

## DISTRIBUTION OF URANIUM IN SOIL PROFILES OF BAHIA STATE, BRAZIL

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### INTRODUCTION

Previous studies have shown that the uranium yields in soils are generally higher than those of the rocks from which they originated (Hansen and Stout 1968). Pliler and Adams (1962) found that the uranium yields in the most advanced horizons of soils are four times higher than those of the underlying fresh rock. They attributed this to the concentration of uranium in heavy minerals, resistant to weathering. Rosholt et al. (1966), who measured the uranium yields of the various horizons of soil profiles and studied the radioactive disequilibrium  $^{234}\text{U}$ : $^{238}\text{U}$ , proposed a complicated model to explain the isotopic evolution of uranium in soil profiles.

These works were based solely on the results of chemical analysis. This kind of ratiocinating is not valuable for weathered rocks and soils, however, unless the loss of matter per unit volume is also taken into account (Millot and Bonifas 1955). In the present work we study five soil profiles and explain the measured uranium concentrations on the basis of an isovolumetric reasoning. The results show that, despite an important loss of uranium to the outgoing solutions when the parent rock is transformed into alterite and soil, the relative concentration in the residual soil increases. To improve our knowledge of the distribution of uranium in the components of the soil, we measured its concentrations in clays and heavy minerals, which are the main bearers of uranium. To explain the phenomena of adsorption and desorption of uranium in clays, we performed, in the laboratory, lixiviation experiments on soil samples washed by water enriched in organic and mineral matter.

### METHODS

Uranium was measured in rocks and soils by  $\alpha$ -ray spectroscopy, after grinding and dissolu-

tion. This rather classic method (Cherdyntsev 1971; Thurber 1962; Labeyrie et al. 1967) gives a precision of  $\pm 5$  percent for uranium concentrations and allows the activity ratio  $^{234}\text{U}$ : $^{238}\text{U}$  of the two natural isotopes of uranium to be determined. The only disadvantage of this method is that it is delicate and time consuming.

The mineralogical separation of the samples was done as follows: the *biotite fraction* was extracted from the rock sample RP 9, which holds 4 percent of this mineral. X-ray diffraction analysis has shown that zircon is associated with this biotite, in small quantities. This result agrees with observations of thin sections. The zircon observed is finely granulated. Another mineral, also associated with biotite in small quantities, is monazite. The determination of the uranium yield of the biotite is difficult because of the presence of these inclusions, which are hard to separate. For the *heavy minerals*, we used the same sample RP 9. These minerals were separated using bromoform. We did not use any other heavy liquid more corrosive, which would have leached the samples and altered their uranium content. Following this method, we obtained those bulk minerals that had a density higher than 2.89. Nevertheless, the efficiency of the extraction is lower than 100 percent. In the fraction obtained, X-ray diffraction analysis showed mainly the presence of zircon, monazite, apatite, and ilmenite. Among these minerals, zircon, apatite, and monazite are known as being "uranium traps."

The heavy minerals and biotite were extracted in the same manner from sample RP 15, and their uranium content was measured. The main heavy minerals obtained were zircon and riebeckite, associated with magnetite and ilmenite.

The mineralogical fraction of soil samples smaller than  $2\mu$ , was extracted by centrifugation



after dispersion by ammonia solution and destruction of organic matter by hydrogen peroxide.

#### DESCRIPTION AND ORIGIN OF THE SAMPLES

The samples were taken in the Preto River basin, located as a mean at 13°30' south latitude and 39°45' west longitude, in the south of Bahia State, located in the northeastern part of Brazil. This basin presents the advantage of a good geological, climatic, and phytologic homogeneity within its 858 km<sup>2</sup> (mean altitude: 200 m).

This basin was described in another work (Moreira-Nordemann 1977); the climate is tropical, having a mean annual rainfall of 1297 mm, without a contrasting season. The annual mean temperature is 27°C. In the major part of the basin, the vegetation is typically that of the tropical forest. The formations of the Precambrian shield represent the geological base of the Preto River basin, with regional, high grade metamorphic rocks of granulitic facies. In all the rocks, quartz is present as flakes with rotating extinction in polarized light. The main accessory minerals are zircon and magnetite, associated with apatite and riebeckite.

The soils of the Preto River basin belong to the class of ferralitic soils, according to the French pedological classification, corresponding to oxisols and ultisols in *Soil Taxonomy* (1975). This kind of soil is frequent in the intertropical zone. Ferralitic soils are formed by intense weathering of the minerals of the "parent" rock (the five profiles come from acid granulite) and by a strong leaching of bases and silica. The profiles are generally A(B)C or ABC, and the horizons have gradual transitions between themselves.

In these soils, organic matter is mainly concentrated in the superficial A horizon, down to about 30 cm. The B horizon contains abundant oxides and hydroxides of iron. Clay minerals belong to the kaolinite family. The soils are acid, and there is a high frequency of good structure.

#### PHYSICOCHEMICAL PROPERTIES

1. Granulometry. Clay contents are lower than 20 percent at the surface level, but may reach 47 percent in the B horizon. Silt contents vary between 20 percent at the surface level and 40 percent in deeper horizons. Fine sand contents reach 50 percent at that surface level, but

are only 10 percent at lower levels. Gross sand contents are never greater than 15 percent.

2. Reaction. These soils are slightly acid; pH is near 5 and decreases with depth.

3. Organic matter. Organic matter contents may reach 3 percent at the surface level, but decrease rapidly to 0.2 percent with depth. The C:N ratio is lower than 10 at the surface level.

4. The saturation grade is greater than 60 percent. The total of exchangeable bases (S) varies between 4 and 8 me percent at the surface level, and the exchange capacity (T) is between 6 and 10 me percent.

The main clay mineral is kaolinite. Montmorillonite has not been observed. Gibbsite exists in small amounts, mainly at the top of the profiles and in the upper region of the basin.

#### RESULTS

Table 1 presents the uranium contents and the <sup>234</sup>U:<sup>238</sup>U ratios of each sample and a short description of the profiles. These measurements were also made for the mother rocks.

It is apparent that the soils are much richer in uranium than is the corresponding mother rock. This result suggests that uranium "concentrates" in soils, which agrees with work previously done in the United States. If, instead of looking at absolute yields (i.e., comparing 1 g of fresh rock to 1 g of soil), however, we make an isovolumetric comparison (which applies only to horizons that maintain their structures), we may calculate that the uranium losses between the fresh rock and the weathered C horizon are 36, 39, 35, 10, and 15 percent in profiles 1, 2, 3, 4, and 5, respectively.

Unfortunately, isovolumetric analysis may be applied only when the rock structure is maintained, i.e., in the lower part of the profiles where, after weathering, the residues occupy a volume equal to that of the rocks from which they originate. In the upper part of the profiles the volume may not be invariant. Loss of matter occurs at the surface because of superficial erosion, which is difficult to measure. A part of the uranium remains behind, either in heavy minerals or in clay, the soluble uranium being removed as shown in the lixiviation experiment. The heavy minerals, being quite indestructible, however, may provide a means of measuring the decrease of volume between the mother rock and the soil.

The heavy minerals content of rock RP 9 is 1

	I
PROFIL	
1. A11	
2. A12	
3. B1	
4. B21	
5. B22	
6. B3	
7. C	
8. rock	RI
PROFIL	
9. A1	
10. B2	
11. alter	ro
12. rock	R
PROFIL	
13. C	RP
14. rock	R
PROFIL	
15. A1	
16. A3	
17. B	
18. C	
19. rock	F
PROFIL	
20. A11	
21. A3	
22. B1	
23. B2	
24. B3	
25. B3	
26. C	
27. rock	
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TABLE 1  
Uranium contents and  $^{234}\text{U}$ : $^{238}\text{U}$  ratios of samples

Horizon	Depth, cm	Description	$^{238}\text{U}$ $\mu\text{g/g}$	$^{234}\text{U}$ : $^{238}\text{U}$
PROFILE 1				
1. A11	0-11	Dark brown (7.5YR 3/2), sandy clay loam, moderate medium granular, slightly hard, few grass roots	4.81	0.98 $\pm$ 0.03
2. A12	11-30	Brown (7.5YR 4/4), sandy clay, weak fine subangular blocky	5.01	0.97 $\pm$ 0.03
3. B1	30-45	Brown (7.5YR 4/4), sandy clay, moderate medium subangular blocky	5.32	0.97 $\pm$ 0.02
4. B21	45-77	Yellowish red (5YR 4/6), medium clay, moderate medium subangular blocky	6.40	0.96 $\pm$ 0.02
5. B22	77-120	Red (2.5YR 4/6), medium clay as above	7.02	0.96 $\pm$ 0.03
6. B3	120-160	Yellowish red (5YR 5/8), clay loam, few medium weathered minerals	5.04	0.98 $\pm$ 0.04
7. C	>160	Much weathered bedrock	2.89	0.93 $\pm$ 0.02
8. rock RP 9		Bedrock: hornblende, microcline, quartz granulate	2.69	1.01 $\pm$ 0.03
PROFILE 2				
9. A1	0-15	Dark brown (10YR 3/3), sandy clay loam, moderate medium granular	4.70	0.97 $\pm$ 0.03
10. B2	100-150	Yellowish brown (10YR 5/6), medium clay, moderate medium subangular blocky	5.10	0.96 $\pm$ 0.04
11. altered rock	200	Yellowish brown weathered bedrock	1.07	0.93 $\pm$ 0.03
12. rock RP 10		Bedrock: quartz, oligoclase, plagioclase granulate	1.04	1.00 $\pm$ 0.03
PROFILE 3				
13. C RP 6		Brown weathered bedrock	1.21	0.96 $\pm$ 0.04
14. rock RP 7		Bedrock: quartz, hypersthene, andesine granulate	1.10	0.94 $\pm$ 0.05
PROFILE 4				
15. A1	0-7	Very dark grayish brown (10YR 3/2) medium clay, moderate medium granular	4.31	0.97 $\pm$ 0.03
16. A3	7-12	Dark grayish brown (10YR 4/2) sandy clay loam, as above	4.22	0.97 $\pm$ 0.02
17. B	12-23	Grayish brown (10YR 5/2) medium clay, moderate fine subangular blocky		
18. C	23-30	Much medium weathered minerals	1.75	0.95 $\pm$ 0.04
19. rock RP 2		Bedrock: quartz, orthoclase, plagioclase granulate	1.15	0.99 $\pm$ 0.03
PROFILE 5				
20. A11	0-10	Brown (10YR 4/2), sandy clay loam, weak fine subangular blocky	5.05	0.98 $\pm$ 0.03
21. A3	10-25	Reddish brown (5YR 4/3) clay loam as above	5.40	0.97 $\pm$ 0.02
22. B1	25-54	Reddish brown (5YR 4/3), clay loam moderate fine subangular blocky	—	—
23. B2	54-75	Yellowish brown (10YR 5/4) sandy clay, as above	7.35	0.96 $\pm$ 0.02
24. B31	75-120	Brown (7.5YR 5/4), medium clay with distinct, coarse yellowish red (5YR 4/8) mottles, moderate subangular blocky	5.02	0.92 $\pm$ 0.02
25. B32	120-162	As above but strong medium subangular blocky	4.05	0.94 $\pm$ 0.03
26. C		As above with increasing amounts of weathering minerals	1.60	0.94 $\pm$ 0.03
27. rock RP 15	250	Weathered bedrock with some yellowish brown medium clay	1.50	1.00 $\pm$ 0.02

percent, and their uranium content is 163.9  $\mu\text{g}/\text{gram}$ , while the uranium content of the rock is 2.69  $\mu\text{g}/\text{gram}$ . From these results we may calculate that 61 percent of the uranium of the rock

is within the heavy minerals. In rock RP 15, 65 percent of the uranium is within the heavy minerals. Table 2 presents the results we obtained, which agree with those of other authors

TABLE 2

Determination of the uranium content of the biotite and heavy mineral fractions and total uranium content of the rock

Mineral fraction	Weight in the rock, %	U, $\mu\text{g/g}$	Percentage to total U	$^{234}\text{U}:^{238}\text{U}$
Sample RP 9: total uranium content = 2.69 $\mu\text{g/g}$				
Biotite	4	12.6	19	0.96 $\pm$ 0.04
Heavy minerals <sup>a</sup>	1	163.9	61	0.92 $\pm$ 0.01
Hornblende				
Hypersthene				
Microcline	95		20	
Quartz				
Oligoclase				
Sample RP 15: total uranium content = 1.50 $\mu\text{g/g}$				
Biotite	4	9.1	24	0.97 $\pm$ 0.02
Heavy minerals <sup>b</sup>	1	98.2	65	0.93 $\pm$ 0.03
Hypersthene				
Quartz	95		11	
Oligoclase				

<sup>a</sup> Heavy minerals: mostly zircons, monazite, apatite, and riebeckite.

<sup>b</sup> Heavy minerals: mostly zircons and riebeckite.

(Picciotto 1950; Leonova and Tautson 1958; Le Van Tiet 1975).

For soil sample A12 (profile No. 1) overlying rock RP 9, the uranium content of the heavy minerals is 158.8  $\mu\text{g/gram}$  (due to the 5 percent uncertainty, this result is approximately equal to the corresponding value for the mother rock). This result is expected, as the X-ray diffraction analysis shows, the heavy minerals of the rock and the soil being the same: zircon, ilmenite, riebeckite, and monazite. Only apatite has a smaller concentration in the soil. Given a total uranium content in the soil of 5.01  $\mu\text{g/gram}$  and a concentration of heavy minerals of 2 percent, this small amount of heavy minerals represents 63 percent of the total uranium of the soil.

The amount of biotite is 4 percent, with a uranium content of 12.6  $\mu\text{g/gram}$ , representing 19 percent of the total uranium of rock RP 9. In the case of sample RP 15, this value is 24 percent, with a total uranium content of 9.1  $\mu\text{g/gram}$ . These results are in agreement with those of Le Van Tiet (1975). Remember that biotite easily weathers to vermiculite and that during this process its uranium is freed to drainage water.

The uranium contents of soil fractions finer than 2  $\mu$  are between 15 and 27 percent of the uranium content of the total sample. This result appears in Table 3. Clay in natural conditions absorbs uranium, as shown by the laboratory experiments of Goldztaub and Wey (1955). It is interesting to note, however, that the uranium contents of the Preto River kaolinite (in natural conditions) are much lower than the uranium

TABLE 3

U contents and  $^{234}\text{U}:^{238}\text{U}$  ratios in the clay of soil samples

No.	Profile no.	Horizon	Clay, %	U, $\mu\text{g/g}$	U% to U <sub>i</sub> in total earth	$^{234}\text{U}:^{238}\text{U}$
1	1	A11	16.2	4.35	15	1.02 $\pm$ 0.02
2	1	A12	24.5	4.84	24	0.99 $\pm$ 0.03
4	1	B21	44.0	3.71	24	0.97 $\pm$ 0.04
6	1	B3	40.0	3.48	27	1.00 $\pm$ 0.02
9	2	A1	16.5	4.75	17	1.04 $\pm$ 0.03
10	2	B3	20.5	6.03	24	1.03 $\pm$ 0.02

absorbed by the H-clay in the laboratory experiments.

Table 4 gives the grain size distribution, the pH, and the organic matter content of the samples for which we measured uranium in the total earth and in the < 2- $\mu$  fraction. The same samples were used for the lixiviation experiments.

#### LIXIVIATION EXPERIMENTS IN SOILS

An important fraction of the uranium of rocks may be mobilized only by the complete dissolution of the heavy minerals, which often contain up to 60 percent of the total uranium present. Depending on the kind of rock, only a small fraction of the uranium is easily dissolved; i.e., that fraction that is slightly bound or present in the joints of the crystals or at the defects or cracks of the crystalline matrix. This uranium is called soluble uranium. We have previously lixiviated rocks with rainwater (Moreira and Lalou 1972) and extracted soluble uranium from the samples. The ratio  $^{234}\text{U}:^{238}\text{U}$  in lixiviation waters

TABLE 4  
Profile no. 1—granulometry, pH, and total organic matter

Horizon	% coarse sand, 200-2000 $\mu$	% fine sand, 50-200 $\mu$	% loam, 2-50 $\mu$	% clay, 0-2 $\mu$	% C	H <sub>2</sub> O	pH KCl N
A11	15.1	51.1	17.6	16.2	2.57	6.0	4.8
A12	13.5	40.2	21.8	24.5	1.27	5.6	4.5
B1	8.5	35.4	22.6	33.5	0.88	5.5	5.0
B21	7.0	21.5	27.5	44.0	0.62	5.3	5.2
B22	6.6	10.8	35.1	47.5	0.54	5.1	4.1
B3	6.0	10.0	44.0	40.0	0.27	5.0	3.8

is greater than 1, which confirms the already known greater solubility of uranium 234 (Cherdynchev 1971).

To determine if uranium absorbed by clay can be easily desorbed, we lixiviated samples of soils in the laboratory. Our purpose being to remain as close as possible to natural conditions, we lixiviated our samples with water enriched in organic matter, using Torumin solution (Tetra Werke), which contains 4.05 mg organic carbon per liter, of which 3.33 mg/liter is humic acids and 0.72 mg/liter is fulvic acids. Mineral ions were added: Na, 1.62 mg/milliliter; Mg, 1.08 mg/milliliter; Ca, 0.65 mg/milliliter, and K, 0.25 mg/milliliter. These concentrations were those measured in rainwater of the same region (Ribeiro 1975). (The uranium content of this solution was measured and found to be lower than the limit of detection 0.01  $\mu$ g.)

We lixiviated sample 9 (profile no. 2, horizon A11) three times and sample 4 (profile 1, horizon B12) (Table 1). We used only 50 g of soil (total earth including organic matter) because of its high uranium content (about 5  $\mu$ g/gram), so that about 235  $\mu$ g of uranium was exposed to the leaching water. The sample was placed in a Büchner funnel (porosity 2), and the solution, rich in minerals and organic matter, was allowed to percolate through the sample. The duration of the contact was 24 h, resulting from the low permeability of the sample.

The amount of organic carbon in the solution was between 2.7 and 121.5 mg/liter, depending on the addition of Torumin solution, which was 1 to 4 times the total carbon content of the most humiferous horizon of the soils of the region. The concentration of the major cations was between 4 and 10 times that of the mean rainwater of the region (Table 4).

The solution that leached the sample was separated and acidified and, after the addition

of the tracer, evaporated. The organic matter was destroyed by a concentrated nitric and perchloric acid mixture at hot temperature, and the residue was dried. Uranium was measured after chemical separation by  $\alpha$ -ray spectroscopy.

In all cases, the amount of uranium in the solution that leached the sample (0.01  $\mu$ g) was lower than the limit of detection. We also extracted 50 g of the < 2- $\mu$  fraction of sample 1 (profile 1, horizon A11). After 38 h of contact between the sample and the solution (with agitation), 1 percent of the total uranium of the soil sample was found in the solution. This is the same amount of uranium that can be obtained by lixiviating fresh rocks with rainwater only.

These experiments show that the uranium is not easily removed from soils by rainwater, and that the organic matter content of the leaching water does not seem to be an important factor in increasing the solubility of uranium.

#### ACTIVITY RATIO $^{234}\text{U}:$ $^{238}\text{U}$

The activity ratio  $^{234}\text{U}:$  $^{238}\text{U}$  is always close to 1 in fresh rocks and in heavy mineral fractions. Uranium 234, being located in a microzone more weathered than that of its grandfather,  $^{238}\text{U}$ , is more soluble, so in weathered mother rocks the ratio  $^{234}\text{U}:$  $^{238}\text{U}$  is lower than 1. The opposite occurs in the solutions that dissolved the uranium and in the runoff waters (the mean value of this ratio for the Preto River waters is 1.24). Clay that gained uranium from these waters should have the same ratio. For these reasons, the total soil (depending on whether the bearers of its uranium are clay or heavy minerals) will have a ratio either greater than or lesser than 1. In fact, uranium in soils is a mixture of both kinds of minerals and, for that reason, one may find intermediate ratios between the value for solutions (greater than 1) and that of the weathered mother rock (less than 1).

## CONCLUSION

This work has explained the high content of uranium in various horizons of tropical soils, and has also shown the role played by clays in the distribution of uranium along the profiles. Uranium is not easily released from clay during laboratory experiments of lixiviation with mineral salts and organic-matter-enriched water. Though most of the experiments and field observations were performed on organic-poor clay, it might be possible that besides ionic links, organic matter has an effect on the retention of uranium by clay, in some of the superficial horizons. It was also shown that the heavy minerals bear the most important fraction of the uranium in soils, confirming the previous hypothesis of Pfler and Adams (1962).

This study of the repartition of uranium in the minerals of rocks and its geochemical behavior in soils was made in conjunction with a larger study to determine the weathering rate of rocks, using uranium as a natural tracer (Moreira-Nordemann 1977).

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