CHAPTER - V

$^{234}\text{U}/^{238}\text{U}$ RADIOACTIVE DISEQUILIBRIUM IN NATURAL WATERS:
SIGNIFICANCE OF PREFERENTIAL SOLUTION THROUGH RECOIL TRACKS

5.1 INTRODUCTION:

In most natural waters, $^{234}\text{U}$ activity exceeds that of its grand parent $^{238}\text{U}$. This radioactive disequilibrium between $^{234}\text{U}$ and $^{238}\text{U}$ is widely used 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. Three mechanisms have been suggested for the commonly observed excess $^{234}\text{U}$ in natural waters (Osmond and Cowart, 1982).

i) Change of the chemical valence state of $^{234}\text{U}$ atom as a result of "hot atom effect" during its radioactive production from $^{238}\text{U}$. It was proposed that $^{234}\text{U}$ is oxidised to $+6$ valence state during this process and is preferentially mobilised during its weathering (Dooley et al, 1966).

ii) Release of $^{234}\text{Th}$ from soil/rock surface into the pore water by direct recoil during alpha decay of $^{238}\text{U}$ and subsequent decay of $^{234}\text{Th}$ to $^{234}\text{U}$ in the pore water (Kigoshi, 1971).

iii) Preferential dissolution of $^{234}\text{U}$ contained in the tracks produced as a result of radiation damage during alpha decay of $^{238}\text{U}$ (Fleischer and Raabe, 1978).
Experimental evidences supporting the various mechanisms are available in literature. However, the quantitative significance of any of them in controlling the $^{234}$U/$^{238}$U activity ratio (AR) in natural waters is not well understood. In this chapter a quantitative model to predict the $^{234}$U/$^{238}$U during track leaching process is developed. Results in support of the model are also presented.

During weathering processes $^{234}$U and $^{238}$U are continually leached from the rock/soil. Except for $^{238}$U, which is added into the solution from the dissolution of the rock matrix, all other daughter nuclides of the series are leached out through the alpha recoil tracks which they are contained in. It is well known that the tracks are etchable much faster than the healthy material (Huang and Walker, 1967; Fleischer et al, 1975). However, the AR leached out may depend upon the nature of the rock, the surface texture, the rock geometry, the size of the rock body or grain in relation to alpha recoil range etc. In the model which is discussed below, calculations for the leachable amounts of $^{234}$U and $^{238}$U for two rock geometries, namely (i) slab type and (ii) sphere type are made. For each one of these geometries, three calculations are effected corresponding to -

a) Zeroth etch
b) continuous etching of the surface to a depth $x$, after zeroth etch, and
c) singularity
Zeroth etch in this discussion is defined as 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 $\varepsilon$ ($\varepsilon$ is assumed to be much smaller relative to the alpha recoil range $L$). After this etch, the rock surface reduces to a weathered surface which can no more offer the zeroth etch contribution. As the rock continually dissolves, it finally attains dimensions comparable to the recoil range. This event is termed as singularity and separate calculation is made for it.

5.2 **MODEL AND ITS ASSUMPTIONS**:

The model is based on the following assumptions:

1) $^{238}U$ and $^{234}U$ are in radioactive equilibrium (i.e. $^{234}U/^{238}U\ AR = 1.0$) in unweathered rocks. Both $^{238}U$ and $^{234}U$ are uniformly distributed within the rock body (Somayajulu et al, 1966).

2) The radioactive mean life of $^{234}U$ is considerably shorter than the annealing time of alpha recoil tracks. This assumption is valid; for Huang and Walker (1967) have shown the annealing characteristics of alpha recoil as well as fission tracks are almost 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.
iii) The etching rate within the recoil track is significantly greater than the rate at which the general rock body is attacked. If the rock body contains the stopping end of the track where $^{234}\text{U}$ atom resides, the atom is extracted in the etch, otherwise the etching of the track does not lead to the recovery of the $^{234}\text{U}$ atom (Fig. V.1).

iv) Track etching is assumed to be isotropic (Fleischer and Price, 1953; 1964).

v) Etching is uniform; etching is always perpendicular to the surface being etched.

The difference between the actual number of tracks and the tracks containing $^{234}\text{U}$ atoms within must be noted. The total number of tracks in a rock body would be about 8 times that of the total $^{238}\text{U}$, $^{235}\text{U}$ and $^{232}\text{Th}$ decays taken place since the formation of the rock whereas the tracks having $^{234}\text{U}$ atoms inside will be only $Q/\lambda_4$, $Q$ being the activity of $^{238}\text{U}$ (and hence $^{234}\text{U}$) per unit volume of the rock (dpm cm$^{-3}$) and $\lambda_4$, the decay constant of $^{234}\text{U}$. The concern here is only with those tracks which contain a recoverable $^{234}\text{U}$ atom inside.

In the zeroth etch, each track containing $^{234}\text{U}$ atom and having an opening at the surface will release its $^{234}\text{U}$ atom in the solution. Since the surface dissolution
Fig. V.1: The rock body AA'B'B is broken at 00' to yield a virgin surface 00'. $^{234}\text{U}$ atoms lie at the positions b and c. Leaching of the parts of the tracks ab and cd in 00'B'B and AA'O'O respectively will not lead to the recovery of the $^{234}\text{U}$ atom.
is minimal in this etch, a large excess of $^{234}$U atoms results from this etching. (The size of the rock leached is greater than the alpha recoil range.) In subsequent leachings, as the dissolution proceeds, new tracks open up and the gain due to deeper seated $^{234}$U atoms coming in the solution is nearly compensated by the loss from the outer layer in the zeroth etch. Actually the loss of $^{234}$U from the outer layer will be a little higher than the gain from the subsequent layer, because, as the rock dissolves, its surface area decreases (assuming no fragmentation). In the last step of etching, when the rock dimension is reduced to a recoil range, there occurs no gain from the deeper layer, since there is no track having a $^{234}$U atom and AR becomes zero. In this way, the initial gain 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.

5.3 SYMBOLS:

The symbols used in the model are:

$L$: Recoil range of $^{234}$Th atom in the rock, following alpha decay of $^{238}$U (cm).

$Q$: Average $^{238}$U activity per unit volume of the rock; (dpm cm$^{-3}$).

$J$: Source strength = $Q/4\pi$, for $^{234}$Th recoils; an operational parameter; (dpm cm$^{-3}$ sterad$^{-1}$).

$A$: Radioactive decay constant; (min$^{-1}$).

$r$: Grain radius; (cm).
\( \rho \) : Average rock density \((g \text{ cm}^{-3})\).

\( x \) : Etched away thickness of either a slab or a grain, always taken perpendicular to the surface; \((\text{cm})\).

\( n(r) \) : Differential size (radius) distribution of grains,
\[
n(r) = \frac{dN}{dr}; \quad (\text{cm}^{-1}).
\]

\( m(r) \) : Differential mass distribution of grains,
\[
m(r) = \frac{dM}{dr}; \quad (g \text{ cm}^{-1}).
\]

\( Z(r,x=\varepsilon) \) : Uranium activity leached out of a unit virgin surface area of a grain of radius \( r \); \((\text{dpm cm}^{-2})\).
This corresponds to the activity leached out in the zeroth etch.

\( Z(t,x=\varepsilon) \) : Same as above, for a slab of thickness \( t \);
\((\text{dpm cm}^{-2})\).

\( \dot{q}(r,x) \) : Total uranium activity leached out per unit area (after the zeroth etch) from a grain of radius \( r \),
in etching from a depth \( x \) to \( x + dx \); \((\text{dpm cm}^{-3})\).

\( \dot{q}(t,x) \) : Same as above for a slab of thickness \( t \);
\((\text{dpm cm}^{-3})\).

5.4 ETCHING OF SLAB :

5.4(a) Zeroth etch :

The rock body AA'B'B was broken/cleaved at 00', to yield a freshly exposed virgin surface (Fig. V.1).
The $^{234}\text{U}$ activity recovered per unit area $Z_A(t, x = \varepsilon)$, from this surface $00'$, corresponding to an infinitesimal etching of the surface ($x = \varepsilon$) of the piece, $00'A'A$, at the test point $P$ (Fig. V.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 $00'B'B$ (like track ab, Fig. V.1).

\[
Z_A(t, x = \varepsilon) = \frac{\pi/2}{4} \int_0^{\pi} J \sin \theta \cos \theta L d\theta = \pi JL
\]  

... (5.1)

It must be noted that the $^{234}\text{U}$ atoms originating as a result of recoils within $00'A'A$ and crossing the surface $00'$ are lost as far as $Z_A$ is concerned. This is to say that only the recoils going upwards and stopping in the rock piece $00'A'A$ contribute to the zeroth etch.

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

\[
Z_B(t, x = \varepsilon) \approx 0
\]  

... (5.2)

5.4(b) **Continuous etching (after zeroth etch):**

After zeroth etch, the new $^{234}\text{U}$ atoms recovered in etching a layer at depth $x$ to $x + dx$ would be due to tracks where the recoiled atom stops anywhere in the channel
Fig. V.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 O0'. P is the test point. Recoils crossing P towards AA' would deposit their $^{234}\text{U}$ atom within a range PQ = L. (It is assumed that the actually recoiled $^{234}\text{Th}$ atom does not move from its emplacement site while it decays to $^{234}\text{U}$.)
QPQ' (Fig. V.3). For tracks with zenith angle from 0 to $\theta$, 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 range of $dx$ sec $\theta$. At zenith angles exceeding $\theta$, the contribution will be from the whole range $L$ from both the hemispheres. The number of atoms of $^{234}$U recovered per cm$^2$ by leaching between $x$ and $x + dx$ would then be given by

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

$$q_4(t,x) = 4\pi J \cos^{-1}(dx/L)$$

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

$$q_8(t,x) = 4\pi J$$

$5.4(c)$ **Singularity**:

Equation (5.3) is valid as long as the thickness of the slab exceeds $L$. For slab thickness $l < L(XA$ in Fig. V.4), it can be shown based on similar arguments as in section 5.4(b) that
Fig. V.3: Continuous etching of a slab after 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 $\theta$ such that $PQ = L$. For $PQ > L$, the range remains fixed at $L$. 

\[ \text{\#} \]
Fig.V.4: Singularity in slab. The thickness $L$ of the slab $AA'B'B$ is less than the recoil range $L$. Recoils with zenith angle $< \theta_1$ will be lost. Contribution to $^{234}\text{U}$ atom would come from the range $dx \sec \theta$ for the zenith angle between $\theta_1$ and $\theta_2$ and from the range $L$ for angles $> \theta_2$. 
\[ q_4(L < L, x) = 4 \pi J \left( \cos^{-1} \left( \frac{dx}{L} \right) \right) \]  

There will be no contribution to \(^{234}\text{U}\) activity from the zenith angle \(0 \leq \theta \leq \cos^{-1} \left( \frac{L}{2r} \right)\) since recoils with \(PQ' \leq L\), will leave the slab (Fig. V.4).

\[ q_8(L < L, x) = 4 \pi J \left( \cos^{-1} \left( \frac{dx}{L} \right) \right) \]  

5.5 ETCHING OF SPHERICAL GRAIN:

5.5(a) Zeroth etch:

Following earlier lines of reasoning, contribution to \(^{234}\text{U}\) activity results from an infinitesimal etching of surface, at the test point \(P\) (Fig. V.5) per cm\(^2\) from range \(L\) for values of \(PQ\) exceeding \(L(0 \leq \theta \leq \cos^{-1} \left( \frac{L}{2r} \right)\)) and from range \(2r \cos \theta\) for \(PQ < L (\cos^{-1} \left( \frac{L}{2r} \right) \leq \theta < \pi/2)\). Recoils travelling downwards do not contribute to \(^{234}\text{U}\) atoms in leaching the grain.
Fig.V.5 : Zeroth etch of a virgin spherical grain.
Recoils crossing the test point P into the grain would deposit their $^{234}\text{U}$ atom within the grain for all zenith angles $<\theta$ from the range L. For $\theta > \cos^{-1}(L/2r)$ the range would be limited by $PQ = 2r \cos \theta$. 
\[
\cos^{-1}(L/2r)
\]
\[
Z_4(r,x = \varepsilon) = \int 2\pi J \sin \theta \cos \theta L \, d\theta
\]
\[
+ \int_{\pi/2}^{\pi/2} 2\pi J \sin \theta \cos \theta 2r \cos \theta \, d\theta
\]
\[
\cos^{-1}(L/2r)
\]
\[
Z_4(r,x = \varepsilon) = \pi J L(1 - L^2/12r^2)
\] ...

(5.7)

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

\[
Z_8(r,x = \varepsilon) \approx 0
\] ...

(5.8)

5.5(b) \textbf{Continuous etching (after zeroth etch)}:

For continuous etching after zeroth etch between $x$ and $x + dx$, the activity of $^{234}\text{U}$ recovered per cm$^2$ would be only from twice the range $PQ(dx \sec \theta)$ till $PQ' = L$ (Fig. V.6).

\[
\cos^{-1}\{L/2(r-x)\}
\]
\[
q_4(r,x)\,dx = 2 \int 2\pi J \sin \theta \cos \theta \, dx \sec \theta \, d\theta
\]
\[
0
\]
\[
q_4(r,x)\,dx = 4 \pi J[1 - \frac{L}{2(r-x)}]; \quad 2(r-x) \geq L
\] ...

(5.9)

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

\[
q_8(r,x) = 4\pi J
\] ...

(5.10)
Fig.V.6: Continuous etching after zeroth etch of a spherical grain. The only contribution to $^{234}\text{U}$ atom arises due to recoils in both directions from a range $PQ$ for all zenith angles $\theta$ such that $PQ' = L$. For larger $\theta$ the atom is lost.
5.5(c) **Singularity:**

Relation (5.9) is valid only as long as \(2(r-x) > L\). When \(2(r-x) \leq L\), the atom recoils out of the rock section (Fig. V.6) and hence

\[
\dot{q}_4(r,x) = 0 \quad ; \quad 2(r-x) \leq L \quad \ldots (5.11)
\]

But in the case of \(^{238}\text{U}\):

\[
\dot{q}_8(r,x) = 4\pi J \quad \ldots (5.12)
\]

The above calculations, equations (5.1) to (5.12) are summarized in Table V.1.

Based on these basic calculations, expressions for the \(^{234}\text{U} / ^{238}\text{U}\) activity ratio obtainable in leaching a slab and spherical grain to a depth \(x\), starting with a virgin surface are derived. In case of spherical grains an expression for \(AR\) is derived for the case of a hyperbolic grain size distribution also.
Table V.1: Theoretically expected amounts of $^{234}$U and $^{238}$U on leaching virgin surface of a rock containing $Q$ dpm of $^{238}$U and $^{234}$U per unit volume of the rock (in equilibrium); ($Q/4\pi = J$). Z and q are the total amounts (dpm) of $^{234}$U (q) or $^{238}$U (8) introduced into the solution, per cm$^2$ surface area ($q = \frac{dq}{dx}$)

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Zeroth etch (dpm cm$^{-2}$)</th>
<th>Continuous etching (after zeroth etch) (dpm cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slab</td>
<td>$Z_4(t, x = \varepsilon)^a) = \pi JL$</td>
<td>$q_4(t, x)^b = 4\pi J$</td>
</tr>
<tr>
<td></td>
<td>$Z_8(t, x = \varepsilon) = 0$</td>
<td>$q_8(t, x) = 4\pi J$</td>
</tr>
<tr>
<td>Sphere</td>
<td>$Z_4(r, x = \varepsilon)^c) = \pi JL(1-\frac{L^2}{12r^2})$</td>
<td>$q_4(r, x)^c) = 4\pi J(1-\frac{L}{2(r-x)})$</td>
</tr>
<tr>
<td></td>
<td>$Z_8(r, x = \varepsilon) = 0$</td>
<td>$q_8(r, x) = 4\pi J$</td>
</tr>
</tbody>
</table>

a) Valid if the initial slab thickness, t exceeds L. For $t = \ell < L$, the value of $Z_4(\ell, x = \varepsilon) = \pi JL/\ell$.

b) Valid if the final slab thickness (ie at x), t, exceeds L. For $t = \ell < L$, the value of $q_4(\ell, x) = 4\pi J \ell/L$.

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

5.6 \(^{234}\text{U}/^{238}\text{U}\) LEACHING FROM A SLAB/GRAIN:

In the following, based on the previous calculations (Table V.1), total amount of leachable \(^{234}\text{U}\) and \(^{238}\text{U}\) and the \(^{234}\text{U}/^{238}\text{U}\) (AR) designated as \(R\) are calculated resulting from leaching a rock with \(^{234}\text{U}/^{238}\text{U}\) (AR) = 1.0 to a depth \(x\). Both the geometries - the slab and the spherical grain, are considered separately. The initial rock surface is assumed to be virgin. A case of the population of grains is also considered. The total amounts of \(^{234}\text{U}\) and \(^{238}\text{U}\) are designated as \(q_4\) and \(q_8\) respectively.

5.6(a) Slab:

Leaching from only one face is considered

\(q = \text{activity recovered } \text{cm}^{-2}\text{ surface leached.}\)

\[
q_4(0-x) = Z_4(t,x = \epsilon) + \int_0^x q_4(t,x) \, dx \quad \cdots (5.13)
\]

\[
q_8(0-x) = \int_0^x q_8(t,x) \, dx \quad \cdots (5.14)
\]

Substituting the values of \(Z_4(t,x = \epsilon), q_4(t,x)\) and \(q_8(t,x)\) from Table V.1 in equations (5.13) and (5.14)

\[
R = \frac{\pi JL + 4\pi Jx}{4 \pi Jx} = 1 + \frac{L}{4x} \quad \cdots (5.15)
\]
This is subject to the thickness of the slab being larger than \( L \) at all times.

5.6(b) Spherical grains:

5.6(b)(i) Single grain:

If \( q(r,x) \) = 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) then,

\[
q_4(r,x) = 4\pi r^2 z_4(r,\varepsilon) + \int_0^x 4\pi (r-x)^2 q_4(r,x) \, dx \quad \ldots(5.16)
\]

\[
q_8(r,x) = \int_0^x 4\pi (r-x)^2 q_8(r,x) \, dx \quad \ldots(5.17)
\]

and

\[
R = 1 - \frac{L}{2} + \frac{L}{4x} (1 - \frac{L^2}{12r^2}) ; (x \ll L) \quad \ldots(5.18)
\]

5.6(b)(ii) Population of grains:

For a population of grains with radii between \( r_1 \) and \( r_2 \) and with a number-radius distribution given by

\[
\frac{dN}{dr} = n(r) = Ar^{-b} \quad \text{(section 4.1(b))}, \text{ the amounts of } ^{234}\text{U and } ^{238}\text{U leached out in etching each grain by } x \text{ are} \]
\[ q_4 \{ n(r); r_1, r_2 \} = \int_{r_1}^{r_2} 4\pi Ar^{-b} z_4 \, dr \]
\[ + \int_{r_1}^{r_2} \int_{0}^{x} \frac{4\pi Ar^{-b}}{(r-x)^2} q_4(r,x) \, dx \, dr \] (5.19)

\[ q_8 \{ n(r); r_1, r_2 \} = \int_{r_1}^{r_2} \int_{0}^{x} \frac{4\pi Ar^{-b} (r-x)^2}{\lambda r^{-b}} q_3(r,x) \, dx \, dr \] (5.20)

\[ R = \frac{q_4 \{ n(r); r_1, r_2 \}}{q_8 \{ n(r); r_1, r_2 \}; (r>> L; x<< r)} \] substituting from 5.19 and 5.20 and simplifying one gets

\[ R = 1 + \frac{L}{4x} \] (5.21)

same as for a slab; equation (5.15)

Fig. V.7 shows the variation of R as a function of the thickness dissolved x.

5.7 EXPERIMENTAL EVIDENCES FOR PREFERENTIAL LEACHING OF ALPHA RECOIL TRACKS:

With a view to check on the significance of enhanced dissolution effects through alpha recoil tracks as a mechanism to produce radioactive disequilibrium among members of the natural radioactive decay chains two sets of laboratory experiments were carried out.

i) Leaching of implanted recoils from annealed and un-annealed mica and

ii) Granite leaching experiment.
Fig. V.7: Theoretically estimated values of the $^{234}\text{U}/^{238}\text{U}(\text{AR})$ from a virgin rock surface as a function of the thickness of the rock dissolved. The lower the dissolution, the higher the activity ratio that can be obtained from the virgin surface in preferential leaching of the alpha recoil tracks.
5.7(a) **Leaching of implanted recoils from mica:**

Mica discs (2.5 cm dia) were irradiated with recoiling \(^{224}\text{Ra}\) and \(^{212}\text{Pb}\) nuclei emanating from a weightless \(^{232}\text{U} - 228\text{Th}\) electrodeposited source (~\(10^4\) dpm). The irradiation was carried out for about four hours in an evacuated chamber at a pressure of about 100\(\mu\)m Hg. For each experiment two discs were irradiated, of which one was heated after irradiation in a furnace at about 350\(^o\)C for 3 to 4 hours to anneal the recoil tracks. The annealed and unannealed discs were assayed for their alpha activity (using a solid state detector coupled to MCA), etched in 48% HF for 0.5 min, washed, dried and recounted. The samples were re-etched for periods of 1-5 mins counted and the process of re-etching and counting repeated for a total etch period of about 20 mins. The \(^{224}\text{Ra}\) and \(^{212}\text{Pb}\) (counted via \(^{212}\text{Bi}\) alphas) remaining in the discs after various etch periods are given in Table V.2 and Fig. V.8.

5.7(b) **Granite leaching experiment:**

Granite of 3 dpm g\(^{-1}\) \(^{238}\text{U}\) concentration was powdered to < 150\(\mu\)m size and was dispersed in 1 liter artificial river water (Strickland and Parson, 1972). It was stirred continuously on a magnetic stirrer for a time period of 5 hours and then the solution was filtered through a millipore. The solution was acidified with nitric acid and processed for uranium after adding \(^{232}\text{U}\) as the yield tracer (section 2.1(c)(i)). The granite residue after the first leach was redispersed in a fresh aliquot of 1 liter
Table V.2: Results of leaching recoil implanted $^{224}$Ra and $^{212}$Pb from mica.

<table>
<thead>
<tr>
<th>Code</th>
<th>Leaching time (mins)</th>
<th>% initial activity remaining on mica (counts per min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Unannealed</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{224}$Ra</td>
</tr>
<tr>
<td>20, 21</td>
<td>0.0</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>29 ± 2</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>12 ± 1</td>
</tr>
<tr>
<td>22, 24</td>
<td>0.0</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>65 ± 3</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>54 ± 2</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>34 ± 1</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>17 ± 1</td>
</tr>
<tr>
<td></td>
<td>17.0</td>
<td>7 ± 1</td>
</tr>
<tr>
<td>25, 26</td>
<td>0.0</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>58 ± 2</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>48 ± 2</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>33 ± 1</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>17 ± 1</td>
</tr>
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<td>17.0</td>
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Fig. V.8: The percent activity of $^{212}\text{Pb}$ and $^{224}\text{Ra}$ remaining in the mica disc for various etch periods. Solid hexagons represent the activity in the unannealed samples and the 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.
artificial river water. After another 5 hours stirring, the solid and the solution phases were separated through millipore and the whole procedure repeated. The results are given in Table V.3. The errors quoted are one sigma uncertainties due to counting statistics.

5.8 DISCUSSION OF RESULTS:

The results on the leaching of $^{224}$Ra and $^{212}$Pb from annealed and unannealed mica (Table V.2, Fig. V.3) show that a recoil track is etched much faster than the healthy material. The decrease in the activity of $^{224}$Ra in the annealed mica (Table V.2), where the tracks produced due to the recoiling $^{224}$Ra atoms from the $^{232}$U - $^{228}$Th source (section 5.7(a)) are annealed due to heating at 350°C, may be due to the mica dissolution. 48% HF is a strong etchant and therefore the dissolution effect could be quite significant. However, the dissolution through recoil tracks is at least 2 to 3 times faster and is almost complete over a period of about 20 to 30 minutes in 48% HF. Fleischer (1980) has shown that the effect of the etchant on preferential leaching is not significant. Thus it would be expected that the natural waters would leach $^{234}$U out preferentially through the recoil tracks in rock bodies as well.

This is indeed shown by the results of the granite leaching experiments (Table V.3). The excess of $^{234}$U in the solution phase arises in each one of the subsequent leaches.
Table V.3: Results of the granite leaching experiments.

<table>
<thead>
<tr>
<th>Leach No.</th>
<th>Period of contact (hrs)</th>
<th>$^{238}\text{U}$ activity in leach (dpm)</th>
<th>$^{234}\text{U}/^{238}\text{U}$ (AR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>$1.03 \pm 0.05$</td>
<td>$1.45 \pm 0.09$</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>$0.77 \pm 0.02$</td>
<td>$1.50 \pm 0.09$</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>$0.91 \pm 0.04$</td>
<td>$1.46 \pm 0.07$</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>$0.74 \pm 0.04$</td>
<td>$1.52 \pm 0.09$</td>
</tr>
<tr>
<td>5</td>
<td>39</td>
<td>$0.82 \pm 0.04$</td>
<td>$1.35 \pm 0.08$</td>
</tr>
</tbody>
</table>
The short period of contact of the granite and water precludes the source of this $^{234}\text{U}$ excess to be the in-situ recoil of $^{234}\text{Th}$ and its decay to $^{234}\text{U}$ (Kigoshi, 1971) and shows that either it could be due to the preferential leaching of the recoil tracks containing $^{234}\text{U}$ or the leaching of $^{234}\text{U}$, from the microcracks, produced as a result of the decay of $^{234}\text{Th}$ emplaced in the cracks by recoil. The present data does not allow to choose between these alternatives.

5.9 $^{234}\text{U}$ Leaching Dynamics in Natural Waters:

**Some Speculations:**

The radioactive disequilibrium between $^{234}\text{U}$ and $^{238}\text{U}$ in natural waters is intimately related to the mechanism of rock weathering. In the previous section it is shown that the excess $^{234}\text{U}/^{238}\text{U}$ ratios are expected to arise by preferential track etching only when a "virgin" surface is leached by an aqueous medium. Subsequent leaches would yield $^{234}\text{U}/^{238}\text{U}$ activity ratio $\sim 1$ until one reaches the point of singularity, i.e., when the dimensions of the rock grain in one of the directions become comparable to the recoil range of $^{234}\text{U}$ nuclei. At this point $^{234}\text{U}/^{238}\text{U}$ (AR) in the leach could be as low as 0.

Weathering results in a continuous fragmentation of the rock which leads to formation of cracks/fissures (Fig. V.9). The character of fissuring will depend on the rock type, the more the density of flaws in a rock body (Gilvarry and Bergstrom, 1962; Logan, 1979), the more would be the fissuring per unit rock dissolution.
Fig. V.9: Cartoon showing the breaking up of grains in yielding virgin surfaces and the excess $^{234}\text{U}$ in a weathering process. Dots represent $^{238}\text{U}$ atoms (shown exaggerated), small rectangles, the alpha recoil tracks and the lines represent the flaws or the microcracks in the body of the grain. (The dotted line shows the extent of dissolution.) Only those tracks with a dot inside have $^{234}\text{U}$ atom within. $^{234}\text{U}$ atom is preferentially extracted out from an exposed track to the surface in weathering. AR stands for $^{234}\text{U}/^{238}\text{U}$ activity ratio.
It is therefore expected that as the exposed surface is leached, connecting virgin surfaces will be exposed. Thus, with the progression of weathering, as exposed surfaces are leached, virgin surfaces would be exposed. During their leaching, further exposure would occur. The fragmentation of a rock into rocklets proceeds at all levels: larger grains breaking down into smaller grains, so forth and so on.

The excess amount of $^{234}\text{U}$ 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, we may quantify the weathering process relevant to excess $^{234}\text{U}$ activity as the ratio of the two parameters:

\[ \kappa = \frac{A}{\xi} \]

where:

- $A$ = the rate at which 'virgin' surface is exposed during weathering ($\text{cm}^2 \text{ min}^{-1}$)
- $\xi$ = the rate of dissolution of an exposed surface during weathering ($\text{g} \text{ min}^{-1}$)

The ratio, $\kappa = \frac{A}{\xi}$, has the dimension of area per unit mass ($\text{cm}^2 \text{ g}^{-1}$) and is a measure of the new surface area exposed per gram rock dissolved. This ratio is independent of the weathering rate of the rock, but is a characteristic property of the rock. In the following I shall relate this rock characteristic ratio, $\kappa$, to the excess $^{234}\text{U}$ obtainable per gram soil dissolution.
The excess concentration of $^{234}\text{U}$ in natural waters is due to the recoil supply of $^{234}\text{Th}$ and that due to the preferential leaching of $^{234}\text{U}$ from the alpha recoil tracks. In preferential leaching, $^{234}\text{U}$ excess is supplied to the aqueous phase only when a virgin rock surface area is leached. The subsequent leaching of the rock does not bring any excess $^{234}\text{U}$, but only near equal amounts of $^{234}\text{U}$ and $^{238}\text{U}$. Thus the $^{234}\text{U}$ excess, supplied via preferential leaching of tracks, would be proportional to the rate at which the new surface area is generated by rock fragmentation in a weathering process (Fig. V.9). The $^{238}\text{U}$ concentration in waters is an index of rock dissolution (section 4.2(a)(i)) and is proportional to the rock weathering rate. Thus $^{234}\text{U}_{\text{ex}}/^{238}\text{U}$ activity ratio in solution would be proportional to $A/t$, the characteristic ratio, $\chi$, of the weathered rock, if the $^{234}\text{U}_{\text{ex}}$ to solution is supplied predominantly by track leaching processes. However, if a significant fraction of the $^{234}\text{U}_{\text{ex}}$ to the aqueous phase is supplied via recoil effects, then the $^{234}\text{U}_{\text{ex}}/^{238}\text{U}$ activity ratio would be an upper limit on $\chi$.

In an attempt to elucidate the factors controlling the $^{234}\text{U}_{\text{ex}}/^{238}\text{U}$ in natural waters, I have statistically analysed the available data (Table V.4; Figs. V.10 and V.11). As can be seen from Table V.4, the ratio of $^{234}\text{U}_{\text{ex}}/^{238}\text{U}$ varies between 0.3 to about 0.8 for Gujarat groundwaters and the Indian river waters. The value of the ratio is also similar to the best fit ratio of
Table V.4: Results of the least squares regression analysis for $\frac{234\text{U}}{238\text{U}}$ activity ratio in waters.

<table>
<thead>
<tr>
<th>Water Type</th>
<th>Observations</th>
<th>$\frac{234\text{U}}{238\text{U}}$</th>
<th>Intercept</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwaters</td>
<td>43</td>
<td>0.88</td>
<td>0.36 ± 0.03</td>
<td>-0.09</td>
</tr>
<tr>
<td>Groundwaters</td>
<td>53</td>
<td>0.81</td>
<td>0.30 ± 0.03</td>
<td>0.22</td>
</tr>
<tr>
<td>River waters</td>
<td>15</td>
<td>0.97</td>
<td>0.70 ± 0.05</td>
<td>-0.21</td>
</tr>
<tr>
<td>River waters</td>
<td>6</td>
<td>0.92</td>
<td>0.55 ± 0.11</td>
<td>-0.1</td>
</tr>
<tr>
<td>River waters</td>
<td>4</td>
<td>1.0</td>
<td>0.29 ± 0.02</td>
<td>0.002</td>
</tr>
<tr>
<td>Groundwaters</td>
<td>25</td>
<td>0.91</td>
<td>0.83 ± 0.08</td>
<td>0.35</td>
</tr>
<tr>
<td>River waters</td>
<td>24</td>
<td>0.92</td>
<td>0.70 ± 0.06</td>
<td>-0.61</td>
</tr>
<tr>
<td>Groundwaters</td>
<td>13</td>
<td>0.93</td>
<td>0.83 ± 0.1</td>
<td>-1.64</td>
</tr>
<tr>
<td>Groundwaters</td>
<td>19</td>
<td>0.94</td>
<td>1.46 ± 0.13</td>
<td>-0.14</td>
</tr>
<tr>
<td>Groundwaters</td>
<td>19</td>
<td>0.52</td>
<td>10.14 ± 4.04</td>
<td>0.64</td>
</tr>
</tbody>
</table>
Fig. V.10: Scattergram of $^{234}\text{U}$ excess-vs-$^{238}\text{U}$ for Indian groundwaters. The correlation co-efficient for the least squares fit is about 0.8 - 0.9 and the slope between 0.3 to 0.8.
Fig. V.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 co-efficient is 0.97 and 0.94 and the slopes 0.7 and 1.5 respectively.
In the granite leaching experiments in the laboratory (Table V.3), which is $0.3 \pm 0.2$.

In river waters, where most of the water is either meteoric or shallow groundwaters, the age of the water is unlikely to be more than a couple of years and the observed excess of $^{234}U$, of the order of 1-2 dpm l$^{-1}$ (Borole et al., 1982) cannot be explained based on the accumulation of $^{234}U$ from the in-situ decay of $^{234}Th$ in water (or the quantitative dissolution of $^{234}U$ formed as a result of the decay of adsorbed $^{234}Th$ on the surfaces of the grains). Laboratory experiments also show an excess of $^{234}U$ in a few hours of granite leaching (Table V.3) which also cannot be of in-situ recoil origin. It must be either due to the preferential leaching of the recoil tracks containing $^{234}U$ or the mobilization of $^{234}U$ from the microcracks where it is produced from the decay of the $^{234}Th$ emplaced by recoil. In both the cases, the excess $^{234}U$ in waters would depend upon the rate at which new surfaces are generated. In groundwaters the observed $^{234}U$ excess could also be explained in terms of the age of the water body (Table IV.7). However, the observation that the slope of the $^{234}U_{ex} - ^{238}U$ plot varies between 0.3 and 0.8, without any systematic trend between river and groundwaters and that the slope is very similar to that observed in laboratory leaching experiments, leads one to speculate that in these samples, most of the $^{234}U$ excess is supplied via track leaching.
In contrast, the slope of the line for Japanese groundwaters (Kigoshi, 1973) and those from Ordovician aquifers (Gilkeson, 1982) are much higher (Table V.4) and have low $^{238}\text{U}$ concentrations. In these cases, either the characteristic of the local aquifer formation could be different leading to higher slope or that recoil could be a major source of $^{234}\text{U}_{\text{ex}}$ to these waters. More laboratory and field data would be required to judge the significance of these different components in regulating the $^{234}\text{U}_{\text{ex}}$ abundances in natural waters. Unless these contributions are properly identified, the $^{234}\text{U}_{\text{ex}}$ dating method based on the recoil models (section 4.4) would subject to major uncertainties.
There is no science without fancy and no arts without facts.

- VLADIMIR NABOKOV