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Poços de Caldas Report No.8

**Natural series radionuclide and
rare-earth element geochemistry
of waters from the Osamu
Utsumi mine and Morro do Ferro
analogue study sites, Poços de
Caldas, Brazil**

JANUARY 1991

An international project with the participation of Brazil, Sweden (SKB), Switzerland (NAGRA), United Kingdom (UK DOE) and USA (US DOE). The project is managed by SKB, Swedish Nuclear Fuel and Waste Management Co.



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Natural series radionuclide and rare-earth element geochemistry of waters from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.

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Abstract

Data are presented on natural series radionuclides and rare-earth elements (REEs) in prefiltered (<450 nm) near-surface and deep groundwaters from the Osamu Utsumi uranium mine and Morro do Ferro (thorium-REE-deposit) analogue study sites.

In the Osamu Utsumi uranium mine, very high concentrations of uranium (up to 10 mg/l) were measured in near-surface waters. In deep groundwaters (60–120 m), concentrations of this element are typically between 3 and 10 µg/l. The reduced concentrations of uranium in the Morro do Ferro host rock are reflected in the considerably lower concentrations of this element in waters from this environment.

The concentrations of ²³²Th in groundwaters from both sites are very low and generally <0.1 µg/l. However, they can be higher, by a factor of 100 or more, in superficial waters rich in humic compounds (Morro do Ferro) or acidic in character (Osamu Utsumi mine).

Pronounced disequilibria were measured between ²³⁴U and ²³⁸U isotopic activities in groundwaters which are characterised by an excess of ²³⁴U due to preferential leaching of this isotope and/or recoil effects. The ²³⁴U / ²³⁸U activity ratio is lower in the superficial waters (1.0 – 1.2) than it is in the deeper groundwaters (1.4 – 2.7). This is because, in moving towards the surface, the groundwater picks up a greater, non-fractionating leach component of uranium in the zone of higher redox potential. Due to the extremely low solubility of thorium and its strong tendency to sorb on suspended particles (mainly composed of hydrous ferric oxides), the ²³⁰Th / ²³⁴U activity ratios in groundwaters are also very low (0.01).

Rare-earth element concentrations in groundwaters from both sites are typically in the range between 1 – 50 µg/l for the light rare-earth elements (LREEs; La, Ce, Nd) and

0.001 – 0.1 µg/l for the heavy rare-earth elements (HREEs; Ho-Lu), but can be much higher in surface waters with high complexation capacities, as observed for thorium. The chondrite-normalised distribution patterns of the REEs in water samples (and in suspended particles) are similar to those observed in the bedrock, indicating congruent dissolution and sorption of these elements. An exception, however, is cerium which shows a very characteristic depletion in oxidising, shallow groundwaters of both sites, probably related to its preferential oxidation and the much lower solubility of Ce(IV) species in natural waters.

With respect to the mobilisation of thorium and the rare-earth elements via a “solution” phase, the data obtained in this study provide further support that solubility limitations (Th) and strong affinities for sorption (Th and the REEs) on particulate and colloidal matter are efficient mechanisms for restricting the dispersion of these elements (and possibly also that of their transuranic analogues) over small distances in porous media. This is best illustrated by the absence of any significant contribution of the Morro do Ferro ore deposit, with its 30,000 t of Th and nearly 100,000 t of LREEs, to the concentrations of these elements in surface drainage waters (<450 nm) collected within a distance of 100 m from the mineralisation zone.

Zusammenfassung

Der Bericht enthält Analysendaten über Radionuklide der U/Th-Zerfallsreihen und Seltene Erd Elemente (SEE) in gefilterterten (<450 nm) Grundwässern der Osamu Utsumi U-Mine und des Morro do Ferro (Th-SEE-Lagerstätte).

In der Osamu Utsumi U-Mine wurden in oberflächennahen Wässern sehr hohe U-Gehalte (bis 10 mg/l) gemessen. Tiefe Grundwässer (60-120 m) enthalten dagegen typisch 3-10 µg/l U. Die niedrigen Konzentrationen von U im Morro do Ferro Wirtgestein spiegeln sich in den wesentlich niedrigeren U-Gehalten der dortigen Wässer wieder.

Die Konzentrationen von Th in den Grundwässern beider Untersuchungsstellen sind sehr niedrig und im allgemeinen <0.1 µg/l. Sie können aber in oberflächennahen Wässern (huminreich am Morro do Ferro, sauer in der Osamu Utsumi U-Mine) um den Faktor 100 oder mehr höher sein.

Ausgesprochene radioaktive Ungleichgewichte für ^{234}U und ^{238}U wurden in Grundwässern gemessen mit dem charakteristischen, durch α -Rückstoss und erhöhte Auslaugbarkeit bedingten Ueberschuss an ^{234}U . Das $^{234}\text{U}/^{238}\text{U}$ Aktivitätsverhältnis ist dabei niedriger in oberflächennahen Wässern (1.0-1.2) als in tieferen Grundwässern (1.4-2.7).

Dies beruht auf einer erhöhten, nicht fraktionierenden Auslaugung von Uran durch die aufsteigenden Grundwässer im oberflächennahen Bereich höherer Redoxpotentiale. Zufolge der extrem geringen Löslichkeit von Thorium und seiner starken Tendenz zur Sorption an suspendierten Partikeln (zur Hauptsache aus Ferrihydriten bestehend) ist auch das $^{230}\text{Th}/^{234}\text{U}$ -Aktivitätsverhältnis in den Grundwässern sehr niedrig (0.01).

Die Konzentrationen an Seltenen Erd-Elementen (SEE) in den Grundwässern beider Untersuchungsstellen liegen typisch im Bereich von 1-50 $\mu\text{g/l}$ für die leichten SEE (LSEE; La, Ce, Nd) und von 0.001-0.1 $\mu\text{g/l}$ für die schweren SEE (SSEE; Ho-Lu), wobei in Oberflächenwässern mit hohem Komplexierungsvermögen, analog zu Th, auch viel höhere Konzentrationen auftreten können. Die chondrit-normalisierten Verteilungsmuster der SEE in den Wasserproben (und den suspendierten Partikeln) sind denjenigen im Umgebungsgestein ähnlich und deuten auf kongruente Auflösung und Sorption dieser Elemente hin. Eine Ausnahme bildet dabei jedoch Cerium, das eine sehr charakteristische Abreicherung in oxidierenden, oberflächennahen Grundwässern beider Untersuchungsstellen aufweist, wahrscheinlich als Folge der Oxidation zu Ce(IV), das in natürlichen Wässern wesentlich unlöslicher ist als Ce(III).

In Bezug auf die Mobilisierung von Th und SEE über die Lösungsphase bestätigen die in dieser Studie erhaltenen Daten, dass geringe Löslichkeit (Th) und starke Tendenz zur Sorption an suspendierten Partikeln (Th und SEE) sehr wirksame Mechanismen darstellen, um die Ausbreitung dieser Elemente (und möglicherweise auch diejenige ihrer Transuran-Analoga) über kurze Strecken in porösem Material zu beschränken. Das zeigt sich am deutlichsten am Fehlen eines nennenswerten Beitrages des Morro do Ferro Erzlagers mit seinen 30 000 t Th und nahezu 100 000 t LSEE zur Konzentration dieser Elemente im exfiltrierenden Drainagewasser (<450 nm), das innerhalb einer Distanz von 100 m vom Erzkörper gesammelt wurde.

Résumé

Le rapport présente les données acquises sur les terres rares (REEs) et les séries naturelles de radionuclides d'eaux souterraines préfiltrées (<450 nm) proches de la surface et profondes récoltées sur les sites d'analogies naturelles de la mine d'uranium de Osamu Utsumi et du gisement de thorium et terres rares de Morro do Ferro.

Dans la mine d'uranium de Osamu Utsumi, on a mesuré des concentrations très élevées en uranium (jusqu'à 10 mg/l) dans les eaux proches de la surface. Dans les eaux plus profondes (60-120 m), la concentration en uranium se situe généralement entre 3 et 10 $\mu\text{g/l}$. A Morro do Ferro, la teneur réduite en uranium dans la roche mère se reflète dans les concentrations très faibles de cet élément dans les eaux souterraines environnantes.

La concentration en ^{232}Th dans les eaux souterraines est très faible sur les deux sites, et généralement inférieure à $0.1\mu\text{g/l}$. Toutefois, on peut trouver des concentrations nettement plus élevées, d'un facteur 100 ou plus, dans les eaux de subsurface riches en composés humiques (à Morro do Ferro) ou à caractère acide (à Osamu Utsumi).

Les eaux souterraines sont caractérisées par un déséquilibre prononcé entre les activités isotopiques de ^{234}U et ^{238}U , se manifestant par un excès en ^{234}U dû au lessivage préférentiel de cet isotope et/ou à des effets de retrait. Le rapport des activités $^{234}\text{U}/^{238}\text{U}$ est plus faible dans les eaux de subsurface (1.0-1.2) que dans les eaux profondes (1.4-2.7). Ceci est dû au fait qu'en se déplaçant vers la surface, les eaux souterraines se chargent dans la zone de potentiel redox accru d'un composé non fractionné du lessivage de l'uranium. Le rapport des activités $^{230}\text{Th}/^{234}\text{U}$ dans les eaux souterraines est également très faible (0.01), en raison de la solubilité extrêmement faible du thorium et de sa forte tendance à être adsorbé sur des particules en suspension, principalement des oxydes ferriques hydratés.

La concentration en terres rares dans les eaux souterraines des deux sites se situe typiquement entre 1 et $50\mu\text{g/l}$ pour les terres rares légères (LREEs; La, Ce, Nd), et entre 0.001 et $0.1\mu\text{g/l}$ pour les terres rares lourdes (HREEs; Ho-Lu), mais peut être nettement plus élevée dans les eaux de subsurface à fort pouvoir de complexation, comme on l'a observé pour le thorium. Les figures de distribution de type chondrite normalisée des terres rares dans les eaux souterraines et les particules en suspension sont semblables à celles observées pour les échantillons de roche, indiquant un comportement congruant de dissolution et d'adsorption de ces éléments. Le cérium, toutefois, fait exception. Il révèle dans les eaux de subsurface des deux sites un appauvrissement caractéristique dû probablement à sa tendance marquée à l'oxydation et à la solubilité très faible des espèces du Ce(IV) dans les eaux naturelles.

En ce qui concerne la mobilisation du thorium et des terres rares via une phase en "solution", les données fournies par la présente étude indiquent que les limites de solubilité du thorium et la forte tendance à l'adsorption du thorium et des terres rares sur les particules en suspension et la matière colloïdale sont des mécanismes efficaces de limitation de la dispersion de ces éléments (et probablement aussi de leurs analogues transuraniens) à de courtes distances en milieu poreux. Le plus bel exemple de ce fait est l'absence de toute contribution significative du gisement de Morro do Ferro (30 000 t de thorium et près de 100 000 t de terres rares légères) à la concentration de ces éléments dans les eaux de drainage (<450 nm) collectées à une distance de 100 m de la zone minéralisée.

Preface

The Poços de Caldas Project was designed to study processes occurring in a natural environment which contains many features of relevance for the safety assessment of radioactive waste disposal. The study area, in the State of Minas Gerais, Brazil, is a region of high natural radioactivity associated with volcanic rocks, geothermal springs and uranium ore deposits. It contains two sites of particular interest on which the project work was focussed: the Osamu Utsumi uranium mine and the Morro do Ferro thorium/rare-earth ore body. The first site is notable in particular for the prominent redox fronts contained in the rock, while Morro do Ferro was already well-known as one of the most naturally radioactive locations on the surface of the Earth, owing to the high thorium ore grade and the shallow, localised nature of the deposit.

The features displayed by these two sites presented the opportunity to study a number of issues of concern in repository performance assessment. The four objectives set after the first-year feasibility study were:

1. Testing of equilibrium thermodynamic codes and their associated databases used to evaluate rock/water interactions and solubility/speciation of elements.
2. Determining interactions of natural groundwater colloids with radionuclides and mineral surfaces, with emphasis on their role in radionuclide transport processes.
3. Producing a model of the evolution and movement of redox fronts, with the additional aim of understanding long-term, large-scale movements of trace elements and rare-earths over the front (including, if possible, natural Pu and Tc).
4. Modelling migration of rare-earths (REE) and U-Th series radionuclides during hydrothermal activity similar to that anticipated in the very near-field of some spent-fuel repositories.

The project ran for three and a half years from June 1986 until December 1989 under the joint sponsorship of SKB (Sweden), NAGRA (Switzerland), the Department of the Environment (UK) and the Department of Energy (USA), with considerable support from a number of organisations in Brazil, notably Nuclebrás (now Urânio do Brasil). The first-year feasibility study was followed by two and a half years of data collection and interpretation, focussed on the four objectives above.

This report is one of a series of 15, summarising the technical aspects of the work and presenting the background data. A complete list of reports is given below. Those in series A present data and interpretations of the sites, while those in series B present the results of modelling the data with performance assessment objectives in mind. The main findings of the project are presented in a separate summary (no. 15).

The work presented in this report is a detailed description of groundwater natural decay series and radiochemistry from the Osamu Utsumi mine and Morro do Ferro environments (objectives 1, 2 and 3).

Poços de Caldas Project Report Series

Series A: Data, Descriptive, Interpretation

Report No.	Topic	Authors (Lead in Capitals)
1.	The regional geology, mineralogy and geochemistry of the Poços de Caldas alkaline caldera complex, Minas Gerais, Brazil.	SCHORSCHER, Shea.
2.	Mineralogy, petrology and geochemistry of the Poços de Caldas analogue study sites, Minas Gerais, Brazil. I: Osamu Utsumi uranium mine.	WABER, Schorscher, Peters.
3.	Mineralogy, petrology and geochemistry of the Poços de Caldas analogue study sites, Minas Gerais, Brazil. II: Morro do Ferro.	WABER.
4.	Isotopic geochemical characterization of selected nepheline syenites and phonolites from the Poços de Caldas alkaline complex, Minas Gerais, Brazil.	SHEA.
5.	Geomorphological and hydrogeological features of the Poços de Caldas caldera and the Osamu Utsumi mine and Morro do Ferro analogue study sites, Brazil.	HOLMES, Pitty, Noy.
6.	Chemical and isotopic composition of groundwaters and their seasonal variability at the Osamu Utsumi and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.	NORDSTROM, Smellie, Wolf.
7.	Natural radionuclide and stable element studies of rock samples from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.	MacKENZIE, Scott, Linsalata, Miekeley, Osmond, Curtis.
8.	Natural series radionuclide and rare-earth element geochemistry of waters from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.	MIEKELEY, Coutinho de Jesus, Porto da Silveira, Linsalata, Morse, Osmond.

Report No.	Topic	Authors (Lead in Capitals)
9.	Chemical and physical characterisation of suspended particles and colloids in waters from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.	MIEKELEY, Coutinho de Jesus, Porto da Silveira, Deguedre.
10.	Microbiological analysis at the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.	WEST, Vialta, McKinley.

Series B: Predictive Modelling and Performance Assessment

11.	Testing of geochemical models in the Poços de Caldas analogue study.	BRUNO, Cross, Eikenberg, McKinley, Read, Sandino, Sellin.
12.	Testing models of redox front migration and geochemistry at the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.	Ed: McKINLEY, Cross, Haworth, Lichtner, MacKenzie, Moreno, Neretnieks, Nordstrom, Read, Romero, Scott, Sharland, Tweed.
13.	Near-field high-temperature transport: Evidence from the genesis of the Osamu Utsumi uranium mine, Poços de Caldas alkaline complex, Brazil.	CATHLES, Shea.
14.	Geochemical modelling of water-rock interactions at the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.	NORDSTROM, Puigdomènech, McNutt.

Summary Report

15.	The Poços de Caldas Project: Summary and implications for radioactive waste management.	CHAPMAN, McKinley, Shea, Smellie.
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1. Introduction

This report summarises measurements of the concentrations and activities of natural series radionuclides and rare-earth elements (REEs) in near-surface and deep groundwaters of the Osamu Utsumi uranium mine and the Morro do Ferro ore deposit, obtained from samples collected between December 1986 and April 1989. The data were intended to improve the general hydrogeochemical understanding of the behaviour of these elements (and of their transuranic analogues) in a natural environment and to assist in achieving other Project objectives mentioned in the Preface. This report concentrates on general observations regarding the aqueous behaviour of uranium, thorium and the rare-earth elements in both environments.

Data on the concentrations of these elements in waters from the Osamu Utsumi mine were practically non-existent at the beginning of the Project. The Th-REE occurrence at Morro do Ferro had been investigated some years earlier with natural analogue and other objectives in mind (Eisenbud *et al.*, 1982 and 1984; Lei, 1984; Miekeley *et al.*, 1982 and 1985; Lei *et al.*, 1986 and Linsalata *et al.*, 1989). However, data on natural series and rare-earth elements in waters have pertained mainly to surface waters of the South Stream (see Fig. 5). This stream represents the major drainage route of water from Morro do Ferro, carrying both storm-water runoff from the highly mineralised southern flank of the hill as well as groundwater from seepage points near the hill's base, also on the southern flank (Eisenbud *et al.*, 1982 and 1984).

Based on the mean concentrations of the elements reported in Table I and on the annual mean discharge during baseflow periods (which accounts for about 85% of the total discharge via the South Stream), the annual transport of these elements in dissolved form (<450 nm) has been shown to be extremely limited, resulting in very small fractional mobilisation rates in terms of the fraction of the total elemental inventories in the ore body per year (Eisenbud *et al.*, 1982 and 1984; Lei *et al.*, 1986 and Campos *et al.*, 1986). The earlier studies thus concluded that the various hydrothermally altered and weathered mineral constituents composing the hill effectively retained or otherwise retarded the transport of Th and the REEs away from the ore body.

The studies performed at Morro do Ferro were focused on obtaining groundwater concentrations of the U/Th decay series elements and the REEs in a series of newly drilled boreholes located at various distances from the mineralisation zone and mechanically packed-off at various depths along the hydraulic gradient (Fig. 5). This was done in the hope of observing real concentration gradients, which could be analysed with

respect to the processes acting to promote or retard element migration (in dissolved, colloidal or particulate forms) along the flow-path.

TABLE I

Concentrations of Th, La, Ce and ^{228}Ra in the South Stream baseflow in data collected from 1981–1982.

Element	Mean filtrate concentration ($\mu\text{g/l} \pm \text{SD}$)	(N)	Annual solution transport ⁽⁴⁾ (tonnes a^{-1})
Th ⁽¹⁾	0.053 ± 0.013	(55)	2.5×10^{-5}
La ⁽¹⁾	0.31 ± 0.04	(17)	1.5×10^{-4}
Ce	0.81 ± 0.09	(17)	3.8×10^{-4}
U ⁽³⁾	0.30 ± 0.18	(43)	1.5×10^{-4}
^{228}Ra (mBq/l) ⁽²⁾	62.9 ± 3.7	(13)	3×10^7 (Bq y^{-1})
$^{234}\text{U}/^{238}\text{U}$	1.26 ± 0.05	(43)	–

¹Eisenbud *et al.* (1984).

²Campos *et al.* (1986).

³NYUMC (unpublished data). Samples collected from various locations in the South Stream between 6/80 and 6/81.

⁴Based on an annual average baseflow of 1300 m^3 per day.

SD = Mean standard deviation.

The scarcity of reliable literature data on thorium and rare-earth elements in natural waters (e.g. Langmuir and Herman, 1980) is partially due to analytical difficulties encountered in the determination of these elements at trace or ultra-trace levels. For this reason, the different experimental methods used throughout this study will be presented in detail.

This report is closely related to Miekeley *et al.* (this report series; Rep. 9), in which the interactions of U, Th and the REEs with particulate (>450 nm) and colloidal (1.5 to 450 nm) phases are discussed. Due to the fact that the chemistries of “solutes” and “solids” are determined by their mutual interaction, no strict separation between these topics can (or should) be made. Some repetition in the presentation of the data was therefore unavoidable.

2. Site descriptions and water characteristics

2.1. Geological setting

The Osamu Utsumi uranium mine and Morro do Ferro analogue sites are situated near the centre of the Poços de Caldas Plateau in the State of Minas Gerais, Brazil, about

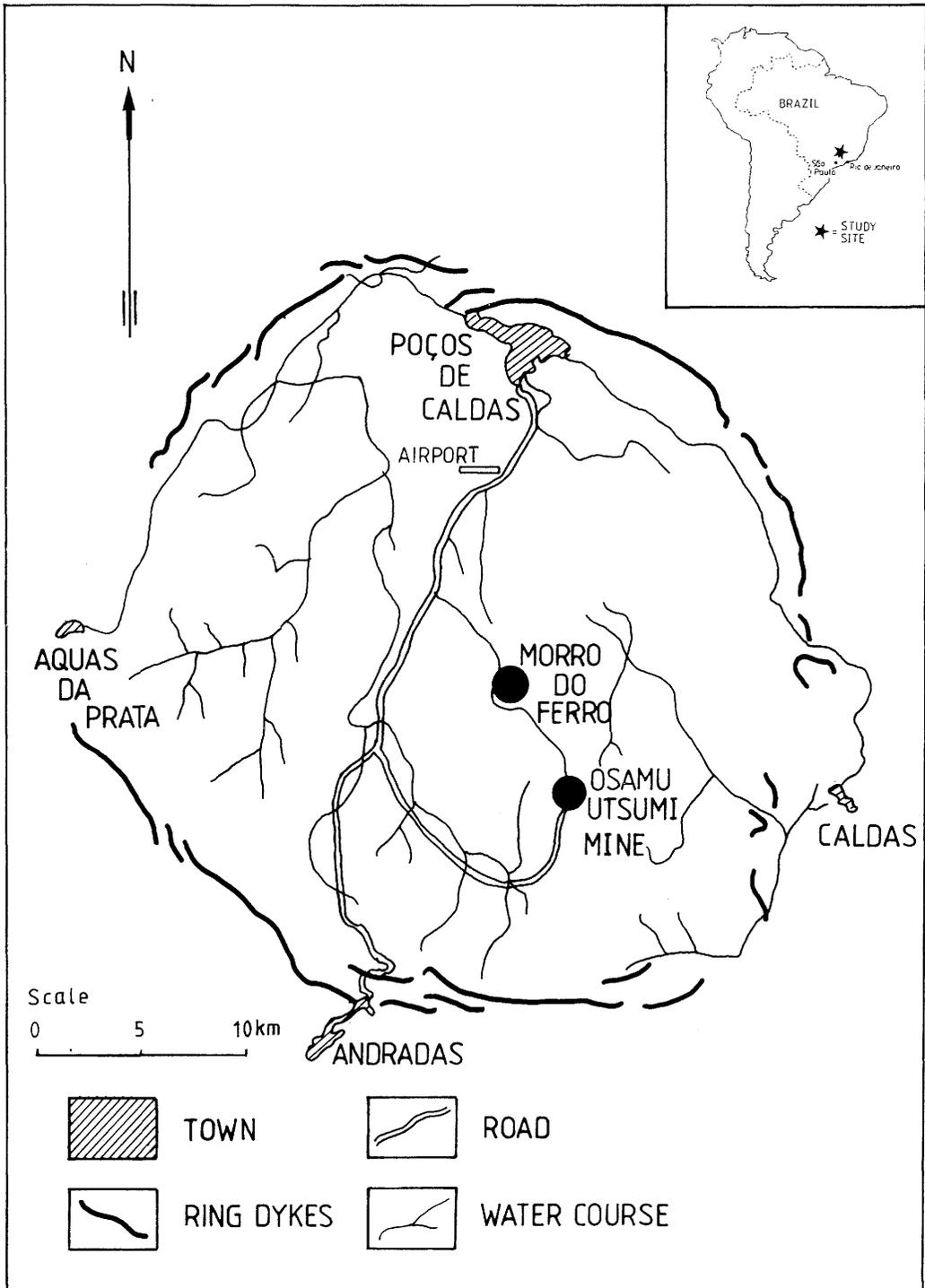


Figure 1. Location of the Osamu Utsumi uranium mine and the Morro do Ferro analogue sites within the Poços de Caldas plateau.

20 km from the city of Poços de Caldas (Fig. 1). The Plateau is believed to be the result of volcanic processes, which occurred about 60 to 80 Ma ago (Bushee, 1971) when igneous alkaline rocks intruded into the Precambrian basement, with subsequent collapse of the central part forming a circular, cauldron-like structure about 35 km in diameter (Schorscher and Shea, Waber *et al.*, Waber and Shea, this report series; Reps. 1-4). Surrounding mountains are 1600 – 1800 m above sea-level and the base of the caldera varies between 900 and 1540 m above sea level. A complex network of faults, fractures and mineralisation zones was formed, generating different radioactive anomalies and mineral deposits (Frayha, 1962; Wedow, 1967) such as the Osamu Utsumi uranium mine and the Morro do Ferro Th-REE deposit.

The local climate is characterised by a dry season (February to August) and a rainy season (October to March). During the rainy season about 80% of the mean annual precipitation (about 170 cm per year) occurs (Holmes and Pitty, this report series; Rep. 5). The precipitation record between 1986 – 1988 is shown in Figure 6.

2.2. The Osamu Utsumi uranium mine: some geological, hydrogeological and geochemical aspects

Deep groundwaters at the uranium mine were sampled predominantly from five reference boreholes of intermediate to greater depth (F1 to F5) and from three shallow boreholes (SW01 to SW03). The locations of these boreholes and their relationship to the local geology, hydrogeology and geochemistry are shown in Figures 2 to 4; some characteristics of the boreholes are summarised in Table II. Additional water sampling was carried out at a piezometer station (PM-22), a flooded mine shaft (Figs. 2 and 3) and at a local reservoir (supply dam) used for water storage following surface accumulation in the mine area during the rainy period.

Analyses of core samples have shown that the bedrock of the mine area is composed predominantly of phonolites and tinguaites which underwent alteration by hydrothermal processes and continuous weathering (Waber *et al.*, this report series; Rep. 2). Characteristic distribution patterns of uranium and some other elements (e.g. Mo and Fe³⁺) developed along redox fronts, which were formed by the downward action of percolating, oxidising waters. Oxidised phonolites/tinguaites are characterised by low sulphide contents (mean [S]: 38 ppm), abundant ferric minerals (hematite, goethite, lepidocrocite, etc.), high concentrations of K-feldspars (50%) and clay minerals (45%), and by minor amounts of accessory minerals (e.g. apatite, zircon). Reduced

TABLE II

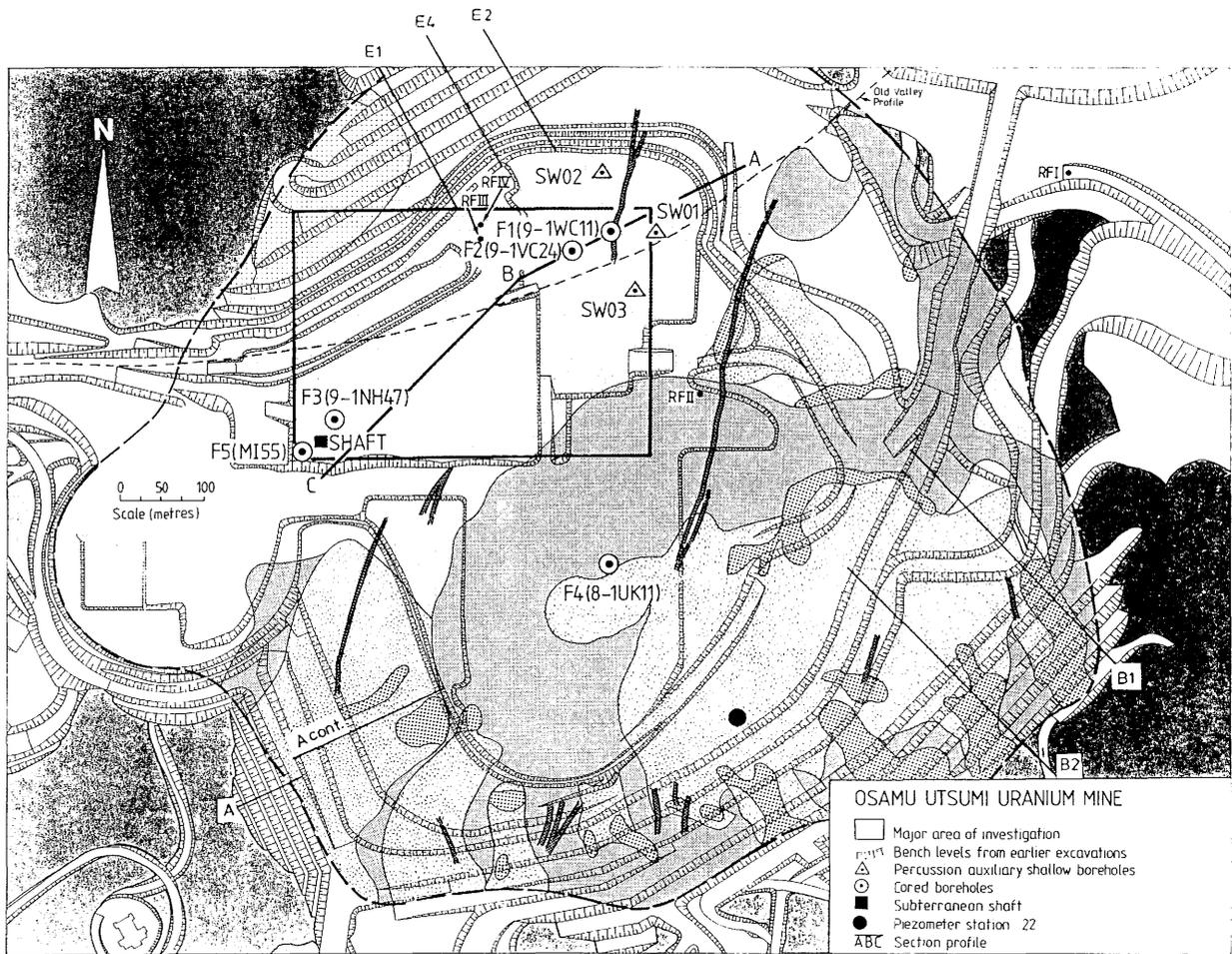
Hydrogeological character of the reference groundwater sampling locations used in this study.

Borehole	Sampled section (metres)	Start of sampling	Main groundwater source
Osamu Utsumi study site			
SW01 SW02 SW03	3–12	Dec/87	Mixing of groundwater from depth with that recently derived from rainfall and flowing at shallow levels.
F1	96–126	Nov/86	From a zone of high conductivity at approx. 110 m; bedrock is porous but not fractured.
F2	45–60	Dec/86	From the borehole section as a whole; conductivity is low and uniform.
F3	50–80	Feb/88	From near the hole bottom (65–80 m) where conductivity is moderately high and uniform.
F4	75–175	Apr/88	From several fracture zones of high conductivity.
F5	275–300	Nov/88	From fracture zone(s) of high conductivity.
Morro do Ferro study site			
MF10	50–74	Dec/86	High hydraulic gradient around the bottom of the borehole.
MF11	30–40	Jan/88	Recharge from the top of the saturated zone.
MF13	60	Dec/88	Recharge from the top of the saturated zone.
MF12	45–71	Jul/87	Zone of low hydraulic conductivity, near-vertical discharge.

NOTE: All boreholes are vertical apart from F4. Although borehole F4 is 415 m long, its vertical extent is only to 175 m depth.

phonolites/tinguaite are typically composed of 62% feldspars, 33% clay minerals, and minor amounts of fluorite and barite. The reduced rocks have generally higher uranium contents (as pitchblende) which are associated with pyrite inclusions (mean [S]: 1.2%). Intersection of these redox fronts occurs at various depths within the boreholes (see Figs. 3 and 4). The mobility and local concentrations of uranium in the rock are controlled by these fronts which are rich in potential scavengers (e.g. Fe(III) oxyhydroxides).

The groundwater flow direction is upwards at the mine site. Hydrogeological studies at the mine, when combined with other information (e.g. topography) obtained prior to



- Limit of mapped area
- (Oldest)
- ▨ Subvolcanic phonolite with very weak hydrothermal alteration; no pyrite impregnation.
 - ▨ Mainly subvolcanic & minor volcanic phonolites, fractured if near 4.
 - ▨ Abyssal & hypabyssal intrusive nepheline syenites (intrusive in 1); fractured if near 4.
 - ▨ Subvolcanic pseudoleucite phonolites (intrusive in 1 and 2); fractured if near 4.
 - ▨ Subvolcanic conduit breccia, locally grading to extremely xenolithic ultra-fine-grained, flow-textured phonolites.
 - End of major hydrothermal event (formation of "potassic rock" and U-Mo-Zr-REE-pyrite hydrothermal mineralisations).
 - (Youngest)
 - ▨ Biotite-lamprophyre dykes (late-stage intrusive).
- RFI, II, III, IV Location of redox fronts for detailed investigations.
- E1, E2, E4 Vertical profiles in ore body 'E'.
- B1, B2 Vertical profiles in ore body 'B'.
- A Vertical profiles in ore body 'A'.

Figure 2. Location map of the principal boreholes at the Osamu Utsumi mine.

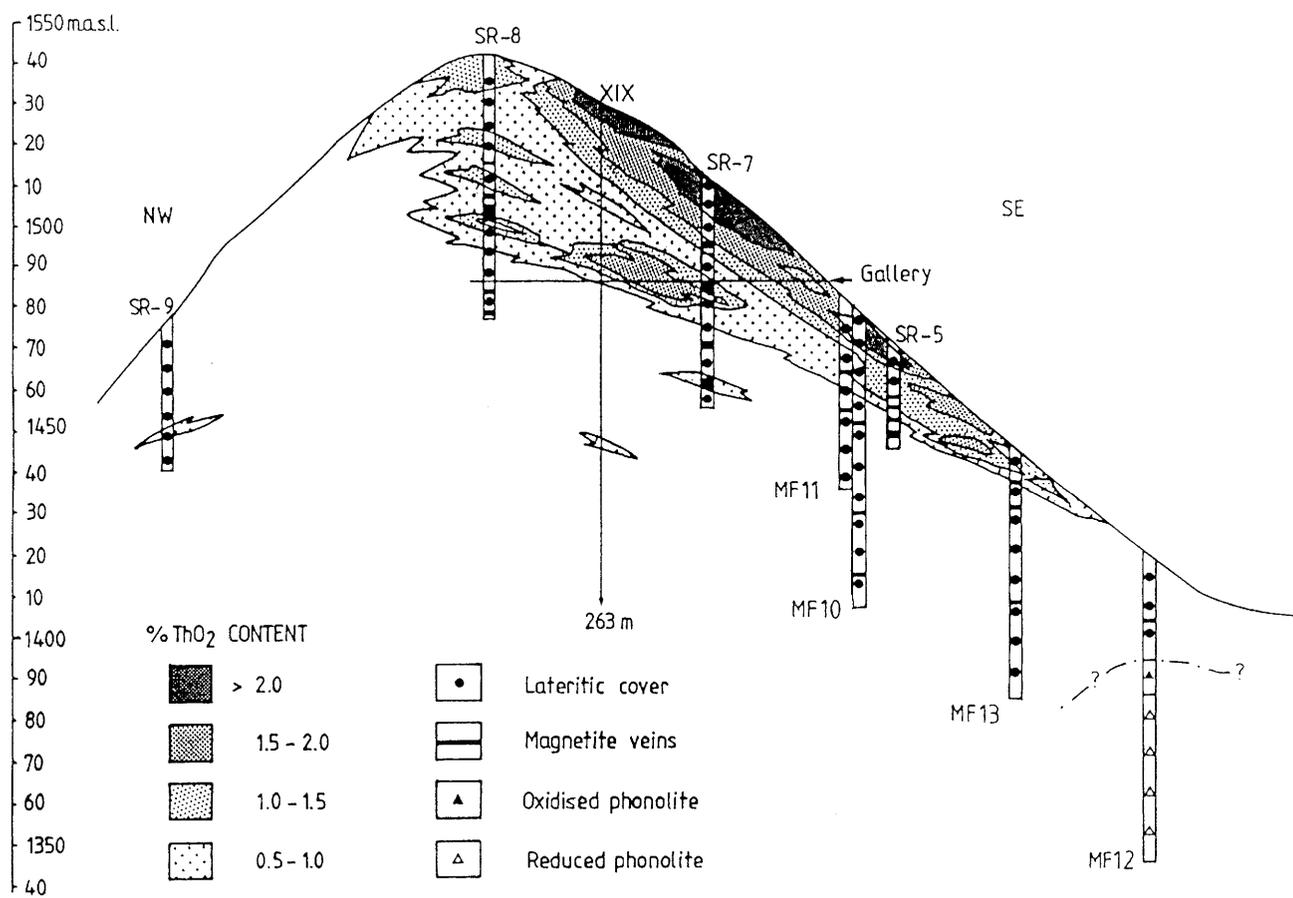


Figure 3. Cross-section of the Osamu Utsumi mine (section ABC; Fig. 2) showing borehole locations, redox fronts, mineralised zones, groundwater reference sampling points and the general direction of groundwater flow.

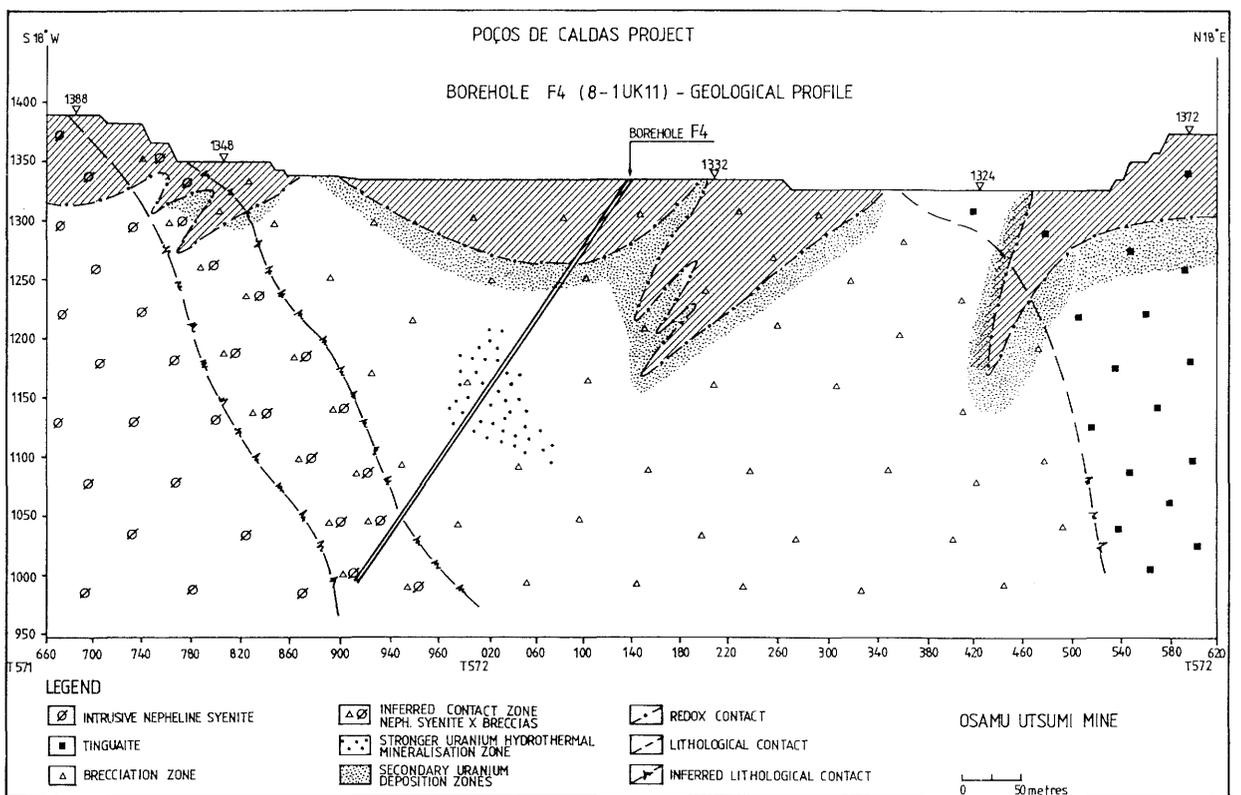


Figure 4. North-south cross-section of the Osamu Utsumi mine showing the relationship of borehole F4 with the breccia pipe and associated uranium mineralisation.

mining operations, permitted the construction of 3-dimensional computer flow models of the situation before and after mine excavation (Holmes *et al.*, this report series; Rep. 5). These models indicate that mine excavation has increased hydraulic gradients and modified flow directions, without drastically changing the vertical flow patterns. Hydraulic conductivities around boreholes F1 to F3 are in the order of 10^{-7} to 10^{-6} m/s, indicating a highly fractured and porous structure for the rock. Zones of higher conductivity are present in borehole F1 between 97 and 124 m and in borehole F3 between 65 and 71 m.

Most groundwaters from the uranium mine can be classified as the 'K-Fe-SO₄' type of oxidising, slightly acidic capacity, and are the result of intense leaching of highly weathered K-rich rock masses (Nordstrom *et al.*, this report series; Rep. 6). Typical groundwater chemical parameters (concentrations in mg/l, except for U, Th and REEs which are in µg/l) are:

[Si]= 13-15, [K]=10-13, [Na]=0.1-1, [Ca]=0.5-2, [Ba]=0.10-0.15, [Sr,Mg]= <0.1, [Fe(tot) and Fe(II)]=0.6-2, [Mn]=0.1-0.3, [U]=4-15, [Th]=0.03-0.07, [ΣREE]=5-40, [SO₄]=10-20, [HCO₃]=8-20, [F]=0.3-2.4, [HPO₄]= ≤0.05, pH= 5.4-6.1 and Eh= +(200-400) mV. [DOC] in the groundwater is low (1-3 mg/l) due to the very scarce vegetation in the mine area. Additional water data are summarised in Tables IX and XIII.

2.3. The Morro do Ferro Th-REE-deposit: some geological, hydrogeological and geochemical aspects

Morro do Ferro (Figs. 1 and 5), which lies 6 km NNW from the uranium mine, is a hill in an advanced state of weathering rising about 140 m above its base. Near the summit is an ore body estimated to contain about 30,000 t of Th, about 33,000 t of La, 49,000 t of Ce, 17,000 t of Nd and about 400 t of U (Frayha, 1962; Linsalata *et al.*, 1989). Secondary enrichment of Th and REEs by weathering and preferential leaching of uranium by percolating oxidising waters are considered as the most probable processes for the pronounced elemental fractionation (Waber and MacKenzie *et al.*, this report series; Repts. 3 and 7). Compared to the uranium mine, Morro do Ferro is in a much more advanced state of weathering; this fact is primarily responsible for a more homogeneous groundwater flow pattern through the deposit.

Although several host minerals for Th and the REEs have been identified (e.g. monazite, cheralite, zircon, thorite), the bulk occurs as sorptions onto clay minerals and hydrous oxides of Fe(III) and Al (probably associated with humic compounds).

Figure 5 is a cross-section through Morro do Ferro showing the water sampling locations and the expected rainwater percolation pathway through the unsaturated and the saturated zones. The boreholes (MF10, MF11, MF12 and MF13) are situated within a magnetite breccia and form a profile which extends from about 50 m below the summit of the hill (MF11) to its base (MF12) and is bounded on both sides by massive magnetite dykes. It is believed that this brecciation zone represents the most conductive part of the deposit and that the boreholes lie along a distinct groundwater flow-path. Hydraulic conductivities are typically in the range of 10^{-7} to 10^{-5} m/s for the weathered zone of laterite and clays, down to 10^{-9} m/s for the unweathered bedrocks near the surface at MF12 (phonolites) (Holmes *et al.*, this report series; Rep. 5).

Information on the groundwater compositions at Morro do Ferro is less detailed than for the Osamu Utsumi uranium mine (Table XVIII). For borehole MF10, which cuts the region of highest Th and REE mineralisation, significantly lower concentrations of major elements (Na, K, Fe) and potential complexing anions (F^- , HCO_3^- , SO_4^{2-}) are found when compared to MF12 or the Osamu Utsumi mine groundwaters, indicating that this water is representative of the highly leached, unsaturated zone of the deposit. The compositions of groundwaters from borehole MF12 are very similar to those of the uranium mine, reflecting the similarity of the bedrock (reduced phonolites). However, when compared with groundwaters from boreholes F1 and F2 (Osamu Utsumi mine), higher concentrations of fluoride and manganese are present in the MF12 waters.

Dissolved organic carbon (DOC) in groundwaters from Morro do Ferro is low (1 to 4 mg/l) due to the scarce vegetation in the deposit area, the intense rainfall during the summer season which favours the leaching of humic matter, and as a result of sorption of these compounds by clays and other adsorbing materials during downward percolation of water (supported by laboratory experiments by Coutinho de Jesus, 1989). From the piezometer holes and shallow percolation waters collected from the gallery (Fig. 5), much higher concentrations of DOC, mainly as humic acids, were occasionally observed. A compilation of some major and trace element concentrations, as well as of the corresponding pH-Eh data of waters from Morro do Ferro, is presented in Table XV and illustrated in Figure 22.

MORRO DO FERRO

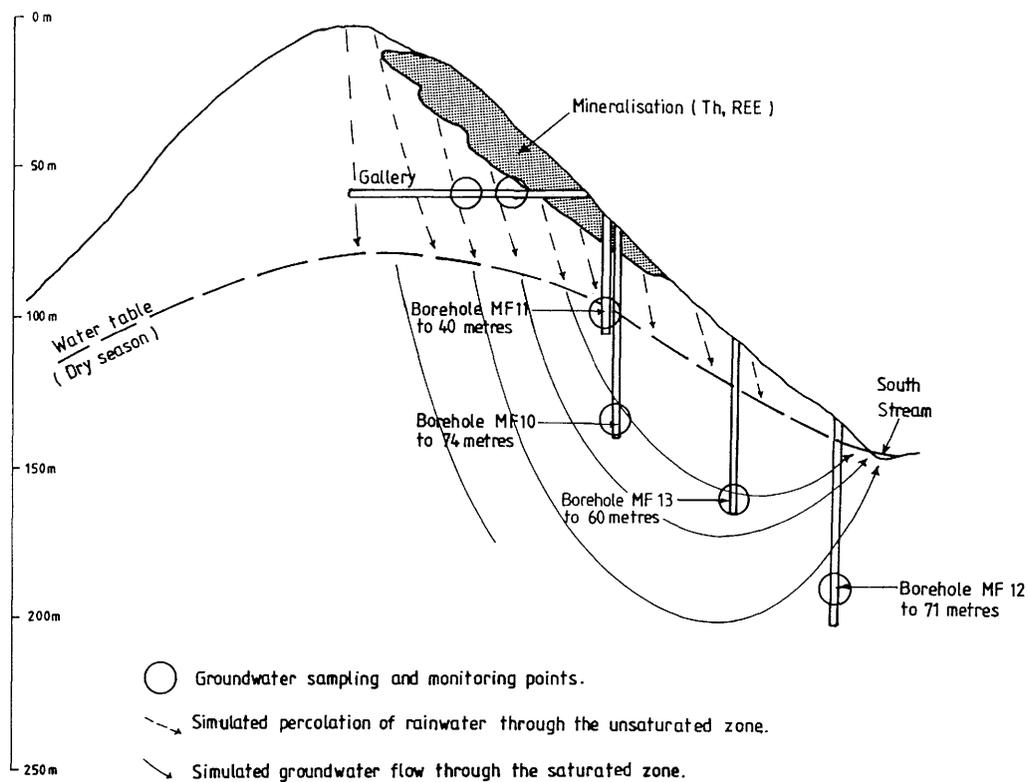


Figure 5. Cross-section of Morro do Ferro illustrating the water sampling locations, the mineralisation zone, and the simulated near-surface percolation and groundwater flows.

3. Materials and methods

3.1. Water sampling and preconcentration procedures

Water sampling at both sites was conducted during the dry, rainy and transitional periods (Nordstrom *et al.*, this report series; Rep. 6). Sampling frequency was quarterly, to coincide with the large seasonal fluctuations illustrated in the subequatorial precipitation pattern shown in Figure 6. With the exception of boreholes SW01 to SW03, PM-22, UC16 and PZ2 (PZ2 from Morro do Ferro), all other boreholes were mechanically packed-off using the double packer technique so that water from a precisely defined depth interval could be collected. Normally a submersible electric pump was used; however, due to the artesian properties of the boreholes F1 and F2 (Osamu Utsumi mine) during the rainy seasons, direct sampling of the outflowing waters could be carried out on these occasions. Prior to sampling, the boreholes were flushed by pumping for at least a few hours, preferably overnight, in order to minimise the effects of adsorptive loss, organic contamination by the plastic casings of the boreholes, and “aging” of the waters. For flushing and sample collection, pumping was done at low rates (<200 ml/min) to avoid “draw-down” of younger waters and to minimise particle disaggregation. An in-line prefilter (Millipore HA, 450 nm; surface area 154 cm²) was used to separate the suspended particle fraction (>450 nm). The prefilters were air-dried and conditioned for further analyses. Eh, pH, DO (dissolved oxygen), S, Fe(tot), Fe(II), temperature and conductivity were monitored routinely at the site. Normally samples of 20 to 40 litres of the prefiltered water were collected in polyethylene containers, to which a sufficient quantity of HCl or HNO₃ was added to acidify the samples to pH <2. The samples were then transported back to the laboratory in Poços de Caldas on the day of collection. In the initial phase of the project, acidification of the samples was done in the laboratory. Volume reduction of the samples to about 500 to 800 ml was performed by evaporation in 5-litre glass beakers in a fume hood. The concentrates, together with precipitated solids, were carefully transferred with deionised and distilled water and small volumes of acid (p.a. HCl or HNO₃) into 1-litre polyethylene bottles and then sent to the analysing laboratories at the New York University Medical Center (NYU) and the Pontifical Catholic University (PUC).

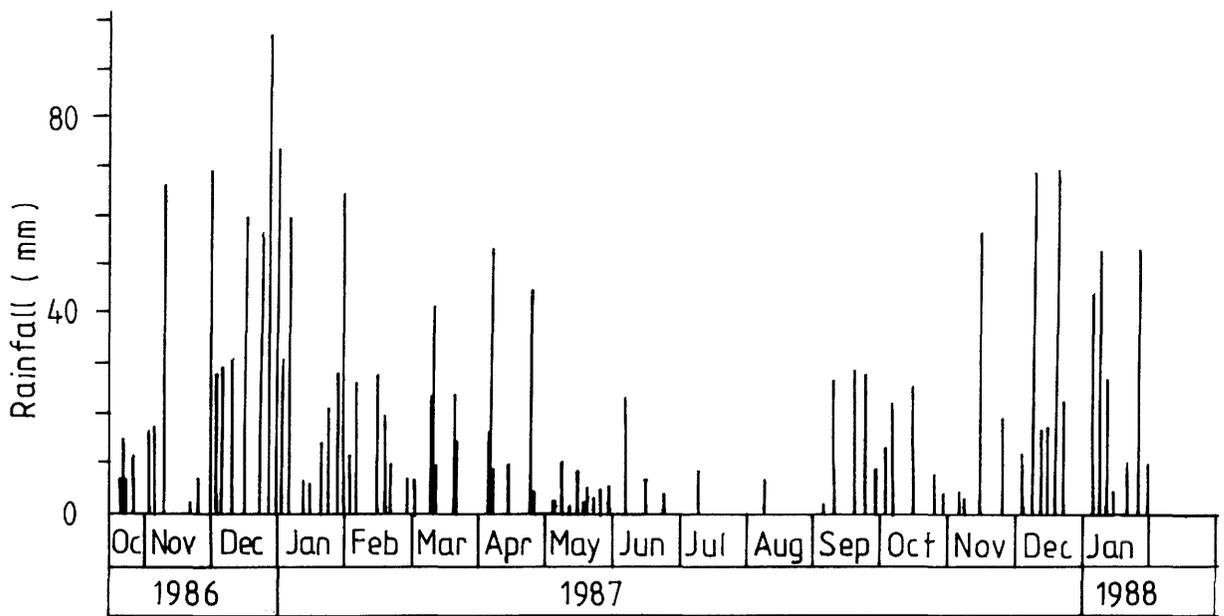


Figure 6. Rainwater precipitation for the investigated area recorded from October 1986 to January 1988.

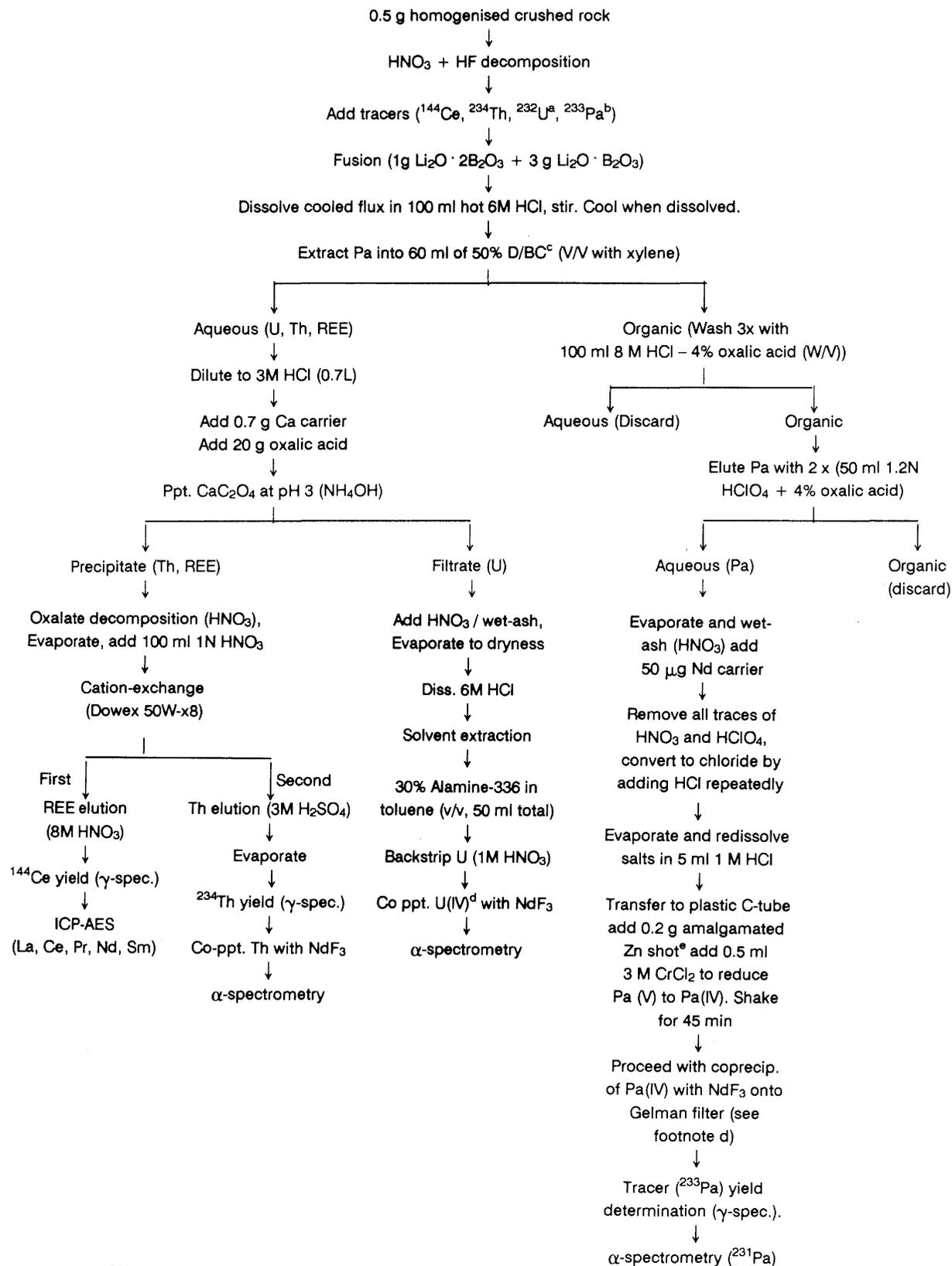
3.2. Analytical methods for the determination of U, Th and the REEs in waters

Throughout this work different preconcentration and instrumental methods have been used for the determination of U, Th and the REEs, for example solvent extraction, coprecipitation, ion-exchange, alpha spectrometry (U, Th), fluorometry (U, Th) and inductively coupled plasma source atomic emission spectroscopy (ICP-AES) (Th, REEs). The analytical protocols for these methods, used by the NYU and PUC laboratories, have been described previously (Silveira, 1986; Linsalata *et al.*, 1987; Miekeley *et al.*, 1987; Coutinho de Jesus, 1989). Therefore, only a brief discussion of the procedures will be presented here.

3.2.1. The New York University Medical Center (NYU) procedure

The procedure used by this group for waters is similar to that shown for the analyses of rock samples (Fig. 7), except for the initial step of sample preparation. Briefly, the sample concentrate is filtered and the collected insoluble matter (mostly precipitated silica) is dissolved using HNO_3/HF , before recombining with the filtrate. Yield tracers (^{234}Th , ^{232}U free of ^{228}Th , and ^{144}Ce) are then added and the solution evaporated and wet-ashed to remove organics. Sufficient ^{234}Th (determined by high resolution gamma spectroscopy) is added such that the contribution of naturally ingrown ^{234}Th from ^{238}U decay is limited to $<1\%$. The remaining salts are dissolved in 3M HCl and Th and the LREEs separated from U by coprecipitation with Ca-oxalate at pH 3. U(VI) does not precipitate under these conditions; it remains in the filtrate, which is reserved for solvent extraction using Alamine-336 in toluene. Thorium and the LREEs are separated by cation-exchange using BioRAD AG 50W X8 resin. Following ^{144}Ce yield determination using High Purity Ge γ -spectrometry (HPGe), the LREEs are then assayed sequentially by ICP-AES. Detection limits (95% confidence interval) range from 0.8 (La and Sm) to 5.0 (Nd) $\mu\text{g}/\text{sample}$. Lower limit of detection (LLD) for U and Th isotopes using alpha spectrometry range between 0.4 and 1.5 mBq/sample with spectrum resolution (Full Width at Half Maximum; FWHM) typically between 50 and 80 keV using a NdF_3 micro-coprecipitation technique (Sill and Williams, 1981).

Following alpha spectrometric determination of Th-isotopes, the coprecipitated Th was then redissolved and assayed again by a fluorometric technique (modified from Sill and Willis, 1962). This alternative procedure was preferred as a result of the failure in many samples to achieve good baseline restoration of the ^{232}Th alpha peak at 4.03 MeV because of tailing from the higher energy alpha emissions of ^{228}Th . The ^{228}Th tailing effect



^a Self-cleaning ²³²U tracer is used (i.e. no ²²⁸Th present).

^b ²³³Pa tracer prepared and purified from its ²³⁷Np parent.

^c Diisobutylcarbinol (DIBC).

^d U(VI) reduced to U(IV) with 10 drops TiCl₃ prior to coprecipitation as the fluoride (Sill and Williams, 1981).

^e The amalgamated Zn serves to keep the Cr reduced and presents a surface for the spontaneous deposition of ²¹⁰Po, which can cause spectral interference with ²³¹Pa.

Figure 7. Analytical flow-sheet for the determination of Th, U, Pa and REEs in core samples (and, with minor modifications, also in waters) used by the NYU laboratory.

was most pronounced in those samples in which the $^{228}\text{Th}/^{232}\text{Th}$ ratios exceeded 100 and peak resolution was greater than 75 keV (see also Miekeley *et al.*, 1987). Severe disequilibrium was due in part to long delay times between sampling and radiochemical analysis, allowing for substantial ingrowth of ^{228}Th from ^{228}Ra decay. Because ^{228}Ra was not determined, ingrowth corrections could not be made and ^{228}Th data are therefore omitted in most of the tables. Although standard estimates of ^{232}Th concentrations by both techniques are reported for most of the samples, the fluorometric results are believed to be more accurate and were generally recorded with greater precision. ^{230}Th concentration estimates are affected to a greater extent by the tailing problem than those for ^{232}Th , which resulted in many non-reportable or “less than” results for this isotope.

As part of the NYU quality assurance programme, full-process, traced reagent blanks were run with each batch of four to six samples. Net reagent blank values, instrument backgrounds and yield estimates were included in all concentration calculations and their associated uncertainties propagated to arrive at the reported total uncertainties, expressed as +/-2 Standard Deviation (SD). Unknowns are processed semi-annually as part of an externally administered quality assurance programme coordinated by the U.S. Department of Energy (DOE). The results reported in Table III indicate reasonable agreement for both ^{238}U and $^{234}\text{U}/^{238}\text{U}$ based on continued interlaboratory comparisons using DOE-prepared water samples. Although standards (IAEA Peruvian Soil, Soil 5) are routinely processed for U, Th and the LREEs in a solid matrix (see MacKenzie *et al.*, this report series; Rep. 7), no standards (other than those solutions used for calibration) were obtainable for Th and the LREEs in water.

TABLE III
NYU quality assurance results on water.

Sample	Certified contents (Bq/l \pm 2SD)*		Measured contents (Bq/l \pm 2SD)	
	^{238}U	$^{234}\text{U}/^{238}\text{U}$	^{238}U	$^{234}\text{U}/^{238}\text{U}$
WANY-8606	1.22 \pm 0.14	1.00 \pm 0.15	1.55 \pm 0.14	1.00 \pm 0.14
WANY-8705	2.63 \pm 0.30	1.00 \pm 0.15	2.55 \pm 0.22	0.90 \pm 0.12
WANY-8905	0.163 \pm 0.016	1.02 \pm 0.15	0.137 \pm 0.015	1.00 \pm 0.076

*Measured by the US DOE. (Environmental Measurements Laboratory) as part of their quality assurance programme (QAP).

3.2.2. The Pontifical Catholic University (PUC) procedure

In this procedure (flow-sheet in Fig. 8), the water concentrate, including the precipitated portion, is wet-ashed first with a mixture of HF-HNO₃-HClO₄ and then with H₂O₂-HNO₃. The residue is then dissolved in 20 to 50 ml of HNO₃ (1M) and an aliquot is traced with ²³⁴Th and ²³²U. Thorium, together with uranium and some other elements, is extracted with 10 ml of Tri-n-octyl phosphine oxide (TOPO) in cyclohexane (0.1 M). Under these conditions, the REEs (including Ce, which is now in the trivalent state), together with other major and trace elements, are retained in the aqueous phase. The organic phase is washed with 10 ml of HNO₃ and the washing solution recombined with the aqueous phase (REEs). Uranium can be determined in small aliquots of the organic phase (100 μl) by a standard fluorometric technique using NaF-LiF beads. This method has an LLD of 0.002 μg per bead or about 0.01 μg/l for a 20-litre processed water sample (Coutinho de Jesus, 1989). Thorium (together with a small fraction of U) is then quantitatively re-extracted with three times 10 ml of H₂SO₄ (0.3 M). From this solution, thorium can be directly coprecipitated with LaF₃ (50 μg) and separated by a membrane filter (0.2 μm), where previously 100 μg of LaF₃ have been deposited to enhance spectrum resolution. The small fraction of the re-extracted U(VI) does not coprecipitate under these conditions. The beta or gamma counting rate of ²³⁴Th can be used to determine the overall chemical recovery. The filters are measured by alpha spectrometry with surface barrier detectors (300 or 450 mm² nominal area) and their ²³²Th activities assayed by comparison with standard filters, prepared by direct coprecipitation of thorium. Energy resolution (FWHM) of the ²³²Th peak is <80 keV, counting efficiency between 15 and 20% and detector/blank background typically between 1 to 4 counts in the peak area in 4 x 10⁴ s. For a 20-litre water sample without “background” interference from ²²⁸Th (see section 3.2.1 and Miekeley *et al.*, 1987), the LLD for ²³²Th is 0.015 μg/l, but can be increased by a factor of four or more in samples with high ²²⁸Th/²³²Th ratios (>100). Table IV shows the results of replicate ²³²Th analyses of a surface water sample from Morro do Ferro obtained by this method and a slightly modified NYU method (Vale, 1982), which indicates that both procedures give reproducible (replicate SD about 11%) and similar concentrations (deviation of the mean values <20%). Figure 9b shows an alpha spectrum of Th-isotopes obtained by the PUC method (sample GW-73).

For water samples with high ²²⁸Th/²³²Th activity ratios, an alternative method was developed for the determination of ²³²Th (Miekeley *et al.*, 1987), which is based on ICP-AES. The membrane filter used for alpha counting is calcined in a platinum crucible and the residue wet-ashed with a few drops of HNO₃-HF-HClO₄, which are then

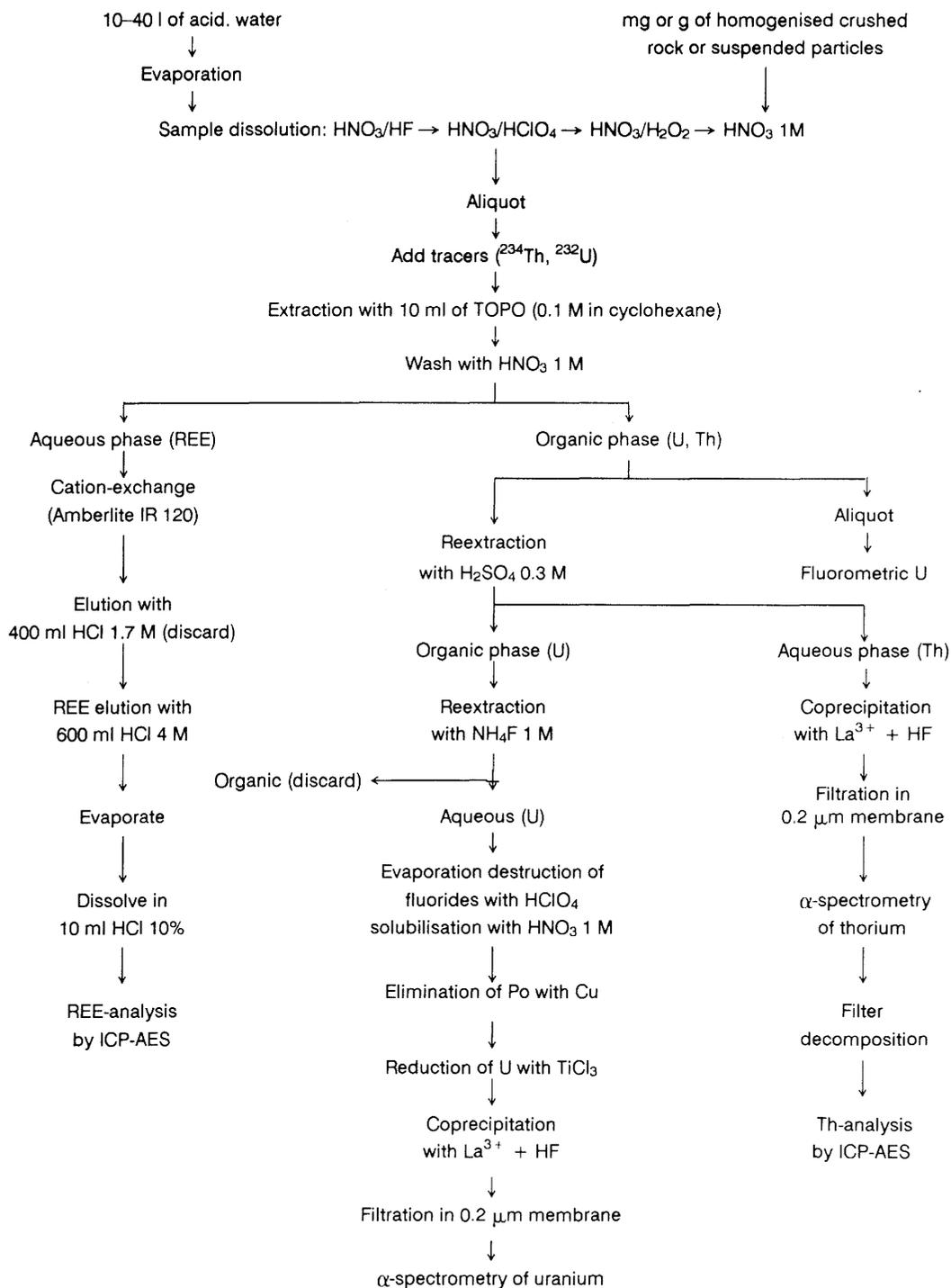


Figure 8. Analytical flow-sheet for the determination of Th, U and REEs in waters and suspended particles used by the PUC laboratory.

evaporated to dryness. The residue is redissolved in 1.0 ml of cold HNO₃ (1 M) by use of an ultrasonic bath and 200 µl of this solution are injected into an ICP using a Babington (GMK)-type nebulizer connected to a peristaltic pump and a small Teflon cup. The analog signal from the emission peak (Th II: 439.1 nm) is registered by a line recorder. Contrary to other possible coprecipitants for thorium (NdF₃, CeF₃), LaF₃ causes no spectral interference with the Th-line and was therefore preferred in this work. The equipment used was a 2 m Paschen-Runge Spectrometer (Analymat 2502 RSV) optically coupled to a Kontron 1000 ICP-source. The practical LLD for this method is 0.25 µg of Th per filter (0.05 µg injected into the plasma), which corresponds to about 0.016 µg/l for a 20-litre processed water sample. Filter dissolution plus micro-injection procedures are very reproducible and have a replicate SD of typically 3%. A comparison of results obtained by alpha spectrometry and micro-injection ICP-AES on samples of water and suspended particles is shown in Table IV.

TABLE IV
PUC quality assurance results on thorium analysis in water and suspended particles.

Sample		²³² Th (µg/l ± 1SD)	
		α-spectrometry	Modified Sill method* ICP-AES
	aliquot		
	1	0.073 ± 0.009	0.064 ± 0.010
	2	0.083 ± 0.009	0.064 ± 0.004
South	3	0.083 ± 0.012	0.050 ± 0.009
Stream	4	0.065 ± 0.012	0.074 ± 0.009
	mean	0.076 ± 0.009	0.063 ± 0.010
PC-GW-39		79 ± 5	81 ± 4
PC-GW-47		36 ± 3	34 ± 2
PC-GW-56		0.094 ± 0.008	0.12 ± 0.01
PC-GW-59		0.071 ± 0.008	0.11 ± 0.01
PC-GW-71		0.49 ± 0.05	0.35 ± 0.02
PC-GW-72		0.13 ± 0.01	0.16 ± 0.01
PC-GW-73		0.10 ± 0.01	0.13 ± 0.01
SP-GW34**		74 ± 4	90 ± 5
SP-GW35**		1270 ± 30	1390 ± 70

* Vale, 1982

** Values in µg/g ± 1SD

Uranium is re-extracted from the TOPO/cyclohexane phase three times with 10 ml of NH_4F and the combined solutions evaporated to dryness in a Teflon beaker. The residue is decomposed with $\text{HNO}_3\text{-HClO}_4$, dissolved with 10 ml of H_2SO_4 (0.3 M), dried again and finally redissolved in 10 ml of H_2SO_4 (0.3 M). ^{210}Po is removed by spontaneous deposition onto Cu-chips. After addition of the lanthanum carrier (similar to the Th-procedure), U(VI) is reduced by a few drops of TiCl_3 and then coprecipitated as U(IV) with LaF_3 by HF (see Fig. 8). Overall efficiency is obtained from the recovered activity of ^{232}U . Alpha spectrum resolution for ^{238}U is between 80 and 100 keV and the LLD about 0.01 $\mu\text{g/l}$.

The method is routinely checked by analyses of standard U-solutions and reference rock samples (IAEA S-2, S-4). Results showing the accuracy of the method are summarised in Table V and a representative alpha spectrum of a groundwater sample is shown in Figure 9a.

TABLE V

PUC quality assurance results on uranium isotopic and ^{230}Th analysis in a reference rock sample (S-2-IAEA).

Analysis	date	^{238}U	^{234}U	^{230}Th	^{234}U	^{230}Th
		(Bq/g \pm 1SD)			^{238}U	^{234}U
1	9/26/86	33 \pm 2	32 \pm 2	31 \pm 1	0.98 \pm 0.07	0.97 \pm 0.06
2	3/11/87	32 \pm 1	35 \pm 2	28 \pm 1	1.09 \pm 0.07	0.80 \pm 0.04
3	6/04/87	33 \pm 2	34 \pm 2	29 \pm 1	1.03 \pm 0.08	0.87 \pm 0.06
4	8/10/87	34 \pm 2	32 \pm 2	33 \pm 1	0.95 \pm 0.07	1.02 \pm 0.06
5	12/10/87	33 \pm 1	32 \pm 1	28 \pm 1	0.96 \pm 0.05	0.90 \pm 0.04
6	2/25/88	33 \pm 1	34 \pm 1	33 \pm 1	1.04 \pm 0.06	0.97 \pm 0.05
7	9/26/88	33 \pm 1	34 \pm 1	38 \pm 1	1.02 \pm 0.06	1.12 \pm 0.05
8	1/09/89	33 \pm 1	33 \pm 1	30 \pm 1	1.01 \pm 0.06	0.91 \pm 0.04
9	4/27/89	33 \pm 1	33 \pm 1	32 \pm 1	1.02 \pm 0.06	0.95 \pm 0.05

The REEs and some other interfering major and trace elements are retained in the aqueous phase of the TOPO extraction step (Fig. 8). This solution (HNO_3 , 1M) is evaporated to dryness, the residue redissolved in 20 ml of HCl (10%) and then slowly adsorbed on an Amberlite IR-120 (100 – 200 mesh) cation-exchange column, previously conditioned with HCl (1M). Interfering elements (e.g. Fe, Ca) are eluted with 400 ml of HCl (1.7 M) and then the REEs and Y are eluted with 600 ml of 4M HCl. This solution is evaporated to dryness and the residue is then redissolved in 10 ml of HCl (10%) and submitted to sequential ICP-AES analysis. The equipment used was an ARL Mod. 35000-C spectrometer. The selected analytical lines and the corresponding detection

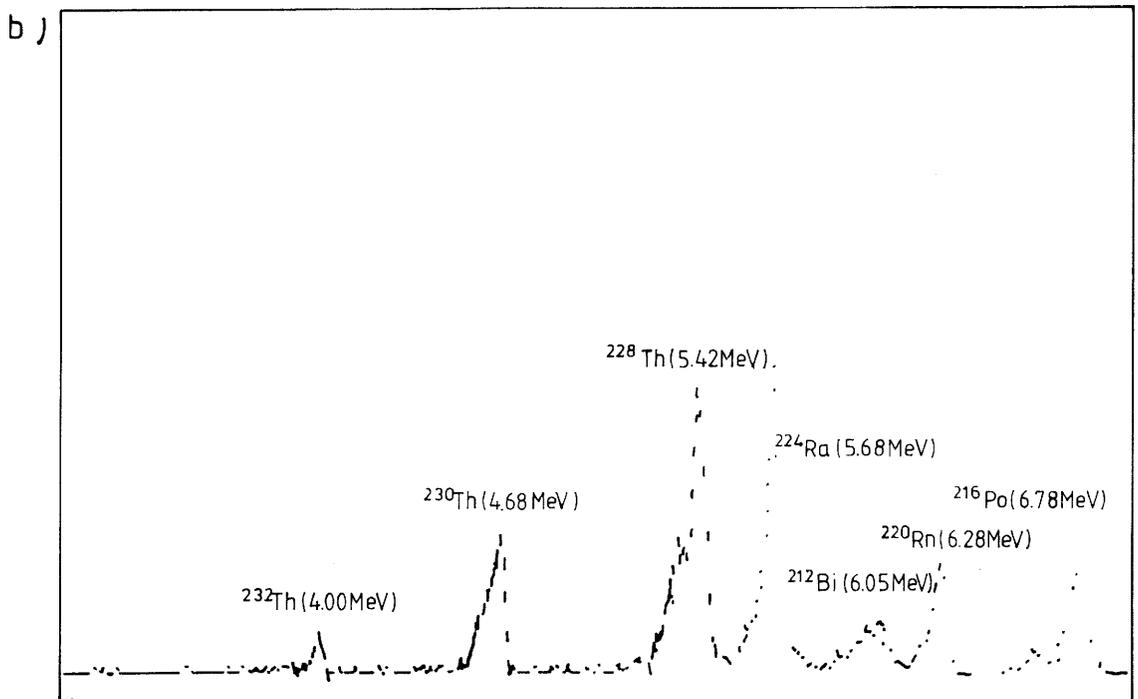
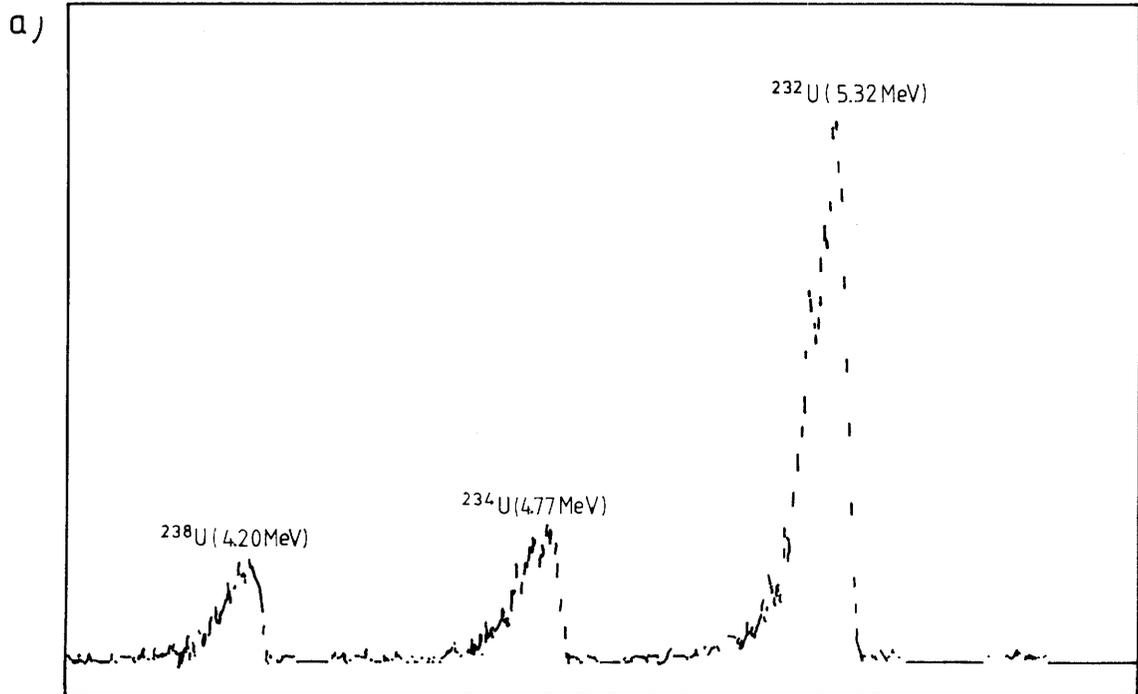


Figure 9.

- a) Alpha spectrum of uranium isotopes in groundwater sample GW-73, obtained by the PUC procedure.
- b) The corresponding spectrum for thorium isotopes.

limits are summarised in Table VI. No radioactive tracers for the REEs were available at PUC when the water samples were analysed. However, previous studies had shown that the procedure has a quantitative chemical recovery of these elements (Silveira P. da, 1986). The accuracy of the method was tested by analysing geological reference materials (BCR-1, NIM-G) and was considered to be adequate for the purpose of this study (see Table VII).

3.2.3. Intercomparison of results obtained by the different analytical procedures

Table VIII summarises analytical results for U, Th and the LREEs obtained by the NYU and the PUC laboratories on water samples from Morro do Ferro. These data were obtained by processing two 20 or 40 litre water aliquots (for details see section 3.1) collected on the same day, at a given location.

Uranium: With only 3 exceptions from a total of 13 samples, where intercomparison was possible, good agreement between the two laboratories was obtained for the 'total uranium' as well as for the $^{234}\text{U}/^{238}\text{U}$ activity ratio data (Table VIII), considering the low concentrations of uranium in these waters (mostly $<1\mu\text{g/l}$).

Thorium: Agreement between the ^{232}Th and ^{230}Th data of both laboratories was less satisfactory (Table VIII and Appendix 1; Table 1-II). Since two analytical techniques for ^{232}Th (alpha spectrometry and ICP-AES at PUC and alpha spectrometry and fluorometry at NYU) produced internally consistent data-sets, one has to question whether or not the sampling and volume reduction techniques produced reliable sample duplicates and, if so, whether or not the initial sample preparation procedures used (including dissolution of insoluble matter within the evaporate) resulted in homogeneous solutions for analyses. Although the good agreement of uranium data for the two laboratories would argue that reliable duplicates were obtained upon sampling, this may or may not hold for thorium, because it is thought to act much less conservatively relative to uranium in the strongly oxidising to slightly oxidising groundwaters typical for the Morro do Ferro environment. Contrary to uranium, most of the thorium in prefiltered groundwaters is in a colloidal state (Miekeley *et al.*, 1989). Variable degrees of retention of colloidal thorium on the prefilters used (sometimes heavily loaded with particulate material $>450\text{ nm}$) and/or contamination of the samples by particulate matter (which has Th-concentrations generally higher by a factor of 100,000 or more than the solution phase; Table XI) could account for the observed greater differences in the thorium concentrations, which appear to be randomly distributed.

TABLE VI

Analytical lines for the determination of rare-earth elements by ICP-AES and detection limits for pure aqueous solutions.

Element	λ (nm)	L_D (mg/l)
La	379.5	0.04
Ce	413.8	0.15
Nd	406.1	0.02
Sm	359.3	0.05
Eu	382.0	0.001
Gd	342.3	0.05
Dy	353.2	0.005
Ho	345.6	0.003
Er	369.3	0.008
Tm	346.2	0.005
Yb	328.9	0.002
Lu	261.5	0.001

TABLE VII

PUC quality assurance data on the determination of rare-earth elements in reference rocks BCR-1 and NIM-G (all values in $\mu\text{g/g}$).

Element	REFERENCE ROCK BCR-1							REFERENCE ROCK NIM-G				
	a	b	c	d	e	f	g	a	b	h	i	
Y	38.6	34	37		35			33	105	100		
La	26	29	26	25	27	25	25	25	106	85	110	105
Ce	54	53	54	48	54	55	54	52	178	160	190	195
Nd	28	29	29	28	30	29	29	29	65	60	72	73
Sa	6.9	6.7	6.6	6.4	6.7	6.7	6.7	6.6	16	20	15	16
Eu	2.02	1.96	1.94	1.9	1.98	1.97	1.95	2.05	0.50		0.40	0.39
Gd	6.5	6.5	6.6	7.0	6.9	6.6	6.6	7.0	13	10		
Dy	6.3	5.9	6.3	5.9	6.7	6.5	6.3	6.4	16	17		
Ho		1.2	1.2	1.1	1.4			1.2	3.4			
Er	3.5	3.4	3.6	3.1	3.8		3.6	3.6	12			
Tm		0.41	0.6	0.48	0.57	0.57		0.50	1.8			
Yb	3.2	3.1	3.4	3.3	3.7	3.5	3.4	3.4	12	12	13	13
Lu	0.50	0.45	0.55	0.50	0.52	0.55	0.54	0.49	1.6		2.0	2.1

- a) ICP-AES; this study
 b) different methods; Flanagan (1973)
 c) ICP-AES; Dutra (1984)
 d) ICP-AES; Crock and Lichte (1982)
 e) INAA; Millard (1981)
 f) IDA-MS; Hanson (1976)
 g) ICP-AES; Crock et al. (1986)
 h) INAA; Croudace (1980)
 i) IDA-MS; Jackson and Strelow (1975)

ICP-AES = Inductively Coupled Plasma Atomic Emission Spectroscopy.
 IDA-MS = Isotope Dilution Mass Spectrometry.
 INAA = Instrumental Neutron Activation Analysis.

TABLE VIII

Intercomparison of data on uranium, thorium and the light rare-earth elements in waters from Morro do Ferro, analysed by the NYU and PUC procedures.

Sample no.	Sampling	Concentration ($\mu\text{g/l} \pm \text{SD}$)						
		U	$^{234}\text{U}/^{238}\text{U}$	Th	Ce	La	Nd	Sm
Near-surface water								
SW-04	7/29/87	0.26 \pm 0.01	1.50 \pm 0.05	0.058 \pm 0.005	1.15 \pm 0.07	0.91 \pm 0.03	0.35 \pm 0.27	0.10 \pm 0.01
		<i>0.35 \pm 0.02</i>	<i>2.04 \pm 0.10</i>	<i>0.088 \pm 0.004</i>	<i>1.2 \pm 0.1</i>	<i>1.2 \pm 0.1</i>	<i>0.36 \pm 0.04</i>	<i>0.07 \pm 0.01</i>
SW-05	8/10/87	0.18 \pm 0.01	1.34 \pm 0.05	0.042 \pm 0.004	0.84 \pm 0.05	0.77 \pm 0.03	0.45 \pm 0.15	0.09 \pm 0.01
		<i>0.16 \pm 0.01</i>	<i>1.50 \pm 0.07</i>	<i>0.074 \pm 0.004</i>	<i>1.0 \pm 0.1</i>	<i>1.6 \pm 0.2</i>	<i>0.31 \pm 0.03</i>	<i>0.03 \pm 0.01</i>
Deep groundwater MF10, 50–74 mbgl								
GW-33	1/27/88	0.071 \pm 0.002	1.26 \pm 0.04	0.056 \pm 0.002	0.93 \pm 0.12	18.1 \pm 0.03	6.0 \pm 0.2	0.67 \pm 0.02
		<i>0.077 \pm 0.005</i>	<i>1.30 \pm 0.07</i>	<i>0.021 \pm 0.001</i>				
GW-48	6/08/88	0.93 \pm 0.04	1.37 \pm 0.04	0.38 \pm 0.03	4.3 \pm 0.1	32.0 \pm 0.6	12.2 \pm 0.8	1.29 \pm 0.03
		<i>1.55 \pm 0.06</i>	<i>1.31 \pm 0.07</i>	<i>0.17 \pm 0.01</i>				
GW-52	9/12/88	0.72 \pm 0.02	1.32 \pm 0.03	0.14 \pm 0.02	3.1 \pm 0.1	43 \pm 1	17.2 \pm 0.4	1.95 \pm 0.04
		<i>0.70 \pm 0.03</i>	<i>1.32 \pm 0.08</i>	<i>0.11 \pm 0.01</i>	<i>3.9 \pm 0.4</i>	<i>29 \pm 3</i>	<i>12 \pm 1</i>	<i>1.2 \pm 0.1</i>
Deep groundwater MF11, 30–40 mbgl								
GW-35	1/28/88	0.037 \pm 0.002	1.17 \pm 0.06	0.077 \pm 0.003	0.48 \pm 0.10	1.7 \pm 0.1	0.54 \pm 0.22	0.08 \pm 0.01
		<i>0.055 \pm 0.004</i>	<i>1.40 \pm 0.10</i>		<i>0.33 \pm 0.03</i>	<i>1.8 \pm 0.1</i>	<i>0.87 \pm 0.09</i>	<i>0.08 \pm 0.01</i>
GW-49	6/13/88	1.40 \pm 0.06	1.38 \pm 0.03	0.24 \pm 0.03	2.2 \pm 0.1	8.6 \pm 0.2	3.6 \pm 0.3	0.41 \pm 0.02
		<i>0.13 \pm 0.01</i>	<i>1.60 \pm 0.10</i>	<i>0.96 \pm 0.03</i>	<i>2.6 \pm 0.3</i>	<i>6.5 \pm 0.7</i>	<i>3.6 \pm 0.4</i>	<i>0.40 \pm 0.04</i>
GW-53	9/13/88	0.83 \pm 0.04	1.48 \pm 0.04	0.14 \pm 0.02	1.06 \pm 0.03	9.4 \pm 0.2	4.7 \pm 0.3	0.58 \pm 0.02
		<i>0.75 \pm 0.03</i>	<i>1.52 \pm 0.09</i>	<i>0.55 \pm 0.03</i>	<i>0.90 \pm 0.09</i>	<i>4.4 \pm 0.4</i>	<i>2.2 \pm 0.2</i>	<i>0.30 \pm 0.03</i>
GW-70	12/12/88	0.40 \pm 0.01	1.37 \pm 0.04	< 0.44	1.02 \pm 0.03	8.4 \pm 0.2	4.0 \pm 0.2	0.60 \pm 0.01
		<i>0.44 \pm 0.02</i>	<i>1.50 \pm 0.10</i>	<i>0.067 \pm 0.003</i>	<i>1.19 \pm 0.12</i>	<i>7.5 \pm 0.8</i>	<i>4.1 \pm 0.4</i>	<i>0.44 \pm 0.04</i>
Deep groundwater MF12, 45–71 mbgl								
GW-18	7/07/87	0.12 \pm 0.01	1.22 \pm 0.05	0.13 \pm 0.02	0.94 \pm 0.05	0.45 \pm 0.02		0.01 \pm 0.01
		<i>0.12 \pm 0.01</i>	<i>1.69 \pm 0.08</i>	<i>0.58 \pm 0.03</i>	<i>1.6 \pm 0.2</i>	<i>0.9 \pm 0.1</i>	<i>0.28 \pm 0.03</i>	<i>0.03 \pm 0.01</i>
GW-30	12/02/87	1.13 \pm 0.03	1.57 \pm 0.03	0.023 \pm 0.001	0.41 \pm 0.10	0.38 \pm 0.02		0.02 \pm 0.01
		<i>1.00 \pm 0.04</i>	<i>1.70 \pm 0.08</i>	<i>0.016 \pm 0.001</i>	<i>0.46 \pm 0.05</i>	<i>0.95 \pm 0.10</i>		<i>0.022 \pm 0.002</i>
GW-34	1/28/88	0.65 \pm 0.03	1.73 \pm 0.06	0.011 \pm 0.001	0.32 \pm 0.09	0.87 \pm 0.02		0.05 \pm 0.01
		<i>0.78 \pm 0.04</i>	<i>1.60 \pm 0.08</i>	<i>0.080 \pm 0.004</i>	<i>1.0 \pm 0.1</i>	<i>1.9 \pm 0.2</i>	<i>0.67 \pm 0.07</i>	<i>0.08 \pm 0.01</i>
GW-71	12/14/88	0.64 \pm 0.03	2.24 \pm 0.06	0.17 \pm 0.01	0.94 \pm 0.03	0.37 \pm 0.01	0.22 \pm 0.02	0.02 \pm 0.01
		<i>0.60 \pm 0.03</i>	<i>2.30 \pm 0.10</i>	<i>0.35 \pm 0.02</i>				

NYU – Normal
PUC – Italics

Rare-earth elements: The agreement between the LREE data obtained by both laboratories is reasonable, e.g. 8 of 10 Ce-concentrations show deviations of +/-30% or less. Intercomparison of the results for Nd and Sm gives a similar picture. However, for some unknown reason, larger discrepancies were observed for La.

Concluding this intercomparison exercise, it can be stated that the different methods used for the analyses of U and LREEs at $\mu\text{g/l}$ -levels in waters produced data which are, in most cases, in reasonable, and sometimes in good, agreement. Due to the lower concentrations of thorium in waters, its greater tendency for association with particulate and colloidal material and the poorer sensitivity of available analytical methods (when compared to U and the REEs), determination of this element still remains a problem. However, there are indications that the large differences observed in the results might be caused by the sampling and pre-treatment procedures, and not by the measuring methods. For this reason, both values (NYU and PUC) will be reported. Duplicate analysis of most of the samples from the Morro do Ferro environment permitted the exclusion of those data which were obviously wrong (i.e. in disagreement with observed concentration trends for a given sampling site, and therefore probably linked with contamination). Intercomparisons for the heavy rare-earth elements (HREEs) could not be made, as only the PUC laboratory was involved.

4. Results and discussions

4.1. Natural series nuclides and rare-earth elements in near-surface and deep groundwaters from the Osamu Utsumi uranium mine

4.1.1. Uranium

Uranium and thorium isotopic data for 41 water samples from the Osamu Utsumi mine are summarised in Table 1-I (Appendix 1), and presented in a more condensed form containing additional chemical data in Table IX.

Total Uranium: As can be expected from such an environment, the uranium concentrations in waters, especially from near-surface regions, are high when compared with data reported for non-uraniferous areas (e.g. 0.5 – 0.6 $\mu\text{g/l}$ in rivers of the USSR; Baturin *et al.*, 1969), but are also high in comparison with other uranium mine waters (typically 15 to 400 $\mu\text{g/l}$; Fix, 1956). In the Osamu Utsumi mine, the concentrations of this element are in the range of 200 to 9000 $\mu\text{g/l}$ in near-surface waters (boreholes SW01 to SW03) and from 3 to 15 $\mu\text{g/l}$ in deep groundwaters (45 to 125 $\mu\text{g/l}$, F2 and F1). Uranium concentrations of up to 73 $\mu\text{g/l}$ were observed in waters from borehole F4

(75–175 mbgl), which cuts a highly conductive brecciated zone, strongly altered by K-metasomatic processes and in which sulphide and fluoride minerals are very abundant (Waber *et al.*, this report series; Rep. 2). This environment is reflected in the hydrochemistry of the borehole which shows oxidising waters (Eh: +233 to +372 mV) containing high concentrations of sulphate (up to 78 mg/l) and fluoride (up to 8 mg/l).

For a given sampling site, small variations in the concentrations of uranium can be observed which can be related to seasonal fluctuations of the precipitation rate in the Poços de Caldas region during dry and rainy periods (see Fig. 6). Maxima in the precipitation rate produce pulses of oxidising waters which penetrate deeper into the bedrock, thus enhancing uranium leaching. Table X summarises mean concentrations of uranium and some other cations and anions in water (SW03, F1 and F2) during wet, transitional and dry periods. Although a somewhat higher mean concentration of uranium is observed in F2 and F1 during the wet period, other ions (SO_4^{2-} , F, K^+ , Fe^{3+}) do not show such a marked trend, which supports a predominantly upward groundwater flow not significantly affected by seasonal effects.

According to Langmuir (1978), Garrels *et al.* (1965) and others, the solubility of U(IV) in natural waters of pH 4 to 7 is generally below 0.05 $\mu\text{g/l}$, reflecting the extreme insolubility of reduced uranium minerals. Slightly higher concentrations are possible in the presence of fluoride, however, at pH <4.0. Typical concentrations of this complexant in groundwaters from the Osamu Utsumi mine are in the range of 0.5 to 8 mg/l. The much higher observed concentrations of uranium in groundwaters of this site indicate that this element is transported predominantly in the hexavalent form (UO_2^{2+}). This interpretation is compatible with the pH-Eh conditions of the different boreholes, showing that all waters of the mine environment are of oxidising character (Fig. 10). The strong tendency of UO_2^{2+} to form stable complexes with inorganic (SO_4^{2-} , HCO_3^- , HPO_4^{2-}) and organic anions (i.e. humic compounds) is well documented (Langmuir, 1978; Bruno *et al.*, 1988; Choppin *et al.*, 1985). Speciation calculations performed by Langmuir (1978) for model groundwaters with similar compositions of complexing anions to those observed in the Osamu Utsumi mine would indicate that the predominant uranium species in groundwater is $\text{UO}_2(\text{HPO}_4)_2^{2-}$, whereas in surface waters of low pH (typically between 3 and 4) and high concentrations of sulphate and fluoride, other species such as UO_2SO_4^0 and UO_2F^+ compete (Fig. 11a). This has been confirmed by Bruno *et al.* (this report series; Rep. 11) for groundwaters from both environments.

The extremely high concentrations of uranium in near-surface waters are to be expected for acidic, oxidising waters in contact with weathered rock with a high residual U-content (which may be predominantly adsorbed or coprecipitated with ferric

TABLE IX

Chemical data for near-surface waters and groundwaters from the Osamu Utsumi uranium mine.

Borehole	Sample	Date (dd/mm/yy)	^{238}U ($\mu\text{g/l}$)	R1	^{232}Th ($\mu\text{g/l}$)	R2	pH	E_h (mV)	Na (mg/l)	K (mg/l)	Fe(II) (mg/l)	Fe(t) (mg/l)	HCO_3^- (mg/l)	SO_4^{2-} (mg/l)	F^- (mg/l)
SW01	PC-GW-37	02/02/88	3200	1.22	360	0.18	3.1	806	1.45	19.0	1.20	5.04	<0.60	780	52.3
	PC-GW-46	07/06/88	4400	1.23	280	0.11	3.32	673	2.03	33.0	35.2	36.8	<0.60	1175	75.2
	PC-GW-57	21/09/88	270	1.23	4.1	0.026	3.92	666	1.40	21.5	<0.10	<0.10	<0.60	3650	10.1
SW02	PC-GW-38	03/02/88	10600	1.0	70	0.025	3.2	858	2.35	39.7	0.33	2.42	<0.60	555	10.7
	PC-GW-39	03/02/88	7400	1.04	79	0.039	3.4	772	2.00	33.4	<0.10	0.14	<0.60	605	10.9
SW03	PC-GW-47	07/06/88	4500	1.02	36	0.016	3.57	751	2.62	25.1	<0.10	0.12	<0.60	445	10.5
	PC-GW-58	22/09/88	250	0.92	0.23	0.001	4.43	614	1.56	13.4	<0.10	<0.10	<0.60	8.8	0.45
	UFSW03-A	25/10/88	6600	1.03	720	0.33	2.85		1.40	29.0	27.0	27.8	<0.60	695	4.07
	PC-GW-66	30/11/88	2400	0.95	42	0.06	3.44	800	1.24	26.0	0.10	0.29	<0.60	430	3.96
	PC-GW-14	06/01/87	5.3	2.3			5.39				1.58	1.67	7.1	17.0	0.51
	PC-GW-15	11/02/87	4.3	2.2	0.030	0.046	5.51				1.62	1.67	13	16.4	0.59
	UFWC11-A	15/02/87	4.3	2.2	0.029		5.36				1.61	1.66	11.4	16.8	0.59
	PC-GW-17	06/05/87	3.0	2.4	0.071	0.029	5.49				1.85	1.87	10.7	17.2	0.84
	UFWC11-B	29/07/87	3.8	2.3	0.065	0.005	5.54				0.75	0.83	10.7	16.4	0.28
	PC-GW-22	20/08/87	4.9	2.1	0.043	0.004	6.05				1.12	1.18	8.1	18.8	0.35
F1	PC-GW-23	17/09/87	3.7	2.2	0.030		5.74				1.24	1.33	7.77	19.0	0.23
	PC-GW-29	10/11/87	4.5	2.3	0.020		5.30				1.15	1.17	9.18	18.0	0.33
	PC-GW-40	08/02/88	7.4	2.2	0.037		5.67	307	0.76	12.5	1.20	1.23	11.3	18.1	0.40
	UFWC11-C	24/05/88	4.9	2.3	0.030	0.004	5.44	379	0.57	10.0	1.15	1.18	8.21	16.6	0.34
	PC-GW-42	01/06/88	4.5	2.2	0.043		5.25	366	0.40	10.0	1.26	1.29	11.4	20.0	0.41
	PC-GW-54	15/09/88	4.0	2.3	0.075	0.012	5.38	277	0.64	14.0	1.78	1.80	8.21	26.6	0.54
	UFWC11-D	25/10/88	4.8	2.3	0.017	0.019	5.81	448	0.56	12.4	1.33	1.34	4.37	21.8	0.61
	PC-GW-63	29/11/88	5.1	2.4	0.120	0.11	5.37	261	0.52	12.0	1.16	1.18	8.11	20.0	0.24
F2	PC-GW-13	15/12/86	15.7	1.5							0.58	0.79	10.3		1.74
	PC-GW-16	12/02/87	14.8	1.5	0.030						0.89	0.95	13.4	11.6	1.88

TABLE IX (contd.).

	Sample	Date (dd/mm/yy)	²³⁸ U (μg/l)	R1	²³² Th (μg/l)	R2	pH	E _h (mV)	Na (mg/l)	K (mg/l)	Fe(II) (mg/l)	Fe(t) (mg/l)	HCO ₃ ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	F ⁻ (mg/l)
	UFWC24-A	16/02/87	14.7	1.5	0.030						0.96	1.03	13.4	11.6	1.88
	PC-GW-20	24/07/87	10.1	1.4	0.076	0.010	5.57				0.56	0.58	10.7	17.4	1.87
	UFWC24-B	06/08/87	8.1	1.4	0.057	0.016	5.97				1.03	1.11	12.1	13.4	2.02
F2	PC-GW-25	28/09/87	6.8	1.6	0.024		5.66		1.46	11.0	0.61	0.73	10.6	16.6	1.15
	PC-GW-31	21/12/87	6.2	1.7	0.036	0.003	5.80	198	1.0	12.0	1.21	1.21	17.0	17.0	2.02
	PC-GW-41	09/02/88	6.4	1.5	0.200	0.089	5.60	559	0.38	9.5	0.98	1.01	14.8	16.8	2.13
	UFWC24-C	31/05/88	5.5	1.6	0.038	0.002	6.09		0.62	12.0	1.42	1.44	15.2	16.4	2.38
	PC-GW-43	02/06/88	5.2	1.7	0.047	0.007	5.72	295	0.45	10.7	1.05	1.11	13.3	16.0	2.18
	PC-GW-60	23/09/88	2.7	1.6	0.031	0.008	5.74	240	0.48	10.6	0.92	0.94	8.84	17.4	1.83
	PC-GW-64	29/11/88	6.7	1.5	0.080	0.020	5.84	261	0.46	12.0	1.50	1.52	20.0	15.0	2.20
	PC-GW-36	01/02/88	25	1.2	0.06	0.004	5.45	420	1.49	34.2	53.4	53.5	18.4	360	4.27
F3	PC-GW-45	06/06/88	16	1.2	6.5		5.21	386	1.52	3.39	76.9	77.9	11.1	605	6.39
	PC-GW-55	16/09/88	0.81	2.2(?)	0.14	0.24	5.06	167	1.90	43.0	89.1	89.9	10.7	615	7.34
	PC-GW-65	30/11/88	4.5	1.3	0.34	0.20	5.10	370	2.10	45.0	98.9	99.4	11.9	835	8.49
F5	PC-GW-62	28/11/88	22	1.8	0.18	0.006	6.25	229	0.96	13.6	9.25	9.35	33.7	55.0	7.76
	PC-GW-72	20/12/88	11	1.8	0.13	0.004	6.30	155	1.24	11.8	9.96	10.6	5.08	33.4	5.44
	PC-GW-44	03/06/88	73	1.4	0.18	0.002	5.71	372	1.00	14.0	4.22	4.24	15.8	78.0	8.33
F4	PC-GW-59	22/09/88	21	1.5	0.07	0.004	6.12	233	1.12	12.4	3.55	3.70	15.8	11.7	7.13
	PC-GW-67	30/11/88	48	1.6	0.20	0.015	6.01	268	1.56	18	5.04	5.06	18.7	43.5	0.32
UC16	PC-GW-21	31/07/87	44	1.14	1.0	0.088									
	PC-GW-24	18/09/87	85	1.0	0.44	0.028									
PM22	PC-GW-19	15/07/87	0.19	2.3	0.087	0.5									
	PC-GW-27	02/10/87	0.44	1.6	0.040	0.1									
sup.D	PC-SW-03	09/07/87	0.43	1.24	0.075	0.16									

Isotopic Activity RatiosR1 = ²³⁴U/²³⁸U, R2 = ²³⁰Th/²³⁴U

UC16 = Pilot Hole

PM22 = Piezometer Station 22 (not shown in Fig. 3)

sup.D = Supply Dam

TABLE X

Mean concentrations of a selection of elements in waters from the Osamu Utsumi mine during wet, transitional and dry seasons.

Borehole	Season	^{238}U ($\mu\text{g/l}$)	R1	^{232}Th ($\mu\text{g/l}$)	R2	pH	E _h	Na (mg/l)	K (mg/l)	Fe(II) (mg/l)	Fe(t) (mg/l)	HCO ₃ ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	F ⁻ (mg/l)
SW03	w	4900	1.00	61	0.050	3.42	786	1.62	29.7		0.22		518	7.43
	t	3425	0.98	360	0.166	3.64	614	1.48	21.2				352	2.26
	d	4500	1.02	36	0.016	3.57	751	2.62	25.1		0.12		445	10.5
F1	w	5.2	2.27	0.039	0.078	5.43	284	0.62	11.5	1.39	1.43	10.0	17.7	0.44
	t	4.1	2.30	0.045	0.016	5.57	368	0.53	12.0	1.47	1.50	7.9	20.2	0.51
	d	4.4	2.20	0.050	0.005	5.61	366	0.44	11.0	1.04	1.10	10.1	18.4	0.35
F2	w	10.8	1.53	0.075	0.037	5.75	339	0.61	11.2	1.02	1.09	14.8	14.4	1.98
	t	5.0	1.60	0.031	0.005	5.83	240	0.85	11.2	0.98	1.04	11.5	16.8	1.79
	d	7.8	1.50	0.060	0.011	5.75	295	0.45	10.7	0.88	0.93	12.0	15.6	2.02

Isotopic Activity Ratios

$$R1 = \frac{^{234}\text{U}}{^{238}\text{U}}$$

$$R2 = \frac{^{230}\text{Th}}{^{234}\text{U}}$$

w = wet
d = dry
t = transitional

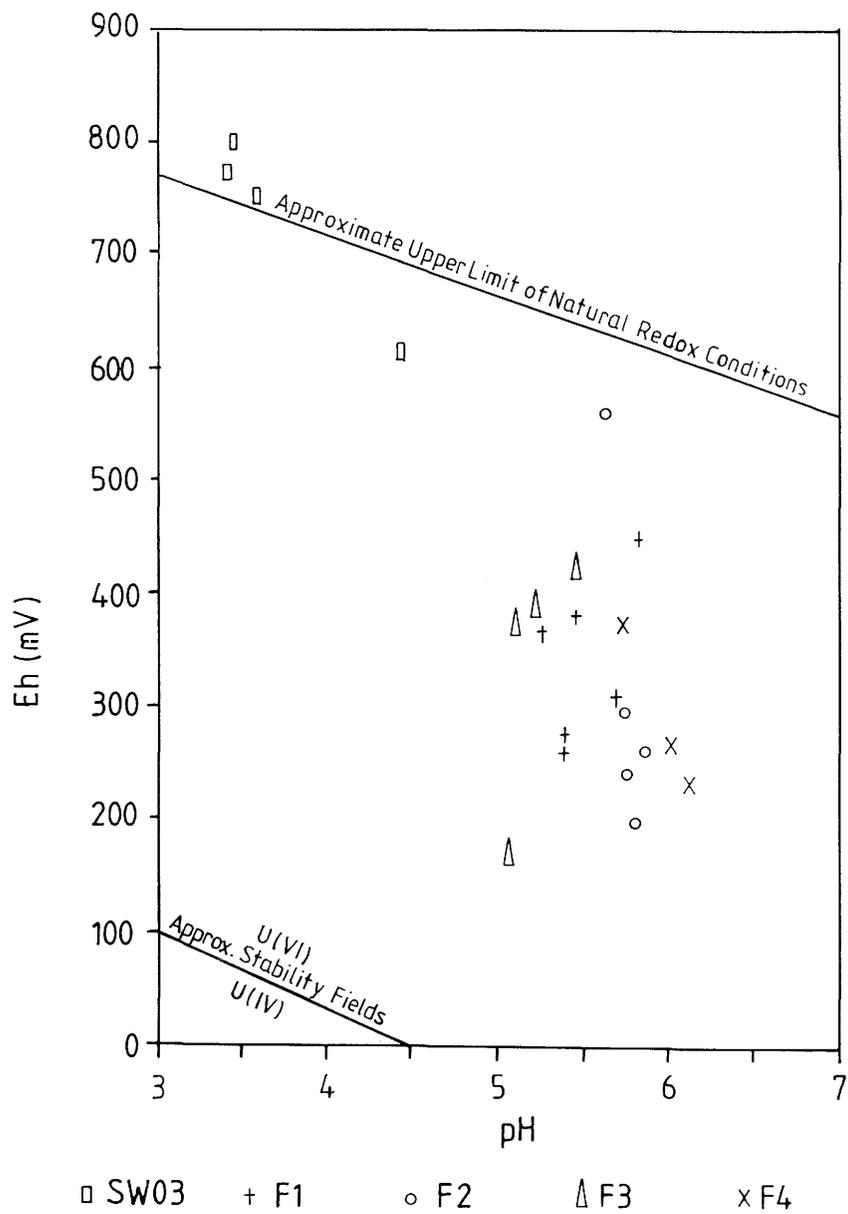
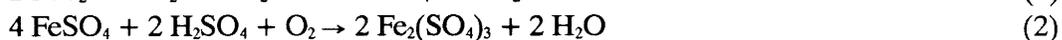


Figure 10. Eh-pH diagram for near-surface and deep ground waters sampled from the Osamu Utsumi mine.

oxyhydroxides (cf. McKinley (Ed.), this report series; Rep. 12). The oxidation of pyrite, which is abundant in the bedrock, promotes the following reactions: 1) the oxidation of pitchblende, 2) the complexation of UO_2^{2+} , and 3) the decrease of the pH of the waters.



Furthermore, the hydrolysis of Fe(III) according to (3) leads to the formation of ferric hydroxides as water-suspended particles and colloids and as surface coatings on the bedrock which may influence, due to their sorption capacities, the partitioning of uranium (and other elements, e.g. Th, REEs) between solution and the solid phases.

Suspended ferric hydroxide particles in groundwaters of the Osamu Utsumi mine are uranium-enriched by a factor of 10,000 to 100,000 when compared to the corresponding waters (Table XI). In near-surface waters which are oxidising and acidic (i.e. SW01 to SW03), sorption of uranium by suspended particles is less effective (Table XII), confirming results of laboratory experiments obtained by Langmuir (1978) and others. Due to the low concentrations of particulate matter (typically <0.5 mg/l), however, more than 90% of uranium in the mine waters is present in a truly “dissolved” form. This dissolved uranium is in exchange equilibrium with suspended particles, as indicated by similarities of the $^{234}\text{U}/^{238}\text{U}$ ratios of both phases.

Oxidation of ferrous iron, hydrolysis of ferric iron and precipitation of ferrihydrites, accompanied or followed by sorption of uranium and other trace elements (and humic compounds), have to be considered as relevant processes which influence the migration behaviour of these elements (and their measured solution concentrations). The observed discrepancies between the measured and predicted concentrations of U, Th and Ra ([Me]-pred. > [Me]-meas.) seem to support these conclusions (Bruno *et al.*, this report series; Rep. 11).

Uranium Isotopic Ratios: $^{234}\text{U}/^{238}\text{U}$ activity ratios in superficial and near-surface waters (SW01 to SW03 and the supply dam) are low and typically between 1.0 and 1.2, due to the severe leaching conditions (high Eh and low pH values, elevated concentrations of complexing agents, mainly sulphate and fluoride) which favour bulk dissolution of uranium instead of preferential leaching of ^{234}U (Rosholt *et al.*, 1963; Fleischer, 1980).

TABLE XI

Uranium and thorium isotopic compositions of suspended particles (> 450 nm) and their corresponding waters from the Osamu Utsumi mine and Morro do Ferro study sites (Miekeley *et al.*, this report series; Rep. 9).

Bore-hole	Sample	Date (dd/mm/yy)	Load (mg/l)	Fluorometry U			²³⁸ U			²³² Th			²³⁰ Th			R1 (w)	R1 (s)	R2 (w)	R2 (s)	R1(w) R1(s)	R2(w) R2(s)
				water (µg/l)	SP (µg/g)	SP _n (µg/l)	water (µg/l)	SP (µg/g)	SP _n (µg/l)	water (µg/l)	SP (µg/g)	SP _n (µg/l)	water (Bq/l)	SP (Bq/g)	SP _n (Bq/l)						
SW03	PC-GW-58	22/09/88	0.8	210	230	0.184	250	270	0.216	0.23	130	0.104	0.0038	4.0	0.0032	0.92	1.43	0.0013	0.85	0.6	0.002
	PC-GW-17	06/05/87	0.05	2.9	830	0.042	3.0	1000	0.050	0.071	490	0.025	0.0027	2.4	0.0001	2.4	2.1	0.029	0.09	1.1	0.322
	PC-GW-22	20/08/87	0.07	4.8	560	0.039	4.9	620	0.043	0.043	1340	0.094	0.0006	2.8	0.0002	2.1	1.8	0.004	0.21	1.2	0.019
F1	PC-GW-40	08/02/88	0.2	7.0	120	0.024	7.4	119	0.024	0.037	620	0.124		2.2	0.0004	2.2	1.8		0.85	1.2	
	UFWC11-C	24/05/88	0.21	4.8	200	0.042	4.9	180	0.038	0.030	290	0.061	0.0006			2.3	2.5	0.004		0.9	
	PC-GW-54	15/09/88	0.15	3.5	140	0.021	4.0	240	0.036	0.075	340	0.051	0.0013	1.1	0.0002	2.3	1.3	0.012	0.28	1.8	0.043
	HFFWC11D	27/10/88	0.14	4.3	190	0.027	4.4	250	0.035	0.012	72	0.010	0.0026	0.59	0.0001	2.6	2.2	0.025	0.09	1.2	0.278
	PC-GW-54	15/09/88	0.15	3.5	140	0.021	4.0	240	0.036	0.075	340	0.051	0.0013	1.1	0.0002	2.3	1.3	0.012	0.28	1.8	0.043
	HFFWC11D	27/10/88	0.14	4.3	190	0.027	4.4	250	0.035	0.012	72	0.010	0.0026	0.59	0.0001	2.6	2.2	0.025	0.09	1.2	0.278
	PC-GW-16	12/02/87	0.2	14	970	0.194	14.8	930	0.186	0.030	400	0.080		15.1	0.0030	1.5	1.46		0.90	1.0	
	UFVC24-B	06/08/87		8	1100		8.1	1030		0.057	91		0.002	7.7		1.4	1.7	0.016	0.36	0.8	0.044
F2	PC-GW-25	28/09/87	0.4	6.8	520	0.208	6.8	550	0.220	0.024	170	0.068		4.6	0.0018	1.57	1.39		0.48	1.1	
	PC-GW-41	09/02/88	0.2	5.5	710	0.142	6.4	720	0.144	0.20	340	0.068	0.0105	9.3	0.0019	1.47	1.54	0.089	0.67	1.0	0.133
	UFVC24-C	31/05/88	0.45	5.3	470	0.212	5.5	410	0.185	0.038	113	0.051		1.6		1.6	1.6	0.002	0.45	1.0	0.004
	PC-GW-60	23/09/88	0.5	2.6	390	0.195	2.7	350	0.175	0.031	146	0.073	0.004	3.3	0.0017	1.55	1.43	0.008	0.53	1.1	0.015
	PC-GW-12	12/12/86	25	1.1	15	0.375	1.06	16.2	0.405	0.060	2320	58	0.0008	0.21	0.0053	1.23	1.14	0.05	0.89	1.1	0.056
	UFMF10-A	25/01/88	4.7	0.27	40	0.188	0.28	44	0.207	0.013	200	0.940	0.0002			1.2	1.5	0.04	0.8		
MF10	PC-GW-33	27/01/88	1	0.061	29	0.029	0.077	31	0.031	0.021	202	0.202	0.0002	0.15	0.0002	1.3	1.4	0.13	0.28	0.9	0.464
	PC-GW-52	12/09/88	0.1	0.65	460	0.045	0.70	480	0.048	0.11	290	0.029	0.0006			1.32	1.5	0.05	0.9		
	UFMF10-B	23/10/88	0.17	0.49	230	0.039	0.56	260	0.044	0.036			0.0004			1.4	1.5	0.04	0.9		
MF11	PC-GW-35	28/01/88	2.8	0.041	27	0.076	0.055	28	0.078		1270	3.556	0.0005	0.26	0.0007	1.4	1.07	0.5	0.69	1.3	0.725
	PC-GW-53	13/09/88	2.1	0.86	39	0.082	0.75	38	0.080	0.55	1240	2.604	0.0014	0.23	0.0005	1.52	1.4	0.1	0.34	1.1	0.294
	PC-GW-18	07/07/87		0.16	57		0.12	57		0.58	550		0.0005			1.7		0.19			
	PC-GW-30	02/12/87	2.8	0.99	58	0.162	1.00	74	0.207	0.016	43	0.120	0.0001	0.69	0.0019	1.72	1.7	0.005	0.45	1.0	0.011
MF12	PC-GW-34	28/01/88	3.1	0.79	54	0.167	0.78	69	0.214	0.080	74	0.229		0.18	0.0006	1.6	1.9		0.11	0.8	
	PC-GW-56	19/09/88	2.6	0.82	65	0.169	0.80	147	0.382	0.094	56	0.146	0.0003	0.21	0.0005	1.9	1.39	0.017	0.08	1.4	0.213
	UFMF12-B	12/10/88	2.3	0.76	40	0.092	0.80	49	0.113	0.035	18	0.041		0.04	0.0001	1.8	2.1	0.03	0.04	0.9	0.750

Isotope Activity Ratios

$$R1 = \frac{^{234}\text{U}}{^{238}\text{U}}, R2 = \frac{^{230}\text{Th}}{^{234}\text{U}}$$

(w) = water; (s) = SP.

SP_n = Suspended concentration normalised to the water volume (= load x SP x 0.001)

TABLE XII

Association ratios (R_a) of uranium and thorium with suspended particles and the percentage fractions (F) of these elements in waters (< 450 nm). (Adapted from Miekeley *et al.*, this report series; Rep. 9).

Borehole	Sample	Date (dd/mm/yy)	U		^{238}U		^{232}Th		^{230}Th	
			R_a (ml/g)	F (%)	R_a (ml/g)	F (%)	R_a (ml/g)	F (%)	R_a (ml/g)	F (%)
SW03	PC-GW-58	22/09/88	1.1E+03	99.9	1.1E+03	99.9	5.7E+05	68.9	1.1E+06	54.3
	PC-GW-17	06/05/87	2.9E+05	98.6	3.3E+05	98.4	6.9E+06	74.3	8.9E+05	95.7
F1	PC-GW-22	20/08/87	1.2E+05	99.2	1.3E+05	99.1	3.1E+07	31.4	4.7E+06	75.4
	PC-GW-40	08/02/88	1.7E+04	99.7	1.6E+04	99.7	1.7E+07	23.0		
	UFWC11-C	24/05/88	4.2E+04	99.1	3.7E+04	99.2	9.7E+06	33.0		
	PC-GW-54	15/09/88	4.0E+04	99.4	6.0E+04	99.1	4.5E+06	59.5	8.5E+05	88.7
	HFFWC11D	27/10/88	4.4E+04	99.4	5.7E+04	99.2	6.0E+06	54.3	2.3E+05	96.9
		PC-GW-16	12/02/87	6.9E+04	98.6	6.3E+04	98.8	1.3E+07	27.3	
F2	UFVC24-B	06/08/87	1.4E+05		1.3E+05		1.6E+06		3.9E+06	
	PC-GW-25	28/09/87	7.6E+04	97.0	8.1E+04	96.9	7.1E+06	26.1		
	PC-GW-41	09/02/88	1.3E+05	97.5	1.1E+05	97.8	1.7E+06	74.6	8.9E+05	85.0
	UFVC24-C	31/05/88	8.9E+04	96.2	7.5E+04	96.8	3.0E+06	42.8		
	PC-GW-60	23/09/88	1.5E+05	93.0	1.3E+05	93.9	4.7E+06	29.8	8.3E+06	19.5
MF10	PC-GW-12	12/12/86	1.4E+04	74.6	1.5E+04	72.4	3.9E+07	0.1	2.6E+05	13.2
	UFMF10-A	25/01/88	1.5E+05	59.0	1.6E+05	57.5	1.5E+07	1.4		
	PC-GW-33	27/01/88	4.8E+05	67.8	4.0E+05	71.3	9.6E+06	9.4	7.5E+05	57.1
	PC-GW-52	12/09/88	7.1E+05	93.4	6.9E+05	93.6	2.6E+06	79.1		
MF11	UFMF10-B	23/10/88	4.7E+05	92.6	4.6E+05	92.7				
	PC-GW-35	28/01/88	6.6E+05	35.2	5.1E+05	41.2			5.2E+05	40.7
MF12	PC-GW-53	13/09/88	4.5E+04	91.3	5.1E+04	90.4	2.3E+06	17.4	1.6E+05	74.3
	PC-GW-18	07/07/87	3.6E+05		4.8E+05		9.5E+05			
	PC-GW-30	02/12/87	5.9E+04	85.9	7.4E+04	82.8	2.7E+06	11.7	6.9E+06	4.9
	PC-GW-34	28/01/88	6.8E+04	82.5	8.8E+04	78.5	9.3E+05	25.9		
	PC-GW-56	19/09/88	7.9E+04	82.9	1.8E+05	67.7	6.0E+05	39.2	7.0E+05	35.5
	UFMF12-B	12/10/88	5.3E+04	89.2	6.1E+04	87.7	5.1E+05	45.8		

Association ratio R_a = $[\text{SP}_n]/[\text{Water}]$

Percentage fraction F = $[\text{Water}]/[\text{Water}] + [\text{SP}_n] \times 100$ (See Table XI for distribution of $[\text{SP}_n]$).

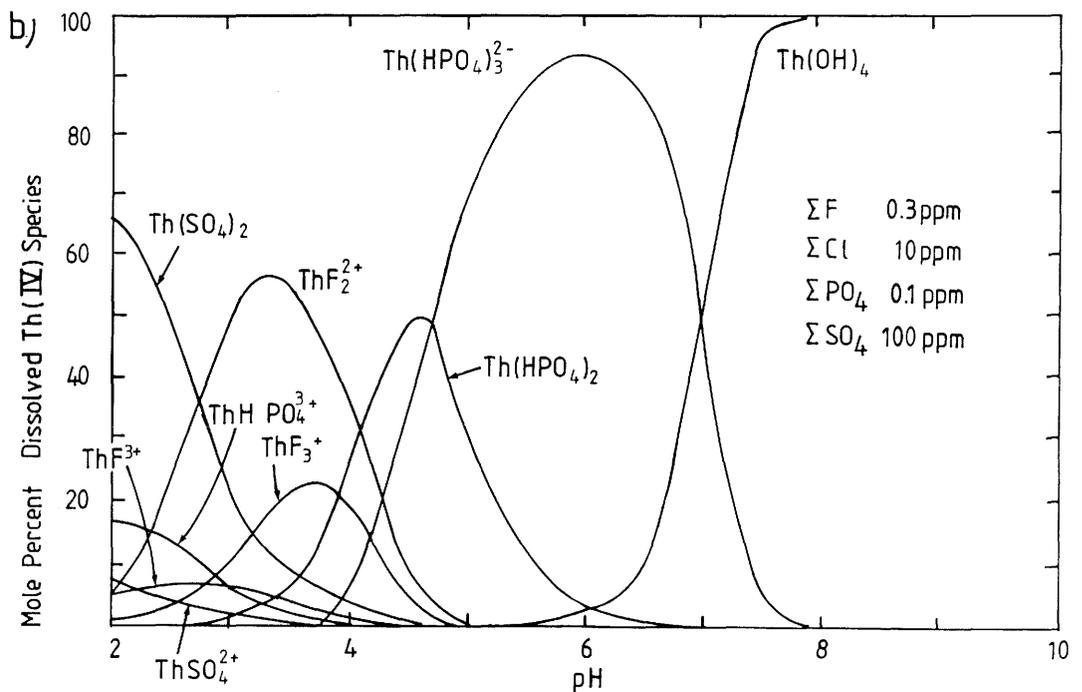
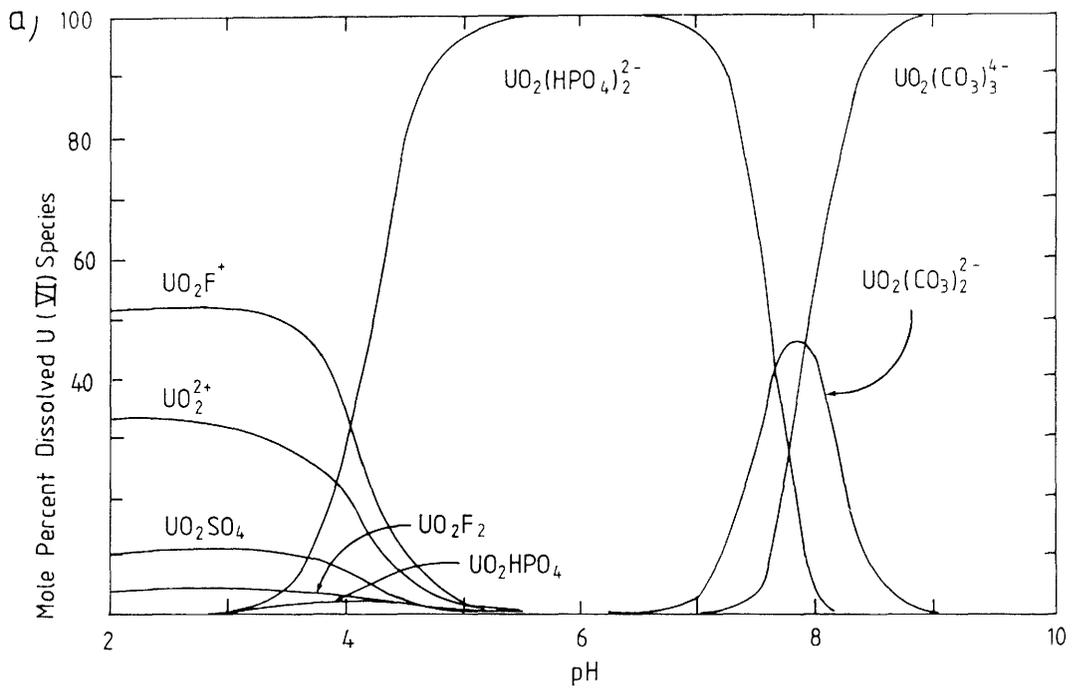


Figure 11.

- a) Speciation diagram for uranium in a model groundwater at 25°C and $p(\text{CO}_2) = 10 \text{ atm}$, according to Langmuir, 1978 ($\Sigma \text{F} = 0.3 \text{ ppm}$; $\Sigma \text{Cl} = 10 \text{ ppm}$; $\Sigma \text{SO}_4 = 100 \text{ ppm}$; $\Sigma \text{PO}_4 = 0.1 \text{ ppm}$; $\Sigma \text{SiO}_2 = 36 \text{ ppm}$).
- b) Similar diagram for the distribution of Th-species at 25°C and with $\Sigma \text{Th} = 0.01 \text{ ppb}$ (Langmuir and Herman, 1980).

In the area of the shallow boreholes, near F1 and F2 (Fig. 3), an increase in the $^{234}\text{U}/^{238}\text{U}$ activity ratios (AR) occurs from the surface down to the sampling depth of borehole F1 which shows the following data sequence:

Sampling location	Depth (m)	Mean of AR ($^{234}\text{U}/^{238}\text{U}$)
SW03	0 – 10	0.99 +/- 0.05 (N=5)
F2	45 – 60	1.54 +/- 0.05 (N=12)
F1	96.5 – 125.7	2.26 +/- 0.08 (N=14)

This increase in the $^{234}\text{U}/^{238}\text{U}$ activity ratios with depth (see also Fig. 12) is not clearly related to the measured Eh-values in boreholes F1 and F2 (Table IX and Fig. 12). Nevertheless, other information, such as dissolved oxygen and mineralogical data, suggest more reducing conditions at the sampling interval of F1. Furthermore, the considerably higher mean concentrations of fluoride in F2 waters (1.93 +/- 0.12 mg/l in F2; 0.43 +/- 0.08 mg/l in F1) should cause this medium to be more aggressive for pitchblende dissolution. This effect could be partly responsible for the observed slightly higher uranium concentration and lower activity ratios in borehole F2, as compared to waters from borehole F1 (see Table IX). An additional reason for the higher $^{234}\text{U}/^{238}\text{U}$ activity ratios in groundwaters from F1 could be the higher leach rates around the zone at 110 m in the past, as indicated by the mineralogy of core samples (Waber *et al.*, this report series; Rep. 2). These could have depleted a larger fraction of the “labile” uranium (as compared to F2), thus enhancing the relative importance of preferential leaching over bulk dissolution.

The relatively low concentrations of uranium in waters from both F1 and F2 (5 to 10 $\mu\text{g/l}$) and the low to moderate $^{234}\text{U}/^{238}\text{U}$ activity ratios (1.5 to 2.3), resulting in low values for “excess ^{234}U ” (Osmond and Cowart, 1982), would indicate that these groundwaters had contact with only weakly mineralised rocks. This seems to be confirmed by analyses of core samples from F1 which showed uranium concentrations close to the water sampling interval which rarely exceeded 100 $\mu\text{g/g}$ (MacKenzie *et al.*, this report series; Rep. 7). However, other reasons could account for the low concentrations of uranium in these relatively oxidising groundwaters: 1) high flow-rates which do not permit equilibration between water and uranium minerals, and 2) scavenging of uranium by iron hydroxides.

Systematic variations in the $^{234}\text{U}/^{238}\text{U}$ activity ratios during dry and wet seasons could not be observed in groundwaters from F1 and F2, which is compatible with the small variations in the total uranium concentrations of these waters (indicating relatively

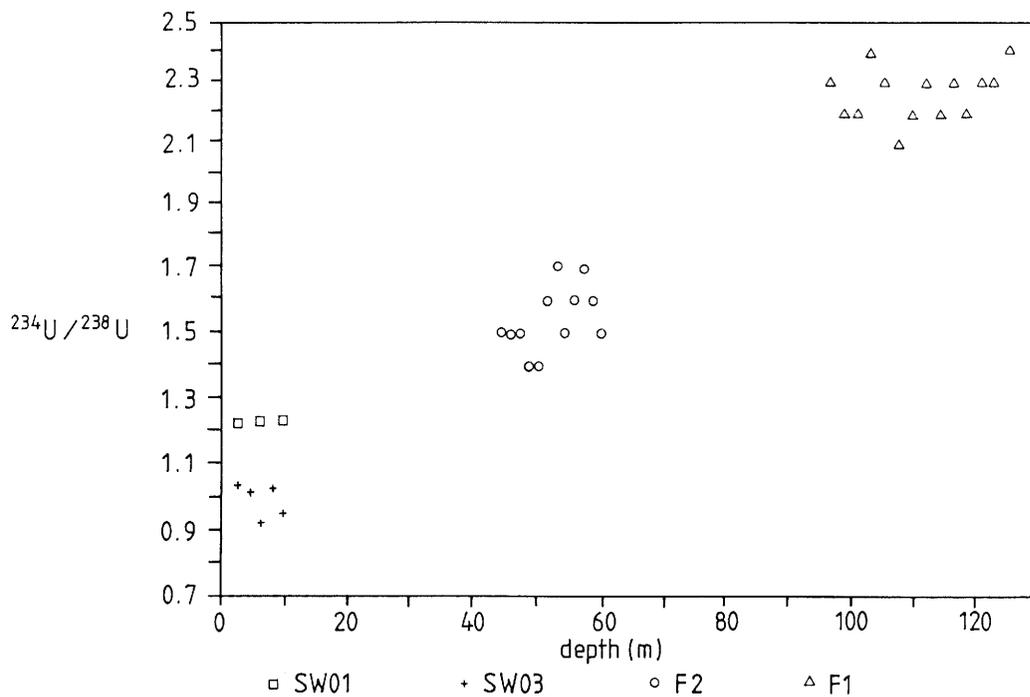


Figure 12. Variations of the $^{234}\text{U}/^{238}\text{U}$ activity ratios of waters from the Osamu Utsumi mine with depth.

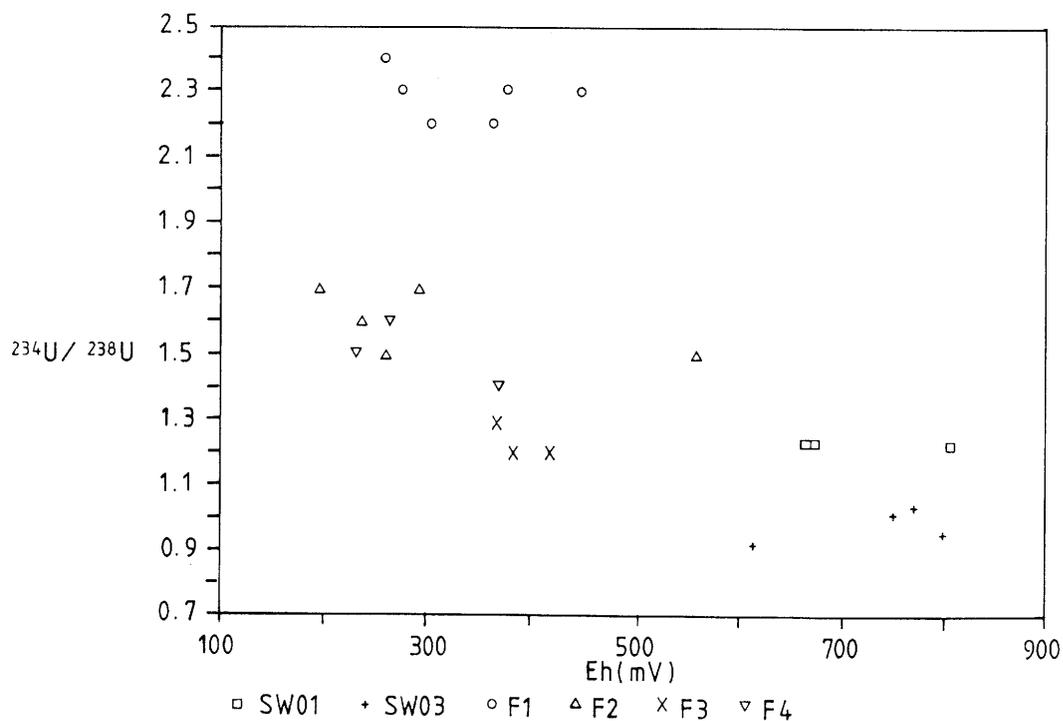


Figure 13. Variations of the $^{234}\text{U}/^{238}\text{U}$ activity ratios of waters from the Osamu Utsumi mine with redox potentials.

uniform leaching conditions due to the upward water flow). Much more drastic variations in the concentrations of total and isotopic uranium, apparently related to larger variations in the Eh conditions of these waters, can be observed in borehole F3. For example, samples PC-GW-36 (01/02/88) and PC-GW-55 (16/09/88) result in the following data (Table IX):

PC-GW-36: tot. [U] = 24.5 $\mu\text{g/l}$; $^{234}\text{U}/^{238}\text{U} = 1.17$; Eh = +420 mV.

PC-GW-55: tot. [U] = 0.81 $\mu\text{g/l}$; $^{234}\text{U}/^{238}\text{U} = 2.20$; Eh = +167 mV.

This example illustrates well the relative importance of two processes: “preferential leaching and recoil gain” versus “bulk leaching”. The inverse relationship between uranium concentrations in water and isotopic ratios is shown in Figure 14 for boreholes SW01, SW03, F1 and F2. According to the model of Osmond *et al.* (1983), groundwater from a single system will exhibit two dissolved uranium components, namely flow-through uranium and locally leached uranium. In this case, the former is at low concentrations and has a relatively high recoil ^{234}U contribution. The latter is at a high concentration and has the activity ratio of the rock (which varies in the Osamu Utsumi mine typically between 0.8 and 1.2; MacKenzie *et al.*, this report series; Rep. 7). On a plot of $^{234}\text{U}/^{238}\text{U}$ activity ratios against reciprocal U concentration (Fig. 14), the data should trend from the lower left (towards the leaching ratio) to the upper right, along a preferential loss slope. The data confirm this trend and, for infinite concentrations ($1/[\text{U}] = 0$), approach the uranium isotopic ratios of the mineralised rocks. The average excess ^{234}U obtained from this graph is about 0.07 Bq/l for F1 and 0.05 Bq/l for F2 waters ($80 \mu\text{g } ^{238}\text{U} = 1 \text{ Bq}$).

Given the flow direction of groundwaters at the mine, the following model can be proposed to account for these isotopic data. Deep groundwater in F1 is relatively “reducing” and may have reached a steady-state of excess ^{234}U (balance between recoil mobilisation, adsorption and decay). Upward movement brings water into a more oxidising environment (F2) where aggressive leaching occurs. This increases the total content of ^{238}U and ^{234}U , but does not result in a material increase in excess ^{234}U . In fact, the excess in F2 is slightly less than in F1, suggesting a somewhat different parent water, and/or some dilution by surface waters. If the water were moving downwards, one would expect the $^{234}\text{U}/^{238}\text{U}$ activity ratios in F1 to be higher (owing to a combination of high concentration of uranium in the host rock and waters that were decreasing in Eh) and the waters in F2 to be lower in uranium concentration but have the same activity ratio, because precipitation is isotopically non-fractionating.

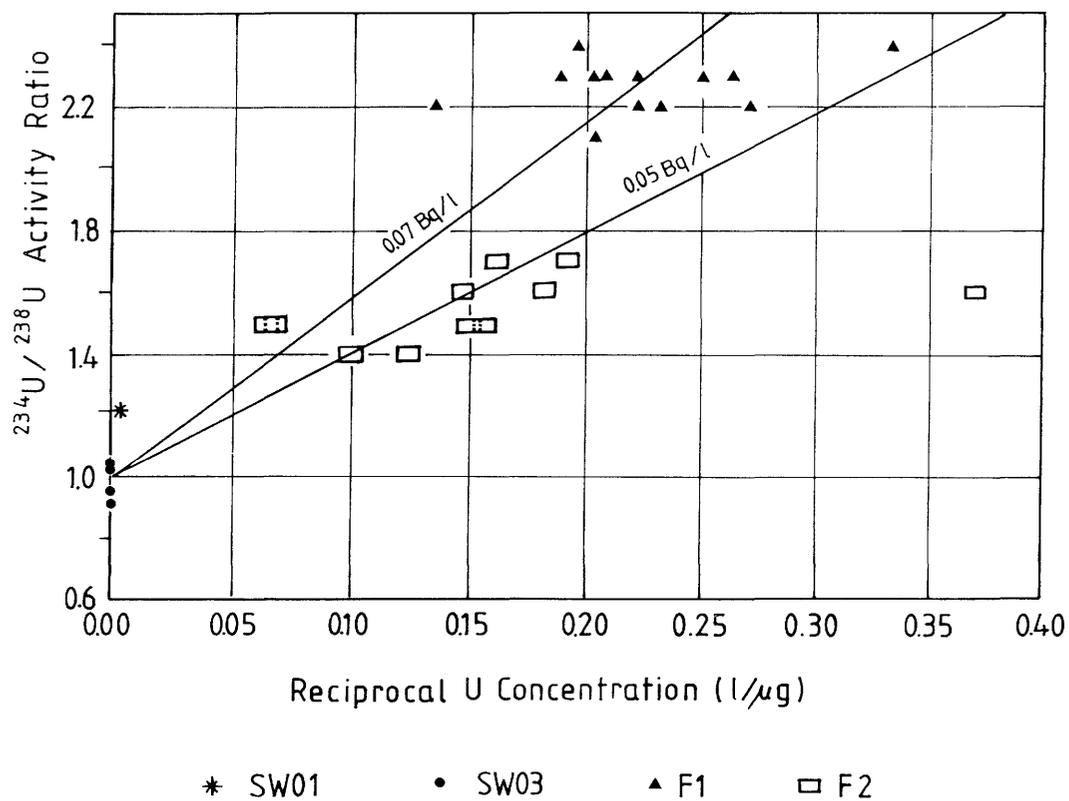


Figure 14. Variations of the $^{234}\text{U}/^{238}\text{U}$ activity ratios of waters from the Osamu Utsumi mine with reciprocal uranium concentration.

The upward flow of groundwater at the F1 and F2 sampling locations, as known from borehole hydraulics (Holmes *et al.*, this report series; Rep. 5) and, indirectly, from the above-described U-isotope systematics, is further supported by the tritium data which show that groundwaters from borehole F1 are younger (and therefore closer to the recharge area) than waters from borehole F2 (Nordstrom *et al.*, this report series; Rep. 6).

Drainage water of the mine collected at the “supply dam”, which can be considered as a composite sample for the whole mine environment, has a $^{234}\text{U}/^{238}\text{U}$ activity ratio of 1.24 (see Table IX), similar to that observed for the strongly oxidising waters from the shallow borehole SW01. Waters from the two other shallow boreholes SW02 and SW03 and from the deeper borehole UC-16, also of oxidising character, have $^{234}\text{U}/^{238}\text{U}$ activity ratios at or very close to secular equilibrium.

Information concerning uranium isotopic systematics of the other boreholes in the mine area is very scarce and does not permit more detailed interpretation. Groundwaters from one of the deeper boreholes, F4 (sampling interval: 75–175 mbgl), which should represent reducing waters, still has Eh-values between +230 and +370 mV, compatible with the stability field of U(VI). The high U-concentrations in these waters and the low $^{234}\text{U}/^{238}\text{U}$ activity ratios (1.4 to 1.6) are indicative of stronger uranium mineralisation in the surrounding bedrock and severe leaching conditions (Table IX).

From the deepest borehole F5 (sampling interval: 275 – 300 mbgl), situated close to borehole F3 (Figs. 2 and 3), only two water samples have been analysed (GW-62 and GW-72; Tables IX and Appendix 1; Table 1-I). The data show the expected trend, when compared to the more shallower waters from F3 (and also from F4), of slightly lower Eh-values and correspondingly higher $^{234}\text{U}/^{238}\text{U}$ activity ratios (1.8 ± 0.1 for both samples). The higher pH-values (6.3) of waters from F5 and their lower concentrations of SO_4^{2-} and Fe^{2+} further indicate that these groundwaters are less “contaminated” by acid mine waters and are therefore perhaps most representative of the deeper aquifer (Nordstrom *et al.*, this report series; Rep. 6).

4.1.2. Thorium

Total Thorium: Tables IX and Appendix 1, Table 1-I summarise results on thorium concentrations and isotopic compositions of waters from the Osamu Utsumi mine. Concentrations of this element in prefiltered groundwaters (<450 nm) are typically between 0.01 and 0.1 $\mu\text{g/l}$. According to Langmuir *et al.* (1980), these concentrations are

much above the expected solubility of thorianite, which would be about 0.01 ng/l as $\text{Th}(\text{OH})_4^0$ in the pH range of the mine groundwaters. Complexation and/or association of thorium with suspended matter are the generally accepted reasons for the observed higher concentrations in natural waters. This has been confirmed by ultrafiltration experiments for waters from the Osamu Utsumi mine and Morro do Ferro (Miekeley *et al.*, 1989 and this report series; Rep. 9). Typically, more than 60% of thorium in prefiltered deep groundwaters is associated with particulate ferrihydrite-organic species of colloidal size ranges (1.5 to 450 nm). This fraction can be even higher in organic-rich near-surface waters from Morro do Ferro and indicates that humic compounds of colloidal size dimensions (>1,000 dalton or 1.5 nm), associated with colloidal hydrous ferric oxides, are the main complexants for thorium. The smaller fraction of “dissolved” thorium, operationally defined as the portion in the <1.5 nm range, is probably associated with low molecular weight fulvic acids and hydroxo, fluoro and phosphato complexes. It can be concluded that the observed thorium concentrations are in very good agreement with those predicted by geochemical models (Bruno *et al.*, this report series; Rep. 11).

Suspended particulate material of larger grain sizes (>450 nm), composed predominantly of clay minerals in near-surface waters and of amorphous hydrous ferric oxides in deeper groundwaters, are the main concentrators of thorium in “unfiltered” waters. These particles have thorium concentrations of up to 1340 $\mu\text{g/g}$, which are higher by a factor of 10^6 or more than those of the corresponding waters (see Table XI). This illustrates convincingly that the hydrochemistry of thorium is greatly influenced, if not completely dominated, by precipitation or sorption reactions. Despite the low concentrations of suspended particles in the Osamu Utsumi mine waters, these particles would be the principal vehicles for the transport of thorium. There are indications, however, that the mobility of these particles is very limited due to the microporous structure of the bedrocks, which seems to provide an efficient migration barrier (Miekeley *et al.*, this report series; Rep. 9).

Water samples collected from the same borehole at different times show considerable variations in the thorium concentrations, but the available data do not permit interpretation in terms of the influence of water chemical compositions and possible seasonal effects. Moreover, due to the extremely low concentrations of thorium in most of these samples, large errors cannot be excluded as most of the results were close to the limit of detection of the methods used (see section 3.2).

The influence of the water chemistry on thorium concentration is, however, clearly visible in near-surface, sulphate-rich waters of low pH (3 to 4), in which up to 720 $\mu\text{g/l}$

of this element were determined (SW01 to SW03, Table IX). These unusually high concentrations are caused by the low pH and, possibly, by complexation with sulphate. Suppression of hydrolysis and sorption of thorium are indicated by two further observations (Miekeley *et al.*, this report series; Rep. 9): 1) when compared to groundwaters, a much smaller proportion of this element is in the colloidal fractions (<10%), and 2) the association ratio of thorium between suspended particles (>450 nm) and the corresponding waters is considerably reduced under low pH- and high [SO₄]²⁻-conditions (Table XII).

Isotopic Ratios: ²³⁰Th activities in deep groundwaters are typically less than 0.01 Bq/l, which corresponds to solution concentrations of about 0.01 ng/l (ppt), and are therefore, on a mass basis, lower by a factor of 1,000 or more than those observed for ²³²Th (Tables IX and Appendix 1; Table 1-I). This reflects the low concentration ratio of ²³⁰Th/²³²Th in the bedrock. The mean concentrations of ²³⁰Th and ²³²Th in core samples in the water sampling interval of borehole F1 are 0.0005 µg/g and 38 µg/g, respectively, which corresponds to a 230/232 mass concentration ratio of about 10⁻⁵. The mean concentrations of both isotopes and their ratio in waters from the same borehole are: ²³⁰Th = 0.002Bq/l = 2.6 x 10⁻⁶ µg/l; ²³²Th = 0.041 µg/l; ²³⁰Th/²³²Th = 6 x 10⁻⁵. The similarities of the ²³⁰Th/²³²Th concentration ratios in rocks and waters confirm that both isotopes have essentially the same reaction chemistry, controlled by solubility limitations and sorption processes. The somewhat higher ²³⁰Th/²³²Th concentration ratio in waters, which seems also to be reflected in a slightly lower association ratio (suspended particles/water) for ²³⁰Th (see Table XII), could be caused by preferential leaching and recoil effects, as this isotope is produced by alpha decay of ²³⁴U.

All of the analysed groundwaters are in strong radioactive disequilibrium with respect to ²³⁴U and ²³⁰Th. The ²³⁰Th/²³⁴U activity ratios are typically between 0.01 and 0.1, reflecting the higher solubility of uranium and the greater tendency of thorium isotopes to sorb onto solid phases.

²²⁸Th/²³²Th activity ratios in waters and suspended material will not be discussed in this report due to the inability to correct the data for the ingrowth of ²²⁸Th from ²²⁸Ra (which has not yet been determined). However, expected trends such as pronounced disequilibria between ²²⁸Th and ²³²Th in aqueous and in particulate phases were clearly visible, similar to those previously observed in other samples from the Morro do Ferro environment (e.g. Lei, 1984; Campos *et al.*, 1986).

4.1.3. Rare-earth elements

Rare-earth element (REE) concentrations for 26 water samples from the Osamu Utsumi uranium mine are summarised in Table XIII.

Similarly to the situation observed for uranium and thorium, very high REE concentrations of up to 29,000 $\mu\text{g/l}$ (ΣLa to Lu) were measured in near-surface waters (e.g. SW03; sample GW-47) of low pH (3.6) and high sulphate concentrations (445 mg/l). These appear to be the highest REE concentrations ever published for natural waters. Concentrations lower by a factor of 30 were reported by Michard (1989) for hydrothermal solutions, which were also rich in sulphate. According to Wood (1990), in moderately acidic waters with $[\text{SO}_4^{2-}] > 1000$ mg/l as observed in the Osamu Utsumi mine (Table IX), the complexation of REEs by sulphate, probably as $\text{Ln}(\text{SO}_4)^+$ species (where Ln represents any REE in the 3⁺ oxidation state), is favoured. As fluoride concentrations are also very high in surficial mine waters (up to 75 mg/l), competition with fluoride complexes, such as LnF_3^0 , LnF_2^+ and LnF^{2+} , is possible (Fig. 15). Complexation affects the distribution of REEs between water and suspended particles, as previously mentioned for uranium and thorium. Suspended particles (>450 nm) in near-surface waters have REE concentrations higher by a factor of 1,000 than the corresponding prefiltered waters (Table XIV). The association ratios (R_a in ml/g) of these elements are in the order of 1,000, with the exception of cerium whose R_a -value is higher by a factor of about 5 to 10. When compared with the association ratios of REEs in groundwaters (e.g. F1, F2), the values of near-surface waters are significantly lower, confirming the influence of pH or sulphate (fluoride) complexation on the partitioning of these elements.

Figure 16 shows the chondrite-normalised distribution patterns of REEs in near-surface waters (SW03) and in a particulate material sample (SP-58 corresponding to GW-58/SW03). A characteristic Ce-depletion can be seen in these water samples, which is probably caused by the much lower solubility of $\text{Ce}(\text{OH})_4$ compared to the trivalent lanthanides (Latimer, 1952) and by the stronger tendency of Ce(IV) to sorb onto solid phases (very much resembling the behaviour of thorium). This seems to be confirmed by the observed higher association ratio (R_a) for cerium (Table XIV, sample SP-58) and (as a consequence of the higher R_a) by the absence of a negative Ce-anomaly in the suspended particle fraction (Fig. 16).

Concentrations of REEs in deep groundwaters from the Osamu Utsumi mine (F1, F2) are much lower than in near-surface waters (Table XIII). The lower complexation capacity of these groundwaters, which results in less effective leaching from the bedrock

TABLE XIII

Rare-earth element concentrations in near-surface and deep ground waters from the Osamu Utsumi mine (all values in $\mu\text{g/l}$).

REE	SW03			F1								
	GW-47	GW-58	GW-66	GW-09	GW-14	GW-15	GW-17	GW-22	GW-40	GW-42	GW-54	GW-63
La	13500	567	12515	3.9	2.9	2.1	0.45	2.7	15.2	4.29	3.89	13.1
Ce	6270	124	5070	6.8	3.2	4.2	0.74	4.9	12.5	6.92	7.24	
Nd	6490	250	6440	1.7		1.2	0.16	1.2	7.75	1.84	2.06	3.36
Sm	764	28.5	734	0.22	0.24	0.14	0.02	0.18	0.90	0.21	0.24	0.41
Eu	206	7.8	200	0.07	0.06	0.05	0.01	0.05	0.25	0.063	0.076	0.11
Gd	585	22.8	555	0.26	0.24	0.13	0.025	0.17	0.73	0.20	0.23	0.31
Dy	595	23.3	530	0.08	0.21	0.14	0.021	0.15	0.75	0.23	0.27	0.34
Ho	130	5.3	115	0.033	0.023	0.001	0.004	0.002	0.14	0.030	0.036	0.075
Er	309	12.2	259	0.055	0.048	0.045	0.009	0.039	0.32	0.052	0.059	0.18
Tb	135	5.5	108	0.022	0.019	0.012	0.003	0.015	0.15	0.018	0.023	0.098
Lu	13.6	0.59	11.9	0.003	0.002	0.001	0.001	0.003	0.016	0.002	0.001	0.009

REE	F2						F3			F4			PM22	SUP .DAM
	GW-13	GW-20	GW-41	GW-43	GW-60	GW-64	GW-36	GW-45	GW-65	GW-44	GW-59	GW-67	GW-19	SD-03
La	1.2	14.2	8.55	1.59	3.0	5.88	12.1	318	11.6	67.4	4.32	65.2	0.5	1.8
Ce	1.7	8.4	6.35	1.61	0.83	8.38	8.73	165	10.5	63.3	4.53	63.4	0.9	1.7
Nd	0.6	4	4.02	0.62	0.49	2.40	2.59	45.7	4.72	19.7	1.32	23.4	0.19	0.41
Sm	0.07	0.48	0.42	0.060	0.038	0.26	0.31	<0.8	0.74	2.59	0.19	3.02	0.018	0.05
Eu	0.03	0.13	0.097	0.020	0.014	0.079	0.10	0.50	0.30	0.78	0.072	0.94	0.009	0.015
Gd	<0.02	0.41	0.22	0.057	0.038	0.24	0.34	<8	1.31	3.08	0.30	3.65	0.029	0.037
Dy	0.06	0.31	0.18	0.079	0.049	0.25	0.29		1.36	2.68	0.42	3.78	0.018	0.02
Ho	<0.001	0.062	0.036	0.014	0.005	0.037	0.054		0.28	0.54	0.088	0.82	0.006	0.007
Er	0.042	0.15	0.087	0.047	0.028	0.073	0.13		0.62	1.04	0.20	1.79	0.011	0.012
Tb	0.016	0.072	0.040	0.033	0.017	0.031	0.068	0.2	0.21	0.26	0.069	0.55	0.005	0.006
Lu	<0.001	0.01	0.006	0.004	0.001	0.002	0.01		0.025	0.027	0.006	0.056	0.002	0.002

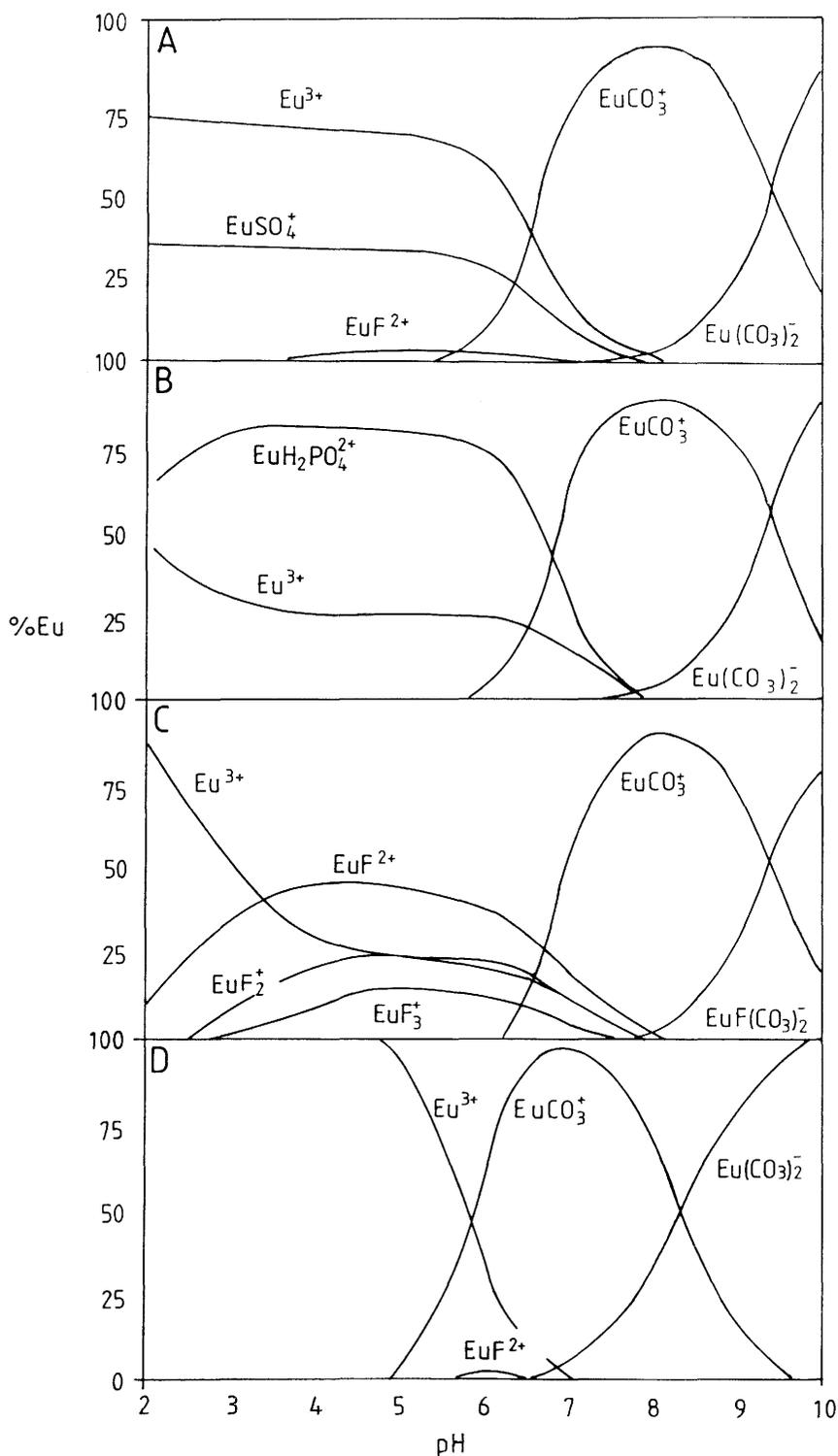


Figure 15. The distribution of Eu^{3+} among inorganic complexes as function of pH in model groundwaters at 25°C and of different compositions, according to Wood (1990). Molal concentrations are expressed as $\log c$.

- A) Eu (-7); F^- (-6); SO_4^{2-} (-4); HCO_3^- (-4); (deviations from A).
 B) SO_4^{2-} (-6); ΣPO_4^{3-} (-2).
 C) F^- (-4); SO_4^{2-} (-6).
 D) SO_4^{2-} (-6); HCO_3^- (-3).

TABLE XIV

Chondrite-normalised rare-earth element concentrations ($\mu\text{g/g}$) in water-suspended particles (>450 nm) of near-surface and deep ground waters from the Osamu Utsumi mine and Morro do Ferro, including calculated association ratios (R_a) and the percentage fractions (F) of REEs in water (<0.45).

Borehole	SW03		F1		F2		MF10		MF11		MF12					
[REE] in suspended particles ($\mu\text{g/g}$)	SP-58	SP-17	SP-40	SP-54	SP-41	SP-60	SP-12	SP-33	SP-52	SP-35	SP-53	SP-18	SP-30	SP-34	SP-56	
La	1025	1110	2270	953	2320	621	1100	1250	3230	3530	3715	837	311	222	128	
Ce	1245	1870	2820	1640	1480	690	2520	513	896	1640	1740	1370	384	297	262	
Nd	547	430	685	355	513	316	636	866	2720	2240	2320	239	140	88.4	61.5	
Sm	65.5	14	56.7	19	43.6	32.8	75	101	359	249	259	19.2	14.8	8.2	5.1	
Eu	16.6	10	18.0	8	13.3	9.4	17.2	24.6	94.5	55.4	57.6	4.8	4.2	2.4	1.7	
Gd	36.0	<100	49.3	<50	<30	16.9	37.7	46.3	174	108	114	<20	8.9	5.2	<5	
Dy	28.9	18	47.3	17	29.7	22.8	22.1	31.2	132	63.5	66.8	5.6	8.6	4.6	3.3	
Ho	2.8		0.7			1.9	4.1	5.1	9.6	11.3	12.5		0.9			
Er	12.3		2.7		9.1	11.3	8.8	10.4	38.4	24.0	25.3		3.0	0.8	0.6	
Tb	15.4	2	4.0	2	13.3	11.2	6.3	7.1	34.2	14.6	15.5	4.0	2.0	1.4	1.1	
Lu	1.5		0.7		0.6	1.3	0.59	0.76	2.7	1.5	1.7	0.4	0.1	0.1	0.1	
Load (mg/l)	0.8	0.05	0.2	0.15	0.2	0.5	25	1	0.1	2.8	2.1		2.8	3.1	2.6	
F (%)	La	99.9	89.0	97.1	96.5	94.9	90.6	3.8	20.9	98.9	15.2	34.7		52.2	73.1	79.5
	Ce	99.2	88.8	95.7	96.7	95.5	70.6	1.9	36.9	97.8	6.7	20.1		30.0	53.0	61.5
	Nd	99.8	88.2	98.3	97.5	97.5	75.6	3.6	97.8	97.8	12.2	30.6		71.0	75.4	
	Sm	99.8	96.6	98.8	98.8	98.0	69.9	3.6	38.8	97.2	10.3	32.3		34.7	76.3	70.7
	Eu	99.8	95.2	98.6	98.4	97.3	74.9	6.5	96.7	96.7	11.4	32.8		43.4	70.8	69.3
	Gd	99.9		98.7			81.8	6.9	43.1	97.4	10.4	36.9			69.7	
	Dy	99.9	95.9	98.8	99.1	96.8	81.1	8.3	27.8	96.9	10.1	39.9		24.9	68.5	63.6
	Ho	100.0		99.9			84.0	5.5	16.4	98.8		43.2				
	Er	99.9		99.8		98.0	83.2	9.1	36.6	97.7		40.4		10.6	54.7	85.2
	Tb	99.8	96.8	99.5	98.7	93.8	75.2	6.5	41.3	95.0	6.8	33.0		26.3	48.0	63.6
	Lu	99.8		99.1		98.0	60.6	11.9	72.5	96.3		21.9		61.7	65.8	
R_a (ml/g)	La	1.8E+03	2.5E+06	1.5E+05	2.4E+05	2.7E+05	2.1E+05	1.0E+06	3.8E+06	1.1E+05	2.0E+06	9.0E+05	9.3E+05	3.3E+05	1.2E+05	9.9E+04
	Ce	1.0E+04	2.5E+06	2.3E+05	2.3E+05	2.3E+05	8.3E+05	2.1E+06	1.7E+06	2.3E+05	5.0E+06	1.9E+06	8.6E+05	8.3E+05	2.9E+05	2.4E+05
	Nd	2.2E+03	2.7E+06	8.8E+04	1.7E+05	1.3E+05	6.4E+05	1.1E+06	2.2E+05	2.2E+05	2.6E+06	1.1E+06	8.5E+05		1.3E+05	1.3E+05
	Sm	2.3E+03	7.0E+05	6.3E+04	7.9E+04	1.0E+05	8.6E+05	1.1E+06	1.6E+06	2.9E+05	3.1E+06	1.0E+06	6.4E+05	6.7E+05	1.0E+05	1.6E+05
	Eu	2.1E+03	1.0E+06	7.2E+04	1.1E+05	1.4E+05	6.7E+05	5.7E+05		3.4E+05	2.8E+06	9.8E+05	4.0E+05	4.7E+05	1.3E+05	1.7E+05
	Gd	1.6E+03		6.8E+04			4.4E+05	5.4E+05	1.3E+06	2.7E+05	3.1E+06	8.1E+05			1.4E+05	
	Dy	1.2E+03	8.6E+05	6.3E+04	6.3E+04	1.7E+05	4.7E+05	4.4E+05	2.6E+06	3.2E+05	3.2E+06	7.2E+05	3.3E+05	1.1E+06	1.5E+05	2.2E+05
	Ho	5.3E+02		5.0E+03			3.8E+05	6.8E+05	5.1E+06	1.2E+05		6.3E+05				
	Er	1.0E+03		8.4E+03		1.0E+05	4.0E+05	4.0E+05	1.7E+06	2.4E+05		7.0E+05		3.0E+06	2.7E+05	6.7E+04
	Tb	2.8E+03	6.7E+05	2.7E+04	8.7E+04	3.3E+05	6.6E+05	5.7E+05	1.4E+06	5.3E+05	4.9E+06	9.7E+05	1.0E+06	1.0E+06	3.5E+05	2.2E+05
	Lu	2.5E+03		4.4E+04		1.0E+05	1.3E+06	3.0E+05	3.8E+05	3.9E+05		1.7E+06	2.0E+05	2.0E+05	2.0E+05	

Association ratio $R_a = [\text{SP}_n]/[\text{Water}]$

Percentage fractions $F = [\text{Water}]/[\text{Water}] + [\text{SP}_n] \times 100$

(For definition of $[\text{SP}_n]$, see Table XI).

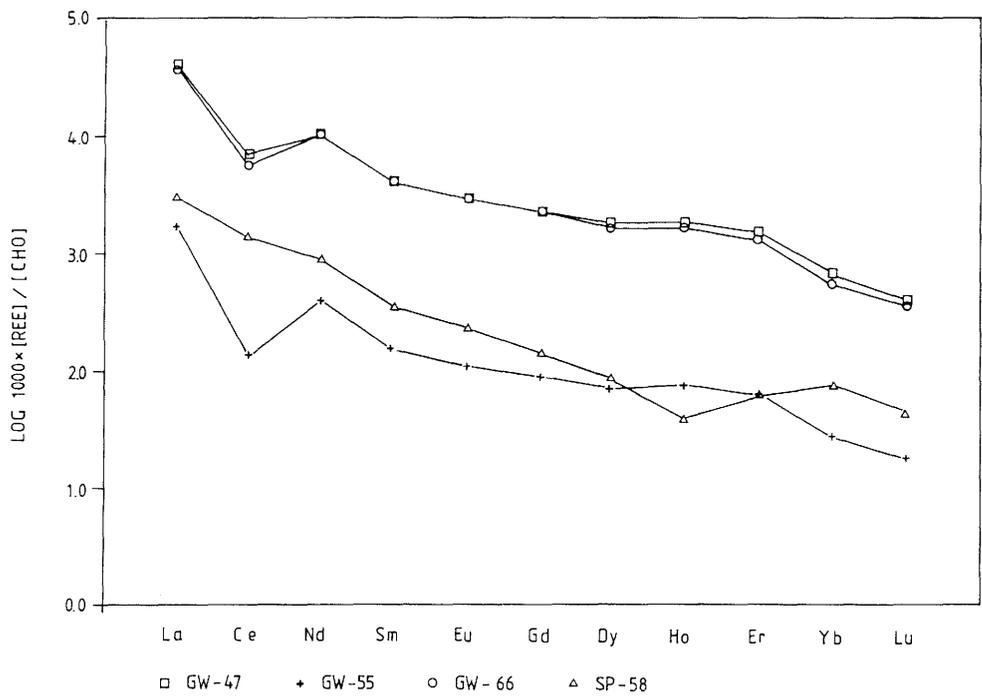


Figure 16. Chondrite-normalised REE distribution patterns in near-surface waters (SW03) and in a corresponding particulate material fraction (>450 nm), Osamu Utsumi mine (the REE concentrations of SP-58 are normalised to fit into the graph, factor: [REE]/1000).

and stronger sorption/hydrolysis of the REEs (indicated by the higher association ratios, Table XIV), is the most probable reason for the observed differences. While uranium concentrations in waters from F1 (and to a lesser degree also from F2) do not exhibit large variations, this is not true for the REEs (e.g. GW-17:La = 0.45 µg/l; GW-40: La = 15.2 µg/l). Seasonal influences on the REE concentrations and/or variations in the ligand concentrations (e.g. SO_4^{2-} , F, HCO_3^-) of these waters were not apparent, so the reason for this large difference in REE concentrations is unknown.

For the typical chemical composition of groundwaters from F1 and F2 (Table IX) one would expect that the REEs would exist predominantly as simple ions Ln^{3+} and as sulphate (fluoride ?) complexes (Fig. 15). Due to the acidic character of the groundwaters from the Osamu Utsumi mine (pH <6), carbonate complexation should be of less importance (Wood, 1990). The formation of simple, low molecular (weight/size) species is in contradiction, however, with experimental results obtained by ultrafiltration techniques (Miekeley *et al.*, this report series; Rep. 9), which indicate that a considerable fraction of the REEs in prefiltered (<450 nm) groundwaters from the Osamu Utsumi mine and the Morro do Ferro environments (up to 50% of the total REE concentrations) is associated with colloidal particles in the 1.5 to 10 nm size range. This could indicate that hydrolytic polymeric species of REEs are of greater importance than believed (Wood, 1990) and/or that complexation/sorption of these elements by humic compounds and/or other colloidal phases (e.g. ferrihydrites) determines, at least in part, the aqueous chemistry of these elements. The expected high complexation constants for REE-humic/fulvic complexes (similar to that reported for actinides, e.g. Choppin *et al.*, 1985) suggest that, even at the low DOC concentrations in groundwaters of both sites (1 to 3 mg/l), organic species could be important. For near-surface DOC-rich waters of Morro do Ferro, this has been confirmed experimentally (Miekeley *et al.*, 1989; this report series; Rep. 9). About 90% of the REEs were associated with humic compounds, predominantly in the form of humic acids.

Data from borehole F4 (samples GW-44 and 67) show that REE concentrations are occasionally much higher than in waters from F1 and F2, which may reflect the expected higher concentrations of these elements in the bedrock and more aggressive leaching conditions as result of higher sulphate concentrations in such waters (Tables IX and XIII). Sample GW-59 from the same borehole (F4), which has a low sulphate concentration, also has a low REE-content. Variations in the fluoride concentrations of these waters do not correlate with REE concentrations, indicating that this ligand is of less importance in REE solubilisation (as would be expected from speciation studies;

Wood, 1990). Due to the small amount of data from this borehole, however, this interpretation is very speculative.

Figures 17 to 19 show examples of chondrite-normalised distribution patterns of groundwaters from boreholes F1, F4 and F2, and Figures 20 and 21 show similar graphic presentations for particulate material (F1, F2) and rock samples. Most of the deeper groundwaters (F1, F4) do not exhibit the characteristic cerium depletion observed in the strongly oxidising waters. Furthermore, they have very similar REE patterns to the bedrock (reduced and/or oxidised phonolites; Fig. 22), showing that leaching occurred without fractionation between the LREEs (La to Sm) and the HREEs (Dy to Lu). This would be in accordance with the redox potential of these waters (Latimer, 1952) and with the similarities in the stability constants of the REE-sulphate complexes [$\log\beta_1$ (La to Lu): 3.64 +/- 0.06], which would not permit elemental fractionation as opposed to the case for carbonate or fluoride complexation (Wood, 1990). However, organic complexation of the REEs cannot be excluded, as already mentioned. In some samples of shallower groundwaters from F2 (GW-41, GW-20), the negative Ce anomaly, characteristic of strongly oxidising waters, is still present and may be caused by the influx of near-surface waters (Fig. 19).

Groundwater-suspended particles, which are composed mainly of amorphous hydrous ferric oxides, are strongly enriched in REEs (Table XIV). Association ratios are higher by a factor of 100 than in near-surface waters and are very similar within the group. This indicates that cerium behaves in groundwaters like the trivalent lanthanides. Whether or not suspended particles are potentially important for the transport of the REEs (and their actinide analogues) depends on the retention capacity of the bedrock for these particles. In each case, however, the low concentrations of suspended matter in groundwaters from the Osamu Utsumi mine and the moderate association ratios (somewhat higher than for U, but lower than for Th) would cause only a small fraction of the total REE concentrations [$\text{REE-tot.} = \text{REE} (>450 \text{ nm}) + \text{REE} (<450 \text{ nm})$] to be transported by particles (Table XIV, Miekeley *et al.*, this report series; Rep. 9).

4.2. Natural series nuclides and rare-earth elements in near-surface and deep ground waters from the Morro do Ferro environment

The composition of groundwaters from Morro do Ferro and the aqueous behaviour of uranium, thorium and the rare-earth elements are qualitatively very similar to those already discussed for the Osamu Utsumi mine. This is a natural consequence of the

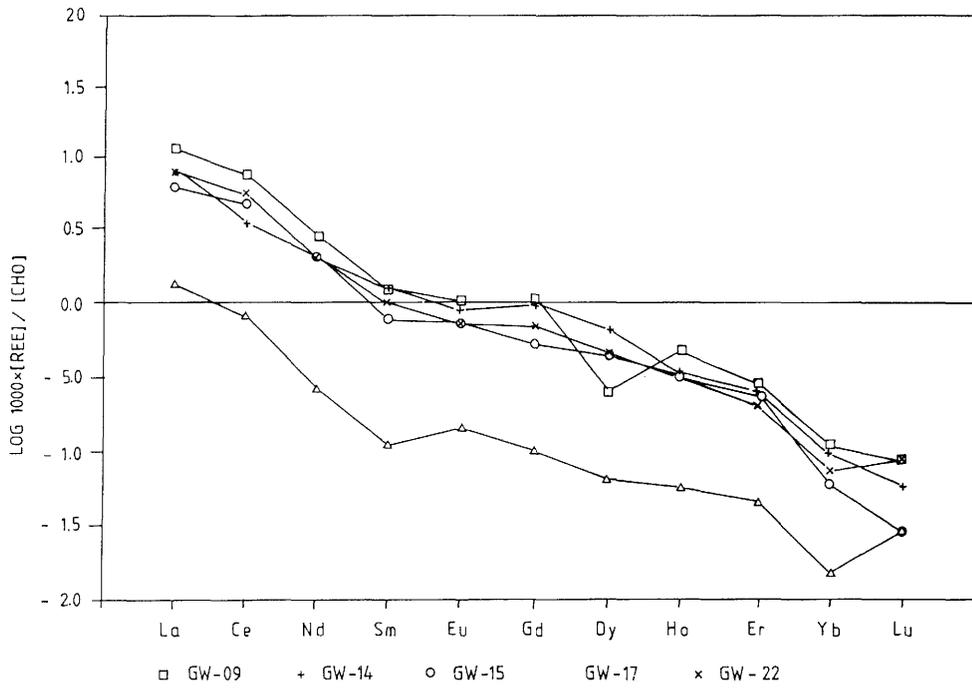


Figure 17a. Chondrite-normalised REE distribution patterns in groundwaters from borehole F1, Osamu Utsumi mine.

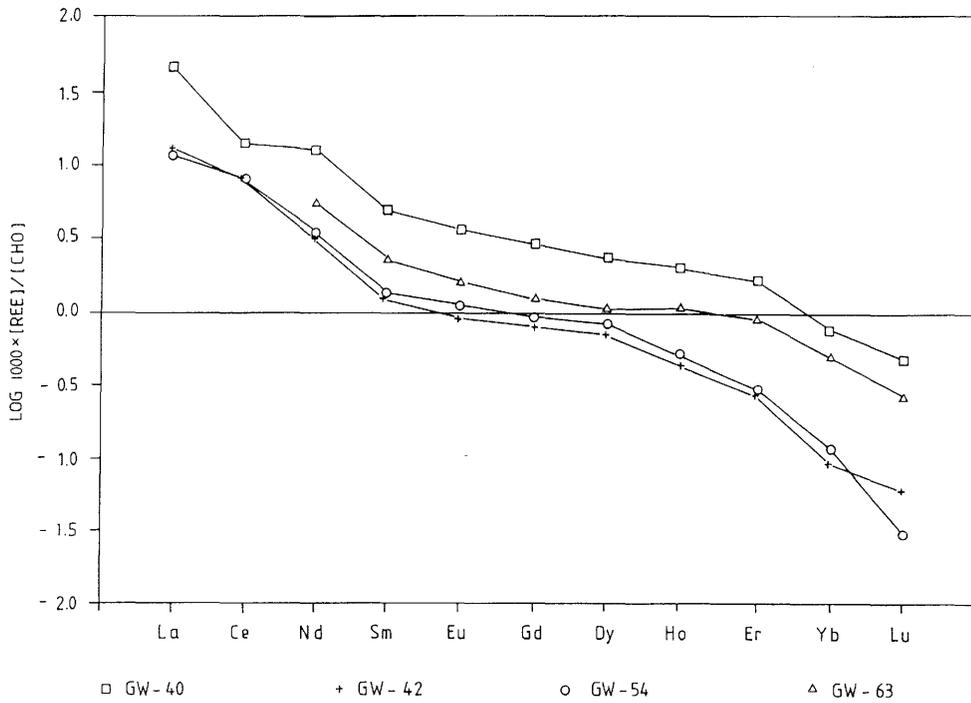


Figure 17b. Chondrite-normalised REE distribution patterns in groundwaters from borehole F1, Osamu Utsumi mine.

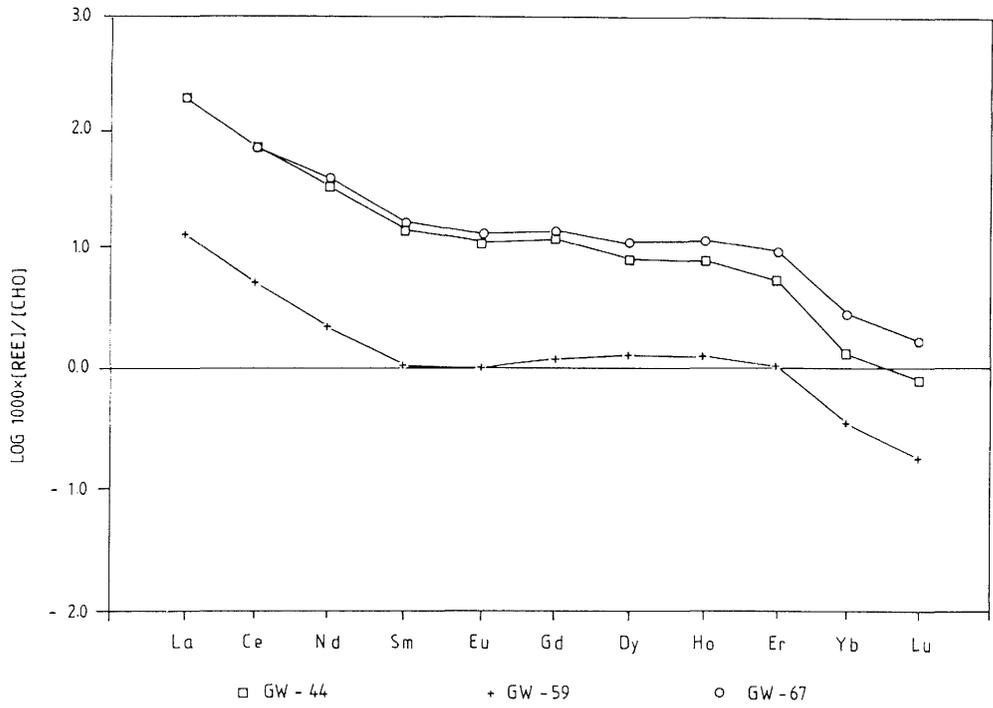


Figure 18. Chondrite-normalised REE distribution patterns in groundwaters from borehole F4, Osamu Utsumi mine.

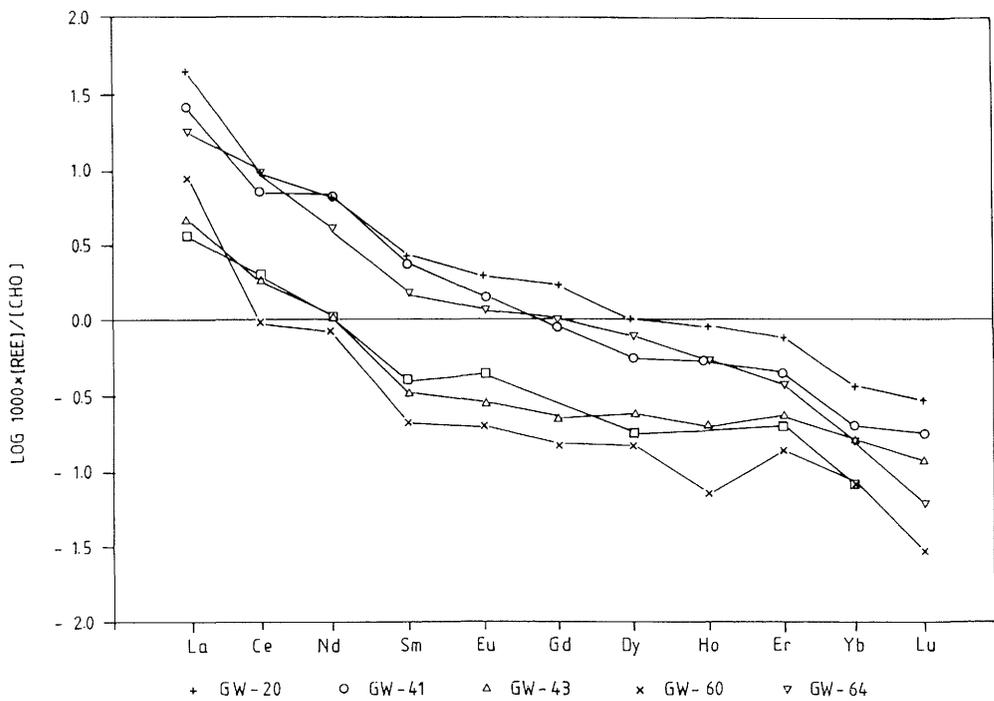


Figure 19. Chondrite-normalised REE distribution patterns in groundwaters from borehole F2, Osamu Utsumi mine.

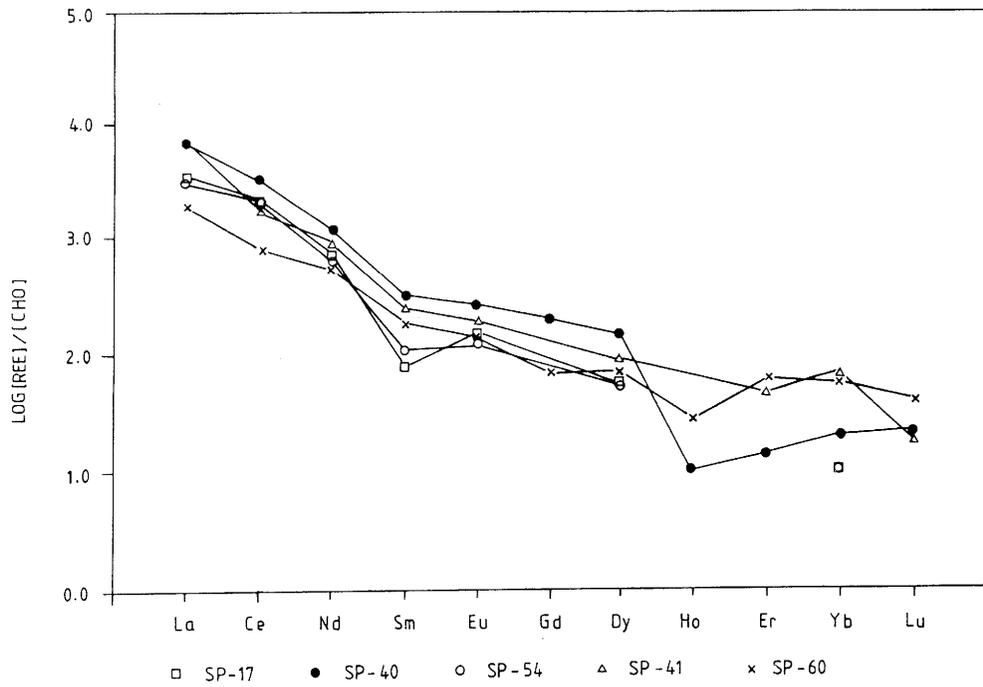


Figure 20. Chondrite-normalised REE distribution patterns in particulate matter (>450 nm) of groundwaters from boreholes F1 and F2, Osamu Utsumi mine (Miekeley et al., this report series; Rep. 9).

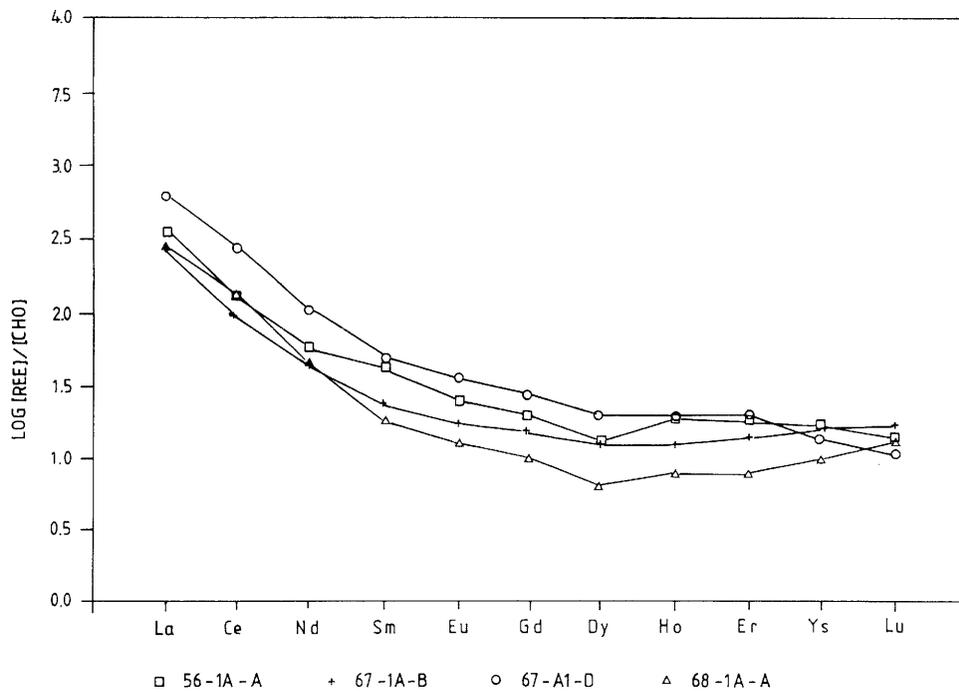


Figure 21. Chondrite-normalised REE distribution patterns in core samples (redox front at 66.2 m) from borehole F1.

similarities in bedrock composition and in the climate at both sites. Differences, mainly of a quantitative nature, were observed in near-surface waters. Due to the more advanced weathering state of Morro do Ferro, which has caused depletion of mobile elements. Waters from the strongly weathered zone of the deposit (MF10, MF11, MF13) have generally lower contents of dissolved solids (and of potential inorganic complexants, such as sulphate, for the less mobile elements, i.e. Th and the REEs), when compared with near-surface waters from the Osamu Utsumi mine. The very high concentrations of Th and REEs detectable in shallow waters of the uranium mine were therefore not measured in Morro do Ferro waters, although the unsaturated zone of this deposit is highly enriched in these elements ([REEs, Th] typically 1–10 mg/g). However, concentrations of DOC in surficial waters from Morro do Ferro are higher than at the Osamu Utsumi mine where there is an absence of any vegetation. For this reason, organic complexation is expected to be more important in Morro do Ferro waters. This aspect is discussed in more detail by Miekeley *et al.* (this report series; Rep. 9).

In the following sections, the available water data from the Morro do Ferro site are analysed in terms of concentration gradients which may occur as a result of the downward migration of Th and the REEs from the highly mineralised saturated zone of the deposit (borehole MF11) to borehole MF12 at the base of the hill (Fig. 5). Further results on the speciation of these elements and their interactions with particulate matter will also be presented.

4.2.1. Uranium

Based on the data of Table XV, mean uranium concentrations in waters from MF10, MF11 and MF12 are essentially identical, about $0.8 \pm 0.2 \mu\text{g/l}$. This is consistent with the relatively small range over which uranium has been measured in core samples (20 to $87 \mu\text{g/g}$, mean: $35 \mu\text{g/g}$; MacKenzie *et al.*, this report series; Rep. 7) and with the noted absence of any significant uranium enrichment in any core samples from Morro do Ferro analysed to date. $^{234}\text{U}/^{238}\text{U}$ mean activity ratios are consistent with time and are similar in MF10 (1.31 ± 0.04), MF11 (1.46 ± 0.08) and MF13 (1.42), but are less than that in MF12 (1.83 ± 0.23).

Although the deep groundwaters of MF11 and MF13, flowing down the hydraulic gradient to the valley bottom, are strongly oxidising (Eh values for MF10 show the same trend, but are widely scattered; Fig. 22), and those of borehole MF12 (which has a strong upward vertical hydraulic component) are less oxidising, no differences in soluble

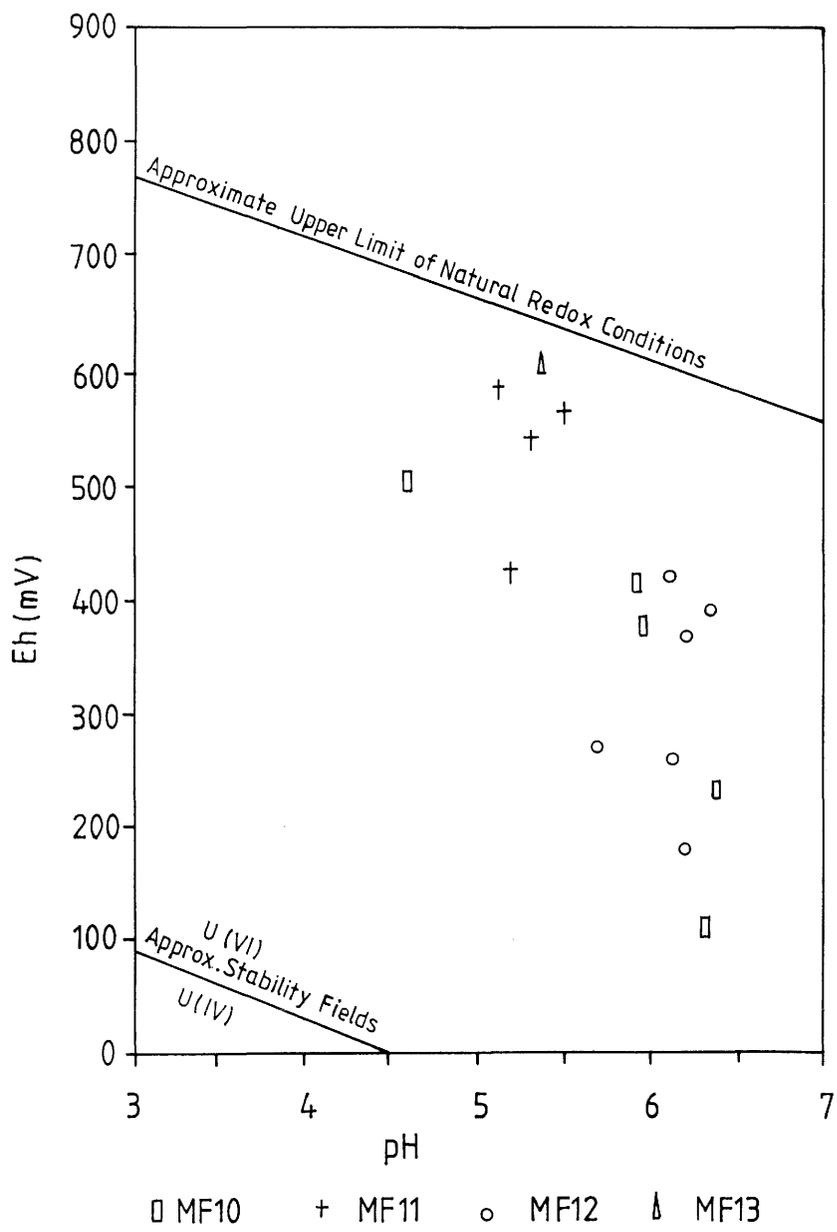


Figure 22. Eh-pH diagram for near-surface and deep ground waters from Morro do Ferro.

uranium concentrations are evident. This may indicate the absence of a significant fraction of labile uranium available for leaching. The higher uranium isotopic ratios in waters from MF12 (which are very close to those observed in borehole F1 of similar bedrock geochemistry) are probably caused by a combination of at least three effects:

- 1) the slightly higher U concentrations in the bedrock (reduced phonolite; MacKenzie *et al.*, this report series; Rep. 7);
- 2) the higher crystallinity of the bedrock as compared to the highly weathered rock, intercepted by boreholes MF10 to MF13, which would enhance the importance of preferential leaching; and
- 3) the somewhat different water composition of MF12 (Eh, SO_4^{2-} , HCO_3^- , F⁻).

For the same borehole, considerable variations in the total uranium concentrations can be observed, which are probably caused by the rapid mixing/dilution of the resident groundwaters with meteoric waters during or after heavy rainfall (see Table XV, samples GW-33, UFMF-10A, GW-35). This effect is shown in Figure 23, which presents the temporal variations of uranium concentrations in three reference boreholes. A strong decline in MF11 in uranium concentrations with the onset of the rainy season (Sept. – Nov.) and a minimum during the peak precipitation period (Dec. – Feb.) is indicated. However, this effect does not influence the uranium isotopic composition of these waters (Table XV), as might be expected (see also section 4.1.1). For borehole MF12, where the seasonal influx of meteoric water would be expected to have less influence on groundwater composition and water table height, fluctuations in the uranium concentrations are less pronounced.

Figure 24, in which $^{234}\text{U}/^{238}\text{U}$ activity ratios are plotted versus reciprocal uranium concentrations, supports the previous observations from the Osamu Utsumi mine on the migration of this element. The MF10 and MF11 samples come from a zone of downward flow and display a combination of congruent uranium leaching and preferential ^{234}U mobilisation. Representative values are 0.012 Bq/l for U concentration and 0.005 Bq/l for excess ^{234}U . For borehole MF12, where the water flow is at least partly upwards and the water is somewhat older, the average U concentration is 0.010 Bq/l and excess ^{234}U is about 0.009 Bq/l. Near-surface waters are more dilute with respect to uranium than the deeper waters, but have similar activity ratios. These data suggest a model in which downward-percolating waters pick up leachable uranium and recoil-mobilised ^{234}U . There is little difference between water from MF10 and MF11, except that samples of

TABLE XV

Chemical data for near-surface and deep ground waters from Morro do Ferro (NYU data in brackets).

Borehole	Sample	Date (dd/mm/yy)	^{238}U ($\mu\text{g/l}$)	R1	^{232}Th ($\mu\text{g/l}$)	R2	pH	Eh (mV)	Na (mg/l)	K (mg/l)	Fe(II) (mg/l)	Fe(t) (mg/l)	HCO_3^- (mg/l)	SO_4^{2-} (mg/l)	F^- (mg/l)
MF10	PC-GW-12	12/12/86 w	1.06	1.23	0.060	0.05									
	UFM10-A	25/01/88 w	0.28	1.2	0.013	0.04	6.37	235	0.37	0.50	0.86	0.92	18.4	14.4	0.21
	PC-GW-33	27/01/88 w	0.077 (0.071)	1.30 (1.26)	0.021 (0.056)	0.13 (<0.26)	4.6	505	0.09	0.14	0.55	0.58	12.0	8.0	0.07
	PC-GW-48	08/06/88 d	1.55 (0.93)	1.31 (1.37)	0.17 (0.38)	0.038 (0.041)	6.37	-121	0.09	0.35	2.31	2.32	18.9	<5.0	0.11
	PC-GW-52	12/09/88 t	0.70 (0.72)	1.32 (1.32)	0.11 (0.14)	0.05 (<0.03)	5.94	384	0.20	0.24	0.62	0.66	10.7	10.0	<.10
	UFMF10-B	12/10/88 t	0.56	1.4	0.036	0.04	6.29	112	0.16	6.36	0.83	1.06	7.73	5.4	0.16
	PC-GW-69	06/12/88 w	0.57 (3.0)	1.35 (1.11)	0.090 (0.30)	0.21 (0.18)	5.91	420	0.10	2.00	0.46	0.52	8.11	<5.0	0.19
	PC-GW-83	05/04/89 t	(1.0)	(1.39)	(<0.1)	(<0.02)									
MF11	PC-GW-35	28/01/88 w	0.055 (0.037)	1.4 (1.17)	(0.077)	0.5 (<0.9)	5.2	430	0.18	0.24	0.19	0.24	26.6	11.2	0.06
	PC-GW-49	13/06/88 d	0.13 (1.40)	1.6 (1.38)	0.96 (0.24)	0.33 (<0.05)	5.12	590	0.16	0.19	<0.10	<0.10	12.0	<5.0	<0.10
	PC-GW-53	13/09/88 t	0.75 (0.83)	1.52 (1.48)	0.55 (0.14)	0.096 (<0.1)	5.30	544	0.12	0.16	<0.10	<0.10	8.84	5.8	0.16
	PC-GW-70	12/12/88 w	0.44 (0.40)	1.5 (1.37)	0.067 (<0.44)	0.20	5.49	568	0.20	0.16	<0.10	<0.10	8.11	<5.0	0.19
	PC-GW-82	04/04/89 t	(0.75)	(1.35)	(0.25)										
MF13	PC-GW-73	20/12/88 w	0.36	1.42	0.10	0.12	5.40	607	0.40	0.70	<0.10	<0.10	24.3	<5.0	1.56
MF12	PC-GW-18	07/07/87 d	0.12 (0.12)	1.7 (1.22)	0.58 (0.13)	0.19 (0.17)	6.21				2.41	2.51	32.9	15.4	6.9
	PC-GW-30	02/12/87 w	1.00 (1.13)	1.72 (1.57)	0.016 (0.023)	0.005 (<0.01)	6.42		1.32	18.0	3.04	3.05	38.9	14.0	5.68
	PC-GW-32	22/12/87 w	1.65	1.64	0.035		6.2	374	0.50	11.0	0.81	1.43	30.4	16.6	7.02
	PC-GW-34	28/01/88 w	0.78 (0.65)	1.6 (1.73)	0.080 (0.011)	(0.004)	5.7	277	1.09	10.5	1.31	1.33	35.3	13.2	5.95
	PC-GW-50	14/06/88 d	0.86 (0.90)	2.0 (1.87)	0.80	0.016	6.19	184	0.97	9.47	0.74	0.79	34.7	13.6	4.96
	PC-GW-56	19/09/88 t	0.80 (0.79)	1.9 (1.97)	0.094 (0.084)	0.017 (0.064)	6.13	265	0.96	1.08	1.25	1.28	27.8	16.2	5.97
	UFMF12-B	12/10/88 t	0.80	1.8	0.035		6.10	425	1.02	11.0	2.00	2.12	28.1	12.6	6.07
	PC-GW-71	14/12/88 w	0.60 (0.64)	2.3 (2.24)	0.35 (0.17)	0.028 (0.020)	6.33	398	0.80	10.4	0.57	0.58	24.9	5.36	7.26
	PC-GW-85	11/04/89 t	(0.67)	(1.93)	(0.052)	(0.010)									
PZ2	PC-GW-26	29/09/87 t	0.49	1.2	0.032										
S.Str.	PC-SS-04	29/07/87 d	0.35 (0.26)	2.0 (1.50)	0.088 (0.058)	(0.16)									
N.Str.	PC-NS-05	10/08/87 d	0.16 (0.18)	1.5 (1.34)	0.074 (0.042)	0.20 (0.068)									

Isotopic Activity Ratios

$$R1 = \frac{^{234}\text{U}}{^{238}\text{U}}$$

$$R2 = \frac{^{230}\text{Th}}{^{234}\text{U}}$$

w = wet
d = dry
t = transitional

OBS: - Errors in isotopic analysis as reported in Table 1-II; Appendix 1.
- NYU data in brackets.

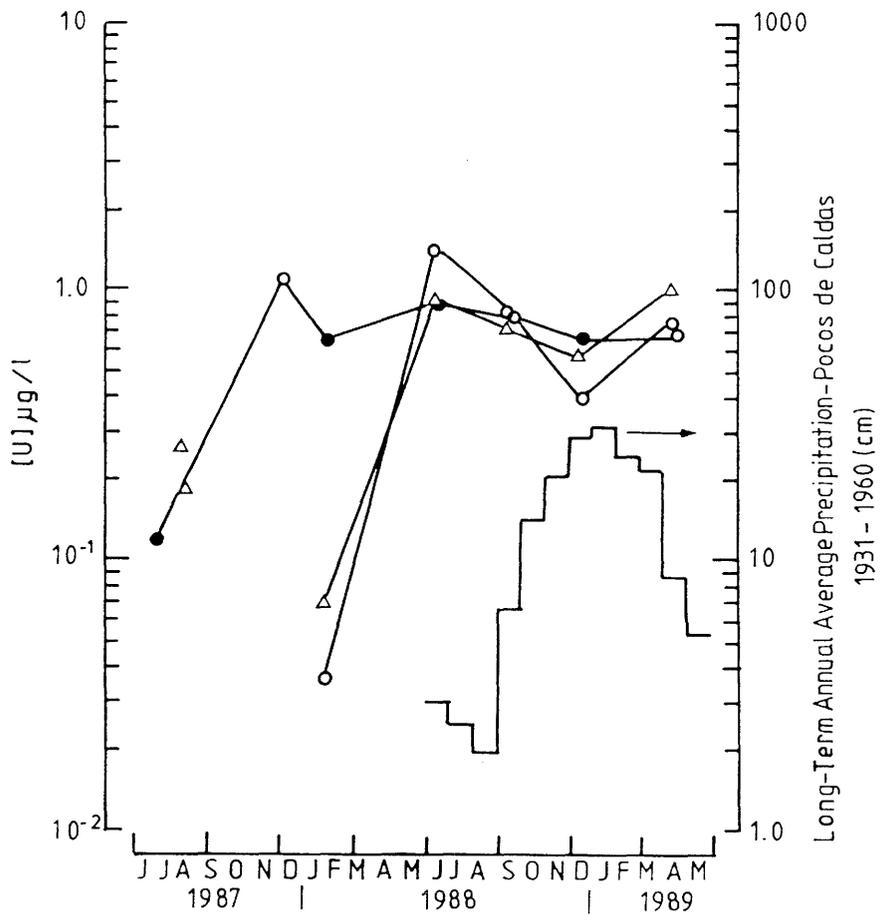


Figure 23. Seasonal variations of uranium concentrations in deep groundwaters from Morro do Ferro. (• MF12; ▲ MF10; ○ MF11; Δ surface water).

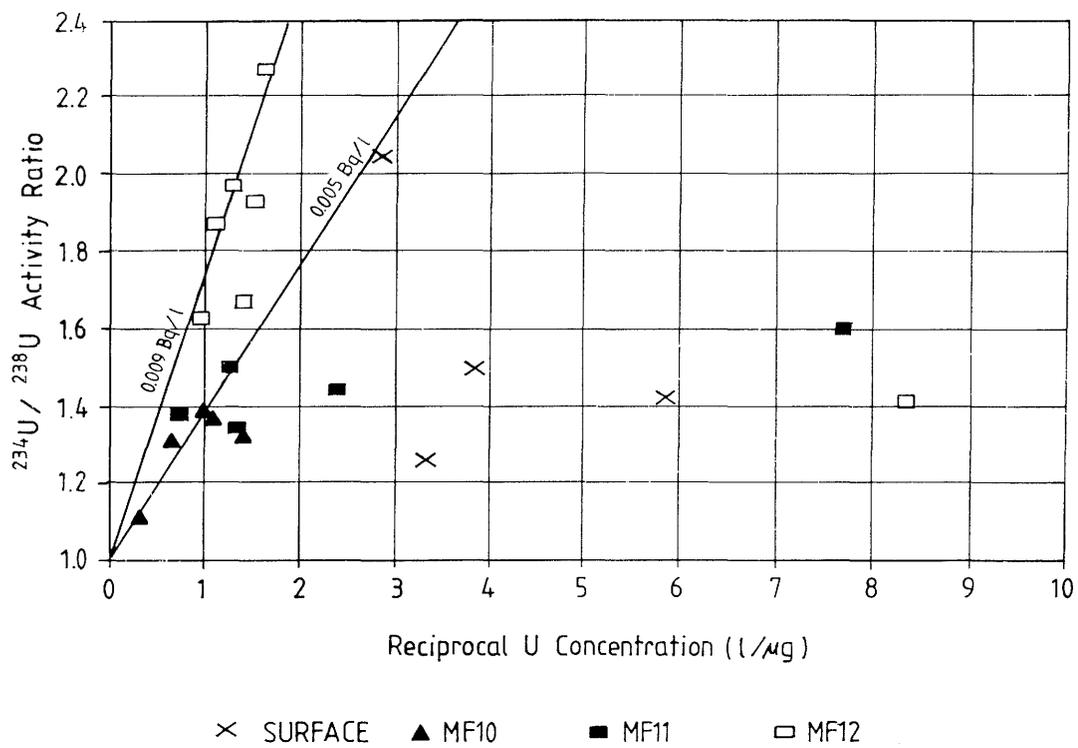


Figure 24. Morro do Ferro uranium isotope data. (The plotted lines represent a "best-fit" with $^{234}\text{U}/^{238}\text{U} = 1.0$ and $1/[U] = 0$ as the origin of the lines).

the latter appear to be more subject to dilution. The older waters (MF12) have gained more excess ^{234}U while losing some ^{238}U , as might be expected during slow groundwater flow conditions under more reducing conditions. Surface waters appear to be mixtures of groundwater and rainwater (pure dilution).

Concerning the association of uranium with particulate material in groundwaters, the situation is very similar to that observed for Osamu Utsumi mine groundwaters, namely: a) isotopic equilibrium between dissolved and particle-associated uranium, b) association ratios (R_a) of the same order of magnitude ($\log R_a = 4$ to 5) and c) predominance of uranium in dissolved form (<1.5 nm). Due to the higher concentrations of suspended material in Morro do Ferro waters, the fraction of “dissolved” uranium as a percentage of the total uranium concentration is, however, slightly lower than in the Osamu Utsumi mine (Table XII).

4.2.2. Thorium

Because of the large interlaboratory differences among individual samples (Table VIII) and the small differences in ^{232}Th concentrations of groundwater from Morro do Ferro (Table XV), one cannot unambiguously confirm the existence of a thorium gradient along the flow-path as intersected by the borehole sampling points MF11, MF10, MF13 and MF12 (Fig. 5). Excluding samples GW-35 (MF11) and GW-33 (MF10), for reasons already discussed in section 4.2.1, it appears that the mean concentrations of ^{232}Th are slightly higher in MF11, MF10 and MF13 than in MF12 (Table XV), which could reflect the much higher concentrations of thorium in the weathered bedrock intersected by the first three boreholes. ^{232}Th concentrations in rocks intersected by MF12 approach background levels for the Poços de Caldas plateau (42 to 129 ppm) and the corresponding water concentrations also do not differ from regional observations (e.g. sample NS-05 from the North Stream). The absence of any significant contribution of “dissolved” thorium to groundwaters in MF12 and to the South Stream from the extremely high thorium concentrations of the ore body shows that “solution” transport of this element is of minor importance due to its very low solubility and its high affinity for sorption. Ultrafiltration experiments have shown that thorium predominates in prefiltered waters (<450 nm) from Morro do Ferro as colloidal ferrihydrite/organic species similar to those observed in the groundwaters from the Osamu Utsumi mine (Mickeley *et al.*, 1989 and this report series; Rep. 9).

Table XI summarises data on the association of ^{232}Th with groundwater-suspended particles ($>450\text{ nm}$). Although a concentration gradient of thorium was not clearly seen in prefiltered waters from the reference boreholes, this is visible in the corresponding suspended particle fraction (SP): SP-MF11 = (1,200 – 1,300) $\mu\text{g/g}$; SP-MF10 = (200 – 300) $\mu\text{g/g}$, and SP-MF12 = (20 – 70) $\mu\text{g/g}$. The fact that the particulate matter from MF12 has background levels of ^{232}Th suggests strongly that groundwater particle transport ($>450\text{ nm}$) of this element is unimportant in this environment. High association ratios for ^{232}Th similar to those observed in the Osamu Utsumi mine were measured in groundwater from Morro do Ferro. This confirms once more that the aqueous chemistry of this element is largely controlled by sorption or precipitation reactions.

4.2.3. Rare-earth elements

Table XVI summarises rare-earth element concentrations of 21 water samples from the sampling locations at Morro do Ferro and from one background location (North Stream). The data indicate an approximate five-fold increase in the LREEs between about 35 mbgl (MF11) and 57 mbgl (MF10), which seems to be related to a broad, high-concentration rare-earth zone in the bedrock at this depth interval (MacKenzie *et al.*, this report series; Rep. 7). With the exception of cerium, the LREE concentrations in groundwaters from MF12 are lower by a factor of about 10 or more and are similar to those observed in the South Stream and the North Stream background reference locations. The concentration gradient for the HREEs in waters from MF11, MF10 (MF13) and MF12 shows a similar trend to that of the LREEs. However, correlations are not so evident, probably due to greater analytical uncertainties in the data for the less abundant rare-earth elements.

These data imply that the REEs are being removed from the saturated, highly mineralised zone of the deposit (due to their much higher solubilities as compared with Th; e.g. solubility products K_{sp} : $\text{Th}(\text{OH})_4 = 10^{-40}$ to $^{-50}$; $\text{Ce}(\text{OH})_3 = 1.5 \times 10^{-20}$; Latimer, 1952), but are redeposited before the groundwater reappears at the surface in the South Stream.

The important role of suspended particles in this process can be deduced from Tables XIV and XVI. LREE concentrations as high as several thousand “ppm” were measured in particulate matter from MF11 and MF10. Whereas in waters from MF11 this particulate material is mostly of clayey composition, and probably derived from weathered bedrock, particulate material from MF10 and MF12 is composed

TABLE XVI

Rare-earth element concentrations in surface, near-surface and deep ground waters from Morro do Ferro (NYU data in brackets; all values in $\mu\text{g/l}$).

REE	MF10						MF11				
	GW-12	GW-33	GW-48	GW-52	GW-69	GW-83	GW-35	GW-49	GW-53	GW-70	GW-82
La	1.1	0.33 (18.1)	(32.0)	28.7 (43.2)	34.4 (50.6)	(42.8)	1.77 (1.7)	6.54 (8.5)	4.14 (9.4)	7.52 (8.4)	(4.4)
Ce	1.2	0.30 (0.93)	(4.3)	3.93 (3.1)	2.92 (14.4)	(1.6)	0.33 (0.48)	2.57 (2.2)	0.92 (1.06)	1.19 (1.02)	(1.6)
Pr		(2.7)	(4.1)	(5.9)	(5.7)	(5.4)	(0.27)	(1.34)	(1.56)	(1.20)	(0.49)
Nd	0.6	(6.0)	(12.2)	12.3 (17.2)	15.3 (17.8)	(16.3)	0.87 (0.54)	3.58 (3.6)	2.15 (4.7)	4.10 (4.0)	(1.6)
Sm	0.07	0.064 (0.67)	(1.29)	1.23 (1.95)	1.57 (1.96)	(1.93)	0.080 (0.08)	0.40 (0.41)	0.26 (0.58)	0.44 (0.50)	(0.24)
Eu	0.03			0.28	0.34		0.020	0.096	0.059	0.10	
Gd	0.07	0.035		0.64	0.74		0.035	0.22	0.14	0.21	
Dy	0.05	0.012		0.41	0.44		0.020	0.17	0.093	0.13	
Ho	0.006	0.001		0.080	0.085			0.032	0.020	0.019	
Er	0.022	0.006		0.16	0.16			0.059	0.036	0.030	
Tb	0.011	0.005		0.065	0.077		0.003	0.028	0.016	0.023	
Lu	0.002	0.002		0.007	0.007			0.002	0.001	0.002	

REE	MF13	MF12						PZ2	South Stream	North Stream
	GW-73	GW-18	GW-30	GW-34	GW-56	GW-71	GW-85	GW-26	SS-04	NS-05
La	18.2	0.9 (0.45)	0.95 (0.38)	1.87 (0.87)	1.29 (12.2)	(0.37)	(0.23)	(10.4)	1.2 (0.91)	1.6 (0.77)
Ce	1.48	1.6 (0.94)	0.46 (0.41)	1.04 (0.32)	1.09 (5.5)	(0.94)	(0.56)	(7.0)	1.2 (1.15)	1 (0.84)
Pr		(0.14)	(0.39)	(0.17)	(1.6)	(0.02)		(2.4)	(0.29)	(0.20)
Nd	13.0	0.28		0.67	0.49	(0.22)	(0.14)	(5.5)	0.36 (0.35)	0.31 (0.45)
Sm	1.51	0.03 (0.01)	0.022 (0.02)	0.082 (0.05)	0.032 (0.63)	(0.02)	(0.01)	(0.82)	0.07 (0.10)	0.03 (0.09)
Eu	0.34	0.012	0.009	0.018	0.010				0.017	0.014
Gd	0.56	< 0.025	< 0.02	0.037	< 0.025				0.032	0.026
Dy	0.33	0.017	0.008	0.031	0.015				0.016	0.014
Ho	0.059	0.004			0.002				0.006	0.005
Er	0.10	0.075	0.001	0.003	0.009				0.009	0.005
Tb	0.048	0.004	0.002	0.004	0.005				0.004	0.004
Lu	0.004	0.002		0.0005	0.0005				0.002	0.002

predominantly of amorphous hydrous ferric oxides, which are probably formed by oxidation of Fe^{2+} in these waters (see also Miekeley *et al.*, this report series; Rep. 9). Ferric hydroxides are known to be good scavengers for the REEs and this is confirmed in this study by the high association ratios in natural waters (Table XIV). These particles also have colloidal size dimensions (1.5 to 450 nm) and experimental results obtained by ultrafiltration techniques also suggest that the REEs in groundwaters from Morro do Ferro are concentrated to some extent in the colloidal fractions (Miekeley *et al.*, this report series; Rep. 9).

Rare-earth element data for water samples and their corresponding particulate fractions are presented as chondrite-normalised distribution patterns in Figures 25 to 29. As observed in the Osamu Utsumi mine, the more oxidising waters (MF11, MF10 and MF13) are characterised by cerium depletion (Figs. 25 and 26), probably for the same reasons as mentioned above. This negative Ce anomaly can also be observed in the corresponding particulate fractions (Fig. 27), but is apparently less pronounced. This could indicate, as already mentioned, the greater preference of Ce(IV) for sorption on particulates, when compared to the other REEs. This characteristic Ce depletion is either completely absent, or only weakly evident in the more reducing groundwaters from MF12 (Fig. 28). In the particulate fractions of groundwaters from this borehole analysed to date, no Ce depletion at all was observed (Fig. 29) and the distribution patterns for the LREEs are very similar to those observed in reduced phonolites close to the water sampling depth of MF12 (45 to 71 m) and also in the same rock type from the Osamu Utsumi mine. This difference in cerium signature between particulate matter from the uphill boreholes (MF11, MF10, MF13) and that from MF12 would provide further support that there is no significant particle transport by groundwaters in this environment (see also Miekeley *et al.*, this report series; Rep. 9). However, more water data and information on the redox and sorption behaviour of cerium in natural waters, including the kinetics of the relevant processes, are necessary to completely confirm these observations.

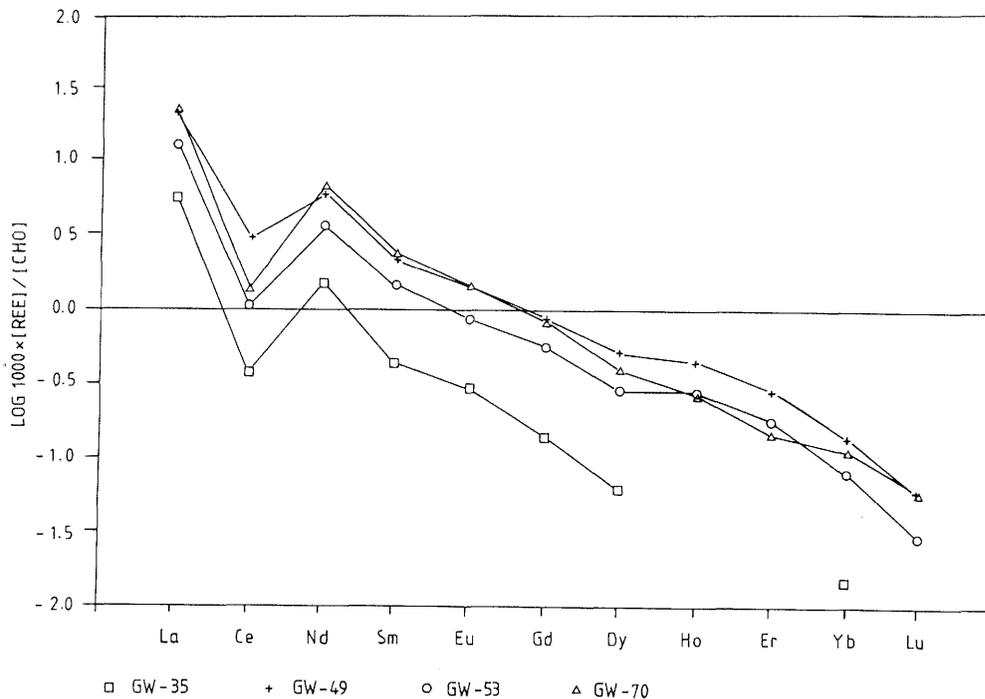


Figure 25. Chondrite-normalised REE distribution patterns in groundwaters from borehole MF11, Morro do Ferro.

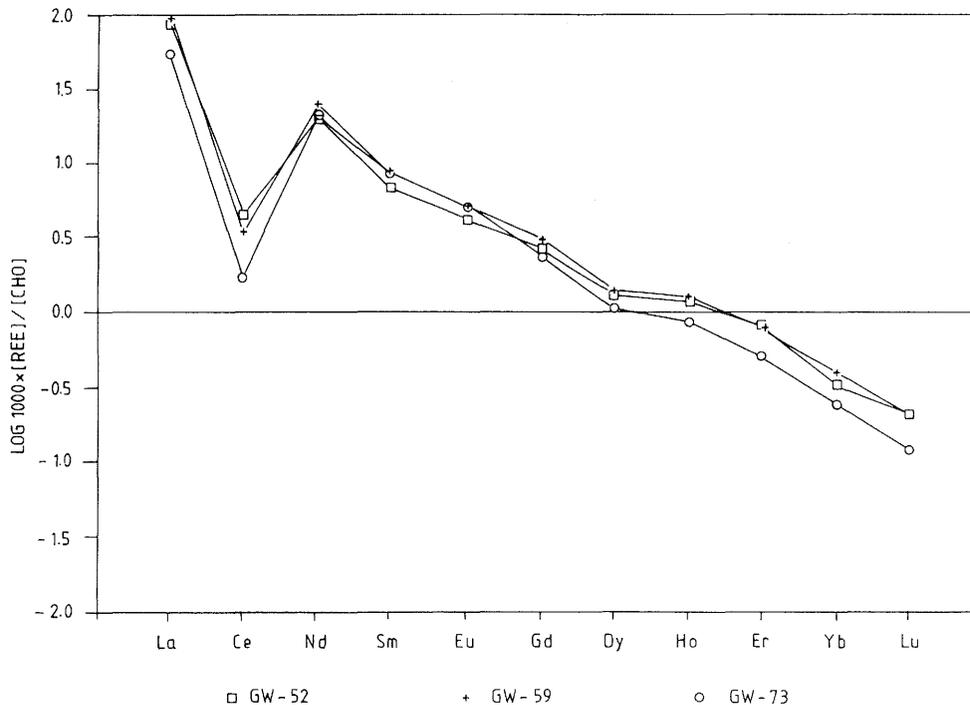


Figure 26. Chondrite-normalised REE distribution patterns in groundwaters from boreholes MF10 and MF13, Morro do Ferro.

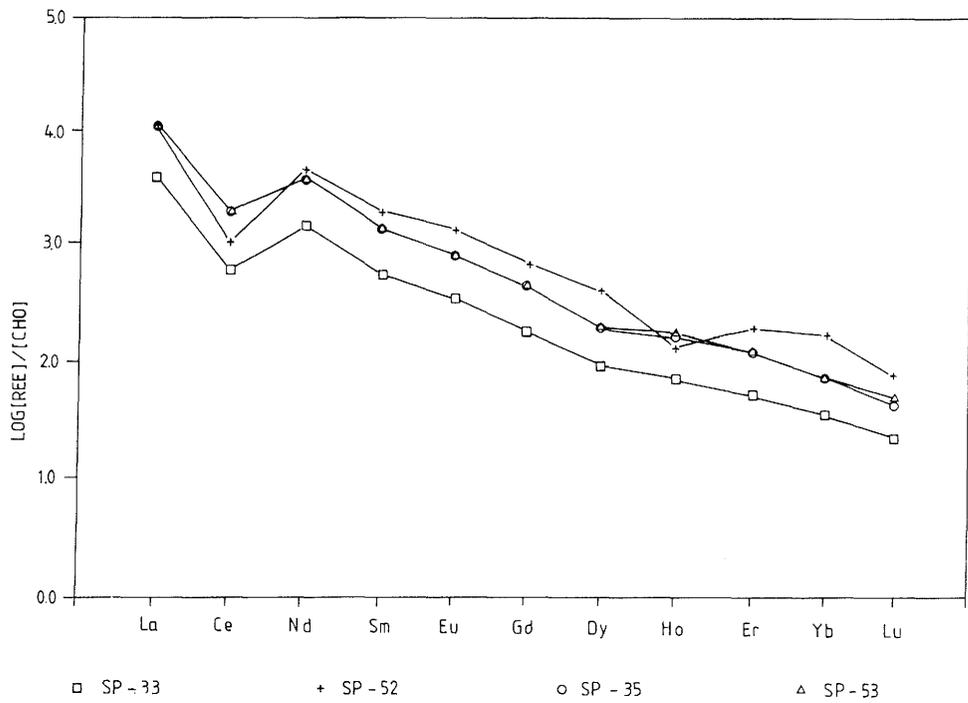


Figure 27. Chondrite-normalised REE distribution patterns in particulate matter (>450 nm) of groundwaters from boreholes MF10 and MF11, Morro do Ferro (Miekeley et al., this report series; Rep. 9.)

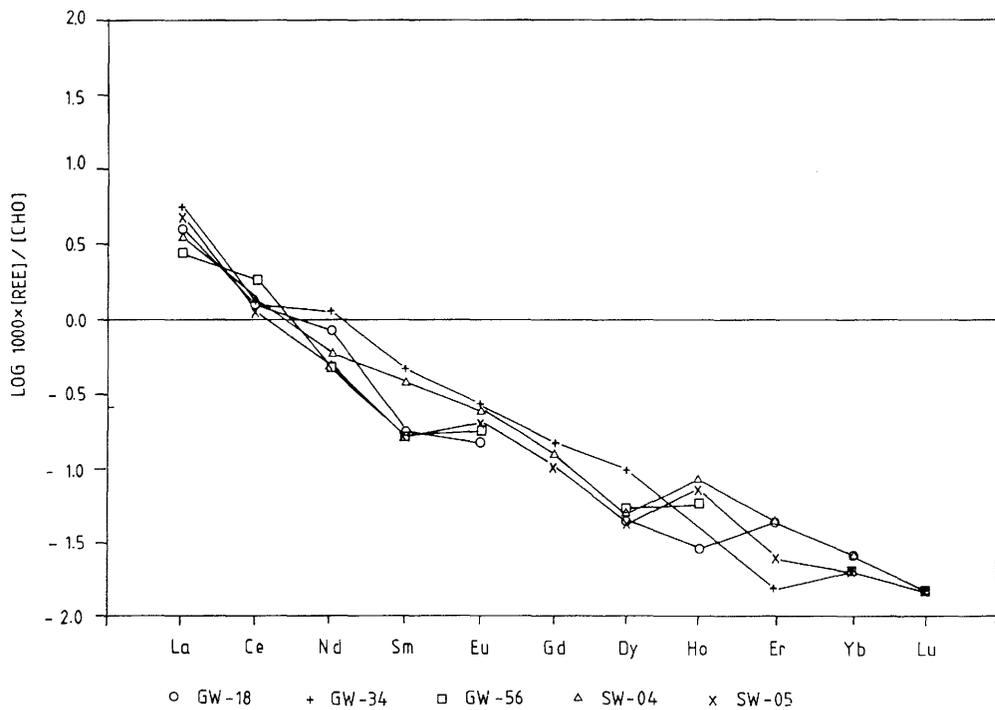


Figure 28. Chondrite-normalised REE distribution patterns in groundwaters from borehole MF12 and in waters from the South and North Streams, Morro do Ferro.

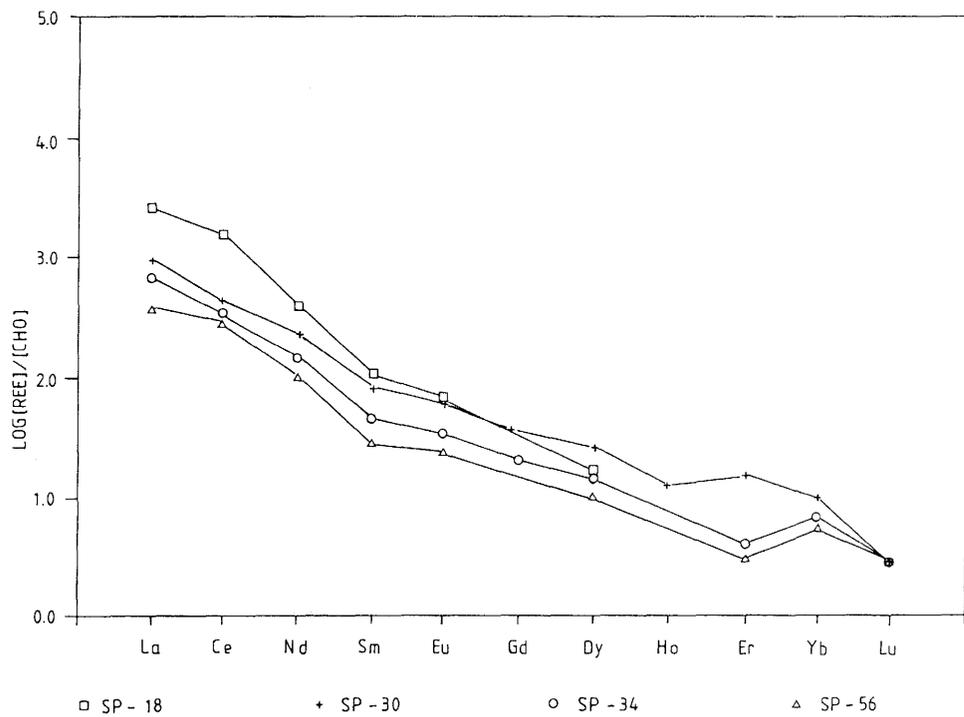


Figure 29. Chondrite-normalised REE distribution patterns in particulate matter (>450 nm) of groundwaters from borehole MF12, Morro do Ferro (Miekeley et al., this report series; Rep. 9).

5. Conclusions

A substantial quantity of data on uranium, thorium and rare-earth element concentrations in prefiltered (<450 nm) near-surface and deep ground waters and in particulate matter (>450 nm) from the Osamu Utsumi mine and Morro do Ferro has been produced. Due to similarities in bedrock geochemistry and climate, the aqueous behaviour of uranium, thorium and the rare-earth elements is shown to be similar in both environments.

Uranium: Due to the oxidising and slightly acidic character of the waters, the chemistry of uranium is determined by that of UO_2^{2+} and its complexes. Consequently, high local concentrations in groundwaters occurring with low to moderate $^{234}\text{U}/^{238}\text{U}$ activity ratios were observed in areas with relatively higher uranium mineralisation. Considerable variations in the $^{234}\text{U}/^{238}\text{U}$ activity ratios of waters with sampling depth have been measured. Interpretation of these data in terms of ^{234}U excess contributed to the formulation of migration models for uranium in both environments. Uptake of uranium occurs on water-suspended hydrous ferric oxide particles (>450 nm). This process is especially efficient in these deep groundwaters. The data show both sites to be dynamic systems in which mobilisation of uranium takes place by leaching and recoil-associated processes, and retardation by sorption, predominantly on hydrous ferric oxides.

Thorium: The aqueous chemistry of this element is completely controlled by solubility limitations and sorption reactions. Even in areas of extremely high thorium concentrations (up to 10 mg/g) in soil and weathered rocks, the deep groundwaters (<450 nm) have very low background concentrations (<0.1 $\mu\text{g/l}$). However, near-surface waters of low pH (<4) and high sulphate or DOC concentrations have much higher thorium concentrations. Unlike uranium, which predominates in prefiltered groundwaters as a simple complexed ion, “dissolved” thorium is mostly associated with colloidal phases. A considerably higher tendency of thorium for sorption on particulate matter is evident. Despite its radiogenic origin, ^{230}Th seems to follow closely the behaviour of ^{232}Th , and, for this reason, low $^{230}\text{Th}/^{234}\text{U}$ activity ratios in waters and high ratios in particulate matter were observed in both environments.

Rare-earth elements: Due to their higher solubilities (when compared to thorium), these elements behave more like uranium in both environments. High local REE concentrations were observed, seemingly caused by the moderate to high sulphate concentrations in most of the waters, which favour the formation of simple ions (e.g. LnSO_4^+). However, similarly to thorium but to a lesser extent, REEs are also associated with colloidal phases. The chondrite-normalised distribution patterns of the REEs in

less oxidising groundwaters resemble those of the surrounding bedrock, indicating that leaching occurs without significant fractionation. Strongly oxidising, near-surface waters show, however, a very characteristic cerium depletion, which could indicate that this element exists as Ce (IV), which is a much less soluble form. This also seems to be indicated by the somewhat greater tendency of cerium to sorb on particulate matter. Low-temperature groundwaters in contact with REE mineralisations may have high REE concentrations. The data from Morro do Ferro suggest, however, that the transport of these elements (and possibly their actinide analogues, e.g. Am and Cm) is strongly limited by sorption reactions.

6. Acknowledgements

This work was financially supported by the Poços de Caldas Project, by the International Atomic Energy Agency (CRP, Pers. Res. Contr. 3937-BR) and by “Financiadora de Estudos e Projetos” (FINEP) and “Conselho Nacional de Desenvolvimento Científico e Tecnológico” (CNPq), Brazil. The ICP-equipment was donated to PUC by the Volkswagen Foundation and by the Society for Technical Cooperation (GTZ), Germany. This work would not have been possible without the scientific and logistic collaboration of J.A.T. Smellie and E. Penna Franca. The help of R. Frayha, P.H. Rabello, S.S. Filho and L. Barroso in field work, and of L.A. Gomiero, W.S. Filho, L.O. Wiikman and M. Dupim in laboratory work is also gratefully acknowledged. Thanks are also due to C.V. Dutra (GEOSOL, Belo Horizonte, BR) for ICP-AES facilities.

The authors (PUC-team) are especially grateful to their laboratory technician D.J. Santos (in memoriam) for his dedicated work during more than ten years of collaboration.

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Appendix 1

Tables 1-I – 1-III: Results on the isotopic compositions of uranium and thorium in waters and particulate material from the Osamu Utsumi mine and Morro do Ferro analogue sites (PUC data).

TABLE 1-1

Results on the isotopic compositions of uranium and thorium in waters from the Osamu Utsumi mine analogue site (PUC data).

SAMPLE ORIGIN (dd/mm/yy)	U-flu. ($\mu\text{g/l}$)	^{238}U (Bq/l) ($\mu\text{g/l}$)	^{234}U (Bq/l)	^{234}U $\overline{^{238}\text{U}}$	^{230}Th $\overline{^{234}\text{U}}$	^{232}Th (Bq/l) ($\mu\text{g/l}$)	^{230}Th (Bq/l)	^{228}Th (Bq/l)	^{228}Th $\overline{^{232}\text{Th}}$
PC-GW-37		39 ± 2	48 ± 2	1.22 ± 0.07	.18 $\pm .01$	1.45 ± 0.06	8.8 ± 0.2	2.12 ± 0.08	1.5 ± 0.1
SW01 02/02/88	2900 ± 300	3200 ± 100				360 ± 20			
PC-GW-46		55 ± 2	67 ± 3	1.23 ± 0.07	.11 $\pm .01$	1.15 ± 0.06	7.4 ± 0.2	2.01 ± 0.09	1.8 ± 0.1
SW01 07/06/88	4000 ± 400	4400 ± 200				280 ± 20			
PC-GW-57		3.4 ± 0.2	4.1 ± 0.2	1.23 ± 0.10	.026 $\pm .002$.017 $\pm .001$.109 $\pm .003$.143 $\pm .003$	8.6 ± 0.4
SW01 21/09/88	220 ± 20	270 ± 20				4.1 ± 0.1			
PC-GW-38		132 ± 8	132 ± 8	1.0 ± 0.1	.025 $\pm .002$	0.28 ± 0.02	3.3 ± 0.1	0.66 ± 0.03	2.3 ± 0.2
SW02 03/02/88	9300 ± 900	10600 ± 600				70 ± 4			
PC-GW-39		92 ± 5	96 ± 5	1.04 ± 0.08	.039 ± 0.002	0.32 ± 0.02	3.8 ± 0.1	0.74 ± 0.03	2.3 ± 0.2
SW03 03/02/88	5600 ± 600	7400 ± 400				79 ± 5			
PC-GW-47		56 ± 3	57 ± 3	1.02 ± 0.08	.016 $\pm .001$	0.14 ± 0.01	0.93 ± 0.04	0.46 ± 0.02	3.2 ± 0.3
SW03 07/06/88	3400 ± 300	4500 ± 200				36 ± 3			
PC-GW-58		3.1 ± 0.1	2.9 ± 0.1	0.92 ± 0.06	.0013 $\pm .0001$	ICP .23 $\pm .01$.0038 $\pm .0004$.049 $\pm .001$	53 ± 3
SW03 22/09/88	210 ± 20	250 ± 10							
PC-GW-66				0.95	0.06	.171 $\pm .005$	1.82 ± 0.04	.361 $\pm .009$	2.1 ± 0.1
SW03 30/11/88	2400 ± 200					42 ± 1			
PC-GW-09		.079 $\pm .006$	0.21 ± 0.01	2.7 ± 0.3				.072 $\pm .002$	
F1 13/11/86	7.3 ± 0.7	6.4 ± 0.4							
PC-GW-14		.066 $\pm .003$.154 $\pm .006$	2.3 ± 0.1				.043 $\pm .001$	
F1 06/01/87	5.3 ± 0.5	5.3 ± 0.2							
PC-GW-15		.054 $\pm .003$.119 $\pm .006$	2.2 ± 0.2	.046 $\pm .003$	ICP .030 $\pm .002$.0054 $\pm .0002$.022 $\pm .001$	180 ± 10
F1 11/02/87	4.6 ± 0.5	4.3 ± 0.2							
PC-GW-17		.038 $\pm .002$.092 $\pm .004$	2.4 ± 0.2	.029 $\pm .005$	ICP .071 $\pm .004$.0027 $\pm .0005$.158 $\pm .004$	550 ± 30
F1 06/05/87	2.9 ± 0.3	3.0 ± 0.2							
PC-GW-22		.062 $\pm .003$.127 $\pm .006$	2.1 ± 0.1	.004 $\pm .002$	ICP .043 $\pm .002$.0006 $\pm .0002$.085 $\pm .002$	490 ± 30
F1 20/08/87	4.8 ± 0.5	4.9 ± 0.2							

TABLE 1-I (contd.).

SAMPLE ORIGIN (dd/mm/yy)	U-flu. ($\mu\text{g/l}$)	^{238}U (Bq/l) ($\mu\text{g/l}$)	^{234}U (Bq/l)	^{234}U $\frac{238\text{U}}{234\text{U}}$	^{230}Th $\frac{230\text{Th}}{234\text{U}}$	^{232}Th (Bq/l) ($\mu\text{g/l}$)	^{230}Th (Bq/l)	^{228}Th (Bq/l)	^{228}Th $\frac{228\text{Th}}{232\text{Th}}$
PC-GW-23		.046 $\pm .002$.103 $\pm .005$	2.2 ± 0.1		ICP		.054 $\pm .001$	440 ± 30
F1 17/09/87	3.5 ± 0.3	3.7 ± 0.2				.030 $\pm .002$			
PC-GW-29		.056 $\pm .002$.128 $\pm .005$	2.3 ± 0.1		ICP		.177 $\pm .004$	2200 ± 100
F1 10/11/87	4.1 ± 0.4	4.5 ± 0.2				.020 $\pm .001$			
PC-GW-40		.092 $\pm .003$.200 $\pm .007$	2.2 ± 0.1		ICP		0.46 ± 0.01	3100 ± 200
F1 08/02/88	7.0 ± 0.7	7.4 ± 0.3				.037 $\pm .002$			
PC-GW-42		.056 $\pm .002$.126 $\pm .005$	2.2 ± 0.1		ICP		.406 $\pm .009$	2300 ± 100
F1 01/06/88	4.1 ± 0.4	4.5 ± 0.2				.043 $\pm .002$			
PC-GW-54		.050 $\pm .002$.113 $\pm .004$	2.3 ± 0.1	.012 $\pm .001$	ICP	.0013 $\pm .0001$.194 $\pm .005$	640 ± 30
F1 15/09/88	3.5 ± 0.4	4.0 ± 0.2				.075 $\pm .004$			
PC-GW-63		.063 $\pm .003$.150 $\pm .006$	2.4 ± 0.1	.106 $\pm .005$	ICP	.0159 $\pm .0005$.42 $\pm .01$	860 ± 40
F1 29/11/88	5.5 ± 0.6	5.1 ± 0.2				.12 $\pm .01$			
PC-GW-13		.196 $\pm .010$	0.29 ± 0.01	1.5 ± 0.1				.0071 $\pm .0003$	
F2 15/12/86	15 ± 1	15.7 ± 0.8							
PC-GW-16		.184 $\pm .009$	0.27 ± 0.01	1.5 ± 0.1		ICP		.0073 $\pm .0003$	60 ± 4
F2 12/02/87	14 ± 1	14.8 ± 0.7				.030 $\pm .002$			
PC-GW-20		.126 $\pm .005$.180 $\pm .008$	1.4 ± 0.1	.010 $\pm .002$	ICP	.0017 $\pm .0003$.0140 $\pm .0005$	46 ± 3
F2 24/07/87	10 ± 1	10.1 ± 0.4				.076 $\pm .004$			
PC-GW-25		.085 $\pm .003$.133 $\pm .005$	1.57 ± 0.09		ICP		.0078 $\pm .0003$	80 ± 5
F2 28/09/87	6.8 ± 0.7	6.8 ± 0.3				.024 $\pm .001$			
PC-GW-31		.077 $\pm .003$.126 $\pm .005$	1.65 ± 0.09	.0028 $\pm .0008$	ICP	.0004 $\pm .0001$.0096 $\pm .0003$	66 ± 4
F2 21/12/87	5.9 ± 0.6	6.2 ± 0.2				.036 $\pm .002$			
PC-GW-41		.080 $\pm .003$.117 $\pm .005$	1.47 ± 0.08	.089 $\pm .005$	ICP	.0105 $\pm .0003$.0254 $\pm .0007$	31 ± 2
F2 09/02/88	5.5 ± 0.5	6.4 ± 0.3				.200 $\pm .010$			
PC-GW-43		.065 $\pm .003$.109 $\pm .004$	1.68 ± 0.09	.007 $\pm .001$	ICP	.0008 $\pm .0001$.0113 $\pm .0004$	59 ± 4
F2 02/06/88	4.5 ± 0.5	5.2 ± 0.2				.047 $\pm .002$			

TABLE 1-I (contd.).

SAMPLE ORIGIN (dd/mm/yy)	U-flu. ($\mu\text{g/l}$)	^{238}U (Bq/l) ($\mu\text{g/l}$)	^{234}U (Bq/l)	^{234}U $\overline{\overline{^{238}\text{U}}}$	^{230}Th $\overline{\overline{^{234}\text{U}}}$	^{232}Th (Bq/l) ($\mu\text{g/l}$)	^{230}Th (Bq/l)	^{228}Th (Bq/l)	^{228}Th $\overline{\overline{^{232}\text{Th}}}$
PC-GW-60		.034 $\pm .001$.052 $\pm .002$	1.55 ± 0.09	.008 $\pm .002$	ICP	.00044 $\pm .00008$.0193 $\pm .0005$	150 ± 8
F2 23/09/88	2.6 ± 0.3	2.7 ± 0.1					.031 $\pm .002$		
PC-GW-64		.084 $\pm .003$.126 $\pm .005$	1.5 ± 0.1	.020 $\pm .002$	ICP	.0026 $\pm .0002$.0285 $\pm .0008$	88 ± 4
F2 29/11/88	6.2 ± 0.6	6.7 ± 0.3					.080 $\pm .004$		
PC-GW-36		0.31 ± 0.01	0.36 ± 0.01	1.17 ± 0.07	.0044 $\pm .0003$	ICP	.0015 $\pm .0001$.0077 $\pm .0002$	31 ± 2
F3 01/02/88	17 ± 2	24.5 ± 1.0					.062 $\pm .003$		
PC-GW-45		0.20 ± 0.01	0.25 ± 0.02	1.2 ± 0.1		ICP		0.19 ± 0.01	7.2 ± 0.4
F3 06/06/88	12 ± 1	16 ± 1					6.5 ± 0.3		
PC-GW-55		.0101 $\pm .0006$.022 $\pm .001$	2.2 ± 0.2	0.24 ± 0.02	ICP	.0052 $\pm .0004$.047 $\pm .001$	83 ± 4
F3 16/09/88	0.74 ± 0.07	0.81 ± 0.05					.14 $\pm .01$		
PC-GW-65		.056 $\pm .002$.074 $\pm .003$	1.32 ± 0.08	0.20 ± 0.01	ICP	.0145 $\pm .0007$.080 $\pm .002$	58 ± 3
F3 30/11/88	4.1 ± 0.4	4.5 ± 0.2					.34 $\pm .02$		
PC-GW-62		0.27 ± 0.01	0.49 ± 0.02	1.8 ± 0.1	.006 $\pm .001$	ICP	.0027 $\pm .0005$.049 $\pm .001$	67 ± 3
F5 28/11/88	17 ± 2	21.5 ± 0.9					.18 $\pm .01$		
PC-GW-72		.135 $\pm .006$	0.24 ± 0.01	1.8 ± 0.1	.004 $\pm .001$.00052 $\pm .00005$.0010 $\pm .0001$.0328 $\pm .0008$	63 ± 6
F5 20/12/88	9.1 ± 0.9	10.9 ± 0.5					0.13 ± 0.01		
PC-GW-44		0.91 ± 0.04	1.28 ± 0.06	1.40 ± 0.09	.0022 $\pm .0002$	ICP	.0027 $\pm .0002$.068 $\pm .002$	94 ± 5
F4 03/06/88	60 ± 6	73 ± 3					.180 $\pm .009$		
PC-GW-59		0.26 ± 0.01	0.37 ± 0.02	1.45 ± 0.10	.0036 $\pm .0003$.00029 $\pm .00003$.0013 $\pm .0001$.0299 $\pm .0008$	100 ± 10
F4 22/09/88	22 ± 2	20.7 ± 1.0					.071 $\pm .008$		
PC-GW-67		0.59 ± 0.03	0.94 ± 0.04	1.6 ± 0.1	.015 $\pm .001$	ICP	.015 $\pm .001$.074 $\pm .002$	91 ± 5
F4 30/11/88	62 ± 6	48 ± 2					.20 $\pm .01$		
PC-GW-21		0.55 ± 0.03	0.63 ± 0.04	1.14 ± 0.10	.088 $\pm .006$	ICP	.055 $\pm .002$.048 $\pm .002$	12 ± 1
UC16 31/07/87	43 ± 4	44 ± 3					1.01 ± 0.05		
PC-GW-24		1.06 ± 0.09	1.10 ± 0.09	1.0 ± 0.1	.028 $\pm .002$	ICP	.031 $\pm .001$.028 $\pm .001$	16 ± 1
UC16 18/09/87	110 ± 10	85 ± 7					0.44 ± 0.02		

TABLE 1-I (contd.).

SAMPLE ORIGIN (dd/mm/yy)	U-flu. ($\mu\text{g/l}$)	^{238}U (Bq/l) ($\mu\text{g/l}$)	^{234}U (Bq/l)	^{234}U $\overline{^{238}\text{U}}$	^{230}Th $\overline{^{234}\text{U}}$	^{232}Th (Bq/l) ($\mu\text{g/l}$)	^{230}Th (Bq/l)	^{228}Th (Bq/l)	^{228}Th $\overline{^{232}\text{Th}}$
PC-GW-19		.0024 $\pm .0001$.0053 $\pm .0002$	2.3 ± 0.2	0.50 ± 0.06	ICP .087 $\pm .004$.0027 $\pm .0003$.0077 $\pm .0003$	22 ± 1
PM22 15/07/87	0.19 ± 0.02	0.19 ± 0.01							
PC-GW-27		.0054 $\pm .0003$.0084 $\pm .0004$	1.6 ± 0.1	0.10 ± 0.02	ICP .040 $\pm .002$.0009 $\pm .0002$.0040 $\pm .0002$	24 ± 2
PM22 02/10/87	0.39 ± 0.04	0.44 ± 0.02							
PC-SD-03		.0054 $\pm .0003$.0067 $\pm .0003$	1.24 ± 0.09	0.16 ± 0.04	ICP .075 $\pm .004$.0011 $\pm .0003$.0011 $\pm .0002$	13 ± 1
Supply D. 09/07/87	0.41 ± 0.04	0.43 ± 0.02							

TABLE 1-II

Results on the isotopic compositions of uranium and thorium in particulate material (>450 nm) from waters of the Osamu Utsumi mine and Morro do Ferro analogue sites (PUC data).

SAMPLE ORIGIN (dd/mm/yy)	U-flu. ($\mu\text{g/g}$)	^{238}U (Bq/g) ($\mu\text{g/g}$)	^{234}U (Bq/g)	^{234}U $\overline{^{238}\text{U}}$	^{230}Th $\overline{^{234}\text{U}}$	^{232}Th (Bq/g) ($\mu\text{g/g}$)	^{230}Th (Bq/g)	^{228}Th (Bq/g)	^{228}Th $\overline{^{232}\text{Th}}$
PC-GW-58		3.3 ± 0.2	4.8 ± 0.2	1.43 ± 0.10	0.85 ± 0.05	0.54 ± 0.04	4.0 ± 0.2	0.95 ± 0.06	1.8 ± 0.2
SW-03 22/09/88	230 ± 20	270 ± 10				130 ± 10			
PC-GW-17		12.4 ± 0.7	26 ± 1	2.1 ± 0.2	0.09 ± 0.01	2.0 ± 0.2	2.4 ± 0.3	17.8 ± 0.6	8.9 ± 0.8
F1 06/05/87	830 ± 80	1000 ± 60				490 ± 40			
PC-GW-22		7.7 ± 0.5	13.5 ± 0.8	1.8 ± 0.2	0.21 ± 0.03	5.4 ± 0.3	2.8 ± 0.3	11.8 ± 0.5	2.2 ± 0.1
F1 20/08/87	560 ± 60	620 ± 40				1340 ± 70			
PC-GW-40		1.48 ± 0.09	2.6 ± 0.1	1.8 ± 0.1	0.85 ± 0.07	2.5 ± 0.1	2.2 ± 0.1	5.7 ± 0.2	2.3 ± 0.1
F1 08/02/88	120 ± 10	119 ± 7				620 ± 30			
UFWC11-C		2.2 ± 0.1	5.7 ± 0.3	2.5 ± 0.2		1.19 ± 0.08		18.1 ± 0.5	15 ± 1
F1 24/05/88	200 ± 20	180 ± 10				290 ± 20			
PC-GW-54		3.0 ± 0.2	4.0 ± 0.2	1.3 ± 0.1	0.28 ± 0.04	1.38 ± 0.09	1.1 ± 0.1	7.9 ± 0.3	5.7 ± 0.4
F1 15/09/88	140 ± 10	240 ± 10				340 ± 20			
HFFWC11D		3.1 ± 0.1	6.8 ± 0.3	2.2 ± 0.1	0.086 ± 0.009	0.29 ± 0.03	0.59 ± 0.06	3.2 ± 0.1	11 ± 1
F1 27/10/88	190 ± 20	250 ± 10				72 ± 7			
PC-GW-16		11.5 ± 0.5	16.8 ± 0.7	1.46 ± 0.08	0.90 ± 0.04	1.61 ± 0.09	15.1 ± 0.4	2.2 ± 0.1	1.4 ± 0.1
F2 12/02/87	970 ± 100	930 ± 40				400 ± 20			
UFVC24-B		12.8 ± 0.6	21.2 ± 0.9	1.7 ± 0.1	0.36 ± 0.02	0.37 ± 0.04	7.7 ± 0.3	0.51 ± 0.05	1.4 ± 0.2
%C= 2.4% 06/08/87	1100 ± 100	1030 ± 50				91 ± 10			
PC-GW-25		6.9 ± 0.3	9.6 ± 0.4	1.39 ± 0.08	0.48 ± 0.03	0.70 ± 0.05	4.6 ± 0.2	1.64 ± 0.08	2.3 ± 0.2
F2 28/09/87	520 ± 50	550 ± 20				170 ± 10			
PC-GW-41		8.9 ± 0.3	13.8 ± 0.5	1.54 ± 0.08	0.67 ± 0.03	1.36 ± 0.07	9.3 ± 0.3	11.1 ± 0.3	8.1 ± 0.5
F2 09/02/88	710 ± 70	720 ± 30				340 ± 20			
UFVC24-C		5.1 ± 0.2	8.1 ± 0.3	1.60 ± 0.10	0.45 ± 0.03	0.46 ± 0.04	3.6 ± 0.2	1.77 ± 0.08	3.9 ± 0.3
F2 31/05/88	470 ± 50	410 ± 20				113 ± 9			
PC-GW-60		4.3 ± 0.2	6.2 ± 0.2	1.43 ± 0.08	0.53 ± 0.03	0.59 ± 0.03	3.3 ± 0.1	2.65 ± 0.09	4.5 ± 0.3
F2 23/09/88	390 ± 40	350 ± 10				146 ± 8			

TABLE 1-II (contd.).

SAMPLE ORIGIN (dd/mm/yy)	U-flu. ($\mu\text{g/g}$)	^{238}U (Bq/g) ($\mu\text{g/g}$)	^{234}U (Bq/g)	^{234}U $\overline{^{238}\text{U}}$	^{230}Th $\overline{^{234}\text{U}}$	^{232}Th (Bq/g) ($\mu\text{g/g}$)	^{230}Th (Bq/g)	^{228}Th (Bq/g)	^{228}Th $\overline{^{232}\text{Th}}$
PC-GW-12		0.20 ± 0.01	0.23 ± 0.01	1.14 ± 0.08	0.89 ± 0.07	9.4 ± 0.2	0.21 ± 0.01	14.3 ± 0.3	1.5 ± 0.1
MF10 12/12/86	15 ± 2	16.2 ± 0.8				2320 ± 50			
UFMF10-A		0.54 ± 0.06	0.79 ± 0.07	1.5 ± 0.2		0.80 ± 0.04		1.46 ± 0.06	1.8 ± 0.1
%C= 5.3% 25/01/88	40 ± 4	44 ± 4				200 ± 10			
PC-GW-33		0.38 ± 0.02	0.55 ± 0.03	1.4 ± 0.1	0.28 ± 0.04	0.82 ± 0.03	0.15 ± 0.02	1.70 ± 0.05	2.1 ± 0.1
MF10 27/01/88	29 ± 3	31 ± 2				202 ± 8			
PC-GW-52		6.0 ± 0.4	8.8 ± 0.5	1.5 ± 0.1		1.2 ± 0.1		1.9 ± 0.2	1.6 ± 0.2
MF10 12/09/88	460 ± 50	480 ± 30				290 ± 30			
UFMF10-B		3.3 ± 0.2	4.8 ± 0.3	1.5 ± 0.1				0.99 ± 0.07	
MF10 23/10/88	230 ± 20	260 ± 20							
PC-GW-35		0.35 ± 0.02	0.37 ± 0.02	1.07 ± 0.10	0.69 ± 0.08	5.2 ± 0.1	0.26 ± 0.02	8.4 ± 0.2	1.6 ± 0.1
MF11 28/01/88	27 ± 3	28 ± 2				1270 ± 30			
PC-GW-53		0.48 ± 0.03	0.67 ± 0.03	1.4 ± 0.1	0.34 ± 0.04	5.0 ± 0.1	0.23 ± 0.02	8.0 ± 0.2	1.6 ± 0.1
MF11 13/09/88	39 ± 4	38 ± 2				1240 ± 30			
PC-GW-18						2.23 ± 0.08		2.80 ± 0.10	1.3 ± 0.1
%C= 7.4% 07/07/87	57 ± 6					550 ± 20			
PC-GW-30		0.92 ± 0.04	1.53 ± 0.07	1.7 ± 0.1	0.45 ± 0.03	0.18 ± 0.01	0.69 ± 0.03	0.33 ± 0.02	1.9 ± 0.2
MF12 02/12/87	58 ± 6	74 ± 4				43 ± 3			
UFMF12-A		18.1 ± 0.7	17.9 ± 0.7	0.99 ± 0.06	0.44 ± 0.02	0.41 ± 0.03	7.8 ± 0.3	1.12 ± 0.06	2.8 ± 0.3
%C= 2.7% 18/01/88	1600 ± 200	1460 ± 60				100 ± 8			
PC-GW-34		0.85 ± 0.04	1.59 ± 0.07	1.9 ± 0.1	0.11 ± 0.01	0.30 ± 0.02	0.18 ± 0.02	0.46 ± 0.02	1.5 ± 0.1
MF12 28/01/88	54 ± 5	69 ± 3				74 ± 4			
PC-GW-56		1.83 ± 0.08	2.5 ± 0.1	1.39 ± 0.09	.083 $\pm .009$	0.23 ± 0.01	0.21 ± 0.02	0.45 ± 0.02	2.0 ± 0.2
MF12 19/09/88	65 ± 7	147 ± 7				56 ± 4			
UFMF12-B		0.61 ± 0.03	1.26 ± 0.05	2.1 ± 0.1	0.04 ± 0.01	.072 $\pm .009$	0.04 ± 0.02	0.37 ± 0.02	5.1 ± 0.7
MF12 12/10/88	40 ± 4	49 ± 3				18 ± 2			

TABLE 1-II (contd.).

SAMPLE ORIGIN (dd/mm/yy)	U-flu. ($\mu\text{g/g}$)	^{238}U (Bq/g) ($\mu\text{g/g}$)	^{234}U (Bq/g)	^{234}U $\frac{^{234}\text{U}}{^{238}\text{U}}$	^{230}Th $\frac{^{230}\text{Th}}{^{234}\text{U}}$	^{232}Th (Bq/g) ($\mu\text{g/g}$)	^{230}Th (Bq/g)	^{228}Th (Bq/g)	^{228}Th $\frac{^{228}\text{Th}}{^{232}\text{Th}}$
G1A		0.74 ± 0.06	1.15 ± 0.07	1.6 ± 0.2		22.3 ± 0.6		78 ± 2	3.5 ± 0.1
GALLERY 11/12/86	110 ± 10	60 ± 4				5500 ± 100			
G1C		0.60 ± 0.04	0.65 ± 0.04	1.09 ± 0.10	0.56 ± 0.07	17.2 ± 0.4	0.37 ± 0.04	26.1 ± 0.6	1.5 ± 0.1
GALLERY 11/12/86	54 ± 5	48 ± 3				4200 ± 100			

TABLE 1-III

Results on the isotopic compositions of uranium and thorium in waters from the Morro do Ferro analogue site (PUC data).

SAMPLE ORIGIN (dd/mm/yy)	U-flu. ($\mu\text{g/l}$)	^{238}U (Bq/l) ($\mu\text{g/l}$)	^{234}U (Bq/l)	^{234}U ^{238}U	^{230}Th ^{234}U	^{232}Th (Bq/l) ($\mu\text{g/l}$)	^{230}Th (Bq/l)	^{228}Th (Bq/l)	^{228}Th ^{232}Th
PC-GW-12		.0132 $\pm .0008$.0162 $\pm .0009$	1.23 ± 0.10	0.05 ± 0.01	ICP	.0008 $\pm .0002$.076 $\pm .002$	310 ± 20
MF10 12/12/86	1.1 ± 0.1	1.06 ± 0.06				.060 $\pm .003$			
PC-GW-33		.00096 $\pm .00007$.00122 $\pm .00008$	1.3 ± 0.1	0.13 ± 0.06	ICP	.00015 $\pm .00007$.0070 $\pm .0002$	82 ± 5
MF10 27/01/88	.061 $\pm .006$.077 $\pm .005$.021 $\pm .001$			
PC-GW-48		.0193 $\pm .0007$.0253 $\pm .0009$	1.31 ± 0.07	.038 $\pm .004$.00067 $\pm .00005$.00095 $\pm .00009$.0264 $\pm .0007$	39 ± 3
MF10 08/06/88	1.8 ± 0.2	1.55 ± 0.06				0.17 ± 0.01			
PC-GW-52		.0087 $\pm .0004$.0115 $\pm .0005$	1.32 ± 0.08	.050 $\pm .008$	ICP	.00057 $\pm .00009$.045 $\pm .001$	101 ± 5
MF10 12/09/88	0.65 ± 0.07	0.70 ± 0.03				.11 $\pm .01$			
PC-GW-69		.0071 $\pm .0003$.0095 $\pm .0004$	1.35 ± 0.09	0.21 ± 0.02	ICP	.0020 $\pm .0001$.0305 $\pm .0008$	84 ± 4
MF10 06/12/88	0.53 ± 0.05	0.57 ± 0.03				.090 $\pm .005$			
PC-GW-35		.00068 $\pm .00005$.00094 $\pm .00006$	1.4 ± 0.1	0.5 ± 0.1		.0005 $\pm .0001$.056 $\pm .001$	
MF11 28/01/88	.041 $\pm .004$.055 $\pm .004$							
PC-GW-49		.00167 $\pm .00009$.0027 $\pm .0001$	1.6 ± 0.1	0.33 ± 0.04	.0039 $\pm .0001$.00089 $\pm .00009$.243 $\pm .006$	63 ± 3
MF11 13/06/88	1.5 ± 0.1	.134 $\pm .007$				0.96 ± 0.03			
PC-GW-53		.0094 $\pm .0004$.0142 $\pm .0006$	1.52 ± 0.09	.096 $\pm .009$.0022 $\pm .0001$.0014 $\pm .0001$.413 $\pm .009$	180 ± 10
MF11 13/09/88	0.86 ± 0.09	0.75 ± 0.03				0.55 ± 0.03			
PC-GW-70		.0055 $\pm .0003$.0082 $\pm .0004$	1.5 ± 0.1	0.20 ± 0.02	ICP	.0016 $\pm .0001$.209 $\pm .005$	770 ± 40
MF11 12/12/88	0.42 ± 0.04	0.44 ± 0.02				.067 $\pm .003$			
PC-GW-73		.0045 $\pm .0002$.0064 $\pm .0003$	1.42 ± 0.09	0.12 ± 0.02	.00041 $\pm .00004$.0008 $\pm .0001$.0047 $\pm .0002$	12 ± 1
MF13 20/12/88	0.38 ± 0.04	0.36 ± 0.02				.10 $\pm .01$			
PC-GW-18		.0015 $\pm .0001$.0026 $\pm .0002$	1.7 ± 0.2	0.19 ± 0.06	ICP	.0005 $\pm .0002$.0164 $\pm .0005$	7.0 ± 0.4
MF12 07/07/87	0.16 ± 0.02	0.12 ± 0.01				0.58 ± 0.03			
PC-GW-30		.0124 $\pm .0005$.0213 $\pm .0008$	1.72 ± 0.10	.005 $\pm .004$	ICP	.00011 $\pm .00009$.0064 $\pm .0002$	99 ± 6
MF12 02/12/87	0.99 ± 0.10	1.00 ± 0.04				.016 $\pm .001$			

TABLE 1-III (contd.).

SAMPLE ORIGIN (dd/mm/yy)	U-flu. ($\mu\text{g/l}$)	^{238}U (Bq/l) ($\mu\text{g/l}$)	^{234}U (Bq/l)	^{234}U $\overline{^{238}\text{U}}$	^{230}Th $\overline{^{234}\text{U}}$	^{232}Th (Bq/l) ($\mu\text{g/l}$)	^{230}Th (Bq/l)	^{228}Th (Bq/l)	^{228}Th $\overline{^{232}\text{Th}}$
PC-GW-32		.0205 $\pm .0008$.034 $\pm .001$	1.64 ± 0.09		ICP		.0043 $\pm .0002$	30 ± 2
MF12 22/12/87	1.6 ± 0.2	1.65 ± 0.07				.035 $\pm .002$			
PC-GW-34		.0097 $\pm .0005$.0159 $\pm .0007$	1.6 ± 0.1		ICP		.0054 $\pm .0002$	17 ± 1
MF12 28/01/88	0.79 ± 0.08	0.78 ± 0.04				.080 $\pm .004$			
PC-GW-50		.0107 $\pm .0004$.0212 $\pm .0008$	2.0 ± 0.1	.016 $\pm .004$.0032 $\pm .0001$.00034 $\pm .00007$.0083 $\pm .0002$	2.6 ± 0.1
MF12 14/06/88	0.98 ± 0.10	0.86 ± 0.03				0.80 ± 0.03			
PC-GW-56		.0099 $\pm .0004$.0188 $\pm .0007$	1.9 ± 0.1	.017 $\pm .004$.00038 $\pm .00003$.00032 $\pm .00007$.0065 $\pm .0002$	17 ± 2
MF12 19/09/88	0.82 ± 0.08	0.80 ± 0.03				.094 $\pm .008$			
PC-GW-71		.0075 $\pm .0003$.0174 $\pm .0007$	2.3 ± 0.1	.028 $\pm .005$	ICP	.00049 $\pm .00009$.0069 $\pm .0002$	4.9 ± 2
MF12 14/12/88	0.54 ± 0.05	0.60 ± 0.03				.35 $\pm .02$			
PC-GW-26		.0061 $\pm .0004$.0075 $\pm .0004$	1.2 ± 0.1		ICP		.0077 $\pm .0003$	59 ± 4
PZ2 29/09/87	0.49 ± 0.05	0.49 ± 0.03				.032 $\pm .002$			
PC-SS-04		.0043 $\pm .0002$.0088 $\pm .0004$	2.1 ± 0.1		ICP		.0087 $\pm .0003$	24 ± 2
South Str. 29/07/87	0.34 ± 0.03	0.35 ± 0.02				.088 $\pm .004$			
PC-NS-05		.0020 $\pm .0002$.0029 $\pm .0002$	1.5 ± 0.2	0.20 ± 0.04	ICP	.0006 $\pm .0001$.00142 $\pm .00008$	4.7 ± 0.3
North Str. 10/08/87	0.17 ± 0.02	0.16 ± 0.01				.074 $\pm .004$			