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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

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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.

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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

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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.

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Abstract

Data are presented on suspended particles and colloids in groundwaters from the Osamu Utsumi mine and the Morro do Ferro analogue study sites. Cross-flow ultrafiltration with membranes of different pore sizes (450 nm to 1.5 nm) was used to prepare colloid concentrates and ultrafiltrates for analyses of major and trace elements and U- and Th-isotopic compositions. Additional characterisation of colloidal and particulate material was performed by ESCA, SEM and X-ray diffraction. The results obtained indicate the presence of low concentrations (<1 mg/l) of colloids (1.5–450 nm) in these waters, composed mainly of iron/organic species. Minor amounts of U and some other trace elements (Si, Ca, Mg, Mn, Cu, Zn, Pb and occasionally Zr and Sn) and significant amounts of Th and REEs were associated with these colloids. U-isotopic measurements indicate element exchange equilibrium between aqueous, colloidal and suspended particle phases. Suspended particles (>450 nm) in the waters show the same trends as the colloids with respect to U, Th and REE associations, but elemental concentrations were typically higher by a factor of 1,000 or more. Calculated association ratios (in ml · g^{-1}*) are in the order of 10*^{4}* to 10*^{5}* for U, 10*^{5}* to 10*^{6}* for the REEs and 10*^{6}* to 10*^{7}* for Th. In waters with low pH and high sulphate content, these ratios are considerably lower. Due to the low concentrations of suspended particles in groundwaters from the Osamu Utsumi U-mine (<0.5 mg/l), these particles carry only a minor amount of U and REEs (<10% of the total concentration of the unfiltered groundwater), but a significant, usually predominant, fraction of Th (30–70%). The suspended particle load in groundwaters from the Morro do Ferro environment is typically higher than in those from the mine by a factor of 5 to 10. This suggests that U and the REEs could be transported predominantly by particulate matter. However, there is chemical and mineralogical evidence that these particles, composed mainly of Fe(III) oxyhydroxides and humic-like compounds, have a low capacity for migration.*

Zusammenfassung

Dieser Bericht stellt Daten über schwebende Partikel und Kolloide in den Grundwässern der Osamu Utsumi Mine und von Morro do Ferro zusammen. Um kolloide Konzentrate und Ultrafiltrate für die Analyse von Haupt- und Spurenelementen sowie von U- und Th-Isotopenzusammensetzungen zu gewinnen, wurden Querfluss-Ultrafiltrationen mit Membranen von unterschiedlicher Porengrösse (450 nm bis 1.5 nm) benutzt. Eine zusätzliche Charakterisierung von Kolloiden und Partikeln wurde durch ESCA, REM und Röntgen-Diffraktion erzielt. Die Ergebnisse deuten auf eine niedrige Konzentration (<1 mg/l) von Kolloiden (1.5-450 nm) in diesen Gewässern hin, die hauptsächlich aus Eisen/organischen Verbindungen zusammengesetzt sind. Geringe Mengen von U und einigen anderen Spurenelementen (Si, Ca, Mg, Mn, Cu, Zn, Pb und teilweise Zr und Sn) sowie bedeutende Mengen von Th und SEE waren in Verbindung mit diesen Kolloiden. U-Isotopen-Messungen deuten auf ein Austauschgleichgewicht zwischen wässeriger und partikulärer Phase hin. Schwebende Partikel (>450 nm) in den Wässern zeigen die gleiche Tendenz wie die Kolloide bezüglich der Anlagerung von U, Th und SEE, aber die Elementkonzentrationen waren etwa um einen Faktor von 1000 oder mehr höher. Berechnete Verteilungsverhältnisse (in $ml \cdot g^{-1}$*) bewegen sich in der Grössenordnung von* 10^4 *bis* 10^5 *für U,* 10^5 *bis* 10^6 *für die SEE und* 10^6 *bis* 10^7 *für Th. In Gewässern mit niedrigem pH Wert und hohem Sulfatgehalt, liegen diese Verhältnisse beträchtlich tiefer. Aufgrund der niedrigen Konzentration schwebender Partikel in den Grundwässern der Osamu Utsumi Uranmine (<0.5 mg/l) tragen diese Partikel nur eine geringe Menge von U und SEE (<10 % der totalen Konzentration des ungefilterten Grundwassers), aber einen beträchtlichen, normalerweise vorherrschenden, Bruchteil von Th (30 %-70 %). Der Gehalt an schwebenden Partikeln in den Grundwässern des Geländes um Morro do Ferro ist typisch 5 bis 10 mal höher als derjenige der Mine. Dies deutet darauf hin, dass U und SEE vor allem durch Partikel transportiert werden könnten. Es bestehen jedoch chemische und mineralogische Beweise, dass diese Partikel, die hauptsächlich aus Fe(III) oxyhydroxyden und huminähnlichen Verbindungen bestehen, nur eine geringe Migrationsfähigkeit haben.*

Résumé

On présente des données sur les particules en suspension et les colloïdes dans les eaux souterraines des sites d'analogies naturelles de la mine d'Osamu Utsumi et de Morro do Ferro. On a utilisé une ultrafiltration à flux transversal à travers des membranes à pores de différents diamètres (450 à 1.5 nm) pour préparer des concentrats colloïdaux et des ultrafiltrats en vue de l'analyse des éléments majeurs et des éléments trace, ainsi que des compositions isotopiques de U et Th. Une caractérisation additionnelle des particules et des colloïdes a été effectuée par spectroscopie électronique (ESCA), par microscopie à balayage (SEM) et par diffraction aux rayons-X. On a ainsi montré que la concentration en colloïdes était faible dans ces eaux, et composée principalement d'espèces du fer et de molécules organiques. Associés à ces colloïdes, on trouve de faibles quantités de U et de quelques éléments trace (Si, Ca, Mg, Cu, Zn, Pb et occasionellement Zr et Sn), et des quantités significatives de Th et de terres rares (TRs). Les mesures isotopiques de U indiquent qu'il y a équilibre d'échange d'éléments entre les phases aqueuse, colloïdale et de suspension. Les particules en suspension (>450 nm) montrent la même tendance que les colloïdes en ce qui concerne les associations de U, Th et TRs, mais révèlent des concentrations en éléments typiquement plus élevées, d'un facteur 1000 ou plus. Les rapports d'association calculés (en ml/g) sont de l'ordre de grandeur de 10^4 à 10^5 pour U, 10^5 à 10^6 pour TRs, et 10^6 à 10^7 pour Th. Dans les eaux très sulfatées et à pH bas, ces rapports sont nettement plus faibles. Du fait de leur faible concentration dans les eaux souterraines de la mine d'uranium d'Osamu Utsumi, les particules en suspension ne contiennent qu'une faible quantité de U et TRs (moins de 10% de la concentration totale de l'eau non filtrée), mais une quantité significative de Th, en général prédominante (30 à 70%). Par rapport à celles de la mine, les eaux souterraines de Morro do Ferro présentent une charge de particules en suspension typiquement plus élevée, d'un facteur 5 à 10. Cela suggère que U et TRs pourraient être tranportés de manière préférentielle par les particules en suspension. Il faut relever toutefois que ces particules, vu leur composition chimique et minéralogique (principalement des oxyhydroxydes de Fe(III) et des composés de type humique), possèdent une faible capacité de migration.

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 description of the role and behaviour of groundwater, suspended particles and colloidal material, with particular reference to the second performance assessment objective of the project.

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 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, Degueldre.
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.

Contents

1. Introduction

The migration of pollutants in the geosphere depends on a complex interplay of processes, related to the chemistry of both the groundwater and the contaminants and physico-chemical interactions of such contaminants with the rock and mineral surfaces. The simplistic view, in which the subsurface transport of a contaminant is described in terms of its partitioning between one mobile aqueous phase and the rock or soil, cannot be applied if mobile suspended particles and colloids are components of a system. These particles and colloids could concentrate potential pollutants by sorption and enhance their mobility through fractured, fissured or porous rock media. Experimental evidence for such a transport mechanism has been reported in the literature (e.g. Nyhan *et al.*, 1985; Nelson and Orlandini, 1986; Short *et al.*, 1988; Hofman, 1989; Alexander *et al.*, 1990). However, there are currently only crude approaches available to quantifying and predicting colloid migration and applying it to transport models. McCarthy and Zachara (1989) have drawn attention to the role of colloids in contaminant transport, to the lack of information about colloidal systems and to the most important questions that require urgent research. These key questions, for which answers were sought in this present study, are listed below (McCarthy and Zachara, op. cit.).

Occurrence and properties of subsurface colloids

- Are colloids present in groundwaters? If so, how can they be sampled without introducing artefacts?
- Can the presence of stable colloids be understood and predicted on the basis of the mineralogy and hydrochemistry of specific subsurface environments?
- What is the composition, physicochemical nature and abundance of colloidal particles in subsurface environments?

Mobility of subsurface colloids

- Do colloids move through rocks?
- Can the chemical and hydrological factors controlling the stabilisation, transport and deposition of colloidal particles be described and incorporated in predictive transport models?

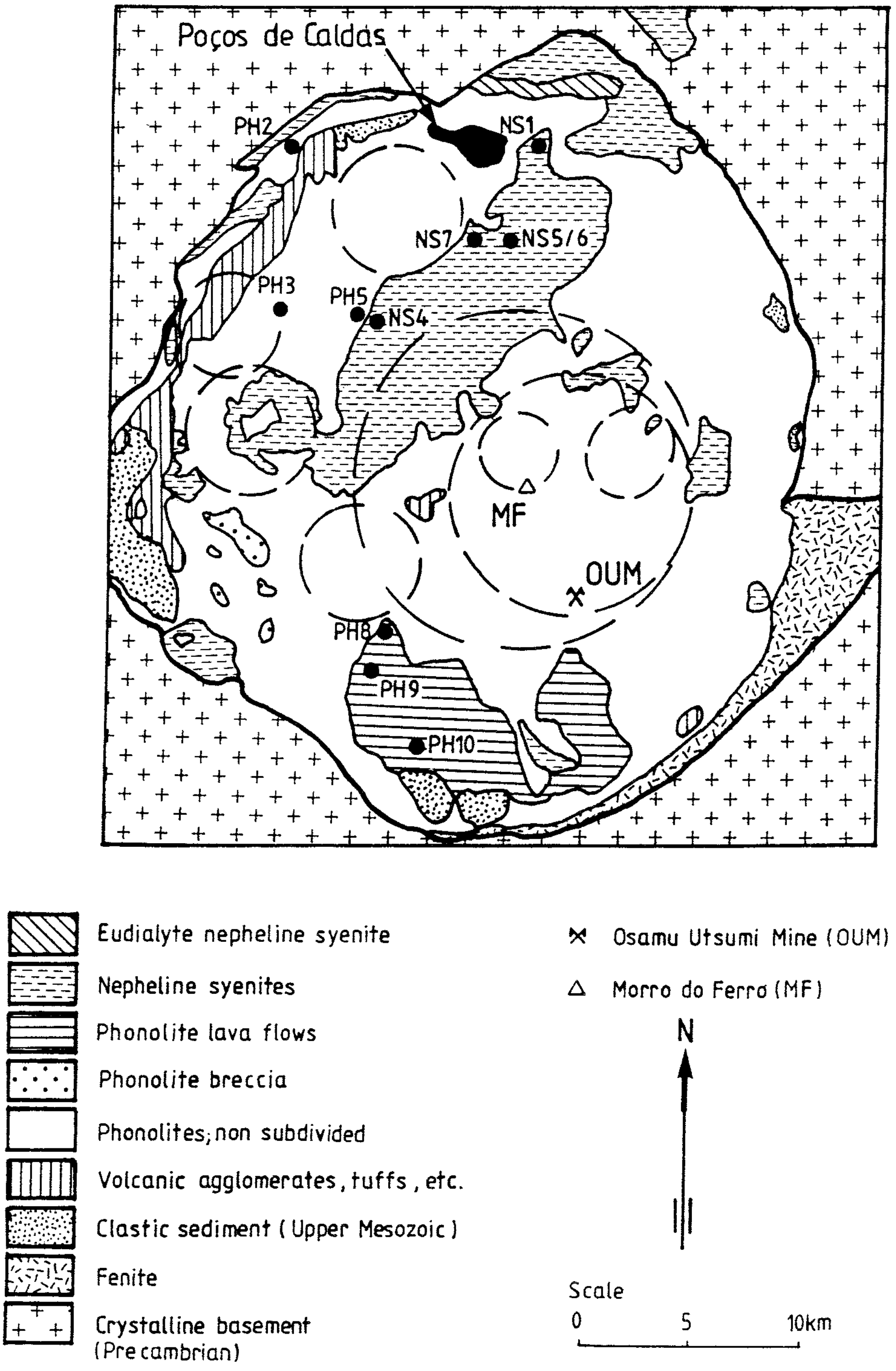


Figure 1. Location of the Osamu Utsumi uranium mine and the Morro do Ferro analogue sites within the Poços de Caldas plateau.

Implications for contaminant transport

- Do mobile colloids sorb and transport contaminants?
- What is the capacity of groundwater colloids to bind contaminants?
- How, and to what extent, do chemical and radioactive wastes either precipitate as colloidal-sized particles or sorb onto other colloidal material?

Implications for waste management

- Can an improved understanding of the geochemistry of subsurface colloids be applied to devise remediation strategies based on manipulation of colloid mobilisation or deposition?

In safety assessment analyses of nuclear waste disposal, these questions are of special importance (e.g. Eichholz *et al.*, 1982; Avogadro and de Marsily, 1984). Radionuclides are expected to be released in very low concentrations in true solution, but waste leaching may directly produce colloids of sparingly soluble elements (e.g. U(IV), Pu(IV), Th(IV), Zr(IV), Sn(IV), III-valent actinides and REEs, etc.) or such elements may sorb onto naturally occurring colloids. Experimental data on the potential role of colloids in radionuclide transport, and on methods of concentrating and characterising them properly, have been published by several investigators (e.g. Degueldre and Wernli, 1987; Degueldre *et al.*, 1989a; Ivanovich *et al.*, 1988; Short *et al.*, 1988; Kim *et al.*, 1987).

This report summarises results on the role of suspended particles (>450 nm) and colloids (1.5–450 nm) in the transport of U, Th and REEs obtained during the Poços de Caldas project. Preliminary results on organic and inorganic colloids in surface- and groundwaters from both Morro do Ferro and the Osamu Utsumi mine have been published previously (Miekeley and Kuechler, 1987; Miekeley *et al.*, 1989).

2. Site descriptions and water characteristics

The Osamu Utsumi mine and the Morro do Ferro study sites are situated approximately in the centre of the Poços de Caldas Plateau (Fig. 1).

At the Osamu Utsumi mine (described in Waber *et al.*, this report series; Rep. 2), uranium (in the form of pitchblende) is being exploited by open-cast methods. Characteristic distribution patterns of uranium and other elements have developed along redox fronts, which are formed by the action of downward-percolating oxidising

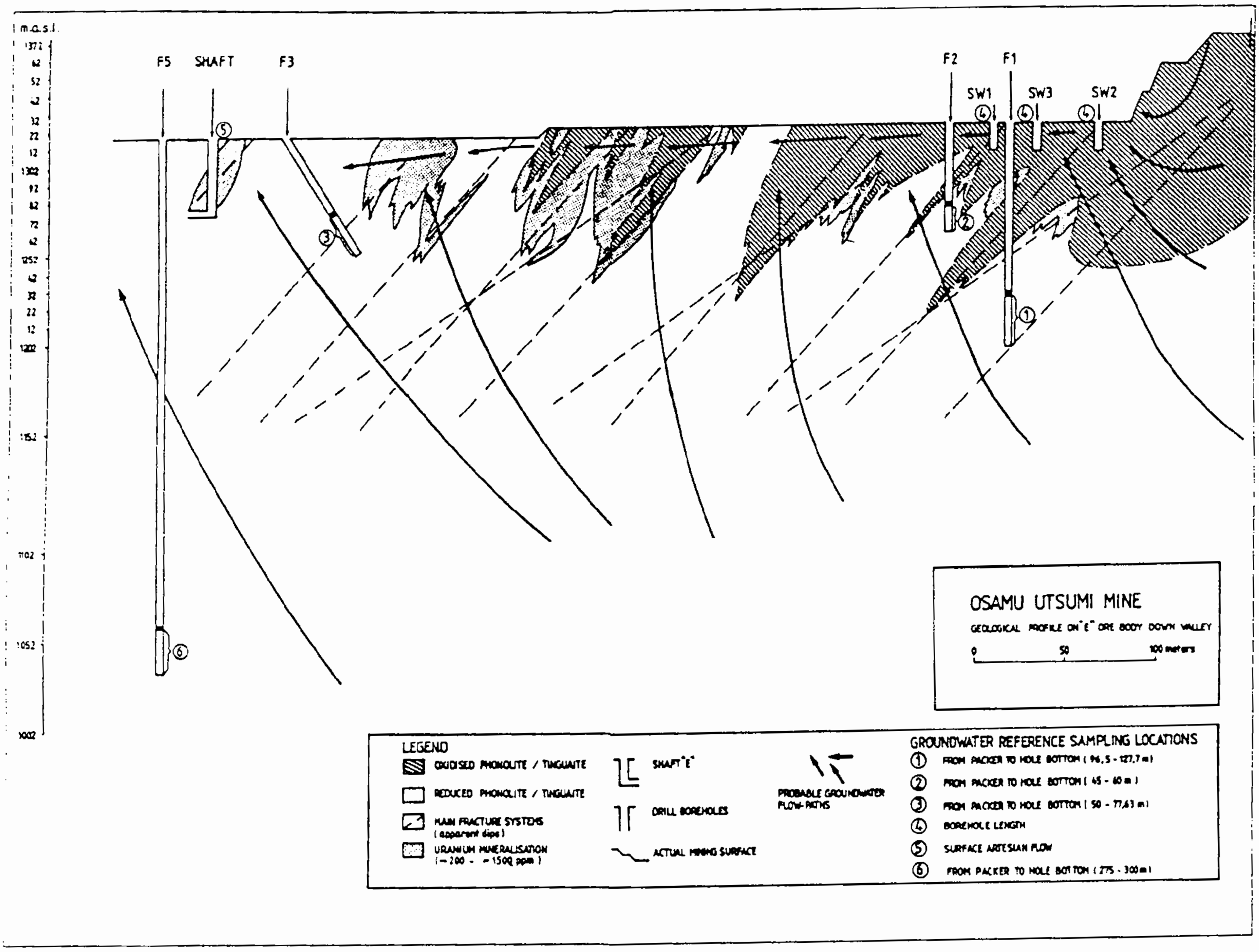


Figure 2. Partial cross-section of the uranium mine illustrating the water sampling locations, the local water flows and the redox fronts.

waters (MacKenzie *et al.*, this report series; Rep. 7). A cross-section of the area in which the colloid sampling was performed is shown in Figure 2. The location of the boreholes for shallow and groundwater sampling (Holmes *et al.*, this report series; Rep. 5) and their position with respect to the redox front and the local water flows (at present upwards) can be seen.

The Th-REE orebody of Morro do Ferro, only 14 km distant from the Osamu Utsumi uranium mine, has been investigated previously as a natural analogue site (e.g. Eisenbud *et al.*, 1982 and 1984; Lei, 1984; Miekeley *et al.*, 1985; Lei *et al.*, 1986). The hill is about 140 m above local stream level and is in an advanced state of weathering (Waber, this report series; Rep. 3). The ore body, near its summit, is estimated to contain about 30,000 t of Th, 33,000 t of La, 49,000 t of Ce, 17,000 t of Nd and about 400 t of U (Frahya, 1962; Linsalata *et al.*, 1989). Few discrete mineral forms of these elements have been identified, and it is believed that most of them are sorbed onto clay minerals and hydrous Fe(III) and Al oxides, which are probably covered with adsorbed organic components. Figure 3 shows a cross-section of Morro do Ferro, indicating the water sampling locations and the expected rainwater percolation flow-paths through the unsaturated and saturated zones (see Holmes *et al.* and Nordstrom *et al.*, this report series; Reps. 5 and 6). The climate of the Poços de Caldas plateau is characterised by a dry season (February to August) and a rainy season (October to March). About 80% of the mean annual precipitation (170 cm per year) occurs during the rainy season.

2.1. Hydrology and water geochemistry of the Osamu Utsumi mine and Morro do Ferro study sites

Although in close proximity to one another, and formed by similar hydrothermal and weathering processes, the two sites have characteristic differences in rock composition, hydrogeology and groundwater geochemistry which make them attractive for comparative studies. Only those aspects which are of relevance for this work will be presented here, the detailed geological and hydrochemical descriptions being found in Schorscher and Shea, Waber *et al.*, Waber, Shea and Nordstrom *et al.* (this report series; Reps. 1–4 and 6). Detailed information on the geochemistry of natural series nuclides and REEs in groundwaters is presented in Miekeley *et al.* (this report series; Rep. 8).

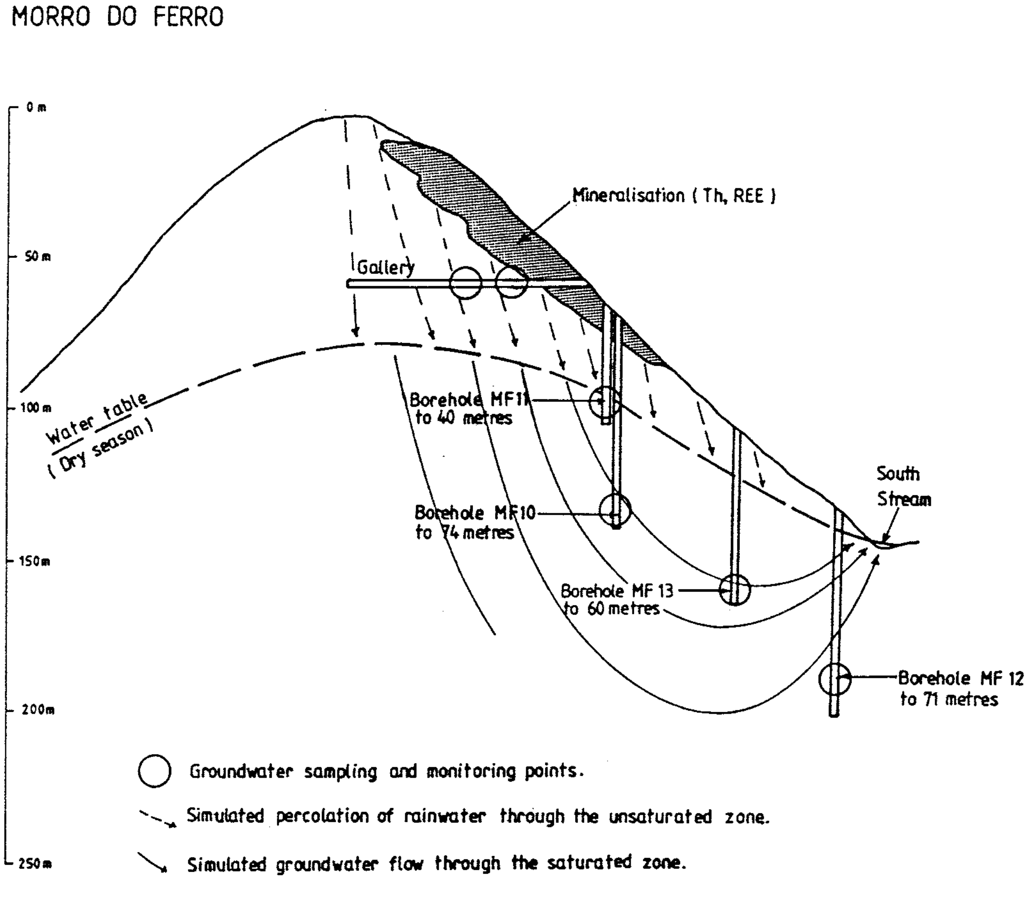


Figure 3. Cross-section of the Morro do Ferro illustrating the water sampling locations, the mineralisation zone and the simulated rain percolation and groundwater flows.

2.1.1. Osamu Utsumi uranium mine

Most groundwaters from the uranium mine can be classified as K-Fe-SO_4 in type, and oxidising and slightly acidic in nature. They are the result of intense weathering processes of highly leached K-rich rock masses (Nordstrom *et al.*, this report series; Reps. 6 and 14). Typical groundwater chemical parameters (concentrations in mg/l, except for U, Th and REEs which are in μ/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, [SO_4]=10–20, [HCO_3]=8–20, [F]=0.3–2.4, [HPO_4] ≤ 0.05 ppm, pH=5.4–6.1 and Eh= + (200–400) mV. The [DOC] (defined here as dissolved organic carbon in the <450 nm fraction, which also contains colloidal organic carbon (COC)) in groundwater is low (1–3 mg/l) due to the very sparse vegetation in the mine area. Additional water data are summarised in Table I.

An interesting hydrogeological feature of the mine area (Holmes *et al.*, this report series; Rep. 5) is the presence of an upward groundwater flow gradient which forces predominantly reducing water to ascend into more oxidising environments (Fig. 2). This process is believed to be responsible for the formation of ferric oxyhydrates, observable as suspended particles (>450 nm) and colloids (1.5–450 nm) in groundwaters and as surface coatings of the rocks.

2.1.2. Morro do Ferro

Compared to the Osamu Utsumi mine, the Morro do Ferro deposit is in a much more advanced state of weathering. The ore body is characterised by very high concentrations of thorium and REEs in soil and weathered rock samples (in certain locations >1%) and much lower concentrations of uranium. Secondary enrichment of thorium and REEs by weathering processes and preferential leaching of uranium by percolating oxidising waters are considered as the most probable processes for the pronounced elemental fractionation.

Morro do Ferro was considered a suitable site for studying the possible migration of suspended particles and colloidal material because of the unperturbed nature of the site (in comparison with the Osamu Utsumi mine) and because there was the possibility of intercepting a simple down-flow groundwater gradient at several points for groundwater sampling and characterisation (Fig. 3).

TABLE I

Chemical data for prefiltered near-surface and ground waters from the Osamu Utsumi uranium mine (adapted from Miekeley *et al.*, 1989).

	SAMPLE	DATE (dd/mm/yy)	^{238}U (ppb)	R1	^{232}Th (ppb)	R2	pH	Eh (mV)	Na (ppm)	K (ppm)	Fe(II) (ppm)	Fe(t) (ppm)	HCO_3 (ppm)	SO_4 (ppm)	F (ppm)
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
SW03	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
	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
F1	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
	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		0.76	12.5	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	0.57	10.0	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	0.40	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	0.44	11.0	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
	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
	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

TABLE I (contd.).

	SAMPLE	DATE (dd/mm/yy)	^{238}U (ppb)	R1	^{232}Th (ppb)	R2	pH	Eh (mV)	Na (ppm)	K (ppm)	Fe(II) (ppm)	Fe(t) (ppm)	HCO3 (ppm)	SO4 (ppm)	F (ppm)
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
F3	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
	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
F5	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
	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
F4	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
	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									

Isotope Activity Ratios

R1 = ^{234}U/^{238}U, R2 = ^{230}Th/^{234}U

UC16 = Pilot Hole
Sup.D = Supply Dam
PM22 = Piezometer Station 22

(Not shown in Fig. 2)

TABLE II

Chemical data for prefiltered near-surface and ground waters from Morro do Ferro (adapted from Miekeley *et al.*, 1990).

	SAMPLE	DATE (dd/mm/yy)	^{238}U (ppb)	R1	^{232}Th (ppb)	R2	pH	Eh (mV)	Na (ppm)	K (ppm)	Fe(II) (ppm)	Fe(t) (ppm)	HCO3 (ppm)	SO4 (ppm)	F (ppm)
MF10	PC-GW-12	12/12/86	1.06	1.2	0.060	0.05									
	UFMF10-A	25/01/88	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	0.077	1.3	0.021	0.13	4.6	505	0.09	0.14	0.55	0.58	12.0	8.0	0.07
	PC-GW-48	08/06/88	1.55	1.3	0.17	0.038	5.37	-121	0.09	0.35	2.31	2.32	18.9	<5.0	0.11
	PC-GUW52	12/09/88	0.70	1.3	0.11	0.05	5.94	384	0.20	0.24	0.62	0.66	10.7	10.0	<.10
	UFMF10-B	12/10/88	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	0.57	1.3	0.090	0.21	5.91	420	0.10	2.00	0.46	0.52	8.11	<5.0	0.19
MF11	PC-GW-35	28/01/88	0.055	1.4		0.5	5.2	430	0.18	0.24	0.19	0.24	26.6	11.2	0.06
	PC-GW-49	13/06/88	0.134	1.6	0.96	0.33	5.12	590	0.16	0.19	<0.10	<0.10	12.0	<5.0	<0.10
	PC-GW-53	13/09/88	0.75	1.5	0.55	0.096	5.30	544	0.12	0.16	<0.10	<0.10	8.84	5.8	0.16
	PC-GW-70	12/12/88	0.44	1.5	0.067	0.20	5.49	568	0.20	0.16	<0.10	<0.10	8.11	<5.0	0.19
MF13	PC-GW-73	20/12/88	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	0.12	1.7	0.58	0.19	6.21				2.41	2.51	32.9	15.4	6.9
	PC-GW-30	02/12/87	1.00	1.7	0.016	0.005	6.42		1.32	18.0	3.04	3.05	38.9	14.0	5.68
	PC-GW-32	22/12/87	1.65	1.6	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	0.78	1.6	0.080		5.7	277	1.09	10.5	1.31	1.33	35.3	13.2	5.95
	PC-GW-50	14/06/88	0.86	2.0	0.80	0.016	6.19	184	0.97	9.47	0.74	1.79	34.7	13.6	4.96
	PC-GW-56	19/09/88	0.80	1.9	0.094	0.017	6.13	265	0.96	1.08	1.25	1.28	27.8	16.2	5.97
	UFMF12-B	12/10/88	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	0.60	2.3	0.35	0.028	6.33	398	0.80	10.4	0.57	0.58	24.9	5.36	7.26
PZ2	PC-GW-26	29/09/87	0.49	1.2	0.032										
S. Str.	PC-SW-04	29/07/87	0.35	2.1	0.088										
N. Str.	PC-SW-05	10/08/87	0.16	1.5	0.074	0.20									

<u>Isotope Activity Ratios</u>

R1 = $^{234}U/^{238}U$, R2 = $^{230}Th/^{234}U$

PZ2 = Piezometer Station 2
S. Str. = South Stream
N. Str. = North Stream

(Not shown in Fig. 3)

This gradient extends from a strongly oxidising (borehole MF11, Eh = + 450–650 mV) to a less oxidising, almost unperturbed environment (borehole MF12, Eh = +200–450 mV). Information on the groundwater geochemistry of the Morro do Ferro site is more sparse than that from the mine (Table II).

The data for waters from borehole MF10, which penetrates the region of highest thorium and REE mineralisation of the deposit, show significantly lower concentrations of major elements (Na, K, Fe) and potential complex-forming anions (F^-, HCO_3^-, SO_4^{2-}) than groundwaters from borehole MF12 (and also from the Osamu Utsumi mine), indicating that this water is representative of the highly leached unsaturated zone of the deposit. The composition of groundwater from borehole MF12 is very similar to most of the groundwater from the uranium mine area, which reflects the similarity of the bedrock chemistry (reduced phonolites).

The DOC concentration in groundwater from the Morro do Ferro site is low (1–4 ppm) due to the sparse vegetation in the area. The intense rainfall during the summer season favours the leaching of humic matter, but sorption of these compounds by clays and other adsorbing materials during downward percolation of water has been shown in laboratory experiments (Coutinho, 1989). In piezometer holes and shallow percolation waters in the unsaturated zone (Fig. 3, gallery), much higher concentrations of DOC (10–20 ppm), mainly as humic acids, were occasionally observed. It could be shown that these compounds with pronounced complexing capacity (e.g. Choppin and Allard, 1986) and colloidal size ranges were the main concentrators for thorium, REEs and other major and trace elements (Kuechler, 1986; Miekeley *et al.*, 1989).

3. Materials and methods

3.1. Water sampling sites and procedures

At the Osamu Utsumi study site, groundwaters from the reference borehole locations (F1, F2, and F3) and from one shallow borehole (SW03) were used in this study. Although not a reference location, borehole F4 was also sampled as it penetrated a highly mineralised area. However, most of the work was concentrated on samples from F1 and F2. Figure 2 shows the location of the sampling points and Table III summarises some of their hydrogeological characteristics. Sampling was performed during the dry, rainy and transitional periods over a period of three years. Normally, a submersible electric pump was used. However, due to the artesian behaviour of boreholes F1 and F2 during

TABLE III

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 extension is only to 175 m depth.

the rainy season, direct sampling of the outflowing waters could be carried out during this period. 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 borehole and other parameters which may influence the groundwater chemistry. For flushing and sample collection, the pumping was done at low rates (<200 ml/min) to avoid draw-down of the water levels and to minimise particle disaggregation. An in-line prefilter (Millipore HA, 450 nm, surface: 154 cm^2) was used to separate the suspended particle (SP) fraction (>450 nm). It is recognised that this size boundary is only an operational definition (based on the traditional use of the 0.45 μm filter) and that this SP-fraction overlaps with the upper end of the colloidal size range. To minimise sorption of colloids by the SP-layer on the prefilter, or retention of the colloids by filtration effects, the surface density of this layer was kept as low as possible by frequent changing of the membrane filters. Because of the low SP concentrations in most of the groundwaters from both sites (see Table VI), it is believed that prefiltering caused no major modifications to the colloid population. The prefilters were air-dried and conditioned for further analyses of the SP-fraction. Eh, pH, and concentrations of dissolved oxygen DO, S, Fe tot., Fe(II), temperature and conductivity were monitored routinely at the site. Groundwater sampling for colloid studies coincided, whenever possible, with the routine sampling programme for the more complete geochemical characterisation of these reference waters.

At Morro do Ferro, sampling was performed in four boreholes (MF10, MF11, MF12 and MF13) and at one location within the experimental mine gallery. All locations are situated within a magnetite breccia which is believed to represent the most hydraulically conductive zone of the area. These boreholes cover a depth interval from 40 to 74 m and probably intercept the same streamlines. Downhill water flow is in the direction from MF11 (40 m) to MF10 (74 m), further downward to MF13 (60 m) and finally to MF12 (71 m) at the base of the hill (Fig. 3). The water sampling procedures were similar to those mentioned above.

3.2. Colloid fractionation and characterisation

3.2.1. Colloid fractionation

Normally, a 40 to 50 l water aliquot, sampled as described above, was used for colloid fractionation. The prefiltered water was collected in polyethylene containers, flushed with nitrogen gas and immediately transported back to a clean laboratory at Poços de Caldas, where it was preferable to perform the colloid fractionation work in order to minimise contamination (more probable under field conditions) and logistic problems. Within the shortest possible time (normally 6 to 12 h after collection) the samples were subjected to a sequential (cascade) cross-flow ultrafiltration procedure using stirred N_2-pressured cells (400 ml) and flat 'Diaflo' membranes with different nominal molecular weight cut-off limits (MWCL) of 100,000, 10,000 and 1,000 daltons (Amicon: YM-100, PM-10 and YM-2; area 41.8 cm^2). Although no exact information on the pore size diameters of these filters is furnished by the manufacturer, the MWCL mentioned correspond to a size interval of about 10 nm to 1.5 nm (see Table IV for some of the characteristics of these membranes).

TABLE IV
Some specifications of the AMICON ultrafiltration membranes used in this study (adapted from Buffle, 1989).

TYPE	Molecular weight cut-off limit (MWCL)	Pore size diameter (nm)	Recommended pressure (atm)	Recommended pressure (psi)	Typical water flux (cm/min)
XM300[1]	300,000	15	1.7	25	0.8–2.0
YM100[2]	100,000	10	1.7	25	0.6–1.5
XM50[1]	50,000	3	3.7	55	1.0–2.0
PM10[3]	10,000	2	3.7	55	2.5–4.0
YM2[2]	1,000	1.5	3.7	55	0.02–0.04

Skin material:
[1] Polyacrylamide, [2] polycarbonate, [3] polysulfane

A protective atmosphere of pure N_2 was applied throughout all operations to minimise oxidation of the waters. Due to the low concentrations of HCO_3^- in waters from both sites (Tables I and II), typically in the range of surface waters, no composite mixture (N_2/CO_2) was used as degassing of CO_2 with subsequent changes in water/colloidal composition was not considered to be a serious problem. Four ultrafiltration cells and 4 pressure containers of 10 l each (when possible, the prefiltered water was directly sampled into these containers, thus avoiding additional transfer operations) were used in parallel to minimise the time span necessary for the completion of the whole fractionation procedure. Even so, 5 to 6 days were normally necessary owing to the low water flux of the YM-2 membrane (see Table IV). The ultrafiltration was interrupted when an enrichment factor of about 50 to 100 was obtained in the colloid concentrates (CC). Small aliquots of the CC were preserved for DOC determination and the rest immediately acidified and stored together with the acid washings of the ultrafiltration cells and membrane filters. A flow-sheet of the particle and colloid separation procedure is shown in Figure 4, and a photograph of the equipment used in Figure 5.

20 to 40 l aliquots of prefiltered water (<450 nm) were also immediately acidified ($pH<1$, HCl or HNO_3) and later concentrated by evaporation for the determination of the total concentrations of uranium, thorium and the REEs.

As already mentioned, colloids are operationally defined in this study as particles which pass through the 450 nm prefilter and are still retained by the YM-2 membrane (1.5 nm). As dissolved species are considered to be those ions or compounds which are concentrated in the ultrafiltrate of YM-2, it has to be emphasised that this is also a purely operational definition.

There is experimental and theoretical evidence that ultrafilters (especially those with the lowest cut-off limits: 1,000 and 500 daltons) can retain truly dissolved components by different processes, such as electrostatic, hydration, electrokinetic, steric and adsorption effects, and by polarisation concentration (e.g. Buffle, 1989). The latter effect, also observed in this study, depends not only on the individual properties of an ion (e.g. hydration energy) but also on the membrane characteristics (e.g. surface charge) and the experimental filtration conditions (pressure, stirring velocity, etc). Correction for this effect may be attempted by different methods, e.g. by extrapolation of the colloid concentration vs. pressure curve to zero pressure (Degueldre *et al.*, 1989b). However, for the YM-2 membrane used in this study, such a procedure was unsuccessful. In the recommended pressure range for this membrane (25–50 psi), no dependence was observed (Kuechler and Miekeley, 1990) when simulated waters of compositions similar to Osamu Utsumi mine waters were used. However, ion retention was indicated. As demonstrated by Buffle *et al.* (1978), and confirmed by Kuechler and Miekeley (1990) with simulated waters, and as shown in this study for natural waters from the Osamu Utsumi mine and Morro do Ferro, ion retention is especially effective for SO_4^{2-}, and best visible at low SO_4^{2-}, as in waters from Morro do Ferro (see Appendix 1, e.g. sample MF10-D). For charge reasons, retention of SO_4^{2-} would also cause retention of cations. To minimise or avoid ion retention by concentration polarisation, membranes with larger pore sizes could be used (e.g. XM-50; MWCL: 50,000 dalton, pore size diameter: 3 nm), in addition to other precautions already applied in this work (e.g. high stirring velocity, low and constant filtration velocity, etc.).

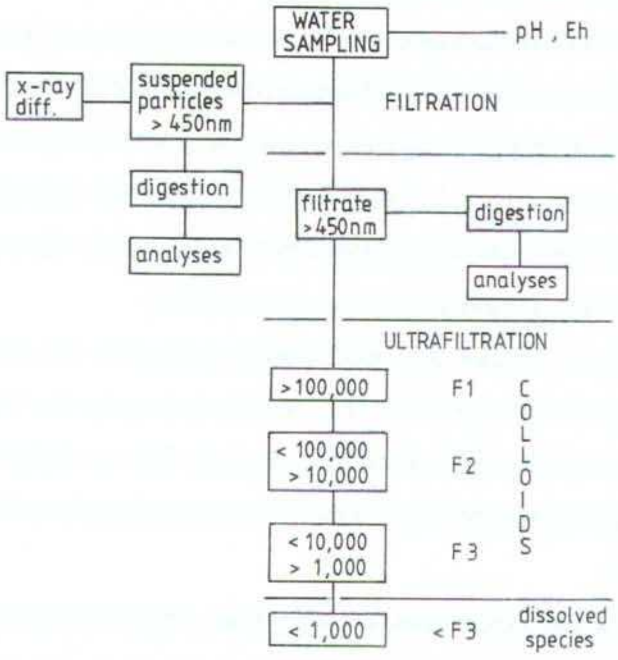


Figure 4. Experimental flow-sheet of the water fractionation procedure.

Figure 5. Photograph of the ultrafiltration equipment used at the Poços de Caldas laboratory.

However, there is also experimental evidence that certain colloids with high binding capacity for trace elements (e.g. humic compounds, hydrous Fe(III) oxides) have particle sizes in the range of 1 to 2 nm or less and are only efficiently retained by low pore size filters such as YM-2 and UM-5 (e.g. Eisenreich *et al.*, 1980; Hoffman *et al.*, 1981; see also section 4.2.1). Ultrafiltration experiments with surface waters of visible high iron colloid content (uranium mine, Fig. 6) and organic colloids, mainly in the form of humic compounds (Morro do Ferro, Fig. 7), have confirmed this effect. Thus, despite the potential errors that may be introduced into the colloid concentration (MW range between 10,000 and 1,000 dalton), which seem difficult to correct adequately in natural waters of varying compositions, the YM-2 membrane was used in this study as it provided the assurance that small colloids (especially of organic origin) would not be overlooked. It should be noted in this experimental approach that the colloid population associated with this size range should therefore be considered as an absolute maximum.

3.2.2. Chemical and size characterisation of colloids

Determinations of major and trace elements were done by standard methods, mainly using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and, additionally, flame Atomic Emission Spectroscopy (AES) and Atomic Absorption Spectroscopy (AAS). Determination of DOC was performed by means of an IR-Total Carbon Analyser. The REEs were determined, after preconcentration by ion-exchange methods, using sequential ICP-AES with continuous aspiration or, for small sample volumes, a micro-injection variation (Miekeley *et al.*, 1987; Silveira, 1986). Thorium was preconcentrated by solvent extraction and coprecipitation procedures and then determined by α-spectroscopy and micro-injection ICP-AES. Uranium was determined by fluorimetry after solvent extraction and by α-spectroscopy. Radioactive tracers (^{232}U, ^{234}Th) were used to correct for chemical recovery and counting efficiency. Blanks were run to check for contamination problems. Estimated analytical errors for the methods mentioned are between 5 and 10%. In one set of water samples, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis was performed with Vacuum Generator equipment in order to obtain additional data on elements not determined by the other methods. The plasma gas was argon and the analytical detection mode was made fully quantitative for aluminium, palladium, tin, thorium and uranium by the use of internal and external standards. The other element concentrations were determined in a

Figure 6. Fe(III) oxyhydroxide colloids in surface water from the Osamu Utsumi mine environment.

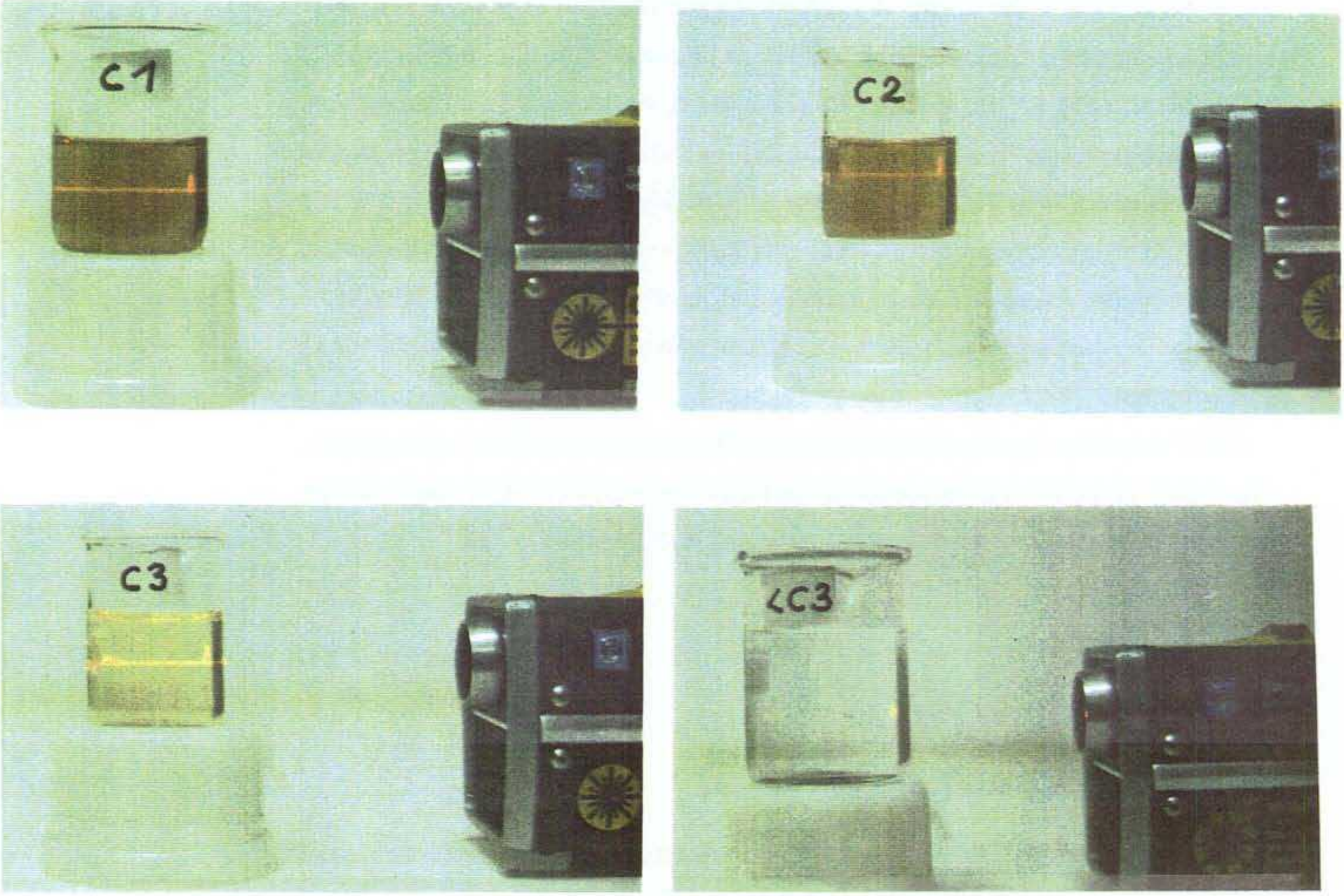


Figure 7. Organic colloids, mainly composed of humic acids, in near-surface water of Morro do Ferro (gallery). The presence of these colloids in different molecular weight fractions can be observed by the scattering of a laser beam.

(C1: 450 nm > MWCL >100,000 dalton; C2: 100,000 > MWCL >10,000 dalton; C3: 10,000 > MWCL >1,000 dalton; <C3: <1,000 dalton).

semiquantitative mode. The precision for the first procedure is about 1 to 2%, for the second one about 10 to 20%.

In the same set of samples, inorganic and organic anions (low molecular weight carboxylic species) were determined by ion chromatography (IC) using a Dionex unit with an AS4A or a APSCEAS1 column and the recommended eluents.

For size and chemical characterisation of colloids by Scanning Electron Microscopy (SEM) and Electron Spectroscopy for Chemical Analysis (ESCA), colloid concentrates (CC) were prepared directly in the field in order to minimise possible alteration effects due to the storage of the waters. 10 to 20 ml of water (prefiltered or unfiltered) were introduced directly into a small ultrafiltration unit (Amicon 80.10, filter PM-10, area 4.1 cm^2) without any air contact and then filtered under N_2-pressure until the filter was dry.

SEM analyses were performed on a Cambridge Instruments S4-10 SEM equipped with a Tracor Northern TN2000 EDS unit. A Cambridge Instruments Quantimet 929 and QUIPS image analysis software (version V05.00) were used to evaluate the colloid size distribution. Artefacts such as bacteria and membrane defects were eliminated manually. The dried membrane filters were coated with a 20 nm layer of gold, carbon or gold/palladium.

ESCA measurements were carried out with a Hewlett-Packard 5950A spectrometer. The sample, mounted on a gold support in the high vacuum chamber of the spectrometer, was irradiated with a monochromatic X-ray beam ($Al(K_\alpha)$: 1486.6 eV).

4. Results and discussions

4.1. Suspended particles (>450 nm)

Prior to the determination of the total concentrations of elements and of the colloidal concentrations, waters are filtered through 0.45 μm membranes. These prefilters retain measurable quantities of solids, which have been considered historically as suspended particles (SP) rather than colloids owing to their larger dimensions. This operational definition was mentioned before, but it is worthwhile repeating it here. The SP are composed mainly of illite, kaolinite, gibbsite, microcline (only in the uranium mine area) and amorphous oxyhydrates of iron-III and aluminium (see Fig. 8 and Table V). In near-surface waters (e.g. percolating water in the unsaturated zone), the crystalline minerals are more frequent in SP while, in deeper groundwaters, amorphous Fe(III) oxyhydroxides are by far the predominant particulate phases. In addition, these SP have

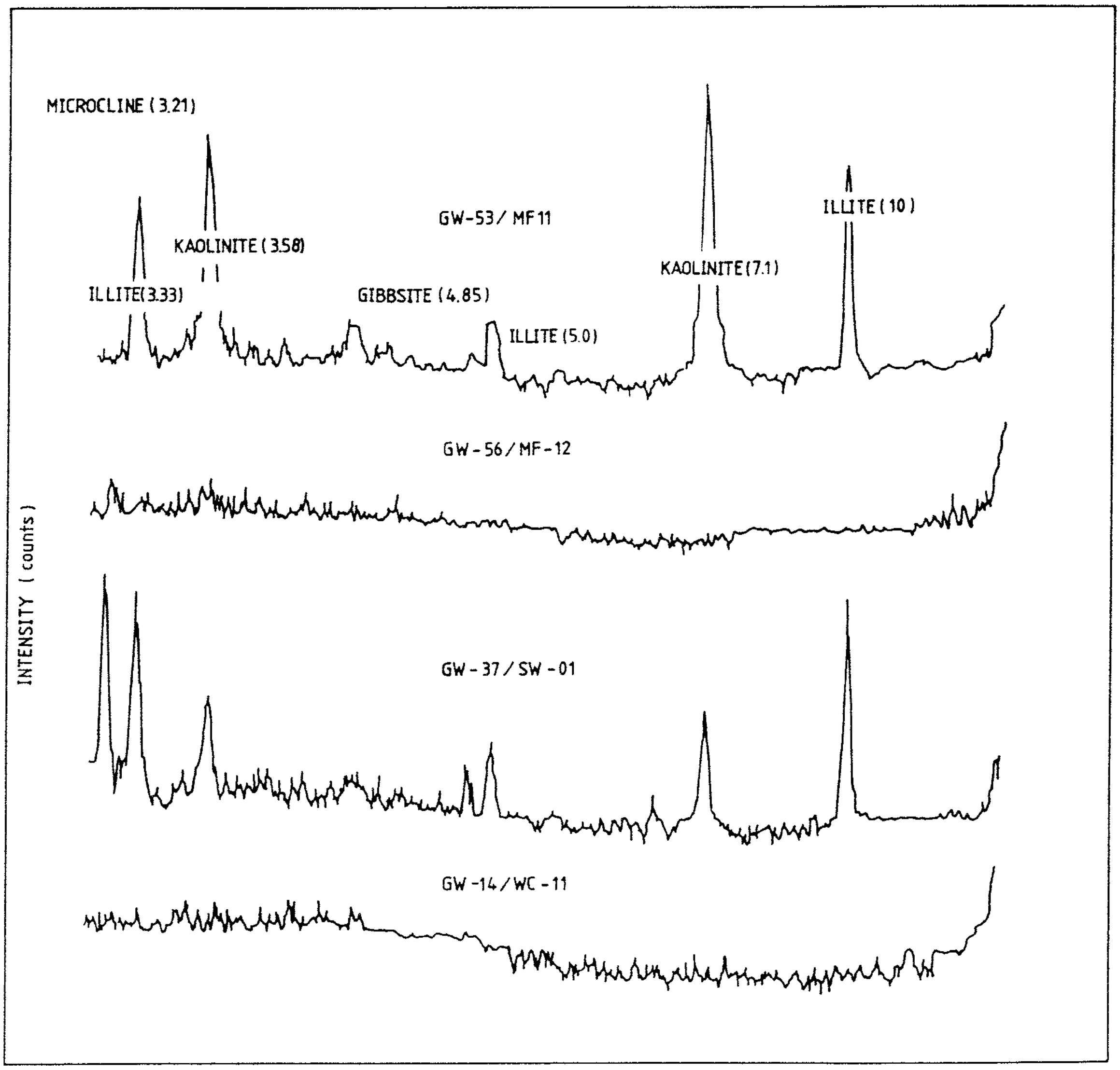


Figure 8. X-ray diffraction patterns of suspended particles (>450 nm) in near-surface and groundwaters from the Osamu Utsumi mine and Morro do Ferro. The amorphous structure of suspended particles (mainly composed of hydrous Fe-III oxides) can be observed.

TABLE V

Qualitative mineralogical data on water-suspended particles (> 450 nm) from the Osamu Utsumi mine and Morro do Ferro sites as obtained by X-ray diffraction (see also Fig. 8).

Sample (location)	Illite	Gibbsite	Kaolinite	Microcline	Amorphous
PC-CW-53 (MF11)	+	+	+	N.D.	
PC-GW-73 (MF13)	+	+	+	N.D.	
UFMF10-A (MF10)	N.D.	N.D.	V.W.S.	N.D.	+
PC-GW-50 (MF12)	N.D.	N.D.	N.D.	N.D.	+
PC-GW-37 (SW01)	+	+	+	+	
PC-GW-16 (F2)	+	N.D.	+	+	
PC-GW-64 (F2)	N.D.	N.D.	N.D.	N.D.	+
PC-GW-14 (F1)	N.D.	N.D.	N.D.	N.D.	+
UFWC11-B (F1	N.D.	N.D.	V.W.S.	N.D.	+
PC-GW-63 (F1)	N.D.	N.D.	N.D.	N.D.	+
PC-GW-36 (F3)	+	N.D.	+	+	
PC-GW-72 (F5)	+	+	+	+	

N.D. = Not Detectable V.W.S. = Very Weak Signal

organic carbon contents in the order of several percent (Coutinho, 1989), probably as surface coatings of humic compounds, as shown by ESCA in this study (Fig. 9). This particulate matter could play an important role in radionuclide partition and transport, due to its known sorption capacity for several elements (e.g. Buffle, 1989).

There are a number of different ways of presenting the analytical data for the SP in order to illustrate their relative significance in this system. For example, Table VI presents data for actinide concentrations in water (i.e. <.45μm) and SP. The latter are presented per gram and normalised per litre groundwater, these values being related by the suspended load. An alternative approach is to express the inventory element (isotope) in the water phase, which is potentially mobile in the system, as a fraction of the total inventory (water + SP). This ratio is denoted by F and is presented for REEs and actinides in Tables VII and VIII.

A further option is an association ratio (R_a) defined as the ratio of the elemental concentration in SP (per g SP) to the groundwater concentration converted into units per ml. This R_a value has units of ml/g and appears similar to the distribution coefficient (Kd) used in transport modelling. It should be emphasised, however, that R_a and Kd are fundamentally different parameters and should not be confused (McKinley and Alexander, 1991). Chondrite normalised plots for the REE compositions of SP and their corresponding waters are shown in Figures 10 and 11.

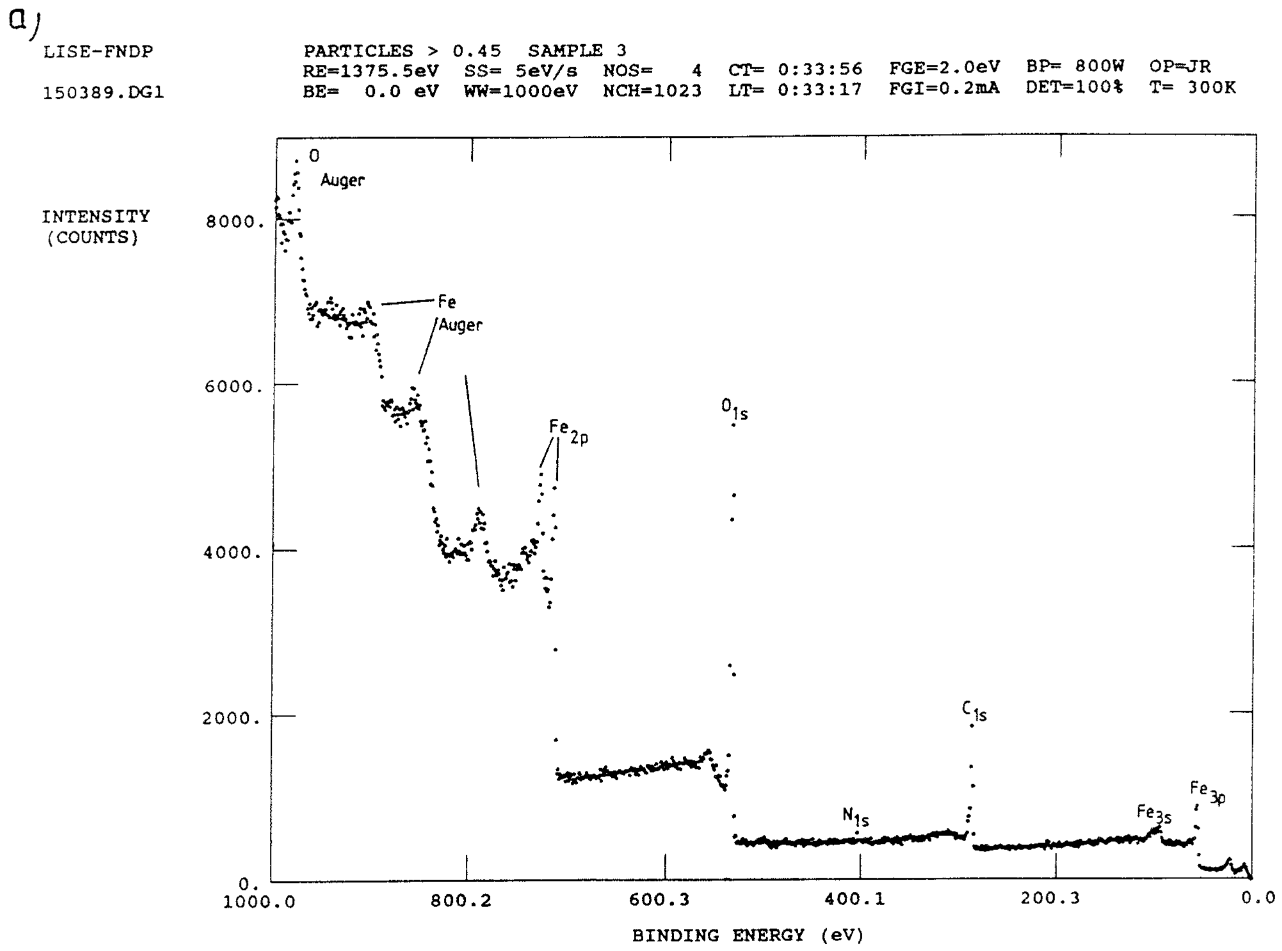


Figure 9. ESCA-spectrum of suspended particles from borehole water MF10, showing a) the predominance of Fe-III, oxygen and carbon in these particles and b) and c) the humic character of the particle-associated carbon. The spectrum c) was obtained from humic acid (reference material supplied by Aldrich). Expected values are shown in parenthesis; the measured values indicate a small energy shift due to the membrane material.

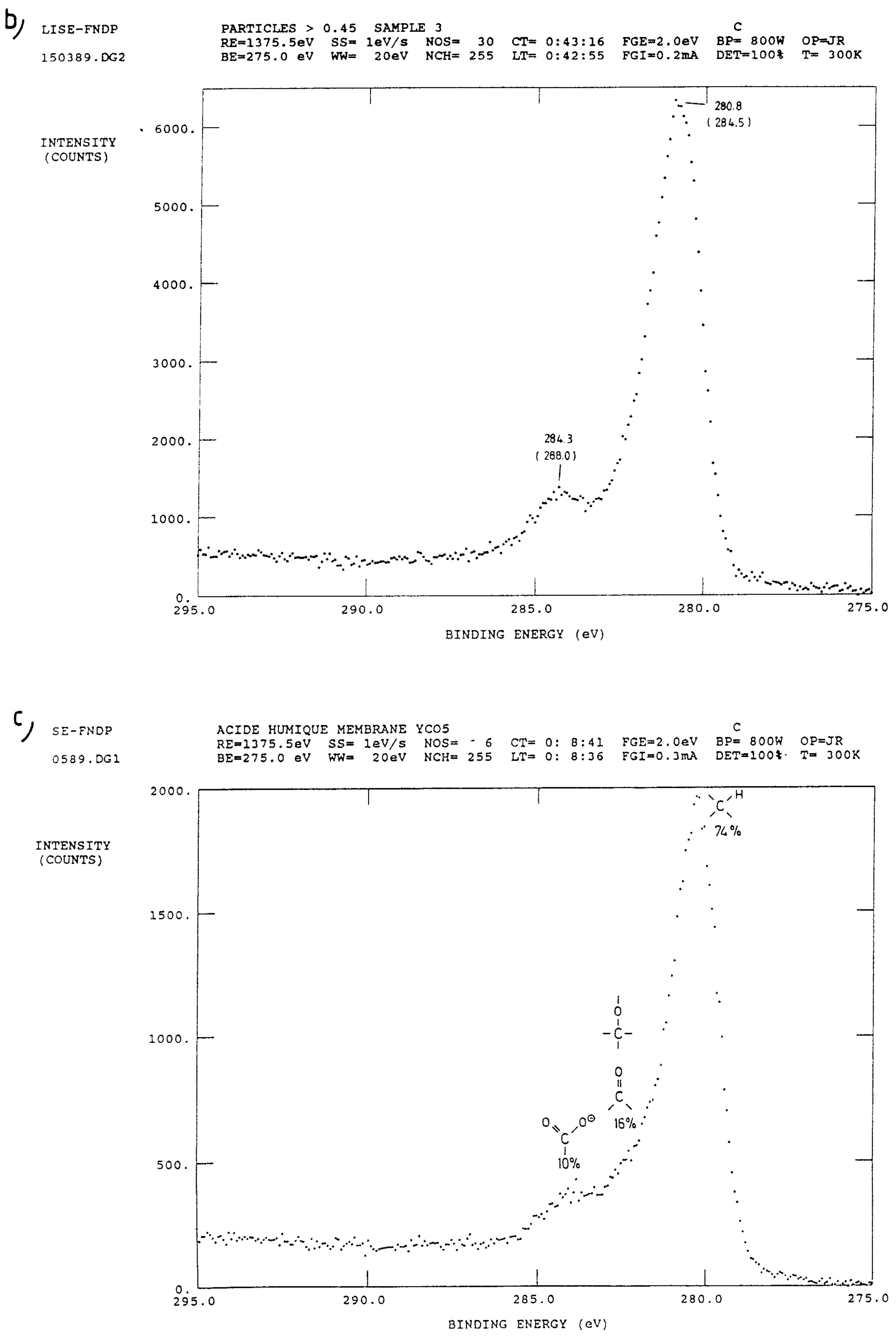


Figure 9 (contd.).

TABLE VI

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.

Borehole	Sample	Date	Load	Fluorimetry U			^{238}U			^{232}Th			^{230}Th							R1(w)	R2(w)
		(dd/mm/yy)	(mg/l)	Water (ug/l)	SP (ug/g)	SP n. (ug/l)	Water (ug/l)	SP (ug/g)	SP n. (ug/l)	Water (ug/l)	SP (ug/g)	SP n. (ug/l)	Water (Bq/l)	SP (Bq/g)	SP n. (Bq/l)	R1 (w)	R1 (s)	R2 (w)	R2 (s)	R1(s)	R2(s)
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
F1	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
	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
F2	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
	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	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
MF10	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		
	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
MF12	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
	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 = $^{234}U/^{238}U$, R2 = $^{230}U/^{234}U$
(w) = water; (s) = SP.

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

TABLE VII

Rare-earth element compositions of suspended particles and their corresponding waters (Osamu Utsumi mine and Morro do Ferro) including calculated association ratios (R_a) and the fractions of REEs in water (F). (See text for definitions).

Borehole		SW03	F1			F2		MF10			MF11		MF12			
REE in suspended particles (µg/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
REE in waters (µg/l)		GW-58	GW-17	GW-40	GW-54	GW-41	GW-60	GW-12	GW-33	GW-52	GW-35	GW-53	GW-18	GW-30	GW-34	GW-56
	La	567	0.45	15.2	3.89	8.55	3.0	1.1	0.33	28.7	1.77	4.14	0.9	0.95	1.87	1.29
	Ce	124	0.74	12.5	7.24	6.35	0.83	1.2	0.30	3.93	0.33	0.92	1.6	0.46	1.04	1.09
	Nd	250	0.16	7.75	2.06	4.02	0.49	0.6		12.3	0.87	2.15	0.28		0.67	0.49
	Sm	28.5	0.02	0.90	0.24	0.42	0.038	0.07	0.064	1.23	0.080	0.26	0.03	0.022	0.082	0.032
	Eu	7.8	0.01	0.25	0.076	0.097	0.014	0.03		0.28	0.020	0.059	0.012	0.009	0.018	0.010
	Gd	22.8	0.025	0.73	0.23	0.22	0.038	0.07	0.035	0.64	0.035	0.14	< 0 .025	< 0.02	0.037	< 0 .025
	Dy	23.3	0.021	0.75	0.27	0.18	0.049	0.05	0.012	0.41	0.020	0.093	0.017	0.008	0.031	0.015
	Ho	5.3	0.004	0.14	0.036	0.036	0.005	0.006	0.001	0.080		0.020	0.004			0.002
	Er	12.2	0.009	0.32	0.059	0.087	0.028	0.022	0.006	0.16		0.036	0.075	0.001	0.003	0.009
	Tb	5.5	0.003	0.15	0.023	0.040	0.017	0.011	0.005	0.065	0.003	0.016	0.004	0.002	0.004	0.005
	Lu	0.59	0.001	0.016	0.001	0.006	0.001	0.002	0.002	0.007		0.001	0.002		0.0005	0.0005

TABLE VII (contd.).

Borehole		SW03		F1		F2		MF10			MF11			MF12		
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	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	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
Ra (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	2.6E+06	1.1E+06	8.5E+0.5		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

TABLE VIII

Association ratios (R_a) of uranium and thorium and their fractions < 0.45 μm (F). (Osamu Utsumi mine and Morro do Ferro.)

Borehole	Sample	Date	U		^{238}U		^{232}Th		^{230}Th	
		(dd/mm/yy)	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
F1	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
	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
F2	PC-GW-16	12/02/87	6.9E+04	98.6	6.3E+04	98.8	1.3E+07	27.3		
	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		
	UFMF10-B	23/10/88	4.7E+05	92.6	4.6E+05	92.7				
MF11	PC-GW-35	28/01/88	6.6E+05	35.2	5.1E+05	41.2			5.2E+05	40.7
	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
MF12	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		

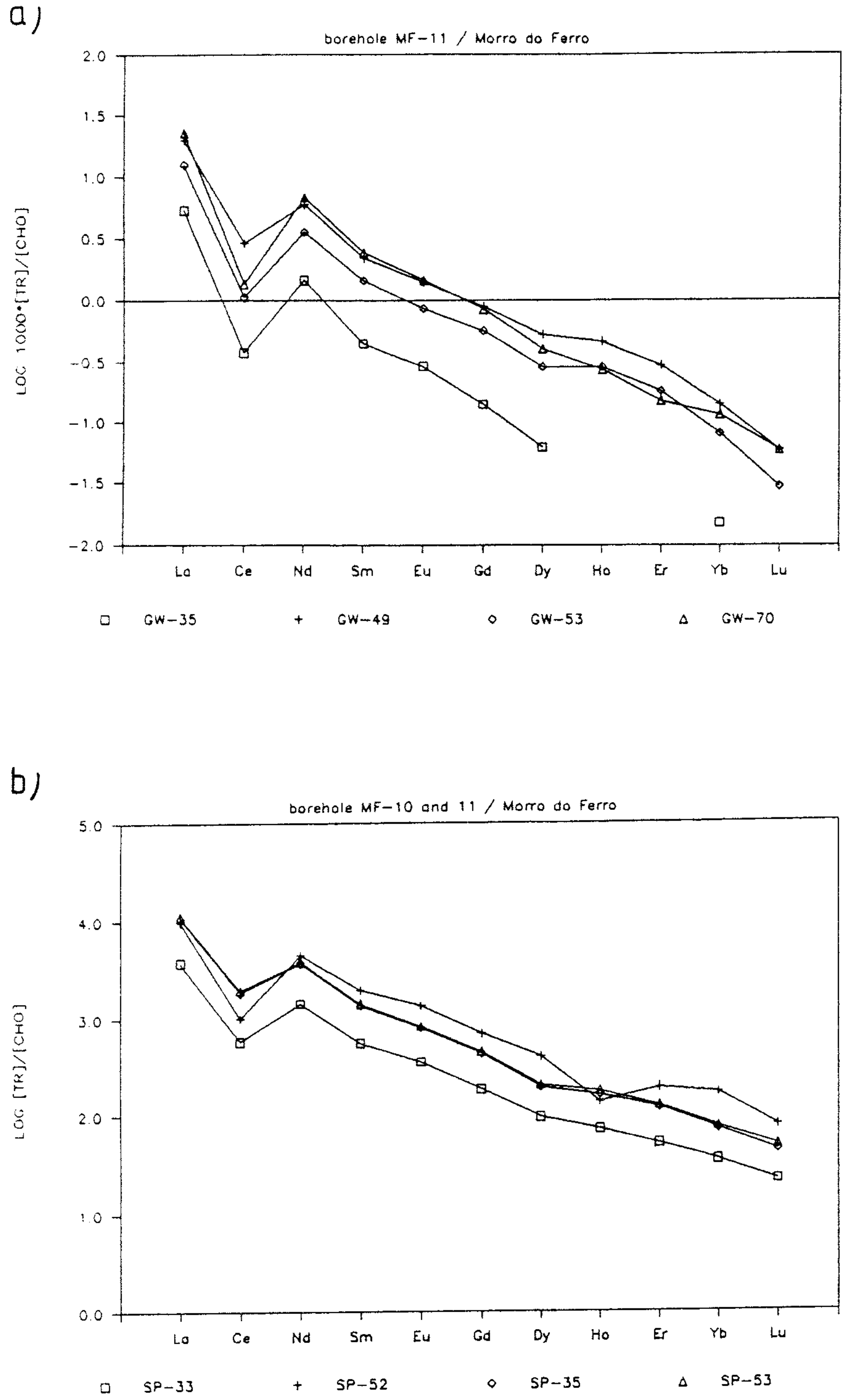


Figure 10. Chondrite normalised REE distribution patterns in near-surface waters from Morro do Ferro (MF11) (a) and in their corresponding suspended particle fractions (b). The negative Ce-anomaly, characteristic for samples from the unsaturated zone, can be observed.

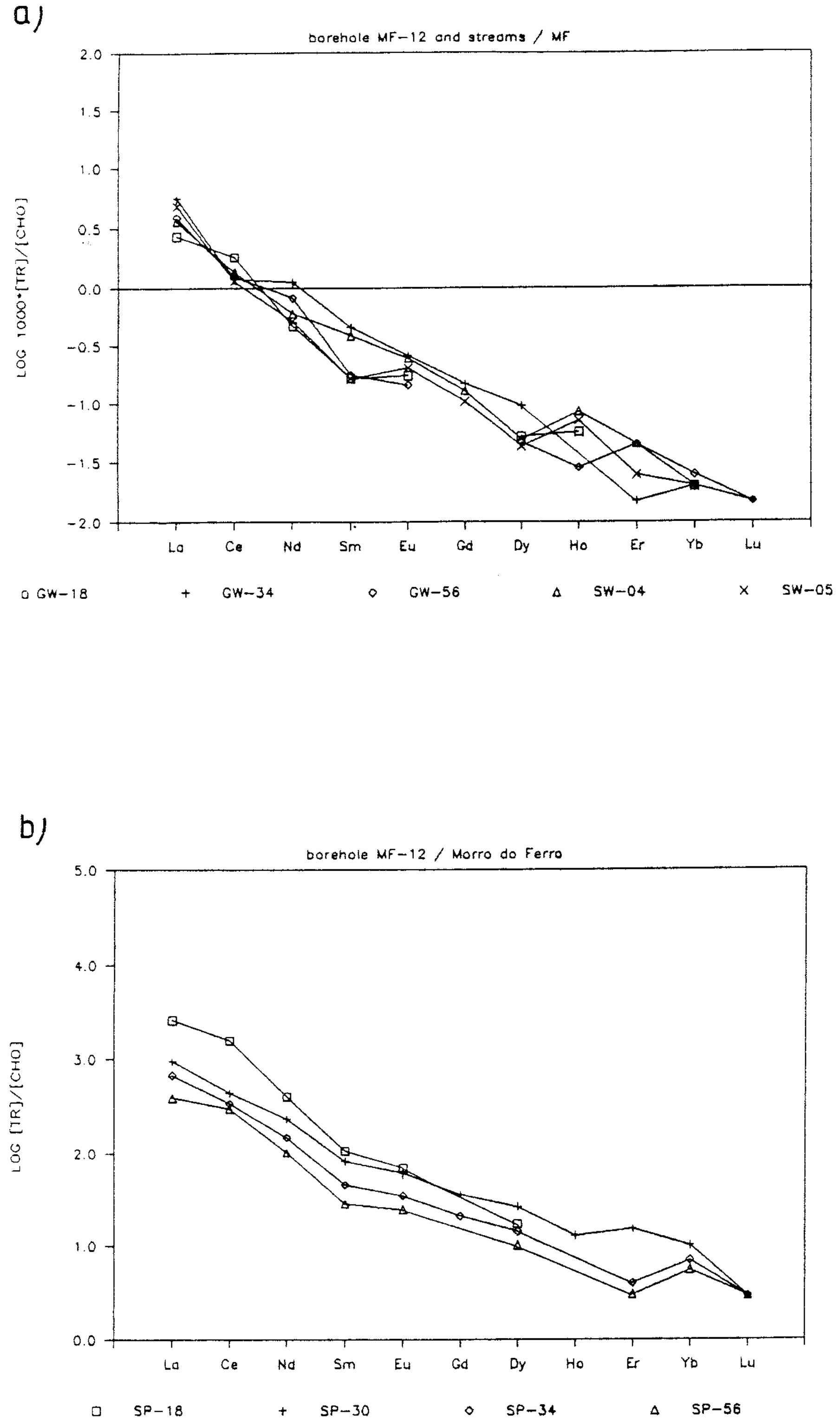


Figure 11. Chondrite normalised REE distribution patterns in groundwaters (MF12) and superficial waters (South Stream) from Morro do Ferro (a) and in their corresponding suspended particle fractions (b). The negative Ce-anomaly is absent in these samples.

The following conclusions can be drawn from these results:

1. Suspended particles have uranium, thorium and REE concentrations that generally exceed those in the corresponding waters by orders of magnitude. The high uranium and thorium contents of this >450 nm particulate matter are in agreement with the observed associations of these elements with the <2 μm grain-size fraction of associated rock samples, which is composed mainly of ferric oxyhydroxides and/or clay minerals with coatings of these oxides (Waber, this report series; Rep. 3). This observation, together with those mentioned below, supports the hypothesis that a large fraction (if not the predominant one) of the uranium and thorium (and probably also of the REEs) is sorbed or coprecipitated by iron minerals from the Morro do Ferro environment.

2. With few exceptions (where experimental errors cannot be excluded), $^{234}U/^{238}U$ activity ratios (R1) in SP and corresponding waters are very similar, indicating possible isotopic exchange equilibrium between the dissolved, colloidal and SP phases. $^{230}Th/^{234}U$ (R2) in SP are typically higher by a factor of 20 or more than in the corresponding filtrates (<450 nm), which may indicate the selectivity of SP in adsorbing ^{230}Th from the solution phase.

3. Association ratios (R_a) in water are typically 10^4 to 10^5 ml/g for U, 10^5 to 10^6 ml/g for the REEs and 10^6 to 10^7 ml/g for thorium. R_a values for uranium and REEs are very similar in waters from both environments, but, for thorium, seem to be somewhat lower in MF12. Whether or not this is a real effect, caused by the different groundwater compositions (e.g. the higher fluoride concentration, favouring thorium complexation) or by different mineral compositions of suspended matter in MF12, needs to be investigated further. Although the usefulness of such R_a values is often criticised, they can nevertheless indicate trends, as best seen in sample PC-GW-58 (SW03). Due to the low pH, high Eh and high SO_4^{2-} concentration in this near-surface water, R_a is reduced by a factor of about 10 to 100 as compared to the deeper groundwater. The R_a values of groundwater derived from field data are surprisingly constant for a specific element (U, Th, REE) and also in both environments. Very similar distribution ratios were reported for uranium in groundwater from the Koongarra uranium deposit (Duerden *et al.*, 1988). R_a values for ^{230}Th seem to be generally lower than for ^{232}Th (exceptions are frequent in MF12 waters). The origin of this isotopic fractionation may lie in the different history of both isotopes (e.g. ^{230}Th is a recoil atom) or the influence of some other mechanism.

4. Although a high value of R_a indicates the tendency of an element to be associated with suspended particles, the relative importance of this process is determined by the concentration of SP in waters and their ability to migrate through the rock. Table VI shows that groundwaters from the Osamu Utsumi mine have SP concentrations typically lower by a factor of 10 than waters from Morro do Ferro. These data, together with the concentrations of uranium, thorium and the REEs in waters and SP, allowed the percentage fractions of these elements that could be transported by the waters if no particulate transport occurs to be calculated. This allowed us to draw the following conclusions:

Uranium: In the deeper groundwaters of the Osamu Utsumi mine (F1), more than 98% of the uranium is in dissolved or colloidal form (<450 nm). This fraction seems to be somewhat smaller in waters from borehole F2 along with their higher SP load (Table VI). SP in groundwaters are composed mainly of amorphous ferric oxyhydroxides, which are probably formed by the oxidation of upflowing, more reducing waters. The SP concentration in borehole F2 appears to be higher in the dry than in the rainy season. This seems to indicate that the SP are generated at depth, by the oxidation process mentioned above, and not by downward migration of material from the surface during rainfall. This interpretation is supported by other mineralogical and chemical evidence (see below). Due to the higher SP load in waters from Morro do Ferro, a larger fraction of the uranium is associated with these solids. However, in most of the waters studied, uranium is predominantly in the solution phase (<450 nm).

Rare-Earth Elements: Owing to their similar R_a values, the behaviour of REEs in waters with low SP concentration, as in the case of the Osamu Utsumi mine waters, is not very different from that of uranium. The major fraction of the REEs is also concentrated in the solution phase. In waters from Morro do Ferro, characterised by higher SP concentrations, the slightly larger R_a values of the REEs as compared to uranium explain why a considerable fraction of these elements (in most cases the predominant one) is concentrated in the particulate phases.

Thorium: Due to its higher R_a, as compared to uranium and REEs, most of the thorium is concentrated in the SP-fraction. This more pronounced tendency of thorium to be associated with solid phases (e.g. sorption on ferric hydroxides) is in agreement with its much lower concentrations in natural waters (Langmuir and Herman, 1980), as indicated also in Tables I and II.

The question as to whether these suspended particles, which could act as potential carriers for thorium and REEs (and, by analogy, for IV and III-valent actinides), are able to migrate through the rock cannot be answered definitely. However, there are indications at Morro do Ferro that their transport through the porous medium of the highly weathered rock mass is limited. This may be explained by the expected distribution of pore sizes in such an environment, with about 40% consisting of residual pores of less than micrometre diameter (Buffle, 1989). Tables V to VII and Figures 8, 10 and 11 illustrate the findings on the limited migration of SP from the thorium-rich mineralised zone around borehole MF11, down-valley to borehole MF12. Suspended material from the mineralised zone (MF11) is characterised by clay minerals and gibbsite, and by high thorium and REE-concentrations (1,000 – 4,000 μg/g). Suspended particles from borehole MF12 are composed predominantly of amorphous ferric oxyhydroxides and have moderate to low concentrations of these elements (20 –300 μg/g). The REE signature of SP gives another hint that substantial transport of particles from MF11 to MF12 has not occurred. As shown in Figures 10 to 12, the chondrite normalised distribution patterns of REEs in core samples, compared to the SP and their corresponding waters, are very similar, indicating that under present conditions the REE content of these particles was obtained by congruent leaching of the rock and sorption of the dissolved REEs from the aqueous phase. This has also been observed in the Osamu Utsumi mine. Waters and SP from the unsaturated, strongly oxidising zone (Eh: + 400 to 600 mV) are characterised by a strong Ce-depletion (Fig. 10 a,b), which may be explained by preferential oxidation and sorption of Ce compared to the other III-valent lanthanides. This interpretation of the negative Ce-anomaly is, however, not without controversy because of the extremely high Eh necessary for Ce-III oxidation (Bonnot-Curtois, 1981; Tlig, 1982). This negative Ce-anomaly was not observed in the more reducing groundwater or associated SP (Fig. 11) from borehole MF12 (Eh: +200 to 450 mV), nor in rock samples close to the water sampling depth interval of 45 to 71 m (Fig. 12). Whether or not these findings on the different REE and thorium signatures of SP from boreholes MF10/11 and MF12 are valid indicators for the immobility of SP depends, however, on slow desorption kinetics for these elements. Preliminary tracer experiments with SP from Morro do Ferro (Coutinho, 1989) and published data on the slow desorption kinetics of other elements, e.g. Pb-II on iron oxides (Lion *et al.*, 1982), indicate such a possibility.

Finally, there is a convincing argument that the suspended particles are formed in situ in the borehole waters and not as an artefact of drilling operations. $^{234}U/^{238}U$ activity ratios (ARs) in groundwaters and SP are quite different from those of the rock (e.g. Osamu

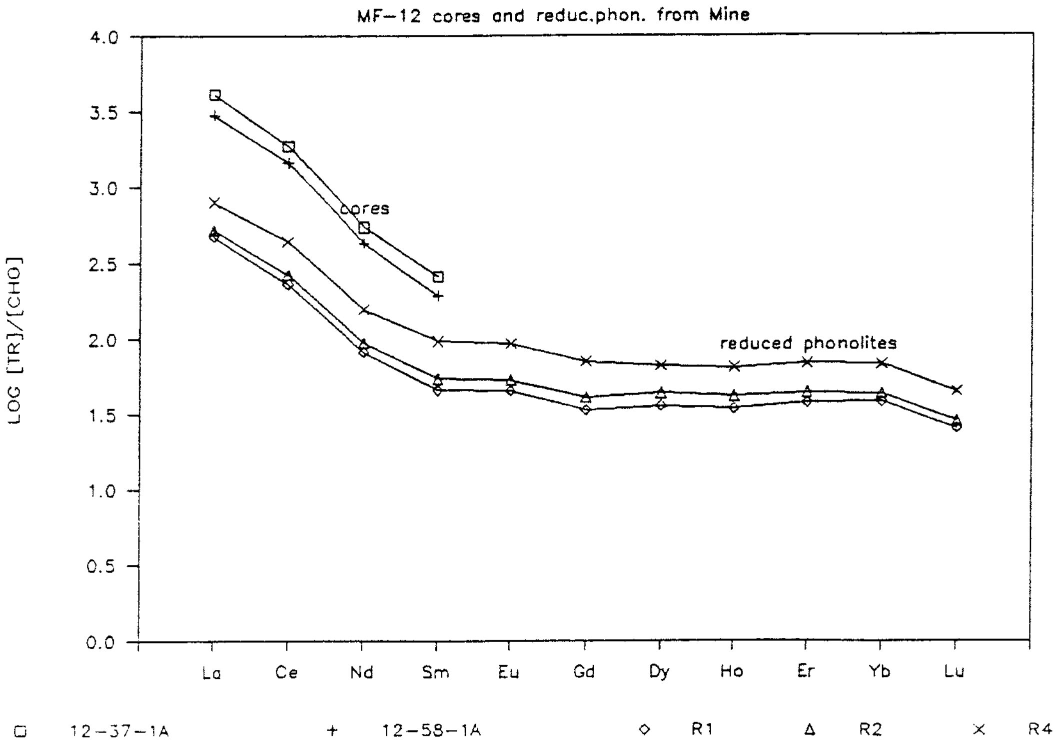


Figure 12. Chondrite normalised REE distribution patterns in two core samples from MF12, close to the sampling interval of the groundwaters. (MacKenzie et al., this report series; Rep. 7).

Utsumi borehole F2 groundwater and SP: ARs = 1.8 to 2.6; rock: ARs = 0.8 to 1.2; Morro do Ferro groundwater and SP: ARs = 1.5 to 2.1; rock: ARs = 0.9 to 1.2).

4.2. Colloids

Information on the distribution characteristics of some major and trace elements in the groundwaters, with respect to different molecular weight cut-off limits (MWCL) (100,000 to 1,000 dalton; equivalent particle size ranges; 10 to 1.5 nm), are summarised in Appendix 1 and in Figures 13 to 18. The presented data include elemental concentrations measured in the colloidal concentrates and ultrafiltrates, colloid concentrations (CC) for each element (corrected for the water volume), total colloid concentrations (TCC) and percentage distributions. As a result of the low CC in groundwater from both sites, the difference between the total concentration (<450 nm) of an element and its dissolved concentration (<1.5 nm) is, in most cases, very small and either at or below the detection limit of the analytical methods used. The inclusion in Appendix 1 of the concentration data, as analysed in the colloidal concentrates, shows, however, that real effects were measured. Nevertheless, the MW or size distribution characteristics of a certain element, obtained by sequential ultrafiltration and chemical analyses, should be considered only as indicative because of the uncertain MWCL of the membranes used for the separation of natural inorganic and organic colloids from waters and the large cumulative errors for the determination of elements at ultratrace level (e.g. thorium). Data obtained by direct counting of the particle size distribution by SEM show, however, that compatible results can be obtained by both methods (see section 4.2.2).

4.2.1. Colloid characteristics of waters from the Osamu Utsumi study site

Although the mine area is in an advanced state of weathering, with potential colloid-forming materials (e.g. clays, oxyhydroxides of Fe-III and Al) being very abundant and groundwaters circulating relatively actively, the concentration of colloids in groundwaters from this site is surprisingly low, being typically <500 ppb (excluding the major ion potassium in the 1,000 to 10,000 MWCL fractions, whose enrichments of typically 2 to 3% are suspected to be the result of ion retention). Ferric oxyhydroxides and DOC are the main contributors to the colloid suite. They behave, probably in the form of colloidal ferrihydrite particles associated (coated?) with humic compounds, as

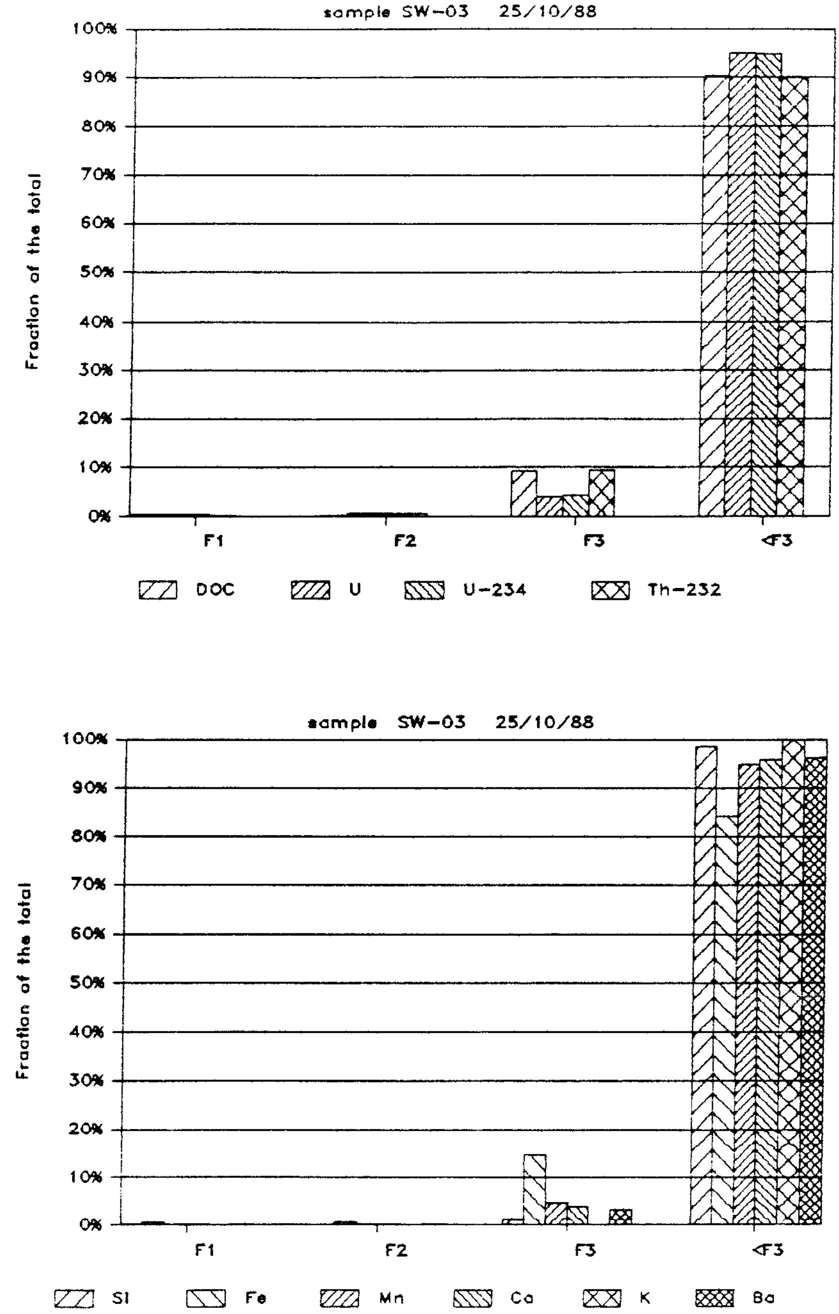


Figure 13. Colloid distribution characteristics of some minor and trace elements in a near-surface water sample from borehole SW03 (Osamu Utsumi mine) of low pH and high SO_4^{2-} *content. (F1: 450 nm > MWCL > 100,000 dalton; F2: 100,000 > MWCL > 10,000 dalton; F3: 10,000 > MWCL > 1,000 dalton; <F3: <1,000 dalton). (F3 values should be considered as maxima due to the possible influence of ion retention; see section 3.2.1).*

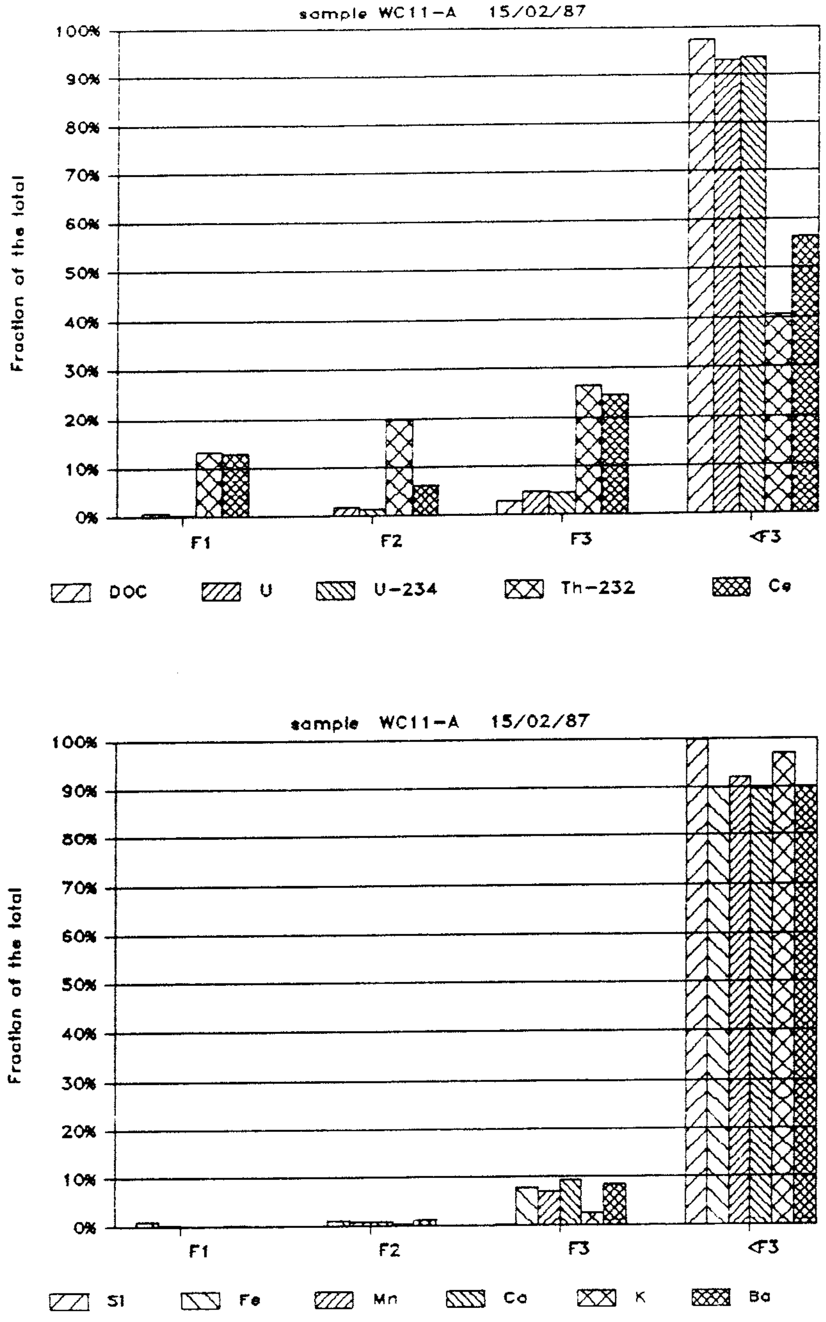


Figure 14. Colloid distribution characteristics of some minor and trace elements in a groundwater sample from borehole F1 (Osamu Utsumi mine). (Molecular weight ranges and limitations of F3-values as specified in Fig. 13).

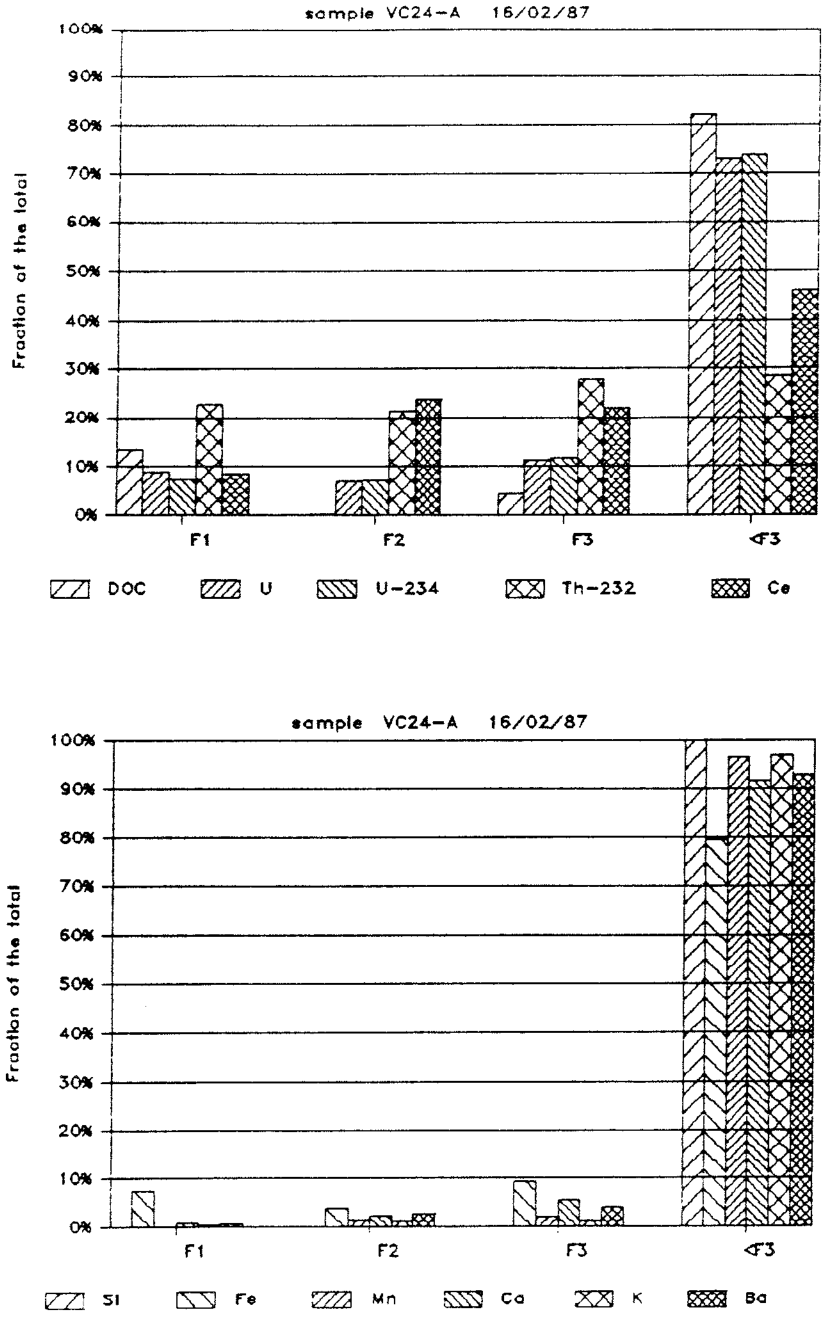
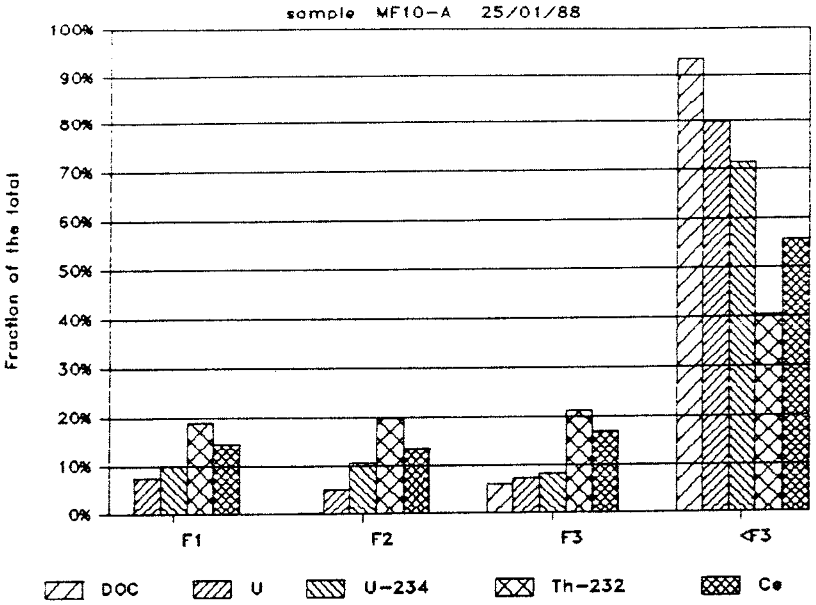


Figure 15. Colloid distribution characteristics of some minor and trace elements in a groundwater sample from borehole F2 (Osamu Utsumi mine), of more oxidising character. The higher proportion of colloids, as compared to sample F1 (Fig. 14), can be observed. (MWCL and limitations of F3-values as specified in Fig. 13.)



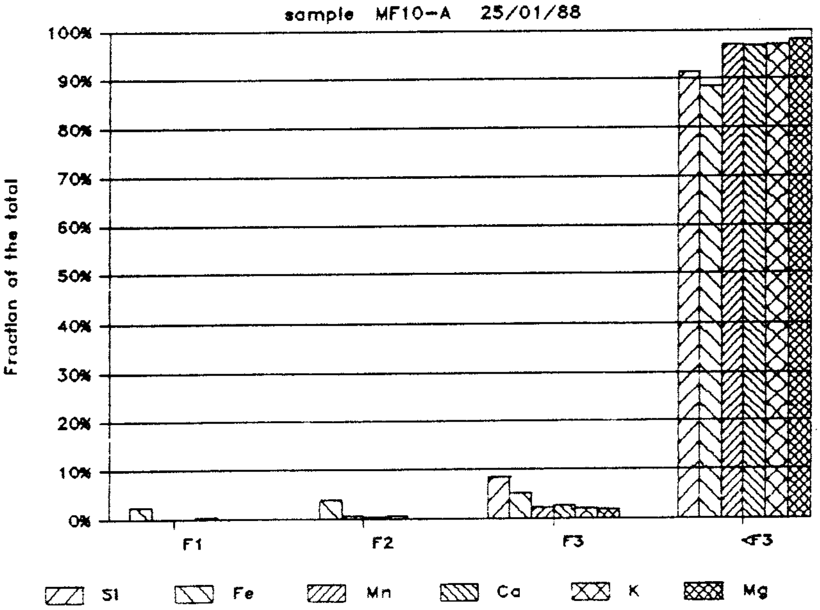


Figure 16. Colloid distribution characteristics of some minor and trace elements in a groundwater sample from borehole MF10 (Morro do Ferro). (Molecular weight ranges as specified in Fig. 13. F2 and F3 values are to be considered as maxima due to the possible effect of ion retention; see section 3.2.1).

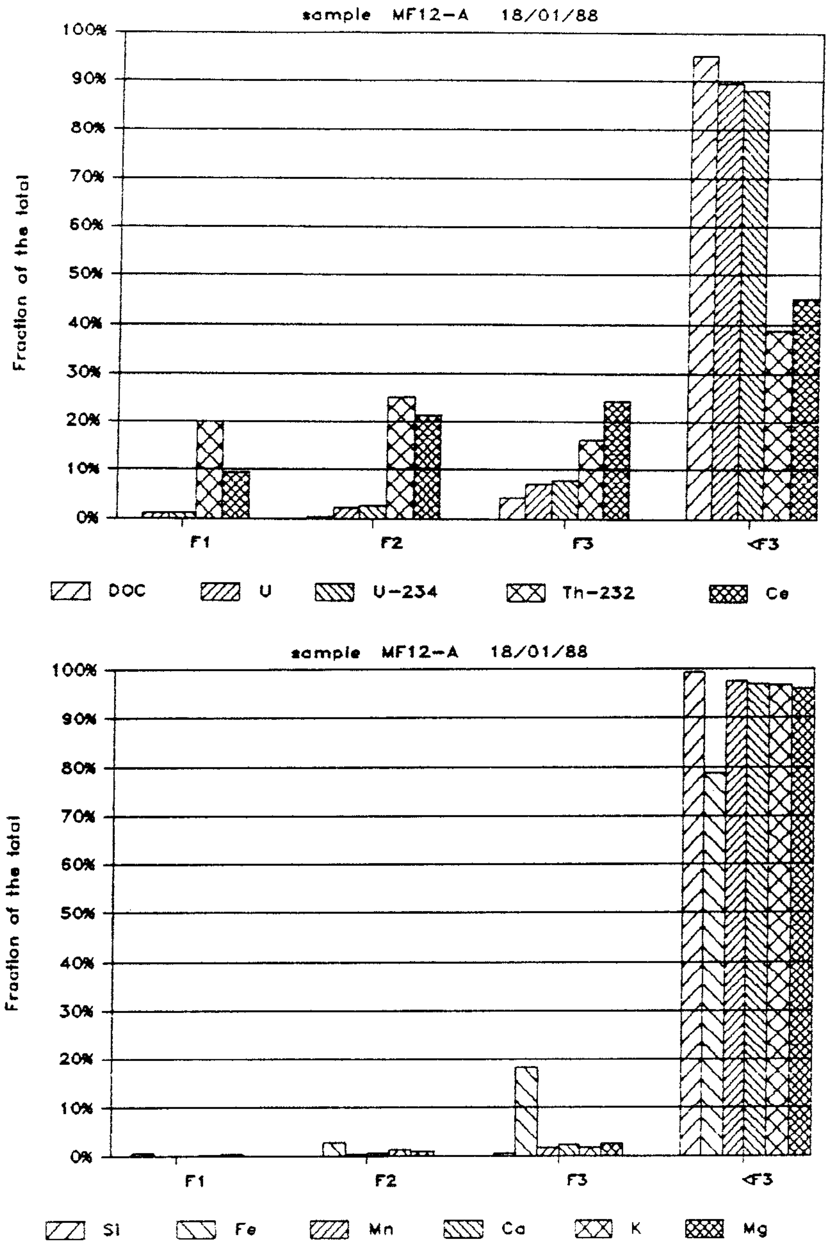


Figure 17. Colloid distribution characteristics of some minor and trace elements in a groundwater sample from borehole MF12 (Morro do Ferro). (MWCL as specified in Fig. 13. F2 and F3 values are to be considered as maxima due to the possible effect of ion retention; see section 3.2.1).

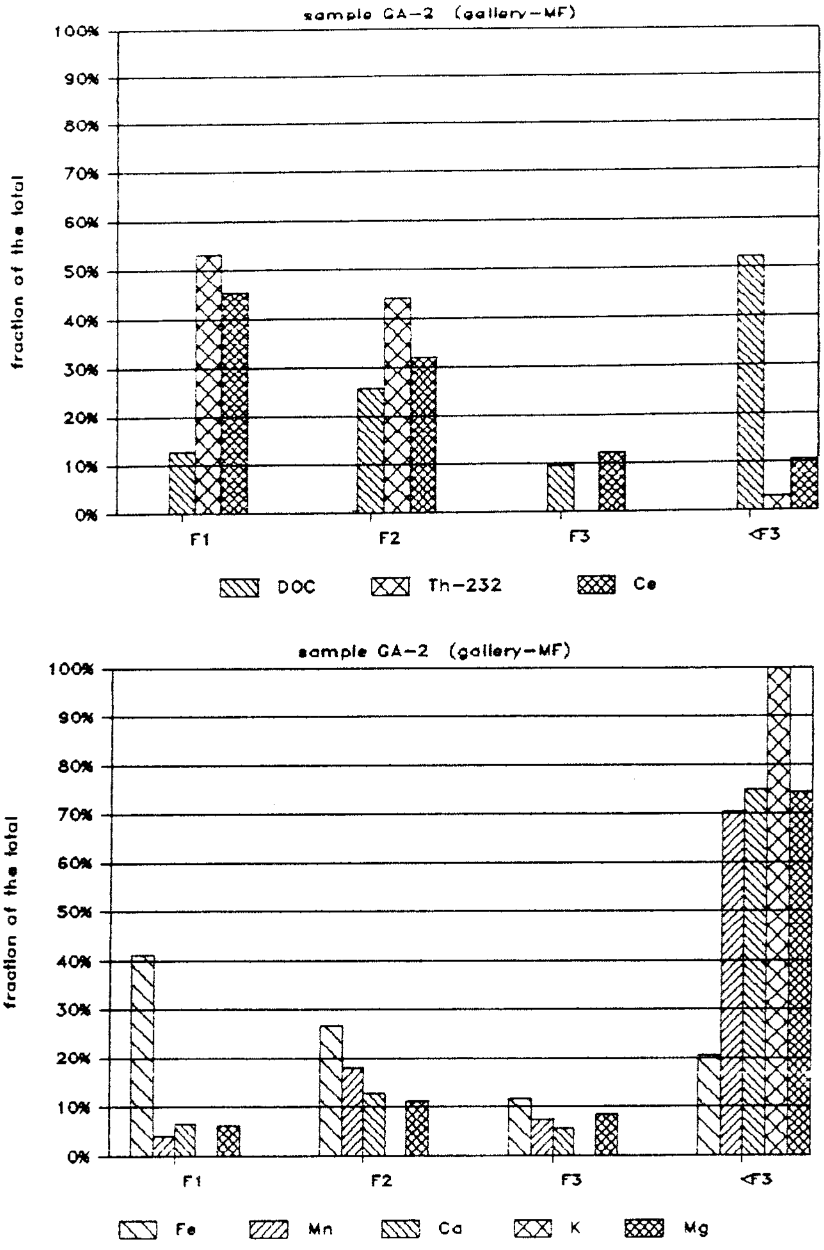
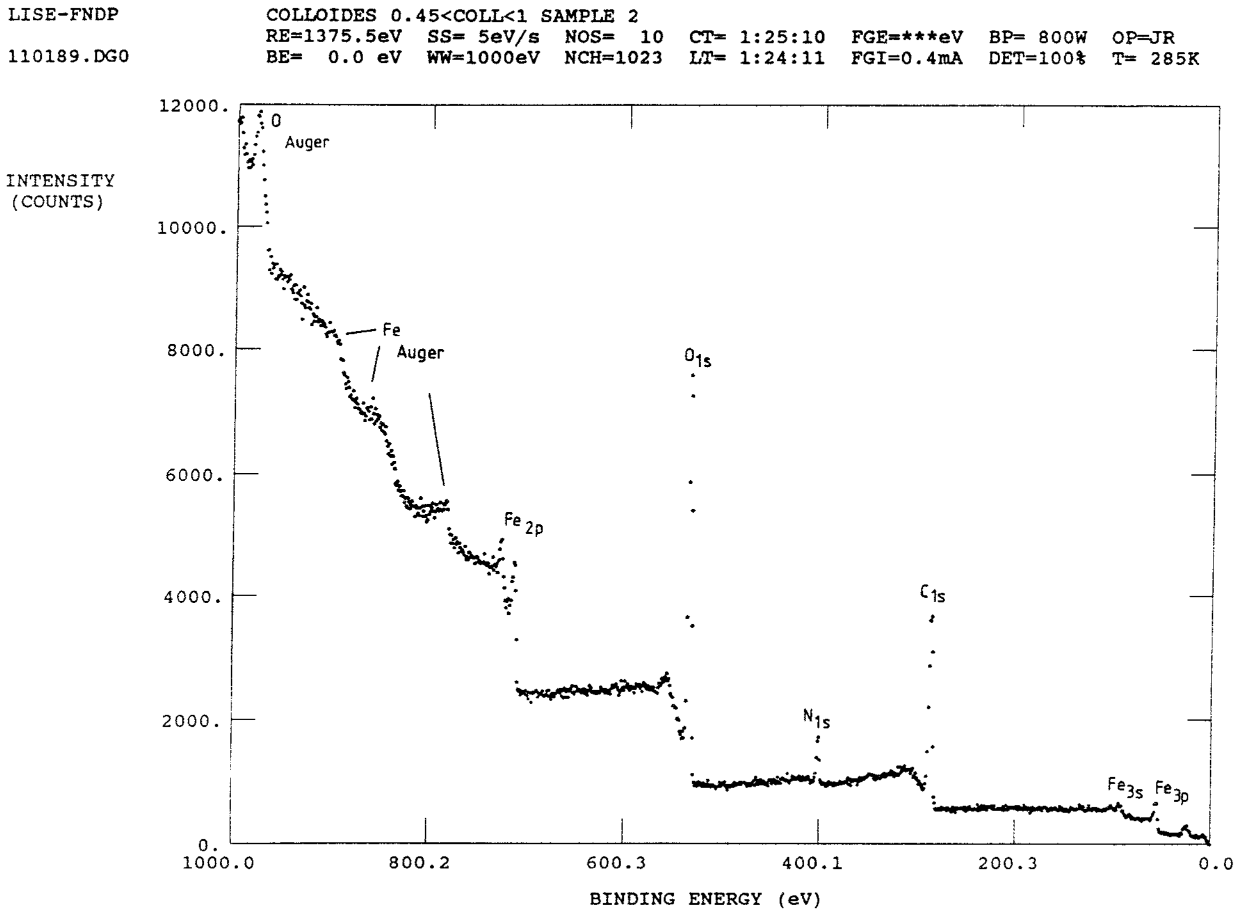


Figure 18. Colloid distribution characteristics of some minor and trace elements in an organic-rich subsurface water sample from an experimental mine addit (gallery, Morro do Ferro). The effect of organic complexation on the distribution of polyvalent metal ions in colloidal fractions can be observed. (F1: 450 nm > MWCL > 300,000 dalton; F2, F3 and <F3 as specified in Fig. 13. Limitations of F2 and F3 are as specified in Fig. 17).



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LISE-FNDP          COLLOIDES 0.45<COLL<1 SAMPLE 2
                   RE=1375.5eV  SS= 5eV/s   NOS=  10   CT= 1:25:10  FGE=***eV   BP= 800W   OP=JR
110189.DGO         BE=  0.0 eV  WW=1000eV   NCH=1023   LT= 1:24:11  FGI=0.4mA   DET=100%   T= 285K
```

Figure 19. ESCA-spectrum of colloidal particles (450 nm > COLL > 10,000 MWCL) from borehole water F1, showing the predominance of Fe-III, oxygen and carbon in these particles.

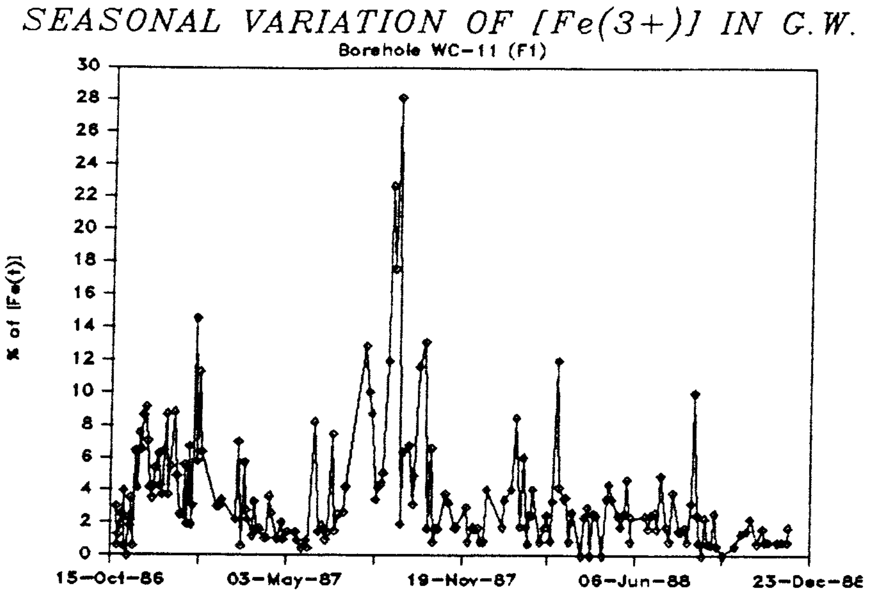
concentrators for the trace elements. The presence of oxidised forms of carbon (C-O and O=C-O), typical of humic carbon, and of iron in these colloidal particles was confirmed by high resolution ESCA (Fig. 19).

Most of the data presented refer to boreholes F1 and F2. In addition, colloid separation was performed once with groundwater from F3 and F4 and twice with near-surface water from SW03. With the exception of SW03 water, no significant differences in colloid behaviour could be observed for the other boreholes.

4.2.1.1. Iron

Typically, maxima of about 8 to 20% of the total Fe was concentrated as colloids, mainly in the smallest colloidal size fraction (1,000 to 10,000 MWCL; Table IX). There are insufficient data available to indicate variations of the colloidal concentration in F1 and F2 groundwaters with respect to season and redox conditions of the water. Figure 20, in which the long-term fluctuations of Fe-III concentration of these groundwaters expressed as a percentage of the total Fe are shown, would suggest, however, that such variations may also exist in the colloidal concentration of iron. The presence of very high concentrations of Fe-colloids in surface or near-surface waters can sometimes be observed by the typical red-brown colour of these waters due to the oxidation of the Fe^{2+} under surface conditions (Fig. 6). Attempts to separate these colloids by ultrafiltration failed, owing to their unstable nature, causing precipitation of Fe-III hydroxides (with loss of uranium, thorium and REEs) and consequent clogging of the membrane filters. It could be observed, however, that these Fe-III colloids have size ranges between 450 nm and less than 1.5 nm. Laboratory experiments have shown that the adsorption of fulvic acids on Fe-III hydroxide colloids can stabilise them as dissolved particles for more than 5 months (Brown *et al.*, 1972). The fact that Fe-III colloids in groundwaters from both sites are predominantly concentrated in the 1,000 to 10,000 MWCL-fraction, where DOC is also enriched and fulvic acids are expected to be concentrated (Kuechler, 1986; Buffle *et al.*, 1978), could be attributed to this stabilising function (e.g. see Figs. 14 to 17). Similar enrichments of DOC and associated minor and trace elements (Fe, Ca, Cu, Cd, Pb and Mn) in the 1,000 to 10,000 MW-fraction have been observed in fresh waters (Hoffman *et al.*, 1981; Buffle *et al.*, 1982) whose DOC-composition was of pedogenic origin; also expected to be the case for surface groundwater from Morro do Ferro and the Osamu Utsumi mine environments.

a)



b)

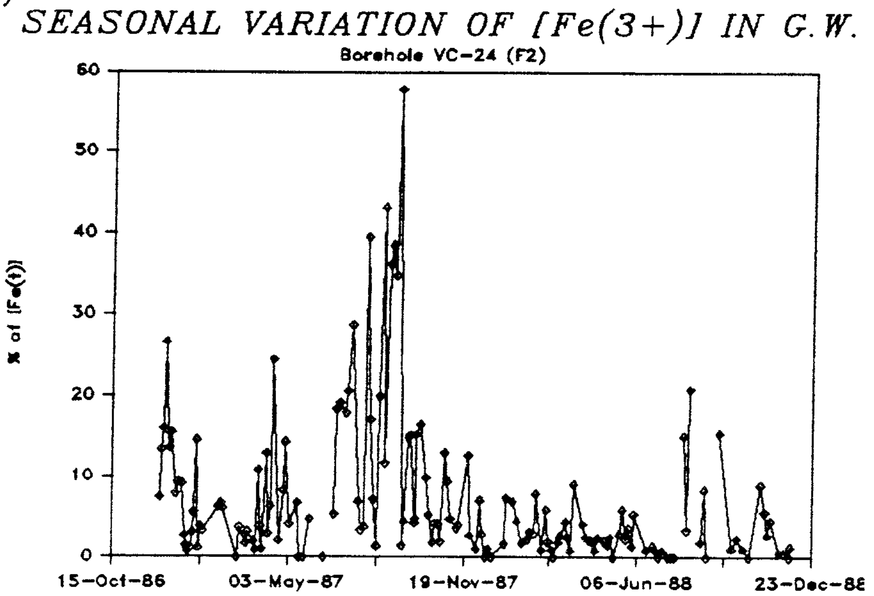


Figure 20. Variations of the Fe(3+) concentrations (expressed as percentage of the total [Fe] in groundwaters from F1 (a) and F2 (b).

The artificial generation of ferric hydroxide colloids during sampling, intermediate storage, and during ultrafiltration procedures, cannot be excluded. However, the natural presence of iron colloids in groundwater is supported by other observations: 1) determinations of total Fe and Fe(II), performed immediately on site showed that a considerable and strongly varying fraction of Fe (2-40%) is in the Fe(III) form (Fig. 20), 2) saturation index calculations indicated a supersaturation of ferrihydrite in F1 and F2 waters (Nordstrom *et al.*, this report series; Rep. 14), 3) discrepancies in the measured and predicted solubilities of some trace elements (e.g. Th, Pb, Ra), known to have a high affinity for uptake on/into ferric hydroxides, could be an indirect indication of the presence of particulate and colloidal ferrihydrite particles and 4) ultrafiltration experiments performed in the field, in which a small volume of water was filtered until dryness through a 2 nm membrane (any contact of the water with air was completely excluded), showed the presence of iron colloids on the filter, as determined by SEM and ESCA.

4.2.1.2. 'Dissolved' organic carbon (DOC)

DOC is in the same range (1 to 4 mg/l) as typically reported for most groundwaters from other regions. About 3 to 10% of the total DOC is concentrated in the MWCL fraction of 1,000 to 10,000 dalton, characteristic of humic compounds. According to Buffle *et al.* (1978), about 70% of the pedogenic refractory organic matter (PROM), in which fulvic acids are predominant, fall in the range of 300 <MW <10,000. (As mentioned earlier, this was the reason for the use of the YM-2 membrane.) On the basis of information to hand it is difficult to present any more specific conclusions on the influence of DOC on the colloidal speciation of the major and trace constituents. The high sorption/complexation capacity of humic compounds for polyvalent trace metals and the affinity of these compounds for sorption on clays, Fe-III oxyhydroxides and other soil inorganic particles is, however, well-documented (e.g. Choppin and Allard, 1986; Schnitzer and Khan, 1972; Stevenson, 1985). As shown by Theng (1976), sorption of fulvic acid and humic acid on solids is a function of the ionic potential of the adsorbed cations. In waters of high DOC concentration (e.g. the Morro do Ferro mine gallery), the importance of these compounds in trace element complexation is clearly visible (e.g. Appendix 1; sample GA2 and Fig. 18).

The major part of DOC, typically more than 90% in groundwater, is concentrated in the <1,000 MW range. Whether this fraction of DOC can be attributed to low MW fulvic acids and other natural organic matter (e.g. carbohydrates, fatty acids, etc.) is still an open question. Low MW organic anions, such as formate, oxalate, acetate, malonate, propionate and butyrate were below the detection limit of ion chromatography (for oxalate: 50 μg/l; for the other anions: 10 μg/l).

4.2.1.3. Silicon

Only a very minor fraction of the total Si (typically <1%) is concentrated as colloids, possibly in the form of clay minerals and SiO_2 (chalcedony ?). Calculations show slight supersaturation of various Si-bearing phases in the mine waters. (Nordstrom *et al.*, this report series; Rep. 14). The very low colloid concentration of silicon is surprising, considering the high total Si in these waters (15-20 mg/l), resulting from the breakdown of K-feldspars and kaolinite. This observation is different from observations in other places where colloidal silicon is a significant contributor to the total colloid population (Short *et al.*, 1988; Vilks *et al.*, 1988).

4.2.1.4. Uranium

As shown in Table I, the total U concentration as well as the $^{234}U/^{238}U$ activity ratios are significantly different in groundwaters from F2 and F1, indicating the more oxidising character of the F2 waters. Varying proportions of this element, typically about 5 to 30% of the total U (<450 nm), are in the 1,000 to 10,000 MW-fraction, apparently correlated with colloidal Fe and DOC. In near-surface waters (sample SW03A) with extremely high concentrations of Fe-colloids (4.6 ppm), exceeding by far colloidal DOC (0.35 ppm), about 300 ppb (5%) of the uranium is associated with the colloidal phase. $^{234}U/^{238}U$ activity ratios in colloids are in most cases identical with those in solution (<1.5 nm), indicating exchange equilibrium between both phases, as already observed for particles of larger sizes (>450 nm). However, as the major proportion of uranium in the colloid concentrations corresponds to dissolved uranium, large errors in the $^{234}U/^{238}U$ activity ratios of the colloidal fractions are involved.

4.2.1.5. Thorium

Total thorium concentrations in groundwaters from both boreholes (F1, F2) are very low (<0.1 µg/l). This complicated the accurate determination of thorium and made contamination of the samples and/or loss due to adsorption more critical. Nevertheless, a trend can be seen, which indicates the greater affinity of this element, when compared to uranium and the REEs, for enrichment in the colloidal fractions. This behaviour is similar to that observed previously for particulate matter. Unlike uranium, which is mostly concentrated in the 1,000 to 10,000 MW fraction, thorium is distributed in more or less equal proportions in all the three size ranges studied. Typically, more than 70% of thorium in groundwater (<450 nm) is present in colloidal form (probably as pseudocolloids of iron-organic (humic) origin). However, clear correlations of thorium with DOC and iron could not be observed. These results on the predominance of thorium in colloidal or particulate forms are in agreement with data reported for other environments, in which dissolved thorium was also predominantly in colloidal form (e.g. Short *et al.*, 1988; Ivanovich *et al.*, 1988).

In near-surface water with extremely high concentrations of thorium (up to 720 µg/l), the proportion of colloidal thorium was low (about 10%), probably due to the effective suppression of hydrolysis and sorption by the very high SO_4^{2-}-content (up to 4,000 ppm) of these waters. The distribution characteristic and proportions of titanium (sample SW03 A) in the colloidal phases were similar to those of thorium, which would be expected from the chemical similarities of both elements. A better correlation between thorium and its potential colloidal host phase is indicated in this sample. Considering that the colloid concentration of Fe (4.6 mg/l) is higher by a factor of 10 than the other colloidal components (including DOC), it seems probable that thorium and most of the other polyvalent trace elements (e.g. REE, Ti, U, Mn, Zn, Cu, Pb) and DOC are adsorbed on, or incorporated in, these hydrous ferric oxides.

In most cases it was not possible to determine $^{230}Th/^{234}U$ or $^{228}Th/^{232}Th$ isotopic ratios with reasonable accuracy. Where it could be done, the data indicate $^{230}Th/^{234}U$ values between 0.002 and 0.009 and $^{228}Th/^{232}Th$ values between 50 and 400 for the original waters (not corrected for the ingrowth of ^{228}Th from ^{228}Ra). The isotopic ratios of $^{230}Th/^{234}U$ could not be determined for the colloidal fractions, but are expected to be higher than for the true solution phase (1,000 MW cut-off), as observed for particulate matter. $^{228}Th/^{232}Th$ ratios are (with one exception) higher in solution than in the colloidal phases, as may be expected from the ingrowth of this isotope from the relatively soluble ^{228}Ra. However, as the ^{228}Th activities were not corrected for the ingrowth of ^{228}Th after sampling, significant errors are possible and further interpretations would be speculative.

4.2.1.6. The rare-earth elements (REEs)

The colloidal behaviour of the REEs is discussed in Appendix 1 using cerium as an example. As the concentrations of cerium in groundwater from the Osamu Utsumi mine are typically higher by a factor of 100 or more than those of thorium and, in addition, the detection method used (ICP-AES) is more sensitive for the former, the enrichment of cerium and other REEs in colloidal fractions could be determined with reasonable accuracy.

Other REEs (Nd to Lu), which were determined occasionally by ICP-AES or ICP-MS, showed similar distribution characteristics. However, lower concentrations of the less abundant elements were sometimes found in colloidal fractions (see sample WC11-A, Appendix 1). In most of the waters studied, the REEs show a higher affinity than uranium for concentration in colloidal fractions (typically 30 to 50% of total concentration, distributed in all the studied size ranges). However, the colloid-forming tendency of the REEs seems to be somewhat less pronounced than that of thorium. This would be in qualitative agreement with the increasing association ratios (U < REE < Th) observed for particulate matter (>450 nm) in both environments (Tables VII and VIII). Correlations between the distribution characteristics of the REEs and those of the anticipated principal carriers (ferrihydrites and DOC) for these elements could not be observed in most of the waters.

4.2.1.7. Other minor and trace elements

Minor proportions of magnesium, calcium, barium and manganese were also observed in the colloidal size range of about 1.5 to 10 nm, but are mostly concentrated in the 1.5 to 2 nm range (1,000 to 10,000 MWCL). Whether this is an artefact of ion retention, or simply reflects the known complexation capacity of humic compounds and/or hydrous ferric oxides for these elements, remains an open question. Ultrafiltration experiments, in which only the 10,000 and 100,000 MWCL membranes were used, confirmed the presence of these and other trace elements (e.g. occasionally Zr and Sn) in >10,000 MW-fractions and showed, in addition, that minor proportions (<10%) of copper, zinc, aluminium and molybdenum (but surprisingly high fractions of lead – up to 27% in groundwater from F1 and 35% in groundwater from MF12) are concentrated in the 2 to 10 nm range. This could reflect the higher ionic potential of lead as compared to manganese, copper and zinc, which would result, for example, in a higher average equilibrium quotient for complexation by fulvic acids and Fe-III hydrous oxides (Buffle *et al.*, 1984).

In waters of very high aluminium concentrations (groundwaters F3: 6 mg/l and SW03B: 67 mg/l) a surprisingly small fraction (<3%) is in the colloidal size ranges >2 nm. The lower size range has not been investigated. As in the case of thorium, this indicates effective suppression of hydrolysis by the high SO_4^{2-} and F^- concentration in these waters.

4.2.2. Colloidal characteristics of waters from the Morro do Ferro study site

The colloidal characteristics of groundwaters from Morro do Ferro (Appendix 1, Figs. 16 to 18) are similar to those already discussed for the Osamu Utsumi mine, namely: 1) a low total concentration of colloids (<1 mg/l), 2) a low fraction of DOC (<10%) in the MW size ranges of humic compounds, especially of fulvic acids (<10,000 MW), 3) a considerable fraction of the total Fe is present in colloidal form (10 to 20%), 4) indications that the tendency to form colloids increases in the order: U< REE <Th, in accordance with the observed association ratios of these elements for suspended matter from this site (Tables VII and VIII) and 5) notwithstanding the large errors involved in the $^{234}U/^{238}U$ ARs of the colloidal fractions, there are indications of an exchange equilibrium of uranium between solution and colloidal phases, as observed for the larger particles (>450 nm).

The colloidal characteristics of the other major, minor and trace elements studied (Si, Mg, Ca, Ba, Mn, Cu, Zn, Mo and Pb) are also similar to those already discussed for the Osamu Utsumi waters. Slightly higher proportions of silicon and aluminium were observed in groundwaters from MF11 and MF10, compared to those from MF12, indicating the presence of colloidal clay minerals (also observed as suspended particles, Fig. 8) in or close to the unsaturated zone of the deposit. This aspect will be discussed further below.

Mn(IV)-oxyhydroxides are considered likely candidates in particle form for the sorption of trace elements in the aquatic environment (e.g. Baes and Mesmer, 1976). Due to the abundance of Mn-oxides (pyrolusite), visible as outcrops in the area of the orebody, the concentrations of manganese are relatively high in the Morro do Ferro waters (MF10: 0.7 mg/l, MF12: 1.7 mg/l). Compared to iron, manganese shows a much lower tendency to form colloidal species (<3% of the total Mn). This observation indicates that the prevalent oxidation state of this element is +2, which seems to be in agreement with the observed pH/Eh conditions in Morro do Ferro groundwaters.

4.2.2.1. Dissolved organic carbon (DOC)

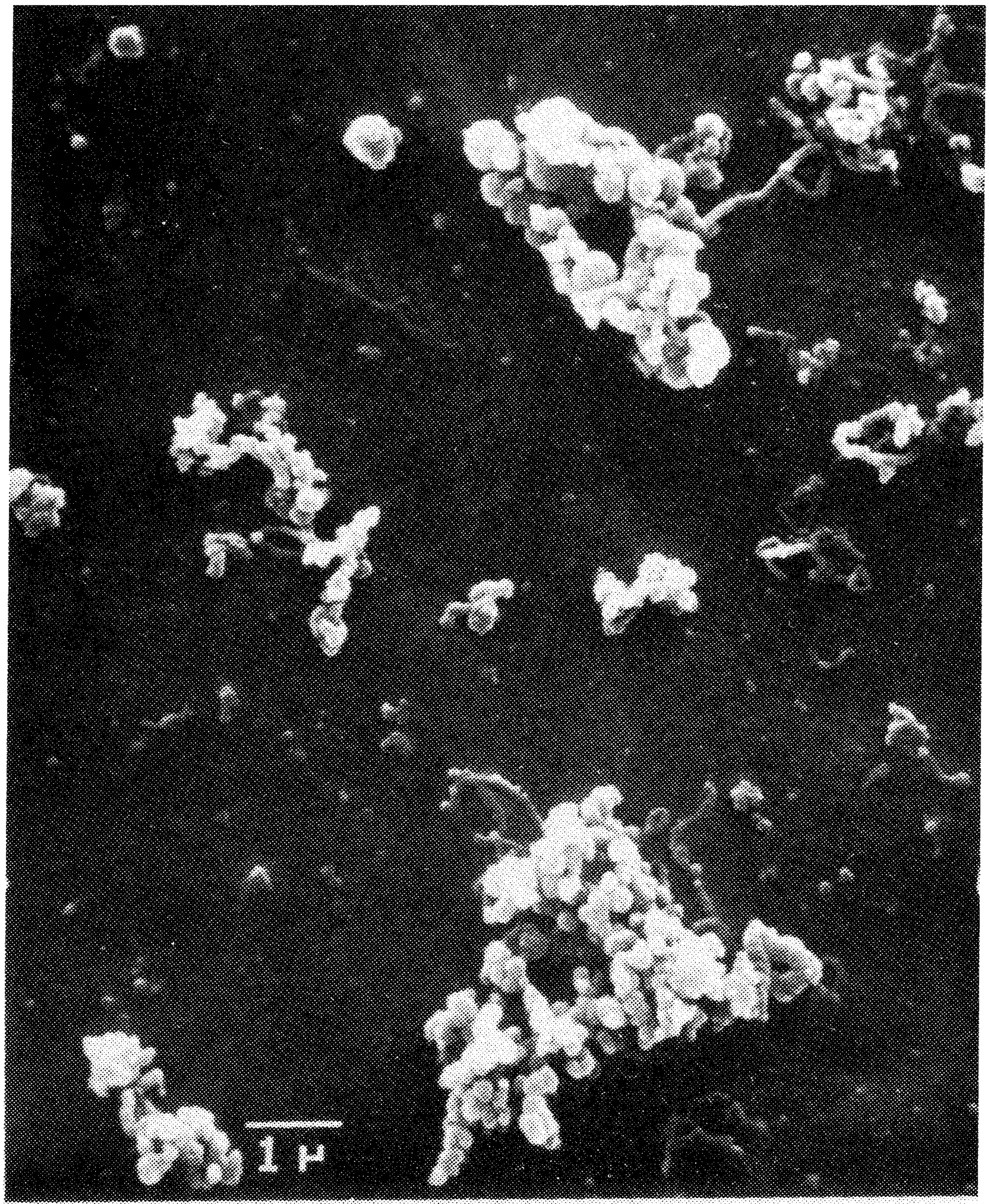
As mentioned earlier, DOC can be much higher in surface and near-surface waters from Morro do Ferro. An example of the colloidal distribution of major and trace elements in an organic-rich percolation water (DOC = 13 ppm), collected from the experimental gallery, is shown in Figure 18 and in Appendix 1 (sample GA-2).

The total colloid concentration (TCC) in this sample is dominated by DOC (TCC = 6.2 mg/l) of MW ranges between 1,000 and >300,000 dalton, typical of humic-like compounds. Extraordinarily high fractions of polyvalent major, minor and trace elements are concentrated in these retentates of colloidal organic carbon (COC), representing about 50% of the total DOC (97% of Th, 80–90% of REE, 80% of Fe and 25–30% of Ca, Mg and Mn). Contamination cannot be excluded as a reason for the equally high concentrations of silicon and sodium in colloidal fractions. These samples were stored in glass bottles for a longer time period. A systematic decrease of the colloidal fraction of an element as a function of valency is observable, which is in accordance with the greater expected stabilities of humic complexes for metal ions of higher ionic potential (e.g. Choppin and Allard, 1986). Acidification of the colloidal concentrates with HCl (pH <2) resulted in the precipitation of brown floccules, identified as humic acids. This process caused a nearly quantitative coprecipitation of thorium (and probably other elements, e.g. the REEs). It is reasonable to expect that a proportion of the DOC, leached from the pedogenic organic matter, reaches the groundwater. Due to the higher adsorption affinity of humic acids on clays and other soil inorganic materials, as compared to fulvic acids, a shift in the MW distribution spectrum to lower MW should be expected. This seems to be the reason why most of the colloidal organic carbon (COC) in groundwater from Morro do Ferro is concentrated in the 1,000 to 10,000 MW range. As has been shown, these colloidal humic compounds (associated with ferrihydrites) are the principal carriers (and complexants) for the major and trace elements studied. This means that only a fraction of the total DOC, namely the COC, is especially effective in the complexation of polyvalent metal ions. The very low COC in water from this site (typically 0.1–0.2 ppm) is probably due to adsorption on clay minerals and other effects, and may be the reason why the estimated 30,000 tons of thorium in the deposit area leave no fingerprints in groundwaters, confirming earlier results of Eisenbud *et al.* (1982). By chemical analogy it may be expected that Pu(IV) species would show similar behaviour.

4.2.2.2. Size characterisation of groundwater colloids from SEM and ESCA studies

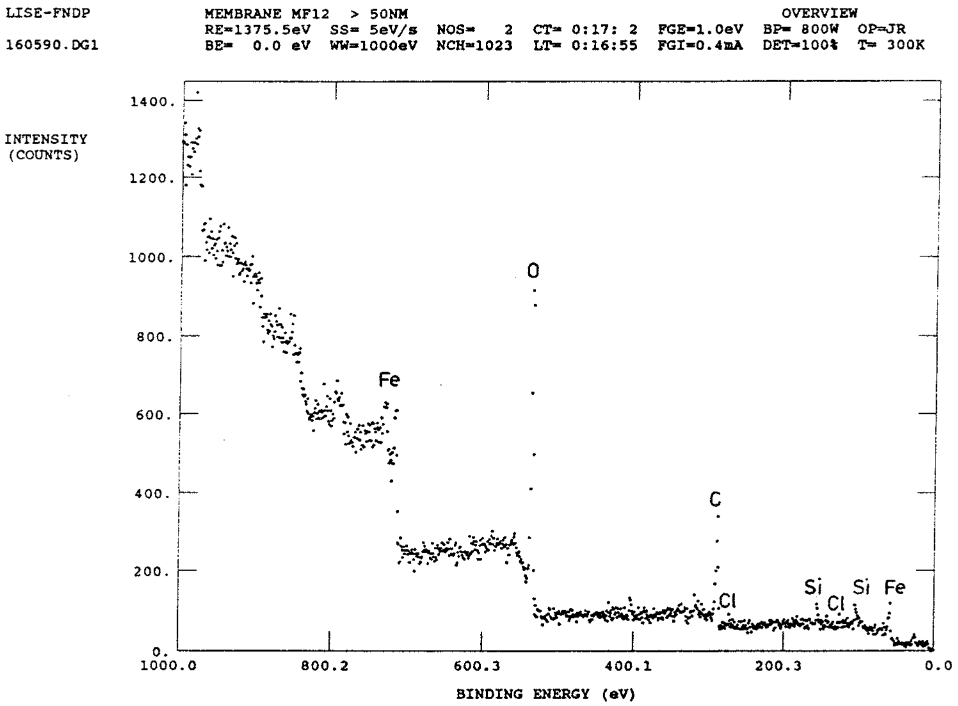
Figure 21 shows a typical microphotograph of colloids from the Morro do Ferro groundwater (MF12), obtained by SEM at an original magnification of 40,000. Large irregular-shaped particles, agglomerates of these particles and long, chain-like aggregates, similar to those observed for humic compounds, are visible. The ESCA-spectrum of this sample (Fig. 22a) shows the predominance of Fe(III), carbon, oxygen, nitrogen and minor amounts of sulphur, silicon and potassium in these particles. For iron and silicon, these results were also confirmed by electron probe microanalysis. The C(1s) high resolution ESCA – spectrum (Fig. 24 b) showed, in addition, that carbon is of humic-like character, with about 8 to 12% carboxylic groups, about 10% of carbon as C-O- and about 80% as aromatic or aliphatic neutral carbon. Similar behaviour is also observed for samples from borehole MF10. The similarity of the spectrum in Figure 22 b with that of Aldrich's humic acid (Na-salt) can be seen in Figure 22 c.

An estimation of the size distribution of colloids from MF12 was performed using SEM microphotographs similar to that shown in Figure 21. A reasonable colloid density was obtained on the membrane by dia-ultrafiltration of about 10 ml of groundwater. The concentration of colloids in the original water sample can be deduced from counting the colloids on several micrographs, to obtain a statistically significant estimate of the number of colloids deposited on the active surface area of the membrane (area = 1.2 cm^2). The estimated number of particles is then related to the volume of the filtered water. Figures 23 a and b present an example of the normal specific size distribution. Since the 'Quantimeter' used can discriminate the elementary particles from their aggregates, two results are presented: uncut and cut. The first profile (uncut) shows the concentration of colloidal aggregates per size class against their corresponding diameter (Fig. 23 a). The second graph shows the same representation for elementary colloidal particles (Fig. 23 b). A more or less regular increase of the colloid population with decreasing particle size diameter can be observed. There is no reason why this distribution should not continue to sizes < 10 nm. With the exception of a slight shift in the concentration/diameter ratio from the uncut to the cut hypothesis, no significant



d. Morro do Ferro MF12 (BZ)

Figure 21. Microphotograph of colloids (composed predominantly of Fe-III oxyhydroxides and humic compounds) from a groundwater sample of borehole MF12 (filtered volume: 9.8 ml, filter PM-10, active surface: 1.2 cm², magnification: 15,000 X).



```
LISE-FNDP            MEMBRANE MF12  > 50NM                                          OVERVIEW
                     RE=1375.5eV  SS= 5eV/s  NOS=   2  CT= 0:17: 2  FGE=1.0eV  BP= 800W  OP=JR
160590.DG1           BE=  0.0 eV  WW=1000eV  NCH=1023  LT= 0:16:55  FGI=0.4mA  DET=100%  T= 300K
```

Figure 22. ESCA-spectrum of colloidal particles (450 nm > COLL > 10,000 MWCL) from borehole water MF12, showing the predominance of Fe-III, oxygen and carbon in these particles.

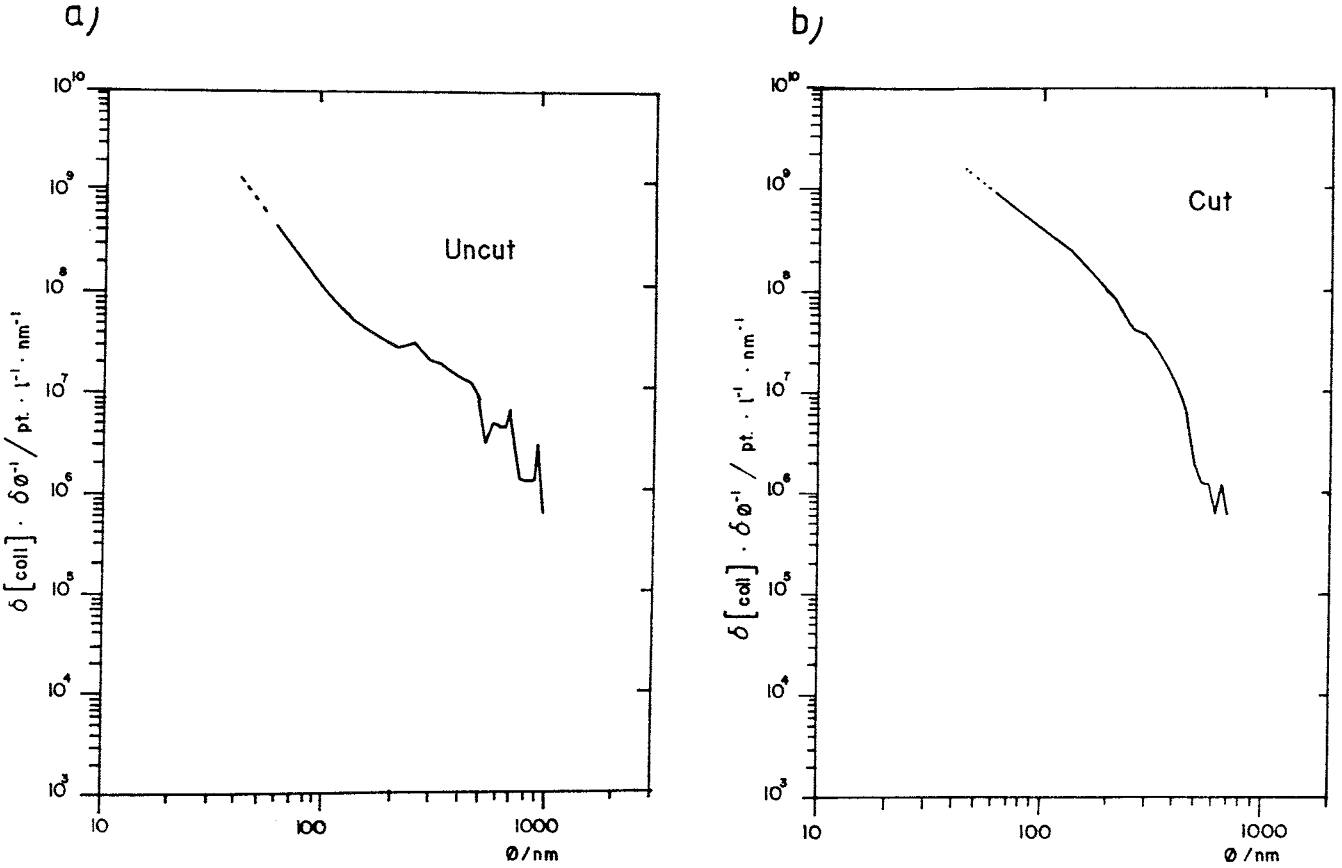


Figure 23. Size distribution of colloids from MF12 groundwater, as obtained from Figure 21: a) uncut, b) cut.

differences in the size distribution characteristics could be observed. Colloidal concentration in particles/l and μg/l, as well as cation exchange capacities (CEC_m = surface site capacity, CEC_M = nanoporous colloid capacity) were calculated on the assumption that the sorption site densities are $3 \cdot nm^{-2}$ and $3 \cdot nm^{-3}$ respectively, and the specific density of the solid is $2x10^{-21}$ $g \cdot nm^{-3}$. Since the lateral resolution of SEM is about 40 nm, the extrapolation to 10 nm is carried out on the basis of a statistical size distribution (Pareto law). The principal results of these calculations are summarised in Table IX. The theoretical background of the procedures involved has been published previously (Degueldre and Wernli, 1987).

TABLE IX

a) Results of a colloid size distribution analysis of a groundwater sample from borehole MF12 (as obtained from Fig. 23).

PARAMETER	Unit	Analysis without cutting	Analysis with cutting
[coll]	pt. 1^{-1}	3.4×10^{10}	8.1×10^{10}
[coll]	ppb	99	164
CEC_m	nM	11	22
CEC_M	μM	0.50	0.80
	Extrapolation (Pareto law), size 10 – 440 nm		
[coll]	pt. 1^{-1}	6.7×10^{10}	2.0×10^{11}
[coll]	ppb	101	167
CEC_m	nM	12	23
CEC_M	μM	0.51	0.80

b) Colloid speciation

[coll]	total	265 ± 65 ppb
[coll]	as $Fe(OH)_3$	50 ppb
[coll]	as $Al_2Si_4O_{11}$	5 ppb

In the size range of 10 to 440 nm, the results for the MF12 sample indicate a colloid concentration of about 2×10^{11} particles/l or about 167 μg/l. These numbers correspond to exchange capacities of 23 and 800 nM for CEC_m and CEC_M respectively. For the same size interval, the total colloidal concentration obtained by chemical methods was about 265 μg/l, composed of 50 μg/l of Fe-colloids, 5 μg/l of clays and about 210 ppb of DOC. For other samples from MF12, the colloid concentration for this size fraction (10 to 440 nm) was lower by a factor of 5 to 10. Extending the size interval up to 1.5 nm (1,000 MWCL), the total colloid concentrations of samples from MF12 and MF10 for the relevant major elements (DOC, Fe, Si, Mg, Ca and Mn) are, however, similar (400 to 600 μg/l; see Appendix 1).

Concerning the question as to whether these colloidal particles are able to migrate through the rocks of Morro do Ferro, similar speculations to those already mentioned for suspended matter can be made by comparing the REE signature of prefiltered water from MF11 (10) and MF12. As about 50% of the REE concentrations of these waters are associated with colloids, a substantial migration of colloids from MF11(10) to MF12 should influence the REE composition of the latter, assuming that the REEs are irreversibly sorbed on the particles during their travelling time. Figure 24 shows an example of how the REE signature of colloids in different size/MW ranges mirror the composition of the corresponding prefiltered water. The characteristic negative cerium anomaly of groundwater from (or close to) the unsaturated zone of the deposit, which also reflects the REE composition of the rock, does not appear in the MF12 groundwaters (Figs. 10 and 11) at the base of the hill, nor in the surface waters of the South Stream, which receives the major part of the drainage water from the area of the ore deposit. In addition, colloidal clay minerals, more frequent in waters from the unsaturated zone, are practically absent from MF12 groundwaters. Both observations may indicate that there is no evidence for ore body degradation/erosion, followed by the subsurface transport of generated colloids (and suspended particles) in groundwaters.

Very similar differences in the REE signatures between near-surface waters (SW03) and groundwaters (F1) have been observed in the Osamu Utsumi mine. However, due to the very complex hydrogeology of this site (Holmes *et al.*, this report series; Rep. 5), a similar hypothesis cannot be established.

The phenomenon that takes place in both environments is probably the true dissolution of trace elements, followed by dispersion in water and sorption on all solid phases such as soil components, rocks, suspended matter and colloids. Within this context, the role of Fe-III oxyhydroxides and humic compounds is of special importance in trace element immobilisation.

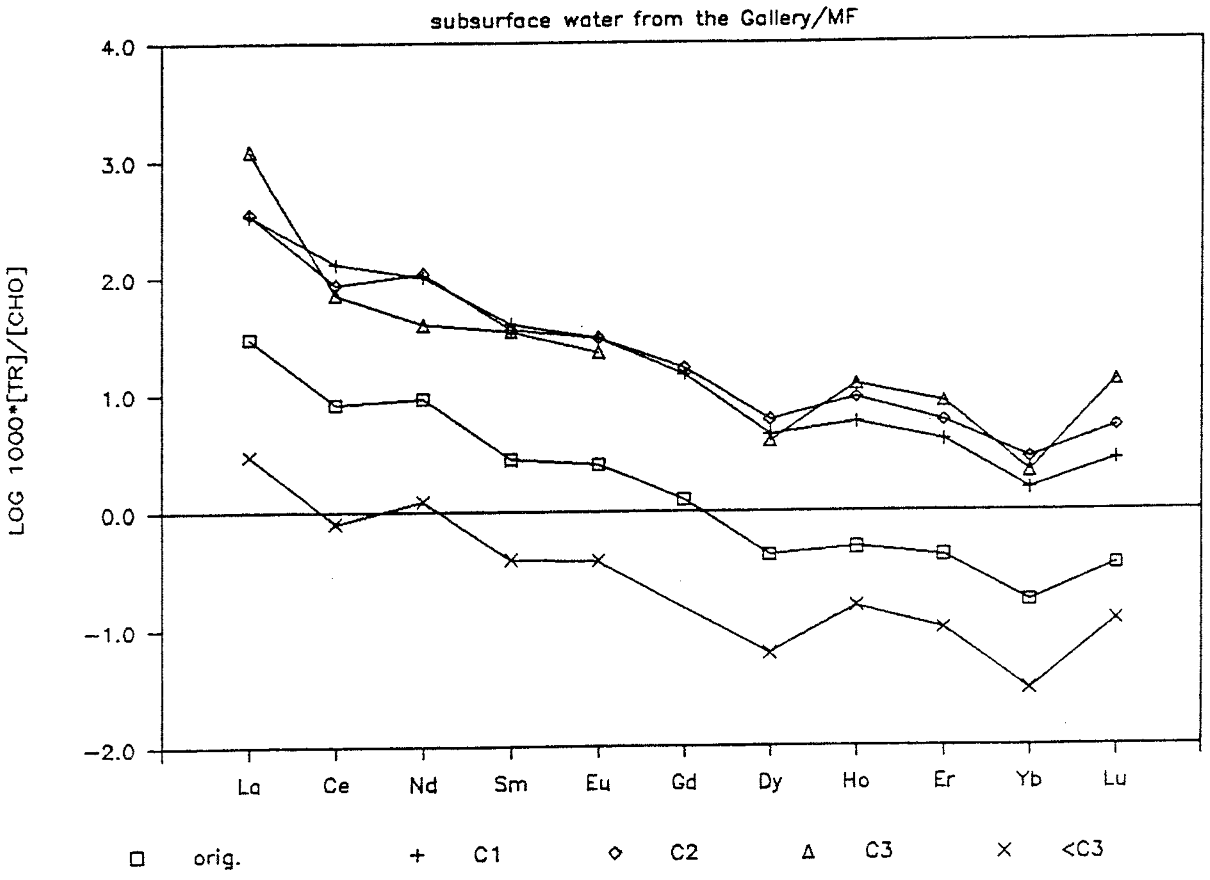


Figure 24. Chondrite normalised REE distribution patterns in a subsurface water from Morro do Ferro (gallery) and in its corresponding colloidal concentrates (F1, F2, F3) and in the ultrafiltrate (<F3). Size ranges as specified in Figure 13.

5. Conclusions

1. Colloidal particles in the size range between 450 nm and 1.5 nm (or less), composed mainly of Fe-III oxyhydroxides and organic, humic-like species, have been identified in prefiltered groundwaters from both the Osamu Utsumi mine and Morro do Ferro study sites. The colloid concentration is, however, low (<1 mg/l), despite both sites being in an advanced state of weathering.

2. Minor fractions of uranium and of some other elements (e.g. Si, Ca, Mg, Mn, Cu, Zn, Pb and also occasionally Zr and Sn), but significant fractions of thorium and the REEs, are concentrated in these colloidal phases. The tendency to form colloidal species increases in the order U <Ce <Th, in accordance with the observed association ratios of these elements for suspended particles (>450 nm).

3. Colloidal organic carbon, mainly as humic-like material, may occur in relatively high concentrations in surface and near-surface waters. The much higher proportions (and concentrations) of polyvalent metal ions (especially Th and REE) in colloidal fractions of organic-rich waters of the Morro do Ferro site were attributed to these compounds.

4. Solution and colloidal phases are in exchange equilibrium with respect to $^{234}U/^{238}U$ isotopic ratios and have identical REE distribution patterns.

5. Unfiltered groundwaters contain suspended particles, which have uranium, thorium and REE contents orders of magnitude higher than the corresponding waters (<450 nm), but their concentration is, typically, low in the Osamu Utsumi mine (0.2–0.4 mg/l) and moderate (1–5 mg/l) at Morro do Ferro. These particles, which are also mainly composed of Fe-III oxyhydroxides and sorbed organics, would be the main reservoirs for thorium and, to a lesser extent, for the REEs. For uranium, they would play no important role, as this element is present almost exclusively in the solution phase (<1.5 nm).

6. All evidence indicates no significant subsurface transport of suspended particles or colloids in either environment.

6. Acknowledgements

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Appendix 1

Elemental concentrations/activities and distribution characteristics in colloidal concentrates and ultrafiltrates of subsurface and ground waters from the Osamu Utsumi mine and Morro do Ferro analogue study sites.

TABLE 1-I

Elemental concentrations/activities and distribution characteristics in colloidal concentrates (C1,C2,C3) and ultrafiltrates (<C3) of subsurface and ground waters from the Osamu Utsumi mine. (C1: 450 nm > MWCL > 100,000 dalton; C2: 100,000 > MWCL > 10,000 dalton; C3: 10,000 > MWCL > 1,000 dalton; <C3: <1,000 dalton; orig. = concentration in the prefiltered water; TCC = total colloid concentration of an element.)

UF: WC11-A	Sampling: 15/02/87									PRINCIPAL ELEMENTS:						
ULT.VOL(1) ?	Volume to calc (1)	DOC (ppm)	U-fluor (ppb)	^{238}U (ppb)	^{234}U (Bq/l)	^{232}Th (ppb)	Ce (ppb)	$^{234}U/^{238}U$	$^{228}Th/^{232}Th$	Si (ppm)	Fe (ppm)	Mn (ppm)	Ca (ppm)	Mg (ppm)	K (ppm)	Ba (ppm)
Orig	43.18	1.7	4.6	4.3	0.12	0.029	4.22	2.2	186	13	1.7	0.29	0.75	0.14	13.6	0.16
C1	0.505	1.6	4.6	4.3	0.098	1.08	63	1.8	23	13.5	2.07	0.29	0.75	0.05	13.1	0.14
C2	0.410	1.3	5.1	8.6	0.21	1.94	39	2.0	24	13.6	2.73	0.42	1.46	0.16	18.9	0.26
C3	0.485	6.1	12	16	0.15	2.19	122	2.2	113	15.7	9.73	1.8	7.71	0.52	43.1	1.04
<C3	41.78	1.8	2.8	2.9	0.083	0.037	3.07	2.3	160	13.6	1.09	0.23	0.74	0.04	12.6	0.11
% Distribution																
C1		0.0%	0.7%	0.5%	0.2%	13.3%	12.9%			0.0%	0.9%	0.3%	0.0%	0.3%	0.0%	0.3%
C2		0.0%	0.7%	1.7%	1.4%	19.8%	6.3%			0.0%	1.3%	0.7%	0.8%	2.4%	0.5%	1.2%
C3		2.6%	3.5%	4.7%	4.7%	26.4%	24.5%			0.2%	8.0%	7.0%	9.5%	11.6%	2.6%	8.5%
<C3		97.4%	95.0%	93.0%	93.8%	40.5%	56.4%			99.8%	89.8%	91.9%	89.7%	85.7%	96.9%	90.0%
TCC (ppb,ppm,Bq/l)		0.044	0.23	0.30	0.007	0.017	1.84			0.023	0.17	0.023	0.077	0.020	0.43	0.016

UF: WC11-B	Sampling: 29/7/87									PRINCIPAL ELEMENTS:						
ULT.VOL(1) 39.05	Volume to calc (1)	DOC (ppm)	U-fluor (ppb)	^{238}U (ppb)	^{234}U (Bq/l)	^{232}Th (ppb)	Ce (ppb)	$^{234}U/^{238}U$	$^{228}Th/^{232}Th$	Si (ppm)	Fe (ppm)	Mn (ppm)	Ca (ppm)	Mg (ppm)	K (ppm)	Ba (ppm)
Orig	38.71	3.4	3.64	3.8	0.11	0.065	7.5	2.3	390		1.0	0.18	3.54	0.66	12	
C1	0.348	15	10.6	13	0.46			2.8			0.56	0.21	1.62	0.88	12	
C2	0.398	10	9.4	9	0.34			3.1			0.71	0.29	1.05	0.08	19	
C3	0.463	14	33	27	0.94			2.8			3.76	1.77	9.21	0.58	59	
<C3	36.50	3.0	3.44	3.49	0.089	0.072	2.9	2.1	290		0.39	0.16	3.0	0.4	10	
% Distribution																
C1		3.3%	1.7%	2.2%	3.2%						0.4%	0.3%	0.0%	1.1%	0.2%	
C2		2.2%	1.6%	1.5%	2.5%						0.8%	0.8%	0.0%	0.0%	0.9%	
C3		4.1%	9.2%	7.4%	9.9%						9.5%	10.9%	2.5%	0.5%	5.6%	
<C3		90.4%	87.5%	88.9%	84.3%						89.4%	88.1%	97.5%	98.4%	93.3%	
TCC (ppb,ppm,Bq/l)		0.33	0.46	0.42	0.017						0.11	0.021	0.088	0.011	0.80	

TABLE 1-I (contd.).

UF: WC11-C		Sampling: 24/5/88								PRINCIPAL ELEMENTS:						
ULT.VOL(1) 42.40	Volume to calc (1)	DOC (ppm)	U-fluor (ppb)	^{238}U (ppb)	^{234}U (Bq/l)	^{232}Th (ppb)	Ce (ppb)	^{234}U/^{238}U	^{228}Th/^{232}Th	Si (ppm)	Fe (ppm)	Mn (ppm)	Ca (ppm)	Mg (ppm)	K (ppm)	Ba (ppm)
Orig	42.13	1.3	4.8	4.9	0.139	0.030	4.3	2.3	320	15.3	1.23	0.13	0.50		11.2	0.16
C1	0.492	1.7	9.5	10.0	0.30	2.7	25	2.4	6.2	15.5	1.20	0.14	0.54		11.5	0.11
C2	0.625	2.3	11	11.5	0.33	1.18	37.5	2.4	42	15.6	2.65	0.30	2.06		24.1	0.30
C3	0.678	7.3	16	18.5	0.50	1.67	25.3	2.2	122	18.1	9.87	1.01	7.00		27.7	0.75
<C3	40.33	1.2	1.6	1.46	0.044	0.017	2.32	2.4	320	15.6	0.94	0.12	0.55		10.4	0.11
% Distribution																
C1		0.5%	4.4%	5.1%	5.0%	33.7%	7.6%			0.0%	0.3%	0.2%	0.0%		0.1%	0.0%
C2		1.2%	7.0%	7.6%	7.3%	18.7%	15.0%			0.0%	2.3%	1.9%	3.3%		1.9%	2.3%
C3		7.4%	11.3%	13.9%	12.4%	29.0%	10.6%			0.3%	12.9%	10.4%	15.4%		2.6%	8.4%
<C3		90.9%	77.2%	73.5%	75.2%	18.6%	66.7%			99.7%	84.5%	87.4%	81.3%		95.5%	89.2%
TCC (ppb,ppm,Bq/l)		0.12	1.10	1.30	0.034	0.025	1.43			0.039	0.19	0.016	0.093		0.51	0.017

UF: WC11-D		Sampling: 25/10/88								PRINCIPAL ELEMENTS:						
ULT.VOL(1) 21.85	Volume to calc (1)	DOC (ppm)	U-fluor (ppb)	^{238}U (ppb)	^{234}U (Bq/l)	^{232}Th (ppb)	Ce (ppb)	^{234}U/^{238}U	^{228}Th/^{232}Th	Si (ppm)	Fe (ppm)	Mn (ppm)	Ca (ppm)	Mg (ppm)	K (ppm)	Ba (ppm)
Orig	21.16	2.50	4.6	4.8	0.137	0.017		2.3	1090	16.4	1.7	0.17	0.30	0.042	11.8	0.14
C1	0.393	2.64	9.0	9.8	0.30	0.56		2.5	123	15.5	1.53	0.18	0.56	0.053	10.8	0.11
C2	0.378	3.65	12	12.6	0.40	0.48		2.5	323	16.5	3.11	0.41	1.53	0.12	21.5	0.25
C3	0.358	8.87	26	30	0.90	0.75		2.4	687	20.8	11.9	1.61	6.85	0.43	47.0	0.74
<C3	20.03	2.14	1.3	1.4	0.039	0.0095		2.3	789	15.7	0.96	0.15	0.43	0.030	9.8	0.072
% Distribution																
C1		0.4%	7.0%	7.0%	7.5%	25.1%				0.0%	0.9%	0.3%	0.4%	1.1%	0.2%	0.8%
C2		1.2%	9.3%	8.9%	9.9%	20.7%				0.1%	3.2%	2.6%	3.5%	4.1%	2.0%	3.6%
C3		5.0%	20.4%	21.6%	22.5%	30.8%				0.5%	15.5%	13.7%	19.4%	17.4%	5.9%	13.0%
<C3		93.4%	63.4%	62.5%	60.1%	23.4%				99.4%	80.4%	83.4%	76.7%	77.3%	92.0%	82.6%
TCC (ppb,ppm,Bq/l)		0.15	0.75	0.84	0.026	0.031				0.10	0.23	0.030	0.13	0.009	0.86	0.015

TABLE 1-I (contd.).

UF: VC24-A		Sampling: 16/02/87								PRINCIPAL ELEMENTS:						
ULT.VOL(1) ?	Volume to calc (1)	DOC (ppm)	U-fluor (ppb)	^{238}U (ppb)	^{234}U (Bq/l)	^{232}Th (ppb)	Ce (ppb)	^{234}U/^{238}U	^{228}Th/^{232}Th	Si (ppm)	Fe (ppm)	Mn (ppm)	Ca (ppm)	Mg (ppm)	K (ppm)	Ba (ppm)
Orig	39.95	2.1	14.8	14.7	0.27	0.030	2.92	1.5	60	13.2	0.99	0.14	1.51	0.03	11.0	0.134
C1	0.520	30	45.8	45.7	0.78	1.62	9.64	1.4	44	10.1	4.90	0.09	1.50	0.039	14.3	0.083
C2	0.508	2.8	36.5	38	0.76	1.57	26.4	1.6	36	14.5	2.88	0.24	2.85	0.042	24.4	0.185
C3	0.425	12.8	58.2	70	1.41	2.42	28.8	1.6	59	12.8	7.18	0.33	6.26	0.154	26.7	0.295
<C3	38.50	2.2	3.9	4.45	0.088	0.026	0.63	1.6	227	13.2	0.6	0.11	0.94	0.03	11.3	0.057
% Distribution																
C1		13.5%	10.0%	8.8%	7.5%	22.6%	8.5%			0.0%	7.4%	0.0%	0.7%	0.4%	0.3%	0.6%
C2		0.3%	7.6%	7.0%	7.1%	21.4%	23.8%			0.1%	3.8%	1.5%	2.4%	0.5%	1.4%	2.6%
C3		4.2%	10.6%	11.4%	11.8%	27.7%	21.8%			0.0%	9.3%	2.1%	5.5%	4.2%	1.4%	4.1%
<C3		82.0%	71.7%	72.8%	73.6%	28.3%	45.8%			99.9%	79.5%	96.5%	91.4%	95.0%	96.8%	92.7%
TCC (ppb,ppm,Bq/l)		0.38	4.18	4.00	0.071	0.022	1.58			0.017	0.20	0.005	0.13	0.002	0.35	0.010

UF: VC24-B		Sampling: 6/8/87								PRINCIPAL ELEMENTS:						
ULT.VOL(1) 41.11	Volume to calc (1)	DOC (ppm)	U-fluor (ppb)	^{238}U (ppb)	^{234}U (Bq/l)	^{232}Th (ppb)	Ce (ppb)	^{234}U/^{238}U	^{228}Th/^{232}Th	Si (ppm)	Fe (ppm)	Mn (ppm)	Ca (ppm)	Mg (ppm)	K (ppm)	Ba (ppm)
Orig	40.10	4.3	8	8.1	0.14	0.057	4.1	1.4	50		0.8	0.2	1.92	0.02	11	
C1	0.351	13.7	18	17	0.85			4.0(?)			1.98	0.28	2.84	0.29	12	
C2	0.483	4.8	15	17.6	0.72			3.3(?)			2.18	0.34	3.71	0.052	17	
C3	0.490	11.9	27	28.4	0.60	1.3		1.8	74		4.94	1.08	13.3	0.25	33	
<C3	37.78	2.9	7.8	8.2	0.15	0.2	4.2	1.5	85		0.78	0.19	1.87	0.02	11	
% Distribution																
C1		3.1%	1.1%	0.9%	3.7%						1.3%	0.4%	0.4%	9.4%	0.1%	
C2		0.7%	1.1%	1.3%	4.2%						2.0%	0.9%	1.1%	1.5%	0.7%	
C3		3.6%	2.9%	2.9%	3.3%						6.1%	5.5%	7.0%	11.2%	2.4%	
<C3		92.6%	94.9%	94.8%	88.8%						90.7%	93.2%	91.5%	77.8%	96.8%	
TCC (ppb,ppm,Bq/l)		0.32	0.41	0.42	0.016						0.075	0.014	0.16	0.004	0.35	

TABLE 1-I (contd.).

UF: VC24-C		Sampling: 31/5/88								PRINCIPAL ELEMENTS:						
ULT.VOL(1) 41.59	Volume to calc (1)	DOC (ppm)	U-fluor (ppb)	^{238}U (ppb)	^{234}U (Bq/l)	^{232}Th (ppb)	Ce (ppb)	$^{234}U/^{238}U$	$^{228}Th/^{232}Th$	Si (ppm)	Fe (ppm)	Mn (ppm)	Ca (ppm)	Mg (ppm)	K (ppm)	Ba (ppm)
Orig	41.27	1.6	5.3	5.5	0.112	0.038	2.14	1.6	20	15.0	1.17	0.23	2.69		12	0.28
C1	0.560	1.6	7.7	9.9	0.22	0.78	5.1	1.8	8.4	14.2	1.19	0.22	2.69		12	0.13
C2	0.600	2.1	12	12.3	0.26	0.59	7.9	1.7	25	14.7	2.11	0.37	4.54		18.8	0.22
C3	0.630	4.6	15	15.7	0.33	0.59	8.2	1.7	60	17.4	5.64	0.82	11.5		30.6	0.53
<C3	39.48	1.7	2.5	2.5	0.051	0.018	0.28	1.7	32	14.7	1.10	0.20	2.34		11.2	0.11
% Distribution																
C1		0.0%	2.4%	3.5%	3.9%	22.6%	11.3%			0.0%	0.1%	0.1%	0.2%		0.1%	0.3%
C2		0.4%	4.8%	4.9%	4.9%	18.3%	19.2%			0.0%	1.2%	1.2%	1.3%		1.0%	1.4%
C3		2.5%	6.7%	6.9%	6.9%	19.3%	21.0%			0.3%	5.8%	4.5%	5.6%		2.5%	5.4%
<C3		97.1%	86.1%	84.7%	84.3%	39.8%	48.5%			99.7%	92.8%	94.2%	93.0%		96.4%	92.9%
TCC (ppb,ppm,Bq/l)		0.046	0.74	0.85	0.017	0.023	1.10			0.042	0.084	0.013	0.19		0.43	0.020

UF: SW03		Sampling: 25/10/88								PRINCIPAL ELEMENTS:						
ULT.VOL(1) 12.72	Volume to calc (1)	DOC (ppm)	U-fluor (ppb)	^{238}U (ppb)	^{234}U (Bq/l)	^{232}Th (ppb)	Ce (ppb)	$^{234}U/^{238}U$	$^{228}Th/^{232}Th$	Si (ppm)	Fe (ppm)	Mn (ppm)	Ca (ppm)	Mg (ppm)	K (ppm)	Ba (ppm)
Orig	12.37	2.9	5500	6600	84	720		1.03	1.2	26.3	27.5	12,3	21.7	5.0	26.7	0.083
C1	0.378	3.6	6400	6400	83	670		1.04	1.3	27.8	30.7	12.5	23.2	5.3	28.0	0.092
C2	0.383	3.4	6300	6900	87	740		1.02	1.3	27.2	30.0	12.6	22.6	5.2	26.8	0.053
C3	0.526	10.9	11000	11500	154	2150		1.07	1.3	35.1	123	25.8	41.9	10.9	27.1	0.154
<C3	11.08	3.2	5000	5700	74	620		1.06	1.2	26.4	24.3	11.7	21.3	4.8	27.5	0.085
% Distribution																
C1		0.3%	0.8%	0.4%	0.4%	0.2%				0.2%	0.7%	0.2%	0.3%	0.3%	0.1%	0.2%
C2		0.2%	0.8%	0.6%	0.5%	0.5%				0.1%	0.6%	0.2%	0.2%	0.2%	0.0%	0.3%
C3		9.2%	4.8%	4.1%	4.4%	9.4%				1.4%	14.5%	4.9%	3.9%	5.1%	0.0%	3.3%
<C3		90.2%	93.7%	94.9%	94.8%	89.8%				98.4%	84.2%	94.7%	95.6%	94.4%	99.9%	96.2%
TCC (ppb,ppm,Bq/l)		0.35	338	305	4.08	70				0.44	4.57	0.65	0.97	0.29	0.015	0.003

TABLE 1-I (contd.).

UF: C1 Sampling: April/89

ULT.VOL(1)	Volume to calc (1)	F^- (ppm)	Cl^- (ppm)	NO_3^- (ppm)	SO_4^{2-} (ppm)	Al (ppb)	Th (ppb)	U (ppb)	Li (ppb)	Na (ppb)	Mg (ppb)	Mn (ppb)	Cu (ppb)	Zn (ppb)	Sr (ppb)	Mo (ppb)	Ba (ppb)	La (ppb)	Pb (ppb)	Rb (ppb)	Y (ppb)
Orig (<450nm)	21.40	0.35	0.189	0.90	31.7	53	0.015	4.12	2.0	181	50	125	14	79	26	11	125	6	1.0	26	0.8
100.000	0.400	0.37	0.217	2.00	26.6	83	0.14	10.9	2.0	204	228	119	27	75	25	11	108	9	1.5	25	1.3
10.000	0.330	0.37	0.200	1.33	35.7	134	0.48	23.6	2.4	382	282	187	56	123	49	44	166	19	17.6	49	3
< 10.000	20.30	0.36	0.203	1.00	16.5	49	0.020	2.79	1.8	190	39	121	12	83	25	9	112	5	0.7	25	0.6
% Distribution																					
100.000		0.1%	0.1%	1.9%	1.1%	1.3%	7.7%	4.7%	0.2%	0.1%	7.7%	0.0%	2.2%		0.0%	0.4%	0.0%	1.4%	1.6%	0.0%	2.0%
10.000		0.0%	0.0%	0.5%	1.8%	2.6%	24.5%	10.0%	0.5%	1.6%	8.2%	0.8%	5.3%		1.5%	5.7%	0.8%	4.1%	27.0%	1.5%	5.8%
< 10.000		99.9%	99.9%	97.6%	97.1%	96.1%	67.8%	85.3%	99.3%	98.3%	84.0%	99.2%	92.5%		98.5%	93.9%	99.2%	94.4%	71.4%	98.5%	92.2%
TCC (ppm, ppb)		0.0003	0.0003	0.0238	0.48	1.95	0.01	0.47	0.01	3.22	7.28	1.02	0.96		0.37	0.58	0.83	0.29	0.28	0.37	0.05

UF: C2 Sampling: April/89

ULT.VOL(1)	Volume to calc (1)	F^- (ppm)	Cl^- (ppm)	NO_3^- (ppm)	SO_4^{2-} (ppm)	Al (ppb)	Th (ppb)	U (ppb)	Li (ppb)	Na (ppb)	Mg (ppb)	Mn (ppb)	Cu (ppb)	Zn (ppb)	Sr (ppb)	Mo (ppb)	Ba (ppb)	La (ppb)	Pb (ppb)	Rb (ppb)	Y (ppb)
Orig (<450nm)	21.16	2.3	0.043	2.2	14.1	168	0.18	5.93	0.8	141	86	213	< 0.5	189	71	5	119	62	0.6	29	10
100.000	0.400	2.3	0.137	0.52	14.3	181	0.86	13.4	0.9	124	49	199	0.7	172	65	5	116	73	2.0	26	11
10.000	0.400	2.5	0.057	0.262	17.0	245	2.47	19.9	0.9	187	67	248	1.6	219	86	6	136	116	2.1	40	18
< 10.000	19.92	2.6	0.144	0.215	14.4	165	0.031	5.31	0.9	135	49	207	< 0.5	188	71	5	124	51	< 0.5	29	8
% Distribution																					
100.000		0.0%	0.0%	2.7%	0.0%	0.0%	17.0%	2.7%	0.0%	0.0%	0.0%	0.0%			0.0%	0.0%	0.0%	0.8%		0.0%	0.7%
10.000		0.0%	0.0%	0.4%	0.3%	0.9%	50.0%	4.9%	0.0%	0.7%	0.7%	0.4%			0.4%	0.4%	0.2%	2.4%		0.7%	2.3%
< 10.000		100.0%	100.0%	56.9%	99.7%	99.1%	32.9%	92.4%	100.0%	99.3%	99.3%	99.6%			99.6%	99.6%	99.8%	96.8%		99.3%	97.0%
TCC (ppm, ppb)		0	0	0.01	0.05	1.51	0.06	0.43	0	0.98	0.34	0.78			0.28	0.02	0.23	1.64		0.21	0.25

TABLE 1-I (contd.).

UF: C3 Sampling: April/89

ULT.VOL(1)	Volume to calc (1)	F^- (ppm)	Cl^- (ppm)	NO_3^- (ppm)	SO_4^{2-} (ppm)	Al (ppb)	Th (ppb)	U (ppb)	Li (ppb)	Na (ppb)	Mg (ppb)	Mn (ppb)	Cu (ppb)	Zn (ppb)	Sr (ppb)	Mo (ppb)	Ba (ppb)	La (ppb)	Pb (ppb)	Rb (ppb)	Y (ppb)
Orig (<450nm)	21.14	11.5	0.170	1.8	760	5900	0.30	2.02	13	1070	3420	20000	<0.5	3590	2800	2	49	33	0.8	103	51
100.000	0.400	11.2	0.144	2.1	761	6500	0.68	3.42	13	1230	6560	21000	1.1	4130	2980	2	58	40	0.9	123	58
10.000	0.400	11.6	0.675	1.8	746	6600	4.69	4.48	14	843	3810	21000	2.3	3450	2940	10	56	34	7.9	98	51
<10.000	19.93	11.6	0.165	5.3	750	6000	0.18	2.21	12	1190	3380	21000	0.5	3370	2910	2	57	34	1.0	97	46
% Distribution																					
100.000		0.0%			0.0%	0.2%	3.5%	1.0%	0.2%	0.1%	1.8%	0.0%		0.4%	0.0%	0.0%	0.0%	0.3%	0.0%	0.5%	0.5%
10.000		0.0%			0.0%	0.2%	31.5%	1.9%	0.3%	0.0%	0.2%	0.0%		0.0%	0.0%	7.2%	0.0%	0.0%	11.7%	0.0%	0.2%
<10.000		100.0%			100.0%	99.6%	65.1%	97.1%	99.5%	99.9%	98.0%	100.0%		99.5%	99.9%	92.8%	100.0%	99.7%	88.3%	99.5%	99.3%
TCC (ppm,ppb)		0			0.21	20.8	0.09	0.07	0.06	0.76	68.3	0		15.9	1.9	0.15	0.02	0.11	0.13	0.51	0.32

UF: C4 Sampling: April/89

ULT.VOL(1)	Volume to calc (1)	F^- (ppm)	Cl^- (ppm)	NO_3^- (ppm)	SO_4^{2-} (ppm)	Al (ppb)	Th (ppb)	U (ppb)	Li (ppb)	Na (ppb)	Mg (ppb)	Mn (ppb)	Cu (ppb)	Zn (ppb)	Sr (ppb)	Mo (ppb)	Ba (ppb)	La (ppb)	Pb (ppb)	Rb (ppb)	Y (ppb)
Orig (<450nm)	21.79	6.2	0.751	1.8	18.9	92	0.033	1.76	2.0	656	240	2050	<0.5	144	189	14	138	2	0.5	21	<0.5
100.000	0.395	6.4	0.079	1.5	20.3	133	0.91	4.82	2.0	753	223	1900	7	158	198	14	102	17	5.7	23	2
10.000	0.360	6.2	0.116	2.6	23.2	382	1.08	11.5	2.3	848	250	1990	6	233	208	20	114	75	3.2	25	9
<10.000	20.76	6.2	0.289	0.87	20.0	139	0.31	3.89	2.0	639	185	2350	4	140	179	12	98	6	4.2	21	1
% Distribution																					
100.000		0.1%		1.3%	0.0%	0.0%	3.3%	0.4%	0.0%	0.3%	0.4%		1.3%	0.2%	0.2%	0.3%	0.1%	2.7%		0.2%	1.6%
10.000		0.0%		3.2%	0.3%	2.8%	3.9%	3.2%	0.3%	0.5%	0.6%		0.8%	1.1%	0.3%	1.1%	0.3%	15.7%		0.3%	11.6%
<10.000		99.9%		95.6%	99.7%	97.2%	92.8%	96.4%	99.7%	99.1%	99.0%		97.8%	98.7%	99.5%	98.6%	99.7%	81.6%		99.5%	86.8%
TCC (ppm,ppb)		0.004		0.04	0.06	4.0	0.02	0.14	0.00	5.52	1.8		0.1	1.9	0.8	0.17	0.34	1.34		0.10	0.15

TABLE 1-I (contd.).

UF: SW-03		Sampling: April/89																			
ULT.VOL(1)	Volume to calc (1)	F^- (ppm)	Cl^- (ppm)	NO_3^- (ppm)	SO_4^{2-} (ppm)	Al (ppb)	Th (ppb)	U (ppb)	Li (ppb)	Na (ppb)	Mg (ppb)	Mn (ppb)	Cu (ppb)	Zn (ppb)	Sr (ppb)	Mo (ppb)	Ba (ppb)	La (ppb)	Pb (ppb)	Rb (ppb)	Y (ppb)
Orig (<450nm)	20.68	24.4	0.212	4.8	909	67000	241	12200	14	917	7400	24000	5	8660	2490	<5	65	53000	1120	127	13000
100.000	0.400	15.5	0.478	6.1	922	83000	234	12300	14	923	7360	29000	7	8990	2520	<5	65	60000	1140	128	15000
10.000	0.400	15.7	0.457	4.6	934	81000	245	12900	14	875	7120	27000	7	8410	2460	<5	70	61000	1170	117	15000
<10.000	19.39	15.7	0.423	4.0	924	71000	221	11700	15	897	7180	25000	7	8420	2450	<5	61	56000	1090	127	14000
% Distribution																					
100.000		0.0%	0.3%	1.0%	0.0%	0.3%	0.1%	0.1%	0.0%	0.1%	0.05%	0.24%	0.0%	0.1%	0.1%		0.1%	0.1%	0.1%	0.02%	0.1%
10.000		0.0%	0.2%	0.3%	0.02%	0.3%	0.2%	0.2%	0.0%	0.0%	0.0%	0.2%	0.0%	0.0%	0.0%		0.3%	0.2%	0.1%	0.0 %	0.1%
<10.000		100.0%	99.6%	98.7%	100.0%	99.4%	99.7%	99.7%	100.0%	99.9%	100.0%	99.6%	100.0%	99.9%	99.9%		99.6%	99.7%	39.8%	100.0 %	99.7%
TCC (ppm, ppb)		0	0.002	0.052	0.19	426	0.72	35	0	0.50	3.5	96.7	0	11.0	1.5		0.25	174	2.5	0.02	38.7

TABLE 1-II

Elemental concentrations/activities and distribution characteristics in colloidal concentrates (C1,C2,C3) and ultrafiltrates (< C3) of subsurface and ground waters from Morro do Ferro (C1: 450 nm > MWCL > 100,000 dalton (resp. 300,000 for sample GA-2); C2: 100,000 > MWCL > 10,000 dalton; C3: 10,000 > MWCL > 1,000 dalton; C3: < 1,000 dalton; orig. = concentration in the prefiltered water; TCC = total colloid concentration of an element.)

UF: MF10-A	Sampling: 25/1/88									PRINCIPAL ELEMENTS:						
ULT.VOL(1) 37.30	Volume to calc (1)	DOC (ppm)	U-fluor (ppb)	^{238}U (ppb)	^{234}U (Bq/l)	^{232}Th (ppb)	Ce (ppb)	^{234}U/^{238}U	^{228}Th/^{232}Th	Si (ppm)	Fe (ppm)	Mn (ppm)	Ca (ppm)	Mg (ppm)	K (ppm)	Ba (ppm)
Orig	36.93	3.8	0.27	0.28	0.0041	0.013	0.34	1.2	137	0.43		0.70	2.38	0.063	9.0	
C1	0.647	3.9	1.8	2.6	0.046	0.62	5.26	1.4	9.5	0.65	0.4	0.65	2.87	0.089	10.6	
C2	0.590	4.4	1.4	2.1	0.052	0.71	5.27	2.0	9	0.65	0.5	0.80	3.63	0.099	11.8	
C3	0.650	17	2.4	2.5	0.038	0.69	6.10	1.2	34	3.70	0.6	1.44	7.33	0.200	19.9	
<C3	34.04	3.7	0.29	0.41	0.0052	0.023	0.34	1.0	37	0.60	0.1	0.61	2.84	0.094	9.0	
% Distribution																
C1		0.1%	7.1%	7.6%	10.0%	18.8%	14.4%			0.1%	2.6%	0.1%	0.0%	0.0%	0.3%	
C2		0.3%	4.7%	5.3%	10.5%	19.8%	13.2%			0.1%	3.7%	0.5%	0.4%	0.1%	0.5%	
C3		6.1%	10.2%	7.3%	8.2%	21.1%	17.0%			8.5%	5.2%	2.4%	2.8%	2.0%	2.1%	
<C3		93.5%	78.8%	79.0%	71.3%	40.3%	55.4%			91.2%	88.4%	97.0%	96.8%	97.9%	97.1%	
TCC (ppb,ppm,Bq/l)			0.25	0.059	0.057	0.001	0.008	0.152			0.038	0.018	0.021	0.077	0.0013	0.26

UF: MF10-B	Sampling: 16/02/87									PRINCIPAL ELEMENTS:						
ULT.VOL(1) 22.18	Volume to calc (1)	DOC (ppm)	U-fluor (ppb)	^{238}U (ppb)	^{234}U (Bq/l)	^{232}Th r(ppb)	Ce (ppb)	^{234}U/^{238}U	^{228}Th/^{232}Th	Si (ppm)	Fe (ppm)	Mn (ppm)	Ca (ppm)	Mg (ppm)	K (ppm)	Ba (ppm)
Orig	22.12	2.5	0.49	0.56	0.0099	0.036		1.4	160	0.41	0.65	0.34	0.04	<0.003	0.18	0.004
C1	0.368	2.9	2.1	3.2	0.062	0.36		1.5	35	0.55	1.29	0.30	0.12	0.012	0.20	0.004
C2	0.383	3.0	3.7	4.5	0.078	0.29		1.4	43	0.66	1.11	0.32	0.18	0.012	0.23	0.006
C3	0.415	9.4	3.8	4.3	0.084	0.24		1.6	135	2.99	5.78	0.79	1.71	0.079	0.41	0.018
<C3	20.95	2.3	0.11	0.13	0.0025	0.023		1.5	129	1.28	0.23	0.26	0.19	<0.003	0.20	0.004
% Distribution																
C1		0.4%	12.1%	15.2%	15.6%	15.0%				0.0%	4.8%	0.2%	0.0%		0.0%	0.0%
C2		0.5%	22.6%	22.6%	20.7%	12.4%				0.0%	4.2%	0.4%	0.0%		0.3%	0.8%
C3		5.4%	25.2%	23.4%	24.2%	10.9%				2.4%	28.4%	3.7%	13.1%		1.9%	6.1%
<C3		93.7%	40.1%	38.8%	39.5%	61.7%				97.6%	62.7%	95.7%	86.9%		97.8%	93.1%
TCC (ppb,ppm,Bq/l)		0.16	0.16	0.21	0.004	0.014				0.032	0.14	0.012	0.029		0.004	0.0003

TABLE 1-II (contd.).

UF: MF12-A		Sampling: 18/1/88								PRINCIPAL ELEMENTS:						
ULT.VOL(1) 38.71	Volume to calc (1)	DOC (ppm)	U-fluor (ppb)	^{238}U (ppb)	^{234}U (Bq/l)	^{232}Th (ppb)	Ce (ppb)	^{234}U/ ^{238}U	^{228}Th/ ^{232}Th	Si (ppm)	Fe (ppm)	Mn (ppm)	Ca (ppm)	Mg (ppm)	K (ppm)	Ba (ppm)
Orig	38.46	3.7				0.024	13.7		44	16.9	0.2	1.66	7.89	0.71	10.0	
C1	0.420	3.5	3.0	3.2	0.058	1.36	8.5	1.5	13	17.2	0.2	1.66	8.16	0.67	11.4	
C2	0.600	4.5	3.7	3.8	0.072	1.19	13.3	1.5	34	17.4	0.4	1.93	10.30	0.83	18.2	
C3	0.655	13	7.4	8.2	0.154	0.73	13.9	1.5	20	21.4	2.0	3.08	17.40	1.24	20.3	
<C3	35.79	3.5	1.5	1.46	0.025	0.029	0.44	1.4	57	16.5	0.1	1.51	7.44	0.50	10.0	
% Distribution																
C1		0.0%	1.0%	1.2%	1.3%	20.0%	9.3%			0.0%	0.6%	0.1%	0.1%	0.4%	0.2%	
C2		0.4%	2.1%	2.3%	2.5%	24.9%	21.2%			0.1%	2.6%	0.6%	0.6%	1.0%	1.3%	
C3		4.5%	6.2%	7.2%	8.0%	16.4%	24.2%			0.5%	18.0%	1.8%	2.3%	2.5%	1.7%	
<C3		95.1%	90.7%	89.3%	88.1%	38.8%	45.3%			99.4%	78.8%	97.7%	97.0%	96.1%	96.8%	
TCC (ppb,ppm,Bq/l)		0.18	0.15	0.17	0.003	0.015	7.50			0.11	0.040	0.039	0.23	0.027	0.32	

UF: MF12-B		Sampling: 12/10/88								PRINCIPAL ELEMENTS:						
ULT.VOL(1) 23.69	Volume to calc (1)	DOC (ppm)	U-fluor (ppb)	^{238}U (ppb)	^{234}U (Bq/l)	^{232}Th (ppb)	Ce (ppb)	^{234}U/ ^{238}U	^{228}Th/ ^{232}Th	Si (ppm)	Fe (ppm)	Mn (ppm)	Ca (ppm)	Mg (ppm)	K (ppm)	Ba (ppm)
Orig	23.20	3.3	0.76	0.80	0.017	0.035		1.8	52	15.9	0.95	1.35	6.67	0.47	8.9	0.001
C1	0.378	4.2	5.3	5.1	0.111	0.30		1.8	92	17.1	10.0	1.44	6.93	0.49	9.9	0.022
C2	0.393	2.7	4.7	7.5	0.147	0.50		1.6	72	17.0	6.91	1.55	7.65	0.52	10.7	0.003
C3	0.388	5.7	4.4	4.8	0.097	0.37		1.6	118	22.6	7.26	2.77	14.5	0.96	15.3	0.012
<C3	22.04	3.0	0.59	0.62	0.014	0.022		1.8	129	16.4	<0.1	1.38	6.91	0.48	9.4	0.003
% Distribution																
C1		0.6%	9.6%	8.3%	8.2%	11.2%				0.1%		0.1%	0.0%	0.0%	0.1%	8.9%
C2		0.0%	8.7%	13.3%	11.7%	20.0%				0.1%		0.2%	0.2%	0.1%	0.2%	0.0%
C3		1.5%	8.0%	7.9%	7.2%	14.4%				0.6%		1.7%	1.8%	1.6%	1.0%	4.4%
<C3		97.9%	73.7%	70.5%	72.8%	54.4%				99.2%		98.1%	98.0%	98.2%	98.6%	86.7%
TCC (ppb,ppm,Bq/l)		0.065	0.21	0.26	0.005	0.018				0.13		0.027	0.14	0.009	0.13	0.0005

TABLE 1-II (contd.).

UF: MF10 Sampling: 6/4/89

ULT.VOL(1)	Volume to calc (1)	F^- (ppm)	Cl^- (ppm)	NO_3^- (ppm)	SO_4^{2-} (ppm)	Al (ppb)	Th (ppb)	U (ppb)	Li (ppb)	Na (ppb)	Mg (ppb	Mn (ppb)	Cu (ppb)	Zn (ppb)	Sr (ppb)	Mo (ppb)	Ba (ppb)	La (ppb)	Pb (ppb)	Rb (ppb)	Y (ppb)
Orig (<450 nm)	22.65	0.061	0.461	0.614	0.115	6.5	0.03	0.29	0.3	46	26	5	2.6	9	1	<0.5	1.5	12	1.3	<0.5	<0.5
100.000	0.375	0.099	0.502	0.515	0.215																
10.000	0.405	0.114	0.591	0.154	0.670	97	0.30	3.18	0.5	124	1250	150	8.0	91	12	<0.5	8.6	126	16	1.0	6.0
<10.000	21.54	0.084	0.661	0.393	0.105	2.8	0.009	0.28	0.4	47	82	131	1.0	76	3	<0.5	4.8	27	0.6	0.5	0.8
% Distribution																					
100.000		0.3%	0.0%	0.5%	1.6%																
10.000		0.6%	0.0%	0.0%	8.8%																
<10.000		99.1%	100.0%	99.5%	89.7%																
TCC (ppm, ppb)		0.001		0.002	0.012																

UF: MF11 Sampling: 6/4/89

ULT.VOL(1)	Volume to calc (1)	F^- (ppm)	Cl^- (ppm)	NO_3^- (ppm)	SO_4^{2-} (ppm)	Al (ppb)	Th (ppb)	U (ppb)	Li (ppb)	Na (ppb)	Mg (ppb)	Mn (ppb)	Cu (ppb)	Zn (ppb)	Sr (ppb)	Mo (ppb)	Ba (ppb)	La (ppb)	Pb (ppb)	Rb (ppb)	Y (ppb)
Orig (<450 nm)	21.08	0.049	0.311	0.108	0.209	2.3	0.003	0.61	0.3	57	29	34	4.2	50	1.0	<0.5	2.8	4.0	2.3	<0.5	
100.000	0.395	0.083	0.490	0.080	0.308	6.9	0.052	2.78	0.3	66	23	32	6.4	49	1.5	<0.5	2.6	24	3.1	<0.5	
10.000	0.400	0.068	0.370	0.046	0.522	13	0.079	2.84	0.4	104	37	46	12	70	2.3	<0.5	3.5	26	3.6	0.5	
<10.000	19.93	0.062	0.238	0.140	0.192	2.4	0.013	0.33	0.3	73	135	29	2.9	44	2.0	<0.5	2.4	1.6	1.6	<0.5	
% Distribution																					
100.000		0.6%	2.0%		1.1%	3.2%	4.9%	11.0%	0.0%			0.2%	2.1%	0.2%			0.2%	17.1%	1.7%		
10.000		0.2%	1.0%		3.2%	7.6%	8.5%	11.4%	0.6%			1.1%	5.6%	1.1%			0.9%	18.9%	2.3%		
<10.000		99.2%	97.0%		9.57%	89.2%	86.6%	77.6%	99.4%			98.7%	92.3%	98.7%			99.0%	64.1%	96.0%		
TCC (ppm, ppb)		0.001	0.007		0.008	0.285	0.002	0.094	0.002			0.38	0.238	0.587			0.025	0.88	0.066		

TABLE 1-II (contd.).

UF: MF12		Sampling: 9/4/89																			
ULT.VOL(1)	Volume to calc (1)	F^- (ppm)	Cl^- (ppm)	NO_3^- (ppm)	SO_4^{2-} (ppm)	Al (ppb)	Th (ppb)	U (ppb)	Li (ppb)	Na (ppb)	Mg (ppb)	Mn (ppb)	Cu (ppb)	Zn (ppb)	Sr (ppb)	Mo (ppb)	Ba (ppb)	La (ppb)	Pb (ppb)	Rb (ppb)	Y (ppb)
Orig (<450 nm)	21.17	5.0	1.9	0.533	9.0	134	0.029	1.15	0.6	325	499	495	0.5	826	126	0.7	1.9	1.2	0.7	16	<0.5
100.000	0.395	4.9	3.0	0.179	8.9	175	1.14	4.94	0.9	371	632	547	4.5	955	138	1.0	3.0	12	8.3	18	1.1
10.000	0.400	8.4	1.4	1.2	12.8	232	0.53	4.38	0.9	436	1540	651	8	1100	173	1.2	4.9	13	9.9	23	2.0
<10.000	19.87	4.9	1.7	0.139	8.8	111	0.011	0.98	0.7	245	179	465	<0.5	746	117	0.8	2.2	0.8	0.6	15	<0.5
% Distribution																					
100.000		0.0%	1.4%	0.5%	0.0%	1.1%	50.6%	6.7%	0.5%	1.0%	4.0%	0.3%		0.5%	0.3%	0.5%	0.7%	15.7%	15.9%	0.4%	
10.000		1.4%	0.0%	12.8%	0.9%	2.0%	23.6%	5.9%	0.5%	1.5%	12.3%	0.8%		0.9%	0.9%	1.0%	2.3%	25.8%	19.4%	1.0%	
<10.000		98.6%	98.6%	86.7%	99.1%	96.9%	25.8%	87.4%	98.9%	97.6%	83.6%	98.9%		98.6%	98.7%	98.6%	97.0%	58.5%	54.7%	98.6%	
TCC (ppm, ppb)		0.07	0.024	0.021	0.08	3.48	0.03	0.14	0.01	5.96	34.17	5.04		10.59	1.45	0.01	0.07	0.55	0.32	0.21	

UF: MF13		Sampling: 9/4/89																			
ULT.VOL(1)	Volume to calc (1)	F^- (ppm)	Cl^- (ppm)	NO_3^- (ppm)	SO_4^{2-} (ppm)	Al (ppb)	Th (ppb)	U (ppb)	Li (ppb)	Na (ppb)	Mg (ppb)	Mn (ppb)	Cu (ppb)	Zn (ppb)	Sr (ppb)	Mo (ppb)	Ba (ppb)	La (ppb)	Pb (ppb)	Rb (ppb)	Y (ppb)
Orig (<450 nm)	22.96	0.073	0.226	0.076	0.122	2.0	0.018	0.47	0.4	34	57	144	1.2	87	3	<0.5	3.9	40	0.9	0.7	1.9
100.000	0.380	0.057	0.605	0.426	0.230	17	0.23	1.76	0.4	598	49	5	3.6	10	1	<0.5	1.7	34	2.5	<0.5	1.1
10.000	0.400	0.069	36	1.6	0.314	19	0.092	1.41	0.6	80	247	5	4.1	9	3	<0.5	1.9	15	1.6	<0.5	0.6
<10.000	21.81	0.052	0.672	0.829	0.113	7.7	0.009	0.35	0.5	89	298	6	2.4	7	2	<0.5	1.8	8	1.4	<0.5	<0.5
% Distribution																					
100.000		0.2%		0.0%	1.7%	1.9%	26.2%	6.0%					0.8%	0.7%				5.1%	1.3%		
10.000		0.6%		1.6%	3.0%	2.5%	10.4%	4.8%					1.2%	0.5%				1.4%	0.2%		
<10.000		99.3%		98.4%	95.3%	95.6%	63.4%	89.2%					97.9%	98.8%				93.4%	98.4%		
TCC (ppm, ppb)		0.0004		0.0134	0.01	0.35	0.01	0.04					0.05	0.08				0.55	0.02		

TABLE 1-II (contd.).

UF: GA2 gallery-MF	Sampling: Oct./82									PRINCIPAL ELEMENTS:						
ULT.VOL(1) 11.00	Volume to calc (1)	DOC (ppm)	U-fluor (ppb)	^{238}U (ppb)	^{234}U (Bq/l)	^{232}Th (ppb)	Ce (ppb)	^{234}U/^{238}U	^{228}Th/^{232}Th	Si (ppm)	Fe (ppm)	Mn (ppm)	Ca (ppm)	Mg (ppm)	K (ppm)	Ba (ppm)
Orig	10.95	13				14	7.14		32		3.2	0.034	1.75	0.051	0.55	0.004
C1	0.295	111				261	115		30		2.35	0.072	7.35	0.32	0.19	0.029
C2	0.310	201				205	76.8		27		1.46	0.23	12.1	0.5	0.25	0.019
C3	0.145	163				0	62.8				1.37	0.21	11.5	0.75	0.52	0.012
<C3	10.20	11				0.38	0.71		78		0.031	0.023	1.73	0.079	0.66	<0.002
% Distribution																
C1		12.8%				53.2%	45.5%				41.2%	4.0%	6.6%	6.1%	0.0%	
C2		25.5%				43.9%	31.8%				26.7%	17.9%	12.7%	11.2%	0.0%	
C3		9.5%				0.0%	12.2%				11.7%	7.6%	5.6%	845%	0.0%	
<C3		52.2%				2.9%	10.5%				20.4%	70.4%	75.1%	74.3%	100.0%	
TCC (ppb,ppm,Bq/l)		6.2				13.6	6.4				2.55	0.010	0.44	0.013	0	

UF: MF-06 (28.62 m)	Sampling: Dec./86									PRINCIPAL ELEMENTS:						
ULT.VOL(1) ?	Volume to calc (1)	DOC (ppm)	U-fluor (ppb)	^{238}U (ppb)	^{234}U (Bq/l)	^{232}Th (ppb)	Ce (ppb)	^{234}U/^{238}U	^{228}Th/^{232}Th	Si (ppm)	Fe (ppm)	Mn (ppm)	Ca (ppm)	Mg (ppm)	K (ppm)	Ba (ppm)
Orig	33.36	1.3	1.6			0.13	5.5		320	0.12	0.06		0.16	0.03	0.60	0.007
C1	0.290	2.3				2.13	507		104			0.046	0.77	0.076	1.06	
C2	0.265	2.9				4.12	10.7		68			0.056	0.48	<0.2	1.66	
C3	0.418	5.7				12.6	16.6		39			0.090	2.27	0.08	1.20	
<C3	31.45	1.2	0.3			1.25	1.21		34	1	0.05	0.055	0.88	0.03	0.31	0.002
% Distribution																
C1		0.8%				0.6%	75.3%					0.0%	0.0%		2.0%	
C2		1.1%				1.6%	1.3%					0.0%	0.0%		3.2%	
C3		4.5%				10.2%	3.3%					0.8%	2.0%		3.4%	
<C3		93.6%				87.6%	20.1%					99.2%	98.0%		91.4%	
TCC (ppb,ppm,Bq/l)		0.083				0.016	4.4					0.0004	0.003		0.052	

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[1]Starprog AB
[2]SKB AB
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Lars Lovius[1], Sven Norman[1], Nils Kjellbert[2]
[1]Starprog AB
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University of Gothenburg, Department of General and Marine Microbiology, Gothenburg
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Lars Werme[1], Patrik Sellin[1], Roy Forsyth[2]
[1]Swedish Nuclear Fuel and waste Management Co (SKB)
[2]Studsvik Nuclear
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Ulla Bergström, Sture Nordlinder
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H. D. Schorscher[1], M. E. Shea[2]
[1]University of Sao Paulo
[2]Battelle, Chicago
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[1]University of Bern
[2]University of Sao Paulo
[3]Scottish Universities Research & Reactor Centre (SURRC), Glasgow
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[1]British Geological Survey, Keyworth
[2]INTERRA/ECL, Leicestershire, UK
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D. K. Nordstrom[1], J. A. T. Smellie[2], M. Wolf[3]
[1]US Geological Survey, Menlo Park
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A. B. MacKenzie[1], P. Linsalata[2], N. Miekeley[3],
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C-L Porto da Silveira[1], P. Linsalata[2], J. N. Andrews[3],
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December 1990