Preferential solution of ^{234}U from recoil tracks and $^{234}\text{U}/^{238}\text{U}$ radioactive disequilibrium in natural waters

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Abstract. A mathematical model to calculate the $^{234}\text{U}/^{238}\text{U}$ activity ratio (AR) in an aqueous phase in contact with rock/soil is presented. The model relies on the supply of ^{238}U by dissolution and that of ^{234}U by dissolution and preferential release from radiation damaged regions (recoil tracks). The model predicts that values of $^{234}\text{U}/^{238}\text{U}$ AR > 1 in the aqueous phase can be obtained only from weathering “virgin” surfaces. Thus, to account for the observed steady-state supply of ^{234}U excess to the oceans by the preferential leaching model, ‘virgin’ rock/soil surfaces would have to be continually exposed and weathered. The ^{238}U concentration and $^{234}\text{U}/^{238}\text{U}$ AR in continental waters allow us to estimate the exposure rates of “virgin” rock/soil surfaces.

Keywords. Uranium isotopes; radioactive disequilibrium; alpha-recoil; preferential leaching.

1. Introduction

In most natural waters, ^{234}U activity exceeds that of its grandparent ^{238}U . This excess of ^{234}U serves as a geochemical tool in the study of the behaviour of uranium in rocks, soils and natural waters and also as a geochronometer for earth surface processes (Ivanovich and Harmon 1982). Three basic mechanisms have been suggested (see for example, Gascoyne 1982) for the commonly observed excess ^{234}U in natural waters, (i) Change of the chemical valence state of ^{234}U atom as a result of the ‘hot atom effect’ during its radioactive production from ^{238}U ; it was proposed that ^{234}U is oxidised to a +6 valence state during this process and is preferentially mobilised during its weathering (Dooley *et al* 1966), (ii) release of ^{234}Th from soil/rock surface into the pore fluids by recoil during alpha decay of ^{238}U (Kigoshi 1971) and subsequent decay of ^{234}Th to ^{234}U , and (iii) preferential leaching of ^{234}U contained in the tracks produced as a result of radiation damage during the alpha decay of ^{238}U (Cherdyntsev 1971). More recently, Fleischer and Raabe (1978) and Fleischer (1982a, b) have demonstrated, based on laboratory experiments, the importance of alpha recoil damage on the preferential release of recoil fragments during etching and its implications on uranium isotopic disequilibrium in natural waters.

In this paper we present a mathematical model to predict the $^{234}\text{U}/^{238}\text{U}$ activity ratio in the aqueous phase, based on the preferential release of ^{234}U from recoil tracks during natural weathering processes. While this work was in progress, Fleischer (1983) suggested a model to estimate the release of alpha recoil nuclei from solid surfaces. This model is based mainly on the equations of Flugge and Zimens (1939) which relate the fractional escape of recoils from the surface of a given grain to its size. On a broader frame work, the model presented in this paper and that of Fleischer (1983) pertain to the

same problem, viz, alpha recoil effects on the $^{234}\text{U}/^{238}\text{U}$ radioactive disequilibrium in nature. However, the models differ greatly both in concepts and details. Fleischer's model calculates the fraction of recoiling nuclei stopped in pore spaces between grains and those implanted onto adjoining grains. These calculations in conjunction with a knowledge of other parameters such as grain size, porosity etc., can be used to derive an estimate of the $^{234}\text{U}/^{238}\text{U}$ activity ratio in the solids (rocks/soil) and the ^{234}U supply to pore fluids via recoil. Our model is to predict the $^{234}\text{U}/^{238}\text{U}$ activity ratio in the aqueous phase resulting from natural weathering of rocks/soils. It considers the release of ^{238}U and ^{234}U by dissolution of rocks and the preferential release of ^{234}U from recoil tracks.

2. Model concepts

In rocks/soils, ^{238}U and its daughter products occupy different sites. The daughter nuclides of ^{238}U are displaced from the site of their production because of recoil effects following alpha decay and would be located in radiation damaged regions (recoil tracks) of the rocks/soil; whereas ^{238}U would be occupying relatively healthier sites. It is well known that radiation damaged areas are etchable relatively faster than the surrounding healthy material (Huang and Walker 1967; Fleischer *et al* 1975; Petit *et al* 1985). This difference in the etching rate between the radiation damaged and healthy regions of rocks/soils results in the preferential mobilization of daughter nuclides relative to the progenitor ^{238}U into the aqueous phase. Thus ^{234}U would be preferentially leached into the aqueous phase following its production from ^{238}U . However, the activity ratio (AR) of $^{234}\text{U}/^{238}\text{U}$ in the aqueous phase resulting from the weathering of rock/soil would depend on several parameters such as the nature of the rock, its surface texture, its geometry, its size in relation to alpha recoil range etc. In the model which is discussed below, calculations are made for the leachable amounts of ^{234}U and ^{238}U for two rock geometries, slab and sphere. For each of these geometries, three calculations are made corresponding to (i) the zeroth etch, (ii) continuous etching of the surface to a depth x , after the zeroth etch and (iii) singularity.

The zeroth etch in this discussion refers to the first etch of an unweathered (virgin) rock surface. In this etch, the tracks having an intersection at the virgin surface would be leached out whereas the surface as a whole would be dissolved to an infinitesimally small depth, ϵ (ϵ is assumed to be much smaller relative to the alpha recoil range L). However this assumption is not critical; the calculations can readily be adjusted to any value of ϵ . After this etch, the rock surface reduces to a weathered surface which can no more offer the zeroth etch contribution. As the rock gets continually weathered, its size becomes comparable to the α -recoil range, which is termed as singularity in our model.

The model is based on the following assumptions: (i) ^{238}U and ^{234}U are in radioactive equilibrium (i.e. $^{234}\text{U}/^{238}\text{U}$ AR = 1.0) in unweathered rocks. Both ^{238}U and ^{234}U are uniformly distributed within the rock body. (ii) The radioactive mean life of ^{234}U is considerably shorter than the annealing time of alpha recoil tracks. This assumption appears to be valid from the data of Huang and Walker (1967) who have shown that the annealing characteristics of alpha recoil tracks and fission tracks are similar. They have also shown that the fission track ages of different micas and their ages based on radioactive decay, upto about 400 million years, are in excellent agreement. However, the recent results of Eyal and Fleischer (1985), indicate that the annealing time of alpha recoil tracks in minerals is $< 10^5$ yr, questioning the validity of

Figure 1. The rock body AA'B'B is broken at OO' to yield a virgin surface OO'. ^{234}U atoms lie at the positions b and c. Leaching of the parts of the tracks ab and cd in OO'B'B and AA'O'O respectively will not lead to the recovery of the ^{234}U atom.

the above assumption. If future experiments certify the recent findings, the calculations given below can be adjusted to include this factor. (iii) The etching rate within the radiation damaged area (recoil track) is much greater than the rate at which the healthy regions of the rock are attacked. However, ^{234}U would be supplied to the leach only if the surface of the grain being weathered, has the stopping end of the recoil track (where ^{234}U resides, figure 1). The number of recoil tracks containing ^{234}U atoms is Q/λ_4 , where Q is the activity of ^{238}U per unit volume (dpm cm^{-3}) and λ_4 the decay constant of ^{234}U (min^{-1}). This number would be considerably less than the total number of recoil tracks per unit volume of rock which is approximately $\{8(^{238}\text{U}) + 7(^{235}\text{U}) + 6(^{232}\text{Th})\}\tau$ where (^{238}U) , (^{235}U) and (^{232}Th) are the activities of these nuclides per unit volume of rock (dpm cm^{-3}) and τ , the storage time of alpha recoil tracks or the age of the rock, if less than τ . (iv) Track leaching is isotropic (Fleischer and Price 1963, 1964).

In the zeroth etch, each track containing a ^{234}U atom and having an opening at the surface will release its ^{234}U atom to the solution. Since the dissolution of the healthy region of the grains is assumed to be much smaller relative to that of radiation damaged zones a large excess of ^{234}U relative to ^{238}U (in activity units) would be supplied to the solution in the zeroth etch. As dissolution/weathering proceeds, new recoil tracks would be revealed and ^{234}U atoms would be continually supplied to the solution along with ^{238}U atoms. The $^{234}\text{U}/^{238}\text{U}$ AR of the solution after the zeroth etch would depend on the geometry of the grain. The surface area of spherical grains decreases as weathering proceeds radially inwards, because of this, the supply of ^{234}U to solution and $^{234}\text{U}/^{238}\text{U}$ AR in solution also decreases. When the grain dimension approximates alpha recoil range, no ^{234}U would be left in the grain and hence $^{234}\text{U}/^{238}\text{U}$ AR in the grain would be zero. In this way, the initial excess of ^{234}U obtained in the zeroth etch of a rock body is compensated and the total ^{234}U and ^{238}U activities leached out from a total rock piece remain equal. For a slab, the leached out activity of ^{234}U does not fall as gradually as in the case of a sphere. Instead, it decreases sharply only after the slab has attained a thickness equal to that of alpha recoil range. In the following, we quantitatively estimate the amounts of ^{234}U and ^{238}U leached out from a unit area of a rock surface as it passes through the above mentioned stages of weathering.

3. Etching of slab

3.1 Zeroth etch

The rock body AA'B'B was broken/cleaved at OO' to yield a freshly exposed virgin surface (figure 1). The ^{234}U activity recovered per unit area Z_4 ($s, x = \epsilon$), from this

Figure 2. Zeroth etch of a virgin slab surface. AA'O'O is a slab type rock piece with a freshly opened up virgin surface at OO'. P is the test point. Recoils crossing P towards AA' would deposit their ^{234}U atom within a range $PQ = L$. (It is assumed that the actually recoiled ^{234}Th atom does not move from its emplacement site while it decays to ^{234}U .)

surface OO' corresponding to an infinitesimal etching of the surface ($x = \varepsilon$) of the piece, OO'A'A, at the test point P (figure 2) would come from atoms stopping between P and Q ($PQ = L$, the recoil range), but only those originating from the part of the rock OO'B'B (like track ab, figure 1)

$$\begin{aligned} Z_4(s, x = \varepsilon) &= \int_0^{\pi/2} 2\pi J \sin \theta \cos \theta L d\theta \\ &= \pi J L, \end{aligned} \quad (1)$$

where $Z_4(s, x = \varepsilon)$ is the ^{234}U activity (dpm cm^{-2}) leached out of a unit virgin surface area of a slab of thickness s ; and J , the source strength $= Q/4\pi$, for ^{234}Th recoils ($\text{dpm cm}^{-3} \text{ sterad}^{-1}$).

It must be noted that the ^{234}U atoms originating as a result of recoils within OO'A'A and crossing the surface OO' are lost as far as Z_4 is concerned. This is to say that only the recoils going upwards and stopping in the rock piece OO'A'A contribute to the zeroth etch.

Since it is assumed that no appreciable surface dissolution takes place during the zeroth etch, the amount of ^{238}U leached out in zeroth etch is almost negligible and hence

$$Z_8(s, x = \varepsilon) \simeq 0, \quad (2)$$

where $Z_8(s, x = \varepsilon)$ is the ^{238}U activity (dpm cm^{-2}) leached out of a unit virgin surface area of a slab of thickness s , in the zeroth etch.

3.2 Continuous etching (after zeroth etch)

After the zeroth etch, the new ^{234}U atoms recovered in etching a layer at depth $x + dx$ would be due to tracks where the recoiled atom stops anywhere in the channel QPQ' (figure 3). For tracks with zenith angle from 0 to θ , where $\theta = \cos^{-1}(dx/L)$, contributions to ^{234}U activity will come from the recoils travelling upwards as well as due to recoils travelling downwards (i.e. from both the hemispheres) corresponding to a

Figure 3. Continuous etching of a slab after the zeroth etch. dx is the infinitesimal thickness. The contribution to ^{234}U comes from a range $dx \sec \theta$, in both the directions, for the zenith angle θ such that $PQ = L$. For $PQ > L$, the range remains fixed at L .

range of $dx \sec \theta$. At zenith angles exceeding θ , the contribution will be from the whole range L from both the hemispheres. The activity of ^{234}U recovered per unit area by leaching between x and $x + dx$ would then be given by

$$q_4(s, x) dx = 2 \int_0^{\cos^{-1}(dx/L)} 2\pi J \sin \theta \cos \theta dx \sec \theta d\theta + 2 \int_{\cos^{-1}(dx/L)}^{\pi/2} 2\pi J \sin \theta \cos \theta L d\theta$$

$$q_4(s, x) = 4\pi J, \quad (3)$$

where $q_4(s, x) dx$ is the total uranium activity leached out per unit area (after the zeroth etch) from a slab of thickness s , in etching from a depth x to $x + dx$.

Since the contribution to ^{238}U in any dissolution is due to the net volume of the rock dissolved, for the case of a slab it can be written as

$$q_8(s, x) = 4\pi J, \quad (4)$$

where $q_8(s, x) dx$ is the total uranium activity leached out per unit area (after the zeroth etch) from a slab of thickness s , in etching from a depth x to $x + dx$.

3.3 Singularity

Equation (3) is valid as long as the thickness of the slab exceeds L . For slab thickness $l \leq L$ (XA in figure 4), it can be shown, based on similar arguments as in the above section, that

$$q_4(l \leq L, x) dx = 2 \int_{\cos^{-1}(l/L)}^{\cos^{-1}(dx/L)} 2\pi J \sin \theta \cos \theta dx \sec \theta d\theta + 2 \int_{\cos^{-1}(dx/L)}^{\pi/2} 2\pi J \sin \theta \cos \theta L d\theta,$$

$$q_4(l \leq L, x) = 4\pi J (l/L). \quad (5)$$

There will be no contribution to ^{234}U activity from the zenith angle 0 to θ_1 $\{ = \cos^{-1}(l/L) \}$ since recoils with $PQ' \leq L$, will leave the slab (figure 4).

Figure 4. Singularity in slab. The thickness of the slab AA'XX' is less than the recoil range L . Recoils with zenith angle $\theta \leq \theta_1$ will be lost. Contribution to ^{234}U atom would come from the range $dx \sec \theta$ for zenith angles between θ_1 and θ_2 and from the range L for angles $\geq \theta_2$.

Figure 5. Zeroth etch of a virgin spherical grain. Recoils crossing the test point P into the grain would deposit their ^{234}U atom within the grain for all zenith angles $\leq \theta$ from range L . For $\theta > \cos^{-1}(L/2r)$, the range would be limited by $PQ = 2r \cos \theta$.

4. Etching of spherical grain

4.1 Zeroth etch

Following earlier lines of reasoning, the contribution to ^{234}U activity results from an infinitesimal etching of a unit surface, at the test point P (figure 5) from range L for values of PQ exceeding $L \{0 \leq \theta \leq \cos^{-1}(L/2r)\}$ and from range $2r \cos \theta$ for $PQ \leq L \{\cos^{-1}(L/2r) \leq \theta \leq \pi/2\}$. Recoils travelling downwards do not contribute to ^{234}U atoms in leaching the grain.

$$Z_4(r, x = \varepsilon) = \int_0^{\cos^{-1}(L/2r)} 2\pi J \sin \theta \cos \theta L d\theta + \int_{\cos^{-1}(L/2r)}^{\pi/2} 2\pi J \sin \theta \cos \theta 2r \cos \theta d\theta,$$

$$Z_4(r, x = \varepsilon) = \pi J L (1 - L^2/12 r^2). \quad (6)$$

And as before, for the case of ^{238}U

$$Z_8(r, x = \varepsilon) \simeq 0. \quad (7)$$

4.2 Continuous etching (after zeroth etch)

For continuous etching after zeroth etch between x and $x + dx$, the activity of ^{234}U recovered per unit area would be only from twice the range $PQ (\simeq dx \sec \theta)$ until $PQ' = L$ (figure 6).

$$q_4(r, x) dx = 2 \int_0^{\cos^{-1}\{L/2(r-x)\}} 2\pi J \sin \theta \cos \theta \sec \theta d\theta,$$

$$q_4(r, x) = 4\pi J \{1 - L/2(r-x)\}; 2(r-x) > L, \quad (8)$$

Figure 6. Continuous etching after zeroth etch of a spherical grain. The only contribution to ^{234}U atom arises due to recoils in both directions from a range PQ for all zenith angles θ such that $PQ' = L$. For larger θ the atom is lost.

And for the case of ^{238}U as before,

$$q_8(r, x) = 4\pi J, \quad (9)$$

4.3 Singularity

Equation (8) is valid only as long as $2(r - x) > L$. When $2(r - x) \leq L$, the atom recoils out of the rock section (figure 6) and hence,

$$q_4(r, x) = 0; \quad 2(r - x) \leq L. \quad (10)$$

But in the case of ^{238}U ,

$$q_8(r, x) = 4\pi J. \quad (11)$$

The above calculations, (1) to (11), are summarised in table 1.

5. $^{234}\text{U}/^{238}\text{U}$ in leaching rock/soil

In the following, based on the previous calculations (table 1), we shall calculate the total amounts of leachable ^{234}U and ^{238}U and the $^{234}\text{U}/^{238}\text{U}$ AR, resulting from leaching a rock with $^{234}\text{U}/^{238}\text{U}$ AR = 1.0 to a depth x . Both the geometries are considered to be with initial virgin surface area. We shall then consider a case of the population of grains also. The total activities of ^{234}U and ^{238}U per unit area leached out are designated as a_4 and a_8 respectively.

5.1 Slab

When a rock of slab geometry of thickness s is leached to a depth x ,

$$a_4(s, x) = Z_4(s, x = \varepsilon) + \int_0^x q_4(s, x) dx \quad (12)$$

$$a_8(s, x) = \int_0^x q_8(s, x) dx \quad (13)$$

Table 1. Theoretically expected amounts of ^{234}U and ^{238}U on leaching virgin surface of a rock containing these isotopes in equilibrium.

Geometry	Zeroth etch (dpm cm ⁻²)	Continuous etching after zeroth etch (dpm cm ⁻³)
Slab	$Z_4(s, x = \varepsilon)^a = \pi J L$	$q_4(s, x)^b = 4\pi J$
	$Z_8(s, x = \varepsilon) = 0$	$q_8(s, x) = 4\pi J$
Sphere	$Z_4(r, x = \varepsilon)^c$ $= \pi J L 1 - L^2/12r^2$	$q_4(r, x)^c$ $= 4\pi J 1 - L/2(r - x)$
	$Z_8(r, x = \varepsilon) = 0$	$q_8(r, x) = 4\pi J$

See text for details of symbols.

^a Valid if the initial slab thickness, s exceeds L . For $s = l \leq L$, the value of $Z_4(l, x = \varepsilon) = \pi J l/L$.

^b Valid if the final slab thickness s (i.e. at x), exceeds L . For $s = l \leq L$, the value of $q_4(l, x) = 4\pi J l/L$.

^c Valid for all values of grain radius, $r > L/2$. For $r \leq L/2$ (3)^{1/2}, $Z_4(r \leq L/2(3)^{1/2}, x = \varepsilon) = 0$ and $q_4(r \leq L/2, x) = 0$.

Substituting the values of $Z_4(s, x = \varepsilon)$, $q_4(s, x)$ and $q_8(s, x)$ from table 1 in (12) and (13), we obtain $R = a_4/a_8$.

$$R = \frac{\pi J L + 4\pi J x}{4\pi J x} = 1 + L/4x \quad (14)$$

where R is the $^{234}\text{U}/^{238}\text{U}$ activity ratio. Equation (14) is subject to the condition that the thickness of the slab s exceeds L .

5.2 Spherical grain

Following the previous arguments, let the total amount of uranium activity released from a virgin grain of radius r in leaching it from its present surface along the radial direction to a depth of x (cm) be represented by $a(r, x)$. Then we obtain

$$a_4(r, x) = 4\pi r^2 Z_4(r, \varepsilon) + \int_0^x 4\pi (r - x)^2 q_4(r, x) dx, \quad (15)$$

$$a_8(r, x) = \int_0^x 4\pi (r - x)^2 q_8(r, x) dx, \quad (16)$$

and

$$R = 1 - L/2r + L/4x \{1 - (L/2r)^2\} \text{ for } x \leq r. \quad (17)$$

If the grain is much larger compared to the recoil range (i.e. $2r \gg L$), (17) would reduce to (14).

For a population of grains with radii between r_1 and r_2 and with a number size

distribution (Lal and Lerman 1973; Lerman *et al* 1977), given by $dN/dr = n(r) = Cr^{-b}$, where C and b are constants, the amounts of ^{234}U and ^{238}U leached in etching each grain to a depth x are

$$a_4 \{n(r); r_1, r_2\} = \int_{r_1}^{r_2} 4\pi Cr^{2-b} Z_4(r, \varepsilon) dr + \int_{r_1}^{r_2} \int_0^x 4\pi Cr^{-b} (r-x)^2 q_4(r, x) dx dr, \quad (18)$$

$$a_8 \{n(r); r_1, r_2\} = \int_{r_1}^{r_2} \int_0^x 4\pi Cr^{-b} (r-x)^2 q_8(r, x) dx dr,$$

and

$$R = a_4 \{n(r); r_1, r_2\} / a_8 \{n(r); r_1, r_2\}. \quad (19)$$

Substituting from (18) and (19), the ratio equals

$$R = 1 + L/4x. \quad (20)$$

Equation (20) is identical to (14). This is expected since as long as the grain size is much larger compared to the recoil range ($2r \gg L$), the effect due to curvature is not prominent. For $2r \sim L$, subtractive terms of $(L/2r)$ and its higher powers, as in (17) would arise.

Now if ε is not infinitesimal as assumed (say 0.1 % of the recoil range L), but is a finite fraction α of L . In this case all the tracks with length l ($l \leq L/1000\alpha$) would be still etched for infinitesimal surface dissolution ε . ($L/1000\alpha$) can be viewed as a new recoil range L' , that would replace L in all expressions for zeroth etch contribution of ^{234}U (i.e. equations 1, 6, 14, 17 and 20). Singularity would also shift to L' instead of L . Calculations for dissolved contributions will be unaffected. Figure 7 shows the variation of R as a function of the thickness of the rock dissolved, starting from a virgin surface, for different assumed values of α .

6. Experimental evidences for preferential leaching of alpha recoil tracks

To check on the validity of the assumptions of preferential leaching of alpha recoil tracks and its role in producing radioactive disequilibrium among members of the natural radioactive decay chains, two sets of laboratory experiments were carried out. These are: (i) leaching of implanted recoils from annealed and unannealed mica, and (ii) granite leaching experiments.

6.1 Leaching of implanted recoils from mica

Mica discs (2.5 cm dia) were irradiated with recoiling ^{224}Ra and ^{212}Pb nuclei emanating from a weightless ^{232}U - ^{228}Th electrodeposited source ($\sim 10^4$ dpm). The irradiation was carried out for about four hours in an evacuated chamber. For each experiment two discs were irradiated, of which one was heated after irradiation in a furnace at $\sim 350^\circ\text{C}$ for 3 to 4 hours to anneal the recoil tracks. The annealed and un-annealed discs were assayed for their alpha activity (using a solid state detector coupled to MCA). After their

Figure 7. Theoretically estimated values of $^{234}\text{U}/^{238}\text{U}$ AR from a virgin rock surface as a function of the thickness of the rock dissolved, for different assumed values of α , the fraction of the recoil range which must be dissolved from the healthy surface in order to etch the complete recoil track. For $\alpha = 0.001$, the total range of the curve shown is available. It decreases for increasing α .

alpha assays, the samples were etched in 48% HF for 0.5 min, washed, dried and recounted. The samples were re-etched for periods of 1–5 min, counted and the process of re-etching and counting repeated for a total etch period of about 20 min. The ^{224}Ra and ^{212}Pb (counted via ^{212}Bi alphas) remaining in the discs after various etch periods are given in table 2 and figure 8 (Hussain 1983).

6.2 Granite leaching experiment

Granite of 4 ppm ^{238}U concentration was powdered to $< 150\mu\text{m}$ size and was dispersed in 1 litre of artificial river water (Strickland and Parsons 1972). It was stirred continuously with a magnetic stirrer for a period of 5 hours and then the slurry was filtered through a millipore. The filtrate was acidified with nitric acid and processed for uranium after adding ^{232}U as the yield tracer (Hussain 1983). The granite residue after the first leach was redispersed in a fresh aliquot of 1 litre of artificial river water. After another 5 hours stirring, the solid and solution phases were separated using a millipore and the whole procedure repeated. The results are given in table 3. The errors quoted are one sigma uncertainties due to counting statistics.

7. Discussion of results

The results on the leaching of ^{224}Ra and ^{212}Pb from annealed and unannealed mica (table 2, figure 8) show that these nuclides are released at a faster rate from the unannealed mica (figure 8). This result is attributable to preferential etching of recoil tracks and subsequent release of ^{224}Ra and ^{212}Pb . The decrease in the activity of ^{224}Ra

Table 2. Results of leaching recoil implanted ^{224}Ra and ^{212}Pb from mica

Code	Leaching time	% initial activity remaining on mica (counts per minute)			
		Unannealed		Annealed	
		^{224}Ra	^{212}Pb	^{224}Ra	^{212}Pb
20, 21	0-0	100	100	100	100
	5-0	29 ± 2	62 ± 3	70 ± 3	91 ± 4
	10-0	12 ± 1	45 ± 2	60 ± 3	83 ± 4
22, 24	0-0	100	100	100	100
	0-5	65 ± 3	94 ± 3	83 ± 4	100 ± 4
	2-0	54 ± 2	87 ± 3	77 ± 4	100 ± 4
	5-0	34 ± 1	80 ± 2	67 ± 3	102 ± 5
	10-0	17 ± 1	58 ± 2	61 ± 4	100 ± 6
	17-0	7 ± 1	37 ± 2	36 ± 3	89 ± 8
25, 26	0-0	100	100	100	100
	0-5	58 ± 2	90 ± 2	80 ± 3	96 ± 4
	2-0	48 ± 2	84 ± 2	69 ± 3	91 ± 4
	5-0	33 ± 1	68 ± 2	65 ± 3	95 ± 4
	10-0	17 ± 1	55 ± 2	58 ± 3	81 ± 4
	17-0	7 ± 1	40 ± 2	49 ± 3	84 ± 4
	22-0	—	—	40 ± 2	74 ± 4

Table 3. Results of the granite leaching experiments

Leach number	Period of contact (hrs)	^{238}U activity in leach (dpm)	$^{234}\text{U}/^{238}\text{U}$ (AR)
1	5	1.03 ± 0.05	1.45 ± 0.09
2	5	0.77 ± 0.02	1.5 ± 0.09
3	5	0.91 ± 0.04	1.46 ± 0.07
4	20	0.74 ± 0.04	1.52 ± 0.09
5	39	0.32 ± 0.04	1.35 ± 0.08

in the annealed mica (table 2), most probably results from mica dissolution. 48% HF is a strong etchant and therefore the dissolution effect could be quite significant. However, the dissolution through recoil tracks is significantly faster and is almost complete over a period of about 20 to 30 min in 48% HF.

The results of the granite leaching experiment (table 3) show the presence of excess ^{234}U in the solution phase in all the leaches. The short period of contact between the granite and the water precludes the source of this ^{234}U excess being the *in situ* recoil of ^{234}Th and its decay to ^{234}U (Kigoshi 1971) and shows that it could only be due to the preferential leaching of ^{234}U , either from recoil tracks or due to higher mobility of ^{234}U . The continued supply of excess ^{234}U to the aqueous phase even after about 70 hours of leaching time (table 3) could be either due to an incomplete etching of all recoil tracks within this duration or that "virgin" surfaces are continually exposed through breaking of existing grains.

Figure 8. The percent activity of ^{212}Pb and ^{224}Ra remaining in the mica disc for various etch periods. Solid hexagons represent the activity in the unannealed samples and open ones that in the annealed samples. The sharper decrease in the residual activity in the unannealed mica shows the effect of preferential solution through alpha recoil tracks.

7.1 ^{234}U leaching dynamics in natural waters

The radioactive disequilibrium between ^{234}U and ^{238}U in natural waters is intimately related to the mechanism of rock weathering. In the previous section it was shown that excess $^{234}\text{U}/^{238}\text{U}$ AR was expected to arise by preferential track leaching only when a 'virgin' surface is leached by an aqueous medium.

Rivers, lakes and groundwaters, by and large, are characterised by $^{234}\text{U}/^{238}\text{U}$ AR > 1 (Scott 1982; Osmond and Cowart 1982). It can be inferred from coral data that the ^{234}U excess in the oceans is in a steady state relative to its supply and removal. Such a continuous supply of ^{234}U excess from the same drainage area is difficult for explanation by the above track leaching model, unless virgin surfaces are made available for preferential supply of ^{234}U .

Almost all known crystalline rocks like granite, dunite or quartzite contain abundant microcracks and cavities known as flaws (Sprunt and Brace 1974; Montgomery and Brace 1975). These are produced mainly as a result of the stress and temperature changes to which an ordinary rock is subjected after its formation. Large differences are expected between rock types since the elastic constants and thermal expansion coefficients of minerals vary appreciably (Nur and Simmons 1970).

Weathering results in a continuous fragmentation of the rock (figure 9). The character of fissuring will depend on the rock type, the greater the density of flaws in a rock body (Nur and Simmons 1970; Tapponier and Brace 1976; Logan 1979), the greater would be the fissuring per unit rock dissolution. It is thus expected that as the exposed surface is leached, simultaneously connecting virgin (fresh) surface will be exposed. With the progression of weathering as exposed surfaces are leached, further exposure would occur. The fragmentation of a rock into rocklets proceeds at all levels, larger grains breaking into smaller grains and so on.

Figure 9. Cartoon showing the breaking up of grains in yielding virgin surfaces and the excess ^{234}U in a weathering process. Dots represent ^{238}U atoms (shown exaggerated), small rectangles, the alpha recoil tracks, and the lines, the flaws or the micro-cracks in the body of the grain (the dotted line shows the extent of dissolution). Only those tracks with a dot inside have a ^{234}U atom within. ^{234}U atom is preferentially extracted from an exposed track to the surface in weathering. AR stands for $^{234}\text{U}/^{238}\text{U}$ activity ratio.

The excess of ^{234}U in leach waters would depend on the rate at which new fissures open up during weathering. Since the rate of leaching would depend on the chemical composition of the waters leaching the rock, and also the chemical composition of the rock itself, we may quantify the weathering process relevant to the supply of excess ^{234}U activity and solution as K , the ratio of two parameters, viz, the rate at which virgin surface is exposed during weathering, $\dot{A}$ ($\text{cm}^2 \text{y}^{-1}$) and the rate of dissolution of an exposed surface during weathering, ξ ($\text{g} \text{y}^{-1}$). $K = \dot{A}/\xi$ has the dimension $\text{cm}^2 \text{g}^{-1}$ and signifies the mean area residing in microcracks per unit rock mass. It is this area which opens up during the mass dissolution of a rock.

In the following we present a model relating the $^{234}\text{U}/^{238}\text{U}$ AR in the aqueous phase resulting from leaching a rock body with a characteristic ratio K . For simplicity we shall consider a spherical grain of a unit surface area and density ρ (g cm^{-3}). The time variation in the ^{234}U and ^{238}U activities in the aqueous phase are given by:

$$da_4/dt = \dot{A} Z_4(r, x = \varepsilon) + q_4(r, x) (\xi/\rho) + \lambda_4 a_8 - \lambda_4 a_4, \quad (21)$$

and

$$da_8/dt = q_8(r, x) (\xi/\rho) - \lambda_8 a_8, \quad (22)$$

t denotes the time parameter, other symbols are as stated earlier.

In general, magnitude of the radioactive production and decay terms in (21) and (22) are negligible relative to leaching and dissolution supply rates. Further for $t \ll \lambda_4^{-1}$, the production of ^{234}U in the leach from a_8 and its decay, will be insignificant and hence the $\lambda_8 a_8$ and $\lambda_4 a_4$ terms in (21) and (22) can be deleted. Substituting $Z_4(r, x = \varepsilon)$, $q_4(r, x)$ and $q_8(r, x)$ from table 1 and solving (21) and (22) we get

$$a_4 = (\dot{A}L + 4\xi/\rho) \pi Jt + a_4^0, \quad (23)$$

and

$$a_8 = 4\pi J \xi t / \rho + a_8^0, \quad (24)$$

where a_4^0 and a_8^0 are the values of a_4 and a_8 at $t = 0$.

At $t = 0$ when the grain comes in contact with the etchant, there is no dissolution and hence $\hat{a}_8 = 0$. However, if the grain had a virgin surface, $\hat{a}_4$ would be the amount of ^{234}U brought into solution in the zeroth etch because the etching through tracks is

Figure 10. Scattergram of ^{234}U excess vs ^{238}U for Indian groundwaters. The correlation coefficient for the least squares fit is about 0.8–0.9 and the slope between 0.3 to 0.8.

Figure 11. Scattergram of ^{234}U excess vs ^{238}U for Indian river waters (Borole *et al* 1982) and groundwaters from Tokyo (Kigoshi 1973). The correlation coefficients are 0.97 and 0.94, and the slopes 0.7 and 1.5, respectively.

assumed to be instantaneous. For a weathered grain, $\hat{a}_4 = 0$. From (23) and (24), we obtain the excess ^{234}U activity $a_4(\text{exc}) (= a_4 - a_8)$ for a virgin grain as:

$$a_4(\text{exc}) = (KL\rho/4)a_8 + \hat{a}_4. \quad (25)$$

Equation (25) is a linear equation and shows that the excess activity of ^{234}U should be linearly dependant on the ^{238}U activity with a slope of $(KL\rho/4)$.

Linear plots of the available data on groundwaters as well as river waters (figures 10 and 11) fit (25). The slope values $(KL\rho/4)$ as estimated through least squares regression analysis for Indian waters range between 0.3 to 0.8 (table 4). Similar analysis for uranium isotopic data for the granite leaching experiments in the laboratory (table 3) also yields the value of the slope as 0.3 ± 0.2 . For typical values of ρ and L as 2 g cm^{-3} and $200 \text{ \AA}$ respectively, the range of the slope corresponds to a range of K , the characteristic ratio of the rock, present in the Indian zone referred here, between 3×10^5 to $8 \times 10^5 \text{ cm}^2 \text{ g}^{-1}$.

^{234}U and ^{222}Rn are produced in a rock at similar sites and at equal rates and thus whatever be the mechanisms of their introduction from rocks into the solution phase,

Table 4. Results of the least squares regression analysis for uranium isotopic data in natural waters to (25) from text.

Water type	Data points	Correlation coefficient	Slope ($\rho LK/4$)	Intercept	References
Ground-waters	43	0.88	0.36 ± 0.03	-0.09 ± 0.23	Hussain (1983)
Ground-waters	53	0.81	0.3 ± 0.03	0.22 ± 0.26	Bhandari <i>et al</i> (1982)
River waters	15	0.97	0.7 ± 0.05	-0.21 ± 0.05	Borole <i>et al</i> (1982)
River waters	6	0.92	0.55 ± 0.11	-0.1 ± 0.28	Bhat and Krishnaswami (1969)
River waters	4	1.0	0.29 ± 0.02	0.002 ± 0.007	
Ground-waters	25	0.91	0.83 ± 0.08	0.35 ± 0.14	
Ground-waters	24	0.92	0.7 ± 0.06	-0.61 ± 0.3	Borole <i>et al</i> (1979)
River waters	13	0.93	0.83 ± 0.01	-1.64 ± 0.54	
Ground-waters	19	0.94	1.46 ± 0.13	-0.14 ± 0.22	Kigoshi (1973)
Ground-waters	4	0.95	7.99 ± 1.93	-1.17 ± 0.42	Gilkeson (1982)
Ground-waters	11	0.85	16.38 ± 3.37	0.65 ± 0.55	

the extent of the rock surface area associated with a unit dissolved activity of either ^{234}U or ^{222}Rn would be the same, provided that both these nuclides are transported from rock into solution quantitatively. Hussain (1983) estimated the specific surface area of the solids in Gujarat aquifers, based on ^{222}Rn measurements, to be $c. 1.6 \times 10^5 \text{ cm}^2 \text{ g}^{-1}$. Accounting for the ^{222}Rn escape factor of 0.235 (Andrews and Wood 1972) the specific surface area of the Gujarat aquifer solids would become $c. 7 \times 10^5 \text{ cm}^2 \text{ g}^{-1}$, which is in excellent agreement with the value of K derived above, based on ^{234}U excess, for similar rocks.

It should be noted that Kulp and Carr (1952) have reported the average specific surface area of the deep sea sediments to be $c. 2.5 \times 10^5 \text{ cm}^2 \text{ g}^{-1}$.

The value of K between $3\text{--}8 \times 10^5 \text{ cm}^2 \text{ g}^{-1}$ is an upper limit, for there could be a finite contribution to the excess ^{234}U used in the calculation, from the direct recoil of ^{234}Th followed by its decay. The importance of recoil becomes particularly significant when the intensity of weathering is low and the time of soil-water contact high. The higher values of the slopes in the case of the Japanese groundwaters (Kigoshi 1973) and the Ordovician aquifer (Gilkesson 1982) (table 4, figure 11) could be due to this effect.

For a given soil-water system, (K_e) is a measure of the rate of opening of new surface area ($\text{cm}^2 \text{ y}^{-1}$). It is possible to estimate this rate on the continents from a knowledge of the continental weathering rate. Using the value of ϵ as the flux of total dissolved solids, $4 \times 10^{14} \text{ g y}^{-1}$ (Garrels and Mackenzie 1971) and K as the average specific surface area of the deep sea sediments, $2.5 \times 10^5 \text{ cm}^2 \text{ g}^{-1}$ (Kulp and Carr 1952), the rate of production of the surface area on the continents can be calculated as $10^{20} \text{ cm}^2 \text{ y}^{-1}$. Implicit in this calculation is an assumption that the surface area produced on the continents through rock weathering is lost to the oceans by the suspended load of the continental run-offs. Based on the total suspended load, $2.5 \times 10^{16} \text{ g y}^{-1}$ (Garrels and Mackenzie 1971), the average specific surface area of the suspended load of rivers works out to be $4 \times 10^3 \text{ cm}^2 \text{ g}^{-1}$. This is the area from which direct recoils are ejected into the waters.

7.2 $^{234}\text{U}/^{238}\text{U}$ activity ratio and rock characteristics

In the previous discussion we have shown that there exists a linear relation between the leachable excess of ^{234}U and total ^{238}U from rocks (25). In terms of $^{234}\text{U}/^{238}\text{U}$ AR leached out from weathered rock ($a_4^0 = 0$), (25) simplifies to:

$$R = 1 + (KL\rho/4). \quad (26)$$

Equation (26) suggests that for a given type of rock ($K = \text{constant}$), the AR obtainable in leaching is fixed and is independent of the rock dissolution. In other words, the leachable AR from a rock characterizes it.

Some results of the laboratory leaching experiments on zircon, granite and limestone, by mild leachants are presented in table 5. In all these, a single respective rock aliquot was leached repeatedly after discarding the zeroth etch. The resistant mineral zircon yields AR close to unity at various stages of its dissolution (varying dissolved ^{238}U), whereas carboniferous limestone yields higher AR. The mean AR for zircon, granite and limestone (table 5) correspond to their respective K values (26) of $0 \pm 5 \times 10^4$, $4 \pm 0.8 \times 10^5$ and $9 \pm 1 \times 10^5 \text{ cm}^2 \text{ g}^{-1}$ ($L = 0.02 \text{ }\mu\text{m}$ and $\rho = 4, 2.5$ and 2.0 g cm^{-3} , respectively). Andrews *et al* (1982) have reported $^{234}\text{U}/^{238}\text{U}$ AR centered around 3 in shallow Stripa groundwaters for dissolved ^{238}U concentrations ranging from 1 to about 90 ppb. This

Table 5. Dissolved $^{234}\text{U}/^{238}\text{U}$ activity ratios in continuous leaches of three rock minerals, zircon, granite and carboniferous limestone.

Rock type	Dissolved activity in solution		Reference
	^{238}U (dpm)	$^{234}\text{U}/^{238}\text{U}$ (AR)	
Zircon	1.0 ± 0.1	0.94 ± 0.1	Hussain (1983)
	3.0 ± 0.3	0.98 ± 0.1	
	5.9 ± 0.5	0.95 ± 0.1	
	6.4 ± 0.6	0.94 ± 0.1	
Granite	0.7 ± 0.1	1.52 ± 0.09	Present Work
	1.0 ± 0.1	1.45 ± 0.09	
Carboniferous* limestone	1.1 ± 0.1	1.81 ± 0.1	Present Work
	1.3 ± 0.1	1.98 ± 0.07	

*From Cornwall, England

constancy of AR in shallow and young groundwaters for their increasing dissolved ^{238}U concentrations, is in an excellent agreement with our model and suggests that Stripa granites from the shallow groundwater zone (Andrews *et al* 1982) can be characterized with their leachable AR of *c.* 3. One of us (NH) is working on the distribution of uranium isotopes in the laboratory leaches of Stripa granites and the preliminary results do seem to confirm the view.

A rock in equilibrium ($^{234}\text{U}/^{238}\text{U}$ AR = 1.0) on leaching cannot yield $R > 1$ ad infinitum as suggested by (26). This apparently perpetual generation of ^{234}U in (26) is an artifact of neglecting the contribution to the excess ^{238}U from the dissolution of singular particles as and when they are produced in the process of rock dissolution-cum-fragmentation. To make an appropriate provision for the excess ^{238}U from singular particles, information about their production rate is essential. For simplicity from the requirement of mass balance of ^{234}U and ^{238}U in the rock, certain deductions can be made. Figure 12 shows qualitatively the variations of the total dissolved ^{234}U and the AR as a function of rock dissolution in a closed system. Curve a is an ideal line for a case where rock dissolution does not produce fragmentation ($K=0$) and the dissolved concentrations of ^{234}U and ^{238}U remain almost in the same proportion as they exist in the parent rock (AR = 1.0) at all stages of its dissolution. When dissolution is followed by fragmentation, the line becomes steeper (curve b), the slope depending on the specific fragmentation per unit dissolution. It is assumed here that the particles with singular dimensions are isolated from dissolution as and when they are produced. Discontinuity in curve b occurs when the singular particles alone are left in the system. Any further dissolution does not add ^{234}U but only ^{238}U and yields curve c. Curve c joins curve a when all the singular particles are dissolved, thus leaving the dissolved concentrations of ^{234}U and ^{238}U the same as existed in the rock. In case the singular particles are not isolated from dissolution but dissolve as and when produced, curve d would result with a curvature depending upon the rate of production of the singular particles. The corresponding variation of AR is shown by curves a', b', c' and d' respectively. Since the rock is assumed to be virgin to start with, for the initial

Figure 12. Variations of cumulative activities of ^{234}U and ^{238}U , and the $^{234}\text{U}/^{238}\text{U}$ activity ratios in leaching a rock, are shown qualitatively. See text for a discussion of the curves a, b, c, d and a', b', c', and d'.

infinitesimal dissolution, AR tends to be very high and comes down to a quasi-steady state value until singular particles start dissolving. $\text{AR} < 1$ in solution is possible when the majority of the particles being leached are of singularity dimensions.

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