottu, the modellers proposed hydroxide, carbonate and phosphate solid phases. The concentrations of REEs calculated from equilibrating the groundwaters with solid hydroxides of carbonates were more than four orders of magnitude larger than the actual measurements. As an alternative approach, the modellers equilibrated the groundwaters with solid REE phosphate phases (REEPO$_4$·10H$_2$O(s)).

The result of equilibrating the groundwater compositions with solid REE phosphates produced a certain overestimation, up to four orders of magnitude, of the actual REE concentrations at Bagombé (Oklo). This overestimation increased with increasing atomic weight, 1 order of magnitude in the case of Nd in sample BAX03, up to four orders of magnitude for Lu in the same sample. 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 structure is documented in the literature (Jones et al., 1996), suggested that the concentration of REEs at Oklo could be explained by coprecipitation with

apatite (Duro et al., 2000b). According to Jones et al. (1996), the incorporation of the lighter REEs in the apatite structure is favoured over the incorporation of the heavier REEs. This is in agreement with the increase in the overestimation of the calculated concentrations versus of the actual REE measurements when increasing the atomic weight. The difference between the measured REE concentration and the REEPO$_4$·10H$_2$O calculated solubility for the REEs included in the Oklo BPM, is shown in Fig. 7a, where up to four orders of magnitude overestimation is observed for the heavier lanthanides (Lu) with respect to the lighter ones (La).

Similar behaviour is observed in the groundwaters of Palmottu, i.e. the difference between the measured REE concentration and the calculated solubility of the pure REE phosphate phase increases when increasing
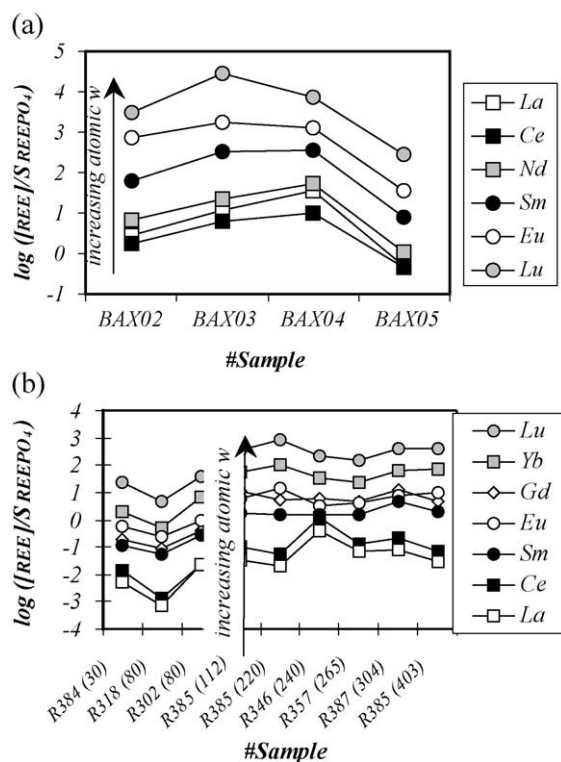

Fig. 7. (a) Difference between the measured REE concentrations and the concentrations calculated by equilibrating the Bagombé (Oklo) groundwaters with pure REEPO$_4$·10H$_2$O. (From Duro et al., 2000b). (b) Difference between the measured REE concentrations and those calculated by equilibrating the Palmottu groundwaters with pure REEPO$_4$·10H$_2$O. (From Bruno et al., 1999a,b).

the atomic weight, but even negative differences are obtained in this case (see Fig. 7b). This means that for the lighter lanthanides it is possible to explain the observed concentrations assuming the precipitation of pure solid phosphates.

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[REE]/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 large phosphate concentrations (from 10^{-5} to 10^{-7} mol/dm^3). Thus, coprecipitation of REEs with apatite explains their behaviour at both the Oklo and Palmottu sites.

4.1.5. 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} mol/dm^3 at all sites. The speciation calculated in the El Berrocal groundwaters is dominated by the neutral complex Th(OH)$_4$(aq) with a predominance of the sulphate complex ThSO$_4^{2+}$ in the sulphate waters sampled in the uraniferous quartz vein (UQV). At Poços de Caldas, the speciation calculated by the modellers is dominated by the neutral species Th(OH)$_4$(aq), fluoride complexes, and the phosphate species when included. The inclusion of Th(IV) phosphate complexes in the calculations gave calculated Th(IV) concentrations values two to three orders of magnitude above the measured data. This is a well-established problem arising from the use of Th(IV) phosphate complexation data determined by Moskvin et al. (1967).

The calculated solubility of Th oxides or hydroxides is in agreement with the Th concentrations (10^{-9}–10^{-11} mol/dm^3) measured at El Berrocal, Palmottu, Poços de Caldas, Cigar Lake and Maqarin.

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 have different crystallinities, which is translated into a large range (up to four orders of magnitude) of solubility constants. (see Table 2). 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) (logK_s = 6.3) is used in the thermodynamic databases, the stability of the aqueous phosphates is suppressed in Poços de Caldas waters and the formation of Th(OH)$_3$CO$_3^-$ is neglected in Palmottu groundwaters.

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

4.1.6. Uranium

Because of its obvious importance to nuclear waste repositories, uranium has been studied in all the BPM exercises performed on the sites. A wide range of concentrations (10^{-5}–10^{-11} mol/dm^3) is observed in the studied sites, due to the variability in redox and alkalinity conditions.

The concentrations measured at El Berrocal and Palmottu (10^{-6} mol/dm^3) 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} mol/dm^3, and the concentrations measured at Maqarin are below the ranges measured at all

Table 2
Solubility constants of thorium oxides and hydroxides found in the literature

Solid	logK_s	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 and 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 and Herman (1980)	ThO$_2$(c) + 4H$^+$ = Th^{4+} + 2H$_2$O

the other sites (10^{-11} mol/dm^3). This fact is an indication that increased alkalinity decreases the expected uranium concentrations in groundwaters. Because of the rather complex chemistry of uranium, it is difficult to make similar generalisations as we have previously done for other elements with a simpler chemistry. Consequently, the geochemical behaviour of uranium will be discussed on a site by site basis.

At El Berrocal, the speciation of uranium is dominated by carbonato-complexes, except for the groundwater sampled in the vicinity of the pyritic quartz vein (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) calculated.

In spite of the similarities between El Berrocal and Palmottu, we found important differences in the redox state that obviously affect the calculated speciation of uranium. The groundwater samples from Palmottu used in the BPM exercise are mainly reducing and 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 uranium speciation are U(VI) fluorides, carbonates and hydroxides. Some of the modellers included uranyl hydrogenphosphates in their databases and calculated a significant amount of these species in the samples.

The Oklo samples are rather heterogeneous in terms of the large range of uranium concentrations measured. Nevertheless, due to the alkalinity of the samples, in most of them, the uranium 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 different Eh values. Whereas oxidising values had been obtained in all the previous campaigns, the 1998 values measured were much more reducing, by almost -300 mV. 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 uranium solubility, highlights the importance of the quality of

the analytical data used on any attempt to predict the solubility of metals in groundwaters. An important effort in this respect was done in the Palmottu project (Blomqvist et al., 2000).

In the Cigar Lake uranium deposit, the calculated speciation is dominated by U(VI) carbonato complexes, as reported in Bruno and Casas (1994). This is interesting since the redox conditions are sufficiently low to keep the solid uranium as UO$_2$(s), but not sufficiently to prevent the formation of hexavalent uranium complexes.

The picture of the uranium 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 UO$_2$(OH)$_4^{2-}$ and/or UO$_2$(OH)$_3^-$ in most groundwaters.

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 uranium 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 Fig. 8, where the actual uranium concentrations in the reducing samples of Oklo and Palmottu (10^{-7}–10^{-8}) mol/dm^3 are compared with the calculated uraninite and coffinite solubility.

In the oxidising samples, the modellers tested the possibility of several other uranium solids controlling the solubility. In those samples from El Berrocal where a uranium-phosphate association was mineralogically reported, equilibrium with autunite provided satisfactory results. However, this conclusion is hampered by the lack of good analytical data on the aqueous phosphate concentrations. 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 uranium in solution. Nevertheless, the results did not agree with the observations and, depending on the groundwater compositions, the discrepancies ranged between one and two orders of magnitude and the calculated values were always larger.

On the other hand, due to the association of uranium with iron(III) oxyhydroxides, the possibility of coprecipitation of these metals was tested, and the results were much closer to the measured values.
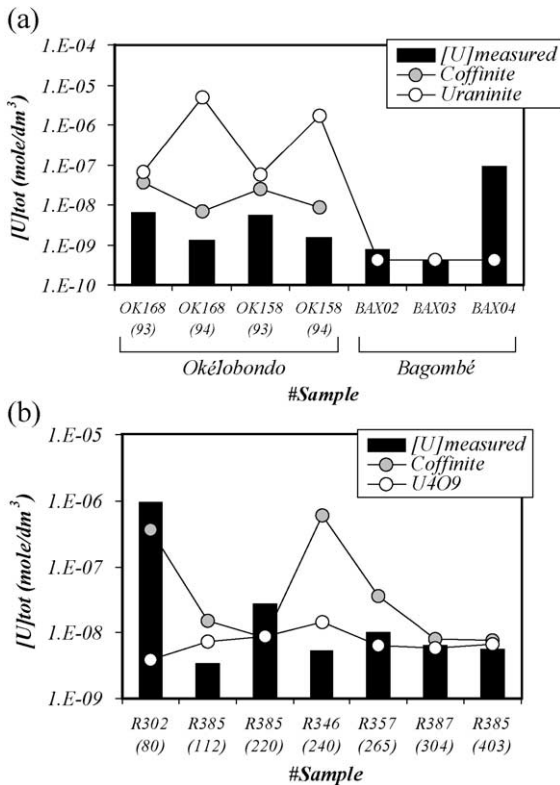
Fig. 8. Comparison between the actual U concentrations measured in the reduced groundwater samples of Oklo (a) and Palmottu (b) and the calculated solubility for uraninite and coffinite.

Therefore, the conclusion was that U(VI)-bearing iron(III) oxyhydroxides 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 iron(III) oxyhydroxides was considered, the calculated concentrations were in close agreement with the measurements (see Fig. 9).

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, 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; Jensen and Ewing, 1998) and the modelling results have been quite satisfactory. Both the actual concentrations and the calculated ones agree within 0.2 logarithmic units and the observed uranium concentration trend are reproduced.

In general, however, it seems that the precipitation of U(VI) silicates, such as uranophane and haiweeite, account for the uranium concentrations observed in the more oxidised samples at Oklo. On the other hand, the association of U with iron(III) oxyhydroxides is able to represent fairly well the concentration of uranium measured in the surface acidic waters of Okélobondo, which was tested by applying a coprecipitation model to a U-bearing iron(III) oxyhydroxide (see Fig. 10).

Finally, in the hyperalkaline groundwaters of Maqarin, the assumption of uranium(VI) oxides and hydroxides as solubility controlling phases resulted in several orders of magnitude overestimations of the actual measurements. The modellers selected the solid phase $CaUO_4$ as likely to control the solubility of uranium at the site. However, the solubility constant for this solid included in the most common thermodynamic databases corresponds to a crystalline solid and,
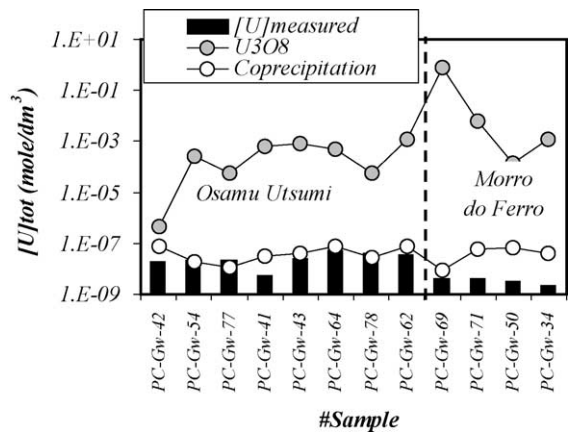

Fig. 9. Comparison of the agreement reached between the actual U concentrations measured in the groundwater samples of Poços de Caldas, the calculated solubility for U_3O_8 and the solubility of U calculated by assuming the coprecipitation of U(VI) with iron(III) oxyhydroxides.
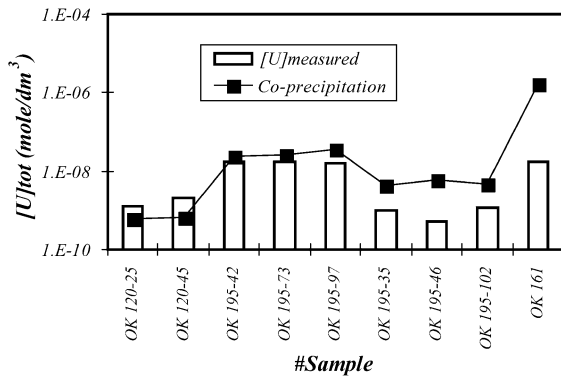
Fig. 10. Comparison between the actual U concentrations measured in the surface-oxidising groundwater samples of Okélobondo (Oklo) and the concentrations calculated by assuming the coprecipitation of U(VI) with iron(III) oxyhydroxides.

consequently, very low U concentrations were calculated. As highlighted in Alexander et al. (1998), an effort should be made to include more amorphous calcium urananates in the databases in order to constrain the solubility of uranium under cementitious environments.

The main conclusions can be summarised as:

- Under reducing conditions, the solid phases controlling the solubility of uranium 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; and

- Under oxidising conditions, U(VI) silicates and/or U(VI)-bearing iron(III) oxyhydroxides are responsible for the aqueous uranium concentrations measured in groundwaters.

5. Discussion and conclusions

As a general trend, carbonate dominates the speciation of all the trace metals studied in alkaline environments, while sulphate complexation is relevant in slightly acidic and oxidising media. This is because most of the elements studied are hard acids and tend to complex with oxo-ligands. 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 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 improvement requirements of thermodynamic databases and/or analytical determinations.

In summary, according to their solubility control, the elements reviewed can be classified into two different groups:

- Elements whose solubility control seems to be exerted by *individual solid phases*:
  Th: apparently controlled by the solubility of $Th(OH)_4(am)$ at all the sites investigated,

Table 3
Degree of agreement between measurements and predictions

Elem. (N)*	Degree of agreement**		Required improvements
	Pure phases	Mixed phases	
Sr (4)	Poor. Overestimation	Good. Linked to Ca	Mineralogical evidence of the association
Ni (6)	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 phosphate data
Th (5)	Fair	Not tested	Improvement of the thermodynamic data base. Internal consistency of aqueous and solid data required
U-reducing	Fair	Not tested	Good Eh measurements
U-oxidising	Fair	Fair. Linked to Fe(III)	Improvement of thermodynamic models

$N*$ = Number of sites where the element has been investigated.

** = Poor: difference of two to three orders of magnitude between measurements and calculations; Fair: difference of one order of magnitude between measurements and calculations; Good: difference of 1/2 orders of magnitude between measurements and calculations.

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;

Trace elements whose *behaviour seems to be linked to the major components of the system*:

Sr, and Zn: controlled by mixed Ca–Sr, or Ca–Zn/Fe(III)–Zn solid phases,

REEs: controlled by incorporation with solid phosphates (apatite),

U under oxidising conditions: partially controlled by its association with Fe(III) oxyhydroxides.

Acknowledgements

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