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Use of $^{234}U/^{238}U$ disequilibrium in measuring chemical weathering rate of rocks

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Abstract—The rate of chemical weathering of rocks has been determined by using uranium as a natural isotopic tracer. The concentration of uranium and $^{234}U/^{238}U$ ratio in natural waters, rocks, and soils of the Preto river basin (Bahia State, Brazil) was measured by alpha-ray spectroscopy.

The activity ratio U234/U238 measured in the various samples indicates the uranium fraction which is dissolved from rocks during the weathering process. The results obtained show that 1 m of rock needs 25,000 yr to be weathered in this region under present climatic conditions.

INTRODUCTION

THE DETERMINATION of the weathering rate of rocks is of great interest in Geophysics and Geochemistry since alteration is one of the most fundamental phenomenon of the superficial Geochemistry leading to the present geomorphology of the continents. An important part of the dissolved load in the water of a river comes from the dissolution of the minerals which takes place during chemical alteration, but another part derives from fall-out in rain. Up to now most studies have used sodium, calcium, potassium, and magnesium concentrations in river waters to set up geochemical balances and/or to determine the weathering rates in the regions investigated (JOHNSON *et al.*, 1968; TARDY, 1969; GIBBS, 1970; MOREIRA-NORDEMANN, 1977). However, the intake of these elements from rain leads to important corrections to obtain their fraction coming from dissolved rocks. Furthermore, for the same region the rates of weathering measured through each element are different because of their various behaviour and rate of solution. I thought of using uranium as a natural tracer of weathering processes because it is not contained in rain (uranium content of the local rain is 0.01 μg/l measured on 30 l, which is 300 times less than the mean content of the river water), it is soluble, and so may be mobilized by rain water, and it is a radioactive element with radioactive descendants.

This last property is the most important for our purpose for it will give us a method for solving the problem produced by the partial solubility of the elements: theoretically, all the radionuclides of the uranium 238 family should be at the secular equilibrium in nature, if short time scale geochemical phenomenon did not interfere. The classical disequilibrium between uranium 238 and uranium 234 has been abundantly described in oceanic river and lacustrine waters, in soils, etc. (THURBER, 1962; KU, 1965; LALOU *et al.*, 1970; CHERDYNTSEV, 1971; OSMOND *et al.*, 1974). This is due to the preferential mobilization of uranium 234 in the course of rock weathering. By measuring the U234/U238 activity ratio in soils and in water, it will be possible to know the uranium fraction dissolved during its weathering (solution coefficient for uranium) and to use these results to obtain the weathering rate of rocks.

EQUATIONS AND MODELS

Determination of the weathering rate

The quantity of weathered matter per unit of surface and per unit of time may be determined by measuring the mean content of the tracer element in the river water (E_E) and in the rocks of the basin (E_R), the mean flow of the river (D) and the surface of the basin (S). The atmospheric fall-out of uranium being negligible the following formula is used:

$$W = E_E D/E_R S \quad (1)$$

Using the density (ρ) of the rocks, I can determine the thickness of rock weathered per unit of time, i.e. the weathering rate of the rocks of the basin (v). This is true in the case of total weathering of the natural tracer during chemical attack. But the natural elements in general are only partly soluble during weathering, so a coefficient of dissolution (k) must be taken into an account, which leads to the following formula:

$$v = W/k\rho = E_E D/k\rho E_R S \quad (2)$$

where the uranium content is expressed in μg/l in water and in μg/g in rocks; the flow of the river is expressed in l/yr, the surface of the basin in cm^2 and the density in g/cm^3. The weathering rate (v) consequently is expressed in cm/yr.

Determination of the coefficient k

Uranium 238 (α emitter half life 4.5×10^9 yr) begets uranium 234 (α emitter half life 2.5×10^5 yr) through

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thorium 234 and protactinium 234 (short half life β emitters). Uranium 238 and 234 are in secular equilibrium in rocks, where their activity ratio is equal to one. To the contrary, this activity ratio measured in river water and in ground water is usually greater than one because of the higher mobility of uranium 234.

Uranium is partly stored in soils and partly removed to the river. In hypothetical steady conditions, uranium in rocks (U_R) is equal to the sum of the quantity of uranium in soils (U_S) and of uranium in water (U_E). However, this removal to the river is a function of time, and so is the storage in soils. But uranium 234 is made from uranium 238 according a fixed time scale (ruled by the half lives of the radioactive elements).

Being given:

U_R = mean uranium content in rocks
U_E = mean uranium content in water
U_S = mean uranium content in weathered rocks (or in C horizons)
A_S = U 234/U 238 in rocks
A_E = U 234/U 238 in water
A_S = U 234/U 238 in weathered rocks (or in C horizons)

We know that:

$$A_R U_R = A_E U_E + A_S U_S \tag{3}$$

But only a fraction of the uranium equal to kU_R is removed. In the weathered rock, it remains a quantity $(1 - k)U_R$. So:

$$U_E = kU_R, \quad A_E U_E = kA_E U_R \tag{4}$$

and

$$A_S U_S = (1 - k)A_S U_R \tag{5}$$

By substitution of (4) and (5) in (3) we obtain:

$$A_R U_R = kA_E U_R + (1 - k)A_S U_R$$

Eliminating U_R and resolving we obtain:

$$A_R = kA_E + (1 - k)A_S$$

$$k = (A_R - A_S)/(A_E - A_S)$$

So the fraction of the weathered uranium can be calculated using only the activity ratios U234/U238 in the river water, in the weathered horizon and in the mother rock itself. The activity ratio being equal to unity in unweathered rocks, the coefficient k is only a function of the activity ratios in the natural water and in the weathered rock of each region. A comparable method has been suggested by OSMOND and COWART (1976) to study world-wide erosion rates.

METHOD

The study was performed in the Preto River basin, in the southern part of the Bahia State, Brazil (Fig. 1.). The choice

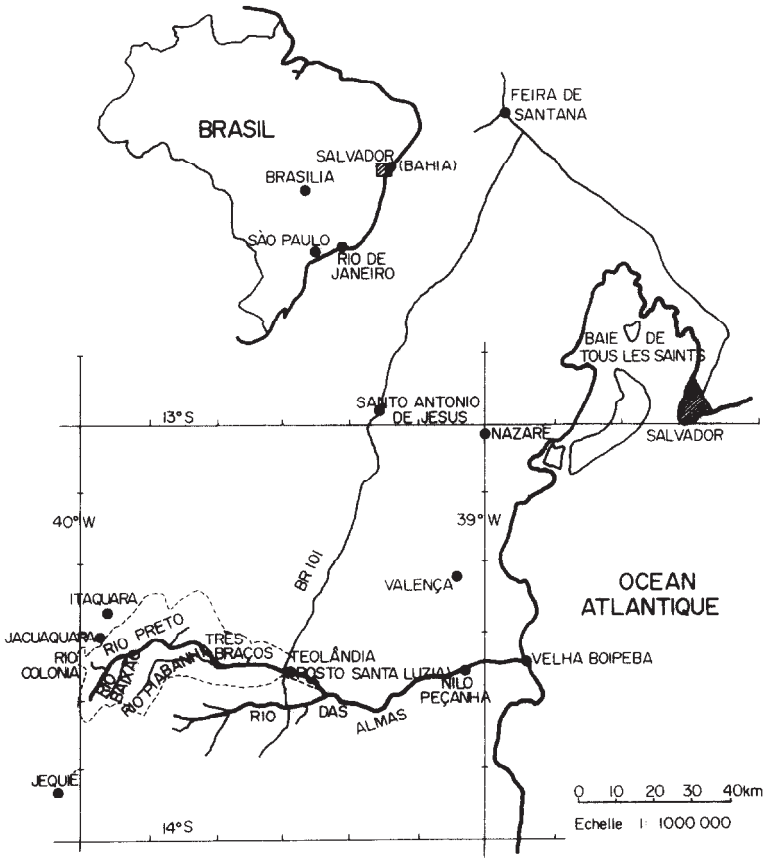

Fig. 1. Geographical situation of the River Preto Basin.

Table 1. General data on the River Preto basin

Surface	858 km²
Localization	13°30′ South latitude 39°45′ West longitude
Mean altitude	200 m
Climate	Tropical
Mean rain fall	11.1×10^{11} l/yr (1297 mm/yr)
Mean temperature	27°C
Vegetation	Tropical forest
Mean flow rate of the river	3.26×10^{11} l/yr
Geology	—High grade metamorphic rocks of granulite facies
Soils	Ferralitic soils corresponding to oxisols and ultisols in soil taxonomy, horizons A B C or A(B) C.
Tributaries	—Colonia, Piabanha, Baixao
The Preto River is a tributary of the Almas River:	

of this basin was made because it is very representative of a humid tropical climate region where chemical weathering is very active. I have used hydrological and pluviometrical observations made by the Water and Electric Energy Authority (D.N.A.E.E., Brazil) over a 20 yr period. It was observed that climatic conditions are very steady. The basin is also very homogeneous from a geological point of view. The hydrology, climate and geology of this area have been reported in detail previously (MOREIRA-NORDEMANN, 1977). However the pertinent background material will be summarized in Tables 1 and 2.

Uranium has been measured in rock and soil samples, and water by means of a U232 tracer and alpha-ray spectroscopy after chemical treatment (MOREIRA-NORDEMANN, 1977). For each sample, the activity ratio U234/U238 has also been measured, 10–20 g of rock were attacked several times by a hot HF-HCl-HNO_3 mixture, the tracer (a mixture of known quantities of U232 and Th 228 at radioactive equilibrium) being added at the beginning of the operation. After complete dissolution of the rock, uranium was coprecipitated with iron by ammonium hydroxide. After centrifugation, the precipitate was dissolved again in 8N HCl and passed through a Dowex 1 × 8–100/200 mesh anion exchange resin column, to separate thorium from uranium fraction. Uranium and iron are recovered from the column by 0.1 N HCl. Uranium is separated from iron by diisopropyl ether extraction. The uranium recovered and purified by this way is deposited on a stainless steel disc with TTA (thenoyltrifluoracetone). Uranium 238 concentration is calculated from the ratio of the counting rates of U238 and U232 peaks, and the quantity of U232 introduced as a tracer.

For water samples, the treatment was made on 20–40 l. Uranium was first concentrated on activated vegetal charcoal, after addition of U232 tracer and of hexamethylenetetramine. After filtration and calcination, the residue containing uranium is dissolved in 8 N HCl and passed through the Dowex 1 × 8 resin column and then after the treatment is the same as rock samples. Analytical techniques in measuring uranium concentrations and U234/U238 activity ratios and treatment of data are reported in detail by OSMOND and COWART (1976).

Water samples have been taken systematically at different flows during one hydrological year at Teolandia (Fig. 1), about 10 km far from the confluency point with the Almas River. The rock samples have been taken on the whole surface of the basin, taking into account the different species of rocks and their surface representations. Uranium was also measured in five profiles of soils from the region.

RESULTS AND DISCUSSION

Uranium in river water.

Table 2 presents the uranium concentrations in various samples of water, their activity ratio U234/U238, the flow of the river for each measurement and the statistic weight of each flow (this statistic weight P_i is the number of cases for which the flow was measured during 20 yr of daily measurements). High statistic weights show that the measurements are really representative of the mean flow of the river.

The uranium concentrations in the Preto River water are low and diminish with increasing flow, which may be explained by the dilution by rain water, with an exception for the measured maximum flow.

Table 2. Uranium concentration in the water of the Preto River

Samples	Flow rate (m^3/s)	238_U* ($\mu g/l$)	$234_U/238_U$**	P_i	Date of sampling
P.10	7.59	0.141	1.33 ± 0.05	527	14–11–73
P.1	8.63	0.123	1.26 ± 0.1	525	12–8–73
P.5	9.68				22–9–73
P.9	9.68	0.075	1.28 ± 0.03	824	17–10–73
P.13	14.8	0.062	1.27 ± 0.05	684	11–12–73
P.12	25.7	0.092	1.07 ± 0.05	367	7–12–73
P.11	66.9	0.191	1.19 ± 0.03	76	1–12–73

* Uncertainty ±5% corresponding to 1 σ.
** Uncertainty corresponding to 1 σ.

Table 3. Uranium concentration of the rocks of the Preto River basin for the seven different mineralogical association and for one sample of quartz

Sampling zone in the basin	Mineralogical associations of the samples	Number of samples measured	U* (μg/g)	$^{234}U/^{238}U$
Mean basin	Hypersthene, quartz, oligoclase, biotite	4	1.50	1.00 ± 0.02
Lower basin	hornblende, hypersthene, microcline, quartz, oligoclase	3	2.69	1.01 ± 0.03
Mean and lower basin	microcline, plagioclase, quartz, hypersthene	2	1.44	0.98 ± 0.04
Higher basin	quartz, hypersthene, andesite	2	1.10	0.94 ± 0.05
Mean basin	biotite, potassic feldspar quartz, plagioclase	4	2.41	1.01 ± 0.02
Mean basin	diopside, quartz, oligoclase	2	1.96	1.02 ± 0.03
Higher basin	quartz, oligoclase, plagioclase	2	1.15	0.99 ± 0.03
	quartz	1	0.36	

* Uncertainty ±5% corresponding to 1 σ.

The mean weighted uranium concentration was calculated by the following formula:

$$E = \sum_i E_i d_i P_i \Big/ \sum_i d_i P_i \qquad (7)$$

E_i = uranium concentration for the i-th measurement
d_i = flow of the river on the day of the i-th measurement
P_i = statistical weight of the i-th flow.

The mean uranium concentration of the river water is 0.102 μg/l. Using formula (7) with the corresponding values of the ratio U234/U238 instead of the concentration E_i, we calculated a mean weighted activity ratio in the water and found it equal to 1.22. This ratio varies for the two highest flows. All the other observed values may be considered as being the same, due to measurement uncertainties.

Uranium in rocks

Table 3 presents the uranium concentrations of seven different mineralogical associations found in the basin, their activity ratio U234/U238 and the number of samples measured for each kind of rock.

The uranium concentration in rocks is a function of the rock genesis and of the geological context of the region. The Preto River basin, being covered by metamorphic rocks of sedimentary origin, presents only low uranium concentrations. This is because the main mineralogical components are quartz and feldspars which are uranium poor minerals. The uranium concentrations vary little due to the geological homogeneity of the region.

Measurements of uranium made on two minerals of these rocks have shown that 60% of the total uranium of the rock is inside the heavy minerals: zircon, monazite, apatite and riebeckite; and 20% in the biotite. The remainder is distributed in fractures and interstices of the crystal matrix and in the principal minerals.

The mean uranium content (1.61 μg/g) of the rocks of the Preto River basin was determined taking into account the spatial representativity of the various mineralogical associations of the granulite family encountered in the region: 35% of hypersthene oligoclase microcline granulite, 13% of charnockite and 17% of hypersthene hornblende oligoclase microline and quartz granulite, the other associations being equally represented in the basin.

The activity ratio U234/U238 in rocks is always equal to one, within the margin of error due to measurement uncertainties.

Uranium in soils and in weathered rocks

Uranium concentrations in samples of soil profiles of the basin were studied in a previous work (MOREIRA-NORDEMANN and SIEFFERMANN, 1979): heavy minerals bearing 60% of the total uranium of the rocks are very resistant to weathering and carry their uranium to the more developed horizons of the profiles. These materials accumulate in soils and so carry more than 60% of the total uranium of the soil.

Alteration clays, in our case kaolinite, absorb uranium and contain between 15 and 27% of the total uranium of the soil.

Lixiviation experiments have been performed on soils in the laboratory and have shown that these clays do not release uranium, even when washed by mineral salts and organic matter rich solutions.

The absolute uranium concentration measured in the samples of five soil profiles have been found greater than the uranium concentrations in the corresponding mother-rock. These results confirm those obtained by PLILER and ADAMS (1962), ROSHOLT *et al.* (1966), HANSEN and STOUT (1968) for soil profiles of North America showing the accumulation of uranium in soils. However, applying the isovolumetric

Table 4. Uranium concentration and U234/U238 activity ratio in C horizon and unweathered rocks for soil profiles in the River Preto basin

Horizon	Depth (cm)	Description	$^{238}U^*$ (μg/g)	$^{234}U/^{238}U$
Profile I				
(7) C	>160	—Much weathered bed-rock	2.89	0.93 ± 0.02
(8) rock RP.9		—Bed-rock: hornblende, microcline, quartz granulite	2.69	1.01 ± 0.03
Profile II				
(11) altered rock	200	—Yellowish brown weathered bed-rock	1.07	0.93 ± 0.03
(12) rock RP.10		—Bed-rock: quartz, oligoclase, plagioclase granulite	1.04	1.00 ± 0.03
Profile III				
(13) C RP.6		—Brown weathered bed-rock	1.21	0.96 ± 0.04
(14) rock RP.7		—Bed-rock: quartz, hypersthene, andesine granulite	1.10	0.94 ± 0.05
Profile IV				
(18) C	23–30	—Much medium weathered minerals	1.75	0.95 ± 0.04
(19) rock RP.2		—Bed-rock: quartz, orthoclase, plagioclase granulite	1.15	0.99 ± 0.03
Profile V				
(26) C		—As above with increasing amounts of weathering minerals	1.60	0.94 ± 0.03
(27) rock RP.15	250	—Weathered bed-rock with some yellowish brown medium clay	1.50	1.00 ± 0.02

* Uncertainty ±5% corresponding to 1 σ.
Complete measurements and description of these profiles appear in a previous work (MOREIRA-NORDEMANN and SIEFFERMANN, 1979).

analysis to the C horizon of alteration with preserved structure, one sees on the contrary that there has been a loss of uranium. High uranium concentrations in A and B horizons may be easily explained when one remembers that one gram of soil comes from several grams of rock. The difference of density between rock and soil may exceed 50%, which shows the importance of losses of matter during weathering processes.

Table 4 shows the uranium concentrations of the C horizons of the profiles and of the corresponding mother-rock and their activity ratio U234/U238. Using the isovolumetric analysis, one may calculate that the losses of uranium between the original rock and the C horizon are 36%, 39%, 35%, 10% and 15% respectively in profiles 1, 2, 3, 4 and 5. Uranium is dissolved at depth and at the beginning of the weathering process.

Weathering rate of the Preto River basin

The weathering rate has been calculated using formula (2) with the missing previously measured data. Table 5 gives the values which have been used. U234/U238 activity ratios in the weathered rock, i.e. in C horizon, are very close. We choose the lower value $A_S = 0.93$ which corresponds to the higher level of mobilization of uranium 234. For this region, the determined k coefficient is equal to 0.24. So, just 24% of uranium is dissolved from rocks during weathering process.

I found that 100 t/km²/yr, of matter are solubilized in the basin of the Preto River basin. This corresponds to 0.04 mm/yr of weathered rock.

I also determined the quantity of soluble matter per unit of surface and per unit of time, measuring sodium concentrations in the same samples and tak-

Table 5. Mean content of uranium in waters and rock samples. Mean activity ratio U234/U238 in rocks, waters and C horizons of soil samples

E_R^*—mean content of uranium in the rocks	1.61 μg/g
E_E^*—mean content of uranium in the waters	0.102 μg/l
A_R—mean activity ratio U234/U238 in rocks	1.00 ± 0.02
A_E—mean activity ratio U234/U238 in waters	1.22 ± 0.04
A_S—mean activity ratio U234/U238 in soils	0.93 ± 0.03
k—coefficient of dissolution of uranium	0.24
ρ—mean density of the rocks	2.7 g/cm³
S—surface of the basin	858 km²

* Uncertainty ±5% corresponding to 1 σ.
These data were employed in equation (2) to determine the weathering rate of the river Preto Basin.

ing into account its atmospheric intake in the basin: I found 115 t/km^2/yr, a value which agrees with the result obtained by the uranium method (MOREIRA-NORDEMANN, 1978). This value is greater than JOHNSON *et al.*'s (1968) for the New Hampshire region which is 80 t/km^2/yr. This may easily be explained by the fact that the Preto River basin is located in an area where the high rain fall-out associated with the effect of equatorial temperatures lead to higher weathering rates.

CONCLUSION

(1) A new method using uranium as a natural isotopic tracer is developed to study the geochemical process of rock weathering and to measure the weathering rate of rocks.

(2) Uranium, which presents the advantage of not being introduced in the basin by rain fall-out, permits the measurement for the basin of a coefficient of partial solution using its natural radioactivity properties.

(3) In the Preto River basin (Bahia State, Brazil), the weathering rate of rocks is found to be 100 t/km^2/yr, which corresponds to 0.04 mm/yr. This result shows that one vertical meter of rock needs 25,000 yr to be weathered under the present climatic conditions.

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