

Merril Eisenbud
711 Bayberry Drive
Chapel Hill, N.C. 27514
FAX/TEL 919-967-4561

July 24 1992

Mr. C. Rick Jones, Director
Office of Health Physics and
Ind.Hyg.Programs
U.S.D.O.E. EH-41
Washington D.C. 20585

Dear Rick:

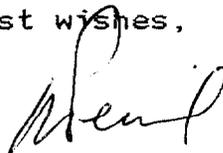
I am glad you suggested that we meet to discuss the Palomares program and its possible relationship to the DOE defence at Rocky Flats. I think we all now have a better understanding of the matter.

We will wait for you or your associates to provide advice on the next steps that should be taken. If the progress report is sent to you before the visit of the Spanish investigators, we would of course like to have a copy of it. If they bring it at the time of their visit, we will rely on your judgement as to how we can best interface with them.

Enclosed is a reprint that summarizes the work we did in Brazil on natural analogues for the transuranic analogues. Our conclusions agreed with what they found at OKLO, they just stay put!

My thanks to you and your associates for taking the time to see us.

With best wishes,



cc: F.Ward Whicker
Walter Lancaster

Natural Analogues for the Transuranic Actinide Elements: An Investigation in Minas Gerais, Brazil

MERRIL EISENBUD

Department of Environmental Medicine
New York University Medical Center
Long Meadow Road
Tuxedo, New York 10987

KONRAD KRAUSKOPF

Stanford University
Stanford, California 94305

EDUARDO PENNA FRANCA

Federal University of Rio de Janeiro
Rio de Janeiro, Brazil

WAYNE LEI, ROBERT BALLAD, PAUL LINSALATA

Department of Environmental Medicine
New York University Medical Center
Long Meadow Road
Tuxedo, New York 10987

and

KENKICHI FUJIMORI

University of São Paulo
São Paulo, Brazil

ABSTRACT / A highly weathered deposit of thorium and rare earth elements located near the summit of a hill in the state of Minas Gerais, Brazil, is being studied as an analogue for a radioactive waste repository that sometime in the distant future may be eroded to the surface or intruded by groundwater. Thorium serves as an analogue for Pu^{4+} , and La^{3+} as an analogue for Cm^{3+} and Am^{3+} . The mobilization rate constants of the analogue elements by groundwater are so slow (of the order of 10^{-9} per year) as to suggest that essentially complete radioactive decay of the transuranic actinides would occur in place even under the relatively unfavorable conditions that exist at a site such as this.

Introduction

An urgent question associated with management of the nuclear fuel cycle is how ancient residues of actinide elements would behave if a nuclear waste repository should be exposed by erosion or be intruded by groundwater. A substantial literature has accumulated concerning the behavior of the transuranic actinide elements in the environment (Watters and others 1980), but most of the research until now has been concerned with fallout from nuclear weapons tests or with contamination in the environs of major atomic energy production plants (IAEA 1976; Hanson 1980; Wrenn 1981). Such studies, useful as they are, leave some questions unanswered because the contaminants have chemical and physical forms different from those that would exist in a nuclear waste repository. Moreover, the fact that these artificial elements were first produced only 40 years ago makes it impossible to consider the effects of geochemical processes over the necessary span of time.

The system of radioactive waste management that is currently most favored involves converting the waste into an insoluble form such as borosilicate glass, packaging the solidified waste in corrosion-resistant canisters, and placing the waste package in deep underground mined cavities, where the wastes must remain isolated from the biosphere long enough to allow decay of most of the radionuclides (NRC 1983). However, many of the nuclides have such long half-lives (i.e., about 25,000 years for ^{239}Pu) that the repository might be breached

by groundwater or, in extreme cases, might erode to the surface, before the radionuclides have decayed sufficiently. The potential risks to the public health in the event of such failures would be determined to a considerable extent by the rates of mobilization, movement in groundwater, and uptake by biota of the transuranic actinide elements, plutonium, americium, curium, and neptunium.

To test whether construction of a proposed repository would entail undue risk to public safety, transport models have been developed that predict the dose to humans in the event of repository failure under a variety of hypothetical circumstances (Denham and others 1973). The dose estimates predicted by those models are subject to uncertainties that may span several orders of magnitude.

Naturally occurring elements that have properties similar to those of the transuranic actinide elements offer a possible means of constructing transport models that are more reliable than those now in use. Two conditions must be satisfied to make such models useful. First, the chemical elements in nature must be shown to be valid analogues for the elements of concern. Second, enough must be known about the chemical and physical forms in which the analogue elements occur, and the geochemical processes involved in their mobilization and transport by environmental processes, to ensure that the information obtained is applicable to proposed repository sites.

An unusually favorable site for such studies exists at the Morro do Ferro (MF) in the state of Minas Gerais, Brazil,

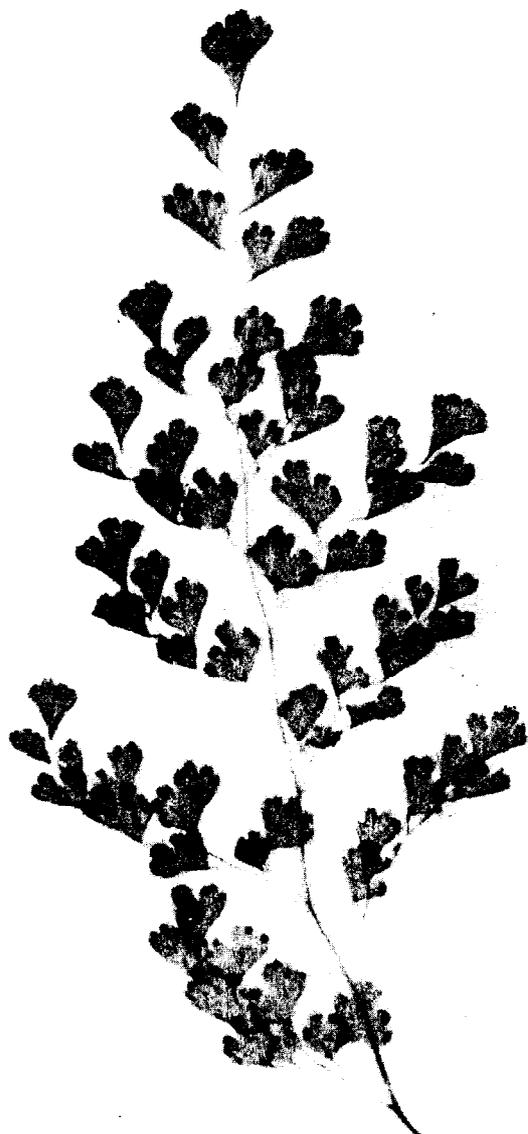


Figure 1. Autoradiograph of a fern, *Adiantum lorentzii*, Hiern, growing on the Morro do Ferro. The radioactivity is due to the uptake of ^{228}Ra , a nuclide in the ^{232}Th decay chain.

where an ore body is located that is rich in Th and rare earth elements (REE) that can be studied as analogues for three transuranic actinide elements. Th is analogous in its behavior to Pu^{4+} , the oxidation state in which Pu exists under many environmental conditions. Nd^{3+} or La^{3+} can serve as an analogue for both Am^{3+} and Cm^{3+} .

General Features of the Morro do Ferro

The MF is a hill near the center of the Poços de Caldas plateau about 300 kilometers north of the city of São Paulo.

The ore body, chiefly confined to the south face of the hill, was discovered in the early 1950s. Estimates of the Th, U, and REE content of the ore body were made independently by Wedow (1967) and Frayha (1962), based on analyses of cores. Some of these cores, the spoils from nine wells recently drilled, and a new core that has been drilled through the ore body to a depth of 450 m, are currently being analyzed, using the more advanced methods now available. As an interim working estimate of the Th content, we use a value of 30,000 tonnes, based on the estimate made by Frayha, whose studies included samples from greater depths than were available to Wedow.

The ambient gamma radiation levels near the summit of the hill range from 1 to 3 mR/hr (100 to 300 times normal) over an area of about 30,000 m^2 (Cullen 1977). The plants on the MF are so radioactive (because of absorption of ^{228}Ra from soil) that they can be autoradiographed (Fig. 1), and the exposure of indigenous burrowing rodents to thoron decay products is estimated to result in an average dose to the basal cells of rat bronchial epithelium of about 3,000 rem per year (Drew and Eisenbud 1966).

The Poços de Caldas plateau, which is roughly circular and about 35 km in diameter, is believed to be a deeply eroded caldera. The MF is near the center of the plateau, rising 140 m above its immediate surroundings. The geology of the area has been described by Wedow (1967), Frayha (1962), Almeida (1977), Ellert (1959), and Bushee (1971). Age determinations by Bushee show that intrusion of molten rock took place over a long period: phonolites and tinguaite give ages between 75 and 87 million years, and foyaite 63 to 64 million years. Thus, the body of alkalic igneous rocks was built up by piecemeal additions over some 20 million years toward the end of the Cretaceous Period. The caldera must have formed later by collapse of the intruded rocks.

The underlying rock of MF shows extensive alteration, due in part to weathering and in part to hydrothermal activity. Material fresh enough for identification is tinguaite (fine-grained nepheline syenite), partly massive and partly brecciated. The only rock outcrops at the MF are magnetite, which occurs as a set of subparallel dikes up to a few meters in thickness on the south face of the hill.

The Th and REE are widespread in the surface material and are especially concentrated near some of the dike contacts. However, the Th-rich material is apparently not directly related to the magnetite. From the studies of Frayha and our recent examination of the gamma ray log of the 450-m drill hole, we conclude that abnormal concentrations of Th exist to depths of nearly 200 m. The reason for the concentration of Th and REE at this one site is a mystery. These elements commonly show slight enrichment in alkalic rocks, but the large concentrations at MF are extraordinary.

Wedow (1967) reported that bastnaesite, thoregummitte,

Table 1. Logarithms of formation constants for thorium and plutonium complexes. Ionic strength 0 except when indicated otherwise in parentheses. (See text for explanation and references.)

Complexing Agent:	F ⁻	SO ₄ ²⁻ (k ₁)	SO ₄ ²⁻ (k ₂)	HPO ₄ ²⁻ (k ₁)	HPO ₄ ²⁻ (k ₂)	C ₆ H ₅ O ₇ ³⁻	EDTA
Pu ⁴⁺	8 ± 1	6 ± 1	10 ± 3	13 ± 1	24 ± 1	15.0 (0.5)	25.7 (0.5)
Th ⁴⁺	8.0	5.4	9.7	10.8 (0.3)	22.8 (0.3)	13.0 (0.5)	25.3 (0.1)

and cerianite were present, but only as secondary minerals associated with magnetite outcrops. In our previously reported study (Eisenbud and others 1982) of thin sections of some of the deeper cores, zircon, monazite, and cheralite, a rare monazite-like mineral, were found to be present in micron-size crystals. However, this information came from cores that were drilled by wet methods about 30 years ago. It now appears that only a minor fraction of these elements is contained in these highly insoluble minerals, and that most of the thorium is associated with claylike material that was washed away in the process of wet drilling. Samples of rich ore had, therefore, not previously been available for mineralogical study. Nine wells were recently drilled dry, and a study of the spoils, which contain ample rich ore, has shown that most of the Th (and presumably the REE) is present on the surfaces of clay and oxide minerals.

The rainfall on the Poços de Caldas plateau averages 170 cm/yr, about 80% of it occurring during a four-month rainy season. The groundwater level is a subdued replica of the surface topography, with recharge from precipitation and discharge into a network of seepages at or near the stream level. The highest point of the water table during the 1981-82 rainy season was about 75 m below the surface of the ridge, or about 75 m above the base of the hill. During the 1981-82 rainy season, in which the rainfall was close to average, the groundwater level in the vicinity of the ore body fluctuated by about 2 m.

Groundwater flow is uniform through much of the deeply weathered ore body, except that near the magnetite dikes it may be controlled by fractures. Permeability measurements in and near the ore body give hydraulic conductivities generally in the range of 10⁻⁴ to 10⁻⁵ cm/sec and average groundwater velocities of 1 cm/day (IPT 1982).

Appropriateness of the Selected Analogues

Thorium as an Analogue for Plutonium

The chemical similarity between Pu⁴⁺ and Th⁴⁺ has been noted by others (Bondietti and Tamura 1980). The outstanding difference between the two elements is that Pu may exist in

several oxidation states, whereas Th is restricted to the 4+ valence.

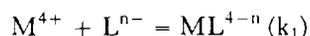
It is to be expected that Pu compounds would exhibit greater solubility than Th compounds under extreme oxidizing or reducing conditions, but that in the moderate range of Eh and pH that characterizes most natural environments, especially those that would be acceptable for a repository, the behavior would be similar. It is difficult to evaluate the degree of similarity in detail because thermodynamic data for the two elements are incomplete and in some cases of uncertain validity.

The two elements in solution should be limited by the solubility of the oxides ThO₂ and PuO₂ in the absence of complexing agents other than OH⁻. The principal Th hydroxy complex at pH levels over 5 is the neutral Th(OH)₄, and, between 3 and 5, Th(OH)₂²⁺ (Langmuir and Herman 1980). The equilibrium concentrations for crystalline ThO₂ in contact with pure water are 10⁻¹⁴ M at pH levels over 4.5 and rising to only about 10⁻¹⁰ M at a pH as low as 3. These concentrations can be as much as five orders of magnitude higher in equilibrium with amorphous oxide, or if complexes are formed with such ions as F⁻, SO₄²⁻, HPO₄²⁻, or organic compounds. Thus, the theoretical concentrations of Th in dilute natural solutions (pH range 4-9) should normally be below 10⁻⁹ M (about 0.2 µg/liter), but in some circumstances can be well above this figure. Actual measured concentrations may differ widely from the theoretical equilibrium values not only because of complexing but also because of slow rates of solution and the presence of colloids.

The situation is more complicated for Pu because of oxidation-reduction reactions, but recent estimates of the solubility of crystalline and amorphous PuO₂ (Eisenbud and others 1982, based on Allard and others 1980; Rai and others 1980a; Rai and others 1980b; Jakubick 1979; Jensen 1980) show that under most Eh-pH conditions to be expected in nature the solubilities are closely similar to those for Th. Only under extremely oxidizing alkaline conditions or extremely reducing acid conditions, such as are not likely in a repository environment, would Pu be markedly more soluble.

Solubilities calculated from thermochemical data for the oxides in pure water have only limited applicability to natural environments because of the frequent presence of complexing

agents besides OH^- . The relative stabilities of complexes formed with commonly occurring ligands are an important consideration when judging the chemical similarities of Th^{4+} and Pu^{4+} . Available data are far from satisfactory, but recent compilations (Langmuir and Herman 1980; Cleveland 1979; Lemire and Tremaine 1980; Moskvina and Poznyakov 1979; Phillips 1982) make possible a rough comparison (Table 1). Numbers in the table are logarithms of equilibrium constants for the reactions



and



Despite the uncertain quality of some of the data, the similarity in constants for the two elements is striking. Where differences exist, they are in the direction that would be expected theoretically—slightly more stable complexes for Pu^{4+} , because its ionic radius (0.98 Å) is a little smaller than that of Th (1.07 Å). Especially notable in the table are the high values for the two organic complexes, reflecting the fact that the solubilities of both elements are markedly increased by the presence of organic materials.*

Neodymium or Lanthanum as Analogues for Curium and Americium

It was recognized early during World War II that the chemical properties of the REE would be similar to those of the transuranic actinides, and the REE were accordingly used to study the chemical properties of the then-scarce artificially produced elements (Seaborg 1958). More recently, Weimer and others (1980) have called attention to the fact that Nd should be an appropriate analogue for Am and Cm. It is to be expected that, like Nd, these actinide elements will exist in the 3+ oxidation state under environmental conditions. The ionic radii are identical for Am^{3+} and Nd^{3+} (1.05 Å), and nearly identical to Cm^{3+} (1.06 Å). Experimental evidence for the analogous behavior of these elements has been provided by

*Additional data that appeared while this paper was in press suggest that under some conditions the analogy may not be complete. Allard (1983) reported a stability constant for PuCO_3^+ that makes this ion the dominant one in equilibrium with solid PuO_2 at pH's below 8 in slightly reducing solutions with high concentrations of CO_3^{2-} ($\log \text{CO}_3^{2-}$ (molar) = 0.76 pH - 10.83, higher than the concentrations in most deep groundwater). The stability of this complex, or other carbonate complexes of Pu^{3+} , is corroborated by measurements (Cleveland and others, 1983) of relative concentrations of plutonium in different oxidation states in the very alkaline (pH 10) and carbonate-rich water of Mono Lake. Under conditions to be expected at most repository sites, however, Allard's calculated solubilities for PuO_2 remain below 10 ppb.



Figure 2. Aerial view of the Morro do Ferro and immediate environs showing the main features discussed in the text.

laboratory and field experiments. The distribution coefficient (K_d) for Nd in aqueous soil suspensions was found to be nearly identical to those for Am and Cm over a wide range of pH and contact times. Uptake factors for plants grown under laboratory conditions were also found to be similar (Weimer and others 1980).

Although similar laboratory comparisons have not been made with La, its chemical properties are known to be similar to those of Nd. We have found close correlations between the concentrations of Nd and La in various samples of soils and water from the MF environs. Because La is present in higher concentrations in the MF environs, and is more easily analyzed by the method to be described, we have chosen La as the analogue of choice for Cm and Am.

General Investigative Approach

The main objectives of our studies are: (1) to estimate the annual mobilization rate, i.e., the fraction of each substance of interest that is removed from the ore body by either erosion or solubilization; and (2) to understand the underlying hydrologic and geochemical influences that determine the mobilization rate.

Most of the drainage at the MF is down its south face into a small stream (South Stream) that rises from the southwestern edge of the hill (Fig. 2). The flow enters the stream mainly via a series of gullies that receive both surface runoff and groundwater seepage. A flume has been constructed in the location shown in Fig. 2, and instruments have been installed that

permit continuous flow measurements and water sampling at a rate proportional to stream flow. The watershed that drains through the flume has an area of only 0.5 km², and there are no impoundments. Surface runoff is thus rapid during a rainfall, and is often accompanied by intense scouring. In a typical shower, the flow in the South Stream can increase in a matter of minutes from a year-round dry weather baseflow of 0.7 m³/min (stage height 3 cm) to flows as high as 66 m³/min (stage height 50 cm). In the absence of additional rain, the flow then returns to its baseline value in less than one day. During periods of baseflow, water reaches the stream by seeping from the ground into small tributaries and thus contains thorium that has been mobilized chemically. Hence the stream water contains Th both in dissolved form and in suspended solids that were eroded during previous brief periods of surface flow. During and immediately following a rainfall, the stream water is largely the accumulation of surface runoff.

A second stream (North Stream) rises from the extreme western edge of the north face but receives less drainage from the ore body than the South Stream. Based on Th and flow volume measurements made during the 1981–82 rainy season, it is estimated that mobilization via the north face of the hill is about 25% of that via the south face.

Nine wells, the locations of which are shown in Fig. 2, have been drilled to permit study of groundwater characteristics, and a meteorological station at the summit of the hill provides a continuous record of rainfall as well as temperature and wind direction and velocity.

A complicating feature is that water passing through the flume has drained not only the MF, but also the hills that rise from the south bank of the stream (opposite hills). The concentrations of Th and REE in the soils and rocks in this portion of the small drainage basin are much less than in the MF, but are a significant addition to the material mobilized from the ore body. An attempt to correct for this contribution has been made in the following way, and is illustrated only for Th.

It is assumed that the amount of thorium mobilized in particulate form is proportional to the concentration of thorium in the surface soil and the area presented to falling rain. We estimate the average Th concentration in soil over the ore body to be 5,660 µg/g and in the remaining portion of the drainage basin to be 180 µg/g. The area of the ore body is estimated to be 6.2 × 10⁴ m². The area of the remaining portion of the drainage basin above the flume is estimated to be 5.0 × 10⁵ m². The ore body thus occupies an area that is about 11% of the area of the drainage basin above the flume. With these assumptions, we calculate that the surface of the ore body contributes 80% of the total mobilized particulate thorium.

The relative contributions of the ore body and surrounding

areas to the soluble fraction of the thorium flux were similarly estimated, assuming that the contributions would be proportional to the quantity of Th contained in the geologic media through which the groundwater passes. The ore body is estimated to have a volume of 6.2 × 10⁶ m³ at an average Th concentration of 1,900 µg/g. The volume of the drainage basin upstream of the flume, but not including the ore body, is estimated to be 1.1 × 10⁷ m³ with an average concentration of 180 µg/g. In this way, we have estimated that the ore body contributes 86% of the Th contained in the filtrate. We recognize that this is at best a coarse estimate: for example, the groundwater could be channeled in passing through the magnetite stockwork associated with the deposit, or the concentration of thorium could be solubility-limited and, therefore, independent of the higher concentration of Th in the ore body. Moreover, thorium is undoubtedly dissolved in surface runoff. However, at this stage of the investigation, we do not have sufficient information to permit more than this first approximation.

Methods of Sampling and Analysis

Because of the low concentrations of Th and REE, 20-liter samples are taken, usually in duplicate. During the past year, periodic grab samples have also been taken from the "North Stream," which drains the north slope of the hill; streams draining into the opposite bank of the South Stream; and a stream outside of the plateau, in the town of São João da Boa Vista.

pH and Eh are measured in the field before the samples are taken to a nearby laboratory where they are filtered through 0.45-µm membrane filters (Millipore). The filtrates are acidified and reduced by evaporation on hot plates from about 20 liter to 0.25 liter to facilitate shipment to New York, where they are analyzed for REE by inductively coupled plasma spectrometry (ICPS), and radiochemically for ²³²Th, ²²⁸Th, and ²³⁰Th.

The analytical procedure for Th in water samples and soils has been modified from that of Sill and others (1974; Sill and Williams 1981). In brief, the sample is dissolved in a potassium fluoride-sodium sulfate fusion. This cake is then dissolved in dilute HCl, and the Th separated by co-precipitation on BaSO₄, which is filtered and dissolved in HClO₄. The Th is purified by extraction into Aliquat-336 (General Mills), washed with 8 M HNO₃, and stripped from the Aliquat with 10 M HCl. The HCl solution is boiled to dryness, and any aliquat and other organics carried over in the extraction are wet-ashed with perchloric-nitric acid. The Th is co-precipitated on cerium fluoride from a 1 M HCl solution of the residue and mounted on a Tuffryn (Gelman) filter for alpha

Table 2. Concentrations of thorium in baseflow water samples compared with two control sites.

Locations	No. Samples	Mean Th concentrations ($\mu\text{g}/\text{l}$)			
		Filtrate ^b	Suspended solids		Total
			As reported	Normalized ^c	
South Stream	55 ^a	0.053 \pm 0.013	0.53 \pm 0.11	0.12	0.59 \pm 0.11
North Stream	14	0.027 \pm 0.006	0.26 \pm 0.03	0.11	0.29 \pm 0.04
Opposite hills	13	0.041 \pm 0.012	0.64 \pm 0.25	0.056	0.68 \pm 0.25
São João do Bôa Vista	5	0.011 \pm 0.004	0.72 \pm 0.33	0.015	0.73 \pm 0.33
Hudson River	5	0.005 \pm 0.001	0.17 \pm 0.10	0.009	0.18 \pm 0.10

^aThe South Stream samples are weekly composites, collected by continuous proportional sampler and by grab sampling. All others are grab samples.

^bDissolved Th is present chiefly in the form of complexes with fluorine and organic material.

^cSee text for normalization procedure.

spectrometry. The chemical extraction for Th is traced internally by the alpha-emitting ²²⁹Th.

The lower limit of detection of ²³²Th at the 95% confidence level is about 0.12 μg , or about 0.006 $\mu\text{g}/\text{liter}$ for a 20-liter sample.

Samples of rock, soil, and suspended solids have also been analyzed by the above procedure or, when a sufficient sample is available, by X-ray fluorescence.

Rare earths in samples of soils, rocks, and suspended solids filtered from our water sample are determined by XRF analysis (Laurer and others 1982). For samples of water and suspended solids, we have adopted the method of Crock and Lichte (1982), in which the Th and REE are separated from the matrix by calcium oxalate precipitation following lithium borate fusion. The REE are separated from Th by sequential elution from a cation exchange resin with 8 M HNO₃ and analyzed by ICPS.

Annual Thorium and Lanthanum Mobilization Rates

Thorium

Our estimates of the annual Th flux cover the period May 1981 through April 1982, during which time the rainfall was 177 cm (similar to the 30-year annual average of 170 cm). Data are available for both the suspended solids and the filtrates.

The flow in the South Stream during much of the year is constant, at 54 m³/hr. This "baseflow" accounts for about 85% of the year-round drainage via the South Stream. The results of Th analysis of samples of the baseflow are given in Table 2, together with analyses of water samples from other locations for reference.

Th carried in suspended particulates ranges between 91% and 99% of the total Th flux for all localities, with the weighted mean being 92%. The flux of particulate Th is highly depen-

dent on the concentration of total suspended solids. The suspended particulate data in Table 2 are given both as μg Th/liter and normalized as μg Th/liter per milligram of suspended solids per liter. The mean concentration of thorium in the filtrate samples varies only from 0.011 $\mu\text{g}/\text{liter}$ at São João da Bôa Vista to 0.053 $\mu\text{g}/\text{liter}$ in the South Stream.

From the data of Table 2, and our knowledge of annual dry weather flow ($4.75 \times 10^5 \text{ m}^3$), we conclude that the annual flux of Th mobilized by the baseflow, including both the North and South Streams, is 0.027 kg in soluble form and 0.26 kg in suspended particulates. We assume the filtrate component during periods of baseflow results from solubilization of Th by groundwater. Based on our estimate that the ore body contains $30 \times 10^6 \text{ kg}$ of Th, groundwater mobilization under baseflow conditions is at a rate of $0.027 / (30 \times 10^6) = 9.1 \times 10^{-10} \text{ yr}^{-1}$. Mobilization of Th in particulate form during periods of baseflow is similarly calculated to be $8.5 \times 10^{-9} \text{ yr}^{-1}$. The total mobilization during dry (baseflow) periods is thus $9.4 \times 10^{-9} \text{ yr}^{-1}$. It is reasonable to assume that much of this fraction is due to resuspension and bank wash of stream sediments.

Fifty-four samples were collected during ten periods of rainfall in the 1981-82 rainy season. The Th flux (ϕ_{Th}) in particulates was found to be highly correlated ($r = 0.9$) with stream flow (Q) according to the following equation:

$$\phi_{\text{Th}} = 5.4 Q^{2.2}$$

where: $\phi_{\text{Th}} = \text{mg Th}/\text{min}$ and $Q = \text{m}^3/\text{min}$

Twenty-five filtrates of the 54 storm samples were also analyzed, but no relationship between Th concentration and flow was evident. The mean filtrate concentration, $0.22 \pm 0.06 \mu\text{g}/\text{liter}$, was assumed to be representative of stormflow filtrates. This value is four times greater than the average concentration ($0.05 \pm 0.01 \mu\text{g}/\text{liter}$) found in the South Stream baseflow filtrates. This may be due to the presence of a greater

quantity of fine particulates ($<0.45 \mu\text{m}$) in the storm water filtrates.

The annual Th flux during periods of rainfall is estimated to be 0.015 kg in "soluble" form, and 27.2 kg as suspended solids. Not surprisingly, 99% of the annual flux of Th particulates is mobilized during periods of rainfall. Mobilization of Th in particulate form is at an annual rate of $27.2/(30 \times 10^6) = 9.1 \times 10^{-7} \text{ yr}^{-1}$. The mobilization rate of soluble Th by stormflow is $5.0 \times 10^{-10} \text{ yr}^{-1}$. The total annual mobilization rate in soluble form is thus $5.0 \times 10^{-10} + 9.1 \times 10^{-10} = 1.4 \times 10^{-9}$.

Lanthanum

There are no previously published estimates of the quantity of La in the ore body, but this can be approximated from our analysis of 101 samples obtained from the well cuttings and exploratory trenches and tunnels. The mean ratio of La to Th in the individual samples is 2.3 ± 0.4 . Applying this ratio to the quantity of Th in the ore body provides an estimate, $2.3 \times 30,000 \text{ tonnes} = 69,000 \text{ tonnes}$, of La.

We have previously estimated that there is about 4,000 tonnes of Th upstream of the flume, but outside of the ore body. The observed La/Th ratio in this region for 71 samples is 7.6 ± 0.5 , which permits an estimate of 30,400 tonnes of La in this portion of the drainage basin.

The observed La/Th ratio in 12 samples of suspended solids taken during storm flow is 2.9 ± 0.2 , similar to the ratio found in the ore body. From this, and knowing the annual Th flux, we estimate that the quantity of La mobilized in particulate form is $2.9 \times 27.2 = 78.9 \text{ kg}$. The annual mobilization rate of La in particulate form is, therefore, 0.079 tonnes per year/ $69,000 \text{ tonnes} = 11 \times 10^{-7} \text{ yr}^{-1}$, which is in close agreement to the $9.1 \times 10^{-7} \text{ yr}^{-1}$ estimated to be the mobilization rate for Th in particulate form.

No samples are available from which the rate of stormflow solubilization of La mass can be determined. However, 20 samples from the baseflow regime have been analyzed, yielding a mean of $0.28 \pm 0.03 \mu\text{g/liter}$, which gives an estimated mobilization rate by groundwater solubilization of 1.6×10^{-9} per year, which is similar to the rate for Th (9.1×10^{-10} per year).

Significance of These Findings

The mobilization rates have been estimated above for two mechanisms, surface erosion by the action of rainfall and solubilization by groundwater. Groundwater intrusion is more relevant to a geological repository, although the possibility of eventual exposure of a deep rock repository due to erosion cannot be excluded.

Table 3. Use of the Th analogue to estimate the concentration of Pu^{+4} in South Stream water.^a

A.	Mass of Th in MF ore body	= 30,000 tonnes
B.	Average concentration of Th ($<0.45 \mu\text{m}$) mobilized by groundwater	= 0.053 $\mu\text{g/l}$
C.	Expected accumulation of ^{239}Pu in U.S. by 2050 (U.S. Dept. of Energy, 1980)	= 2,000 tonnes
D.	Predicted $^{239}\text{Pu}^{+4}$ concentration in South Stream water ^a	= $\text{CB}/\text{A} = 0.0035 \mu\text{g/l}$
E.	Maximum allowable concentration of ^{239}Pu in waste water (Code of Federal Regulation)	= 0.08 $\mu\text{g/l}$

^aBased on assumptions given in text.

The mobilization rates of the natural analogues of Pu, Am, and Cm have been found to be so low that despite the long half-lives of some of the actinide isotopes, essentially complete decay would take place in situ if the analogues we have studied are valid. For example, if we assume that the annual groundwater mobilization rate of ^{239}Pu will remain constant at the present rate for Th, the mean life of the deposit would be $7 \times 10^8 \text{ yr}$ compared to $3.4 \times 10^4 \text{ yr}$ due to radioactive decay of ^{239}Pu .

It is all the more remarkable that the mobilization rates are so low in view of the characteristics of the ore body and its environs. Site selection criteria for geological repositories (NRC 1978) require that they be placed at great depths in unweathered rock, under hydrological conditions that would assure long transit times for nuclides carried by groundwater. The MF ore body meets none of these requirements—depth of burial, condition of the host rock, or transit time of groundwater to potable water. Moreover, preliminary results of speciation studies conducted by Miekeley and others (1982) suggest that a major fraction of the Th in groundwater filtrates is complexed with organic acids which presumably form from the decomposition products of vegetation that percolate to the groundwater through the porous rock. Nevertheless, the mobilization rate for Th is so low that if the Th-Pu analogy is valid, the South Stream filtrates would meet the presently accepted waste discharge standards if all the Pu expected to exist in the United States by 2050 (U.S. DOE 1980) were to be emplaced under conditions comparable to those existing at the MF. We come to this conclusion in the manner shown in Table 3, in which it is estimated that under such conditions the Pu concentration would be about 5% of the maximum permissible concentration (CFR, Title 10) allowed by the regulations of the Nuclear Regulatory Commission.

This conclusion would be particularly valid if the actinide wastes were not exposed so directly to atmospheric oxidation as

is the MF deposit, since this exposure might lead to a change in the oxidation state of plutonium, and hence to greater mobility. Measured Eh (+400 to +700) and pH (4.4 to 7.1) in soil and water at MF, despite exposure to air, are within the field where plutonium has the same valence as thorium and should be similarly immobile (Eisenbud and others 1982). Nevertheless, access to air always offers the possibility of oxidation of some of the plutonium. For a repository well sited and deep underground, such access of air by deep erosion is extremely unlikely. A more probable scenario for repository breaching would be invasion by groundwater, which implies no extremes of either Eh or pH, and in this case the behavior of plutonium should closely mimic that of its analogue.

If neptunium is also present in the waste, the need to site a repository so as to minimize the chance of exposure by erosion is still more urgent, because neptunium is more easily oxidized than plutonium, and because its half-life is longer (2.1×10^6 yr for ^{237}Np). Quadrivalent neptunium is not as close a chemical analogue of thorium as is plutonium, but still should be similarly immobile as long as conditions remain reducing. Thus, the data on thorium migration at MF indicate clearly that none of the transuranic elements would be appreciably mobilized by groundwater contact with the waste in a repository.

Our finding that these analogues of the transuranic actinide elements are so extraordinarily immobile is consistent with findings at the site of the natural reactor in the Oklo uranium mine in Gabon, West Africa (Cowan 1976; Curtis and others in preparation). It is known that about 1.8 billion years ago, conditions in this uranium deposit were such as to sustain criticality for an estimated 10^4 to 10^5 years. The transuranic elements produced by this lengthy episode have long since decayed, but the stable isotopes of the end products of decay have remained, and mass spectrographic studies of rock samples collected in the vicinity of the ore body have shown that minimal migration of actinide elements occurred.

The investigations at Oklo and MF are not yet complete, but the data obtained thus far from both studies suggest that, although the actinide elements are hazardous when absorbed into the body, there are geochemical barriers that would, under ordinary conditions, block these elements from leaving a waste repository and being incorporated into food and water.

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