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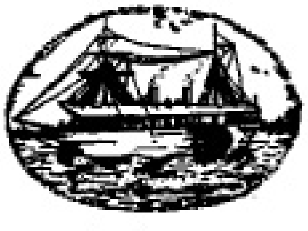

*The Investigator*

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# URANIUM SERIES INEQUILIBRIUM AND THE GEOCHEMICAL PROCESSES OCCURRING ON THE SURFACE OF COASTAL SEDIMENTS

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## ABSTRACT

Remarkable anomaly has been observed between $U^{238}$ and $U^{234}$ in the marine environment by a mumber of workers in the field. But little information is available regarding the $U^{238}$, $U^{235}$ and $U^{234}$ activities in coastal sediments.

The present work deals with the ratio of the activities of $U^{234}/U^{238}$ and $U^{235}/U^{238}$ from the coastal sediments of the west coast of India from Bombay (19°N, 73°E) to the southern tip of India up to Kottilppad near Manavalakurichi (8°N, 77°E) in the monazite bearing area of Kerala State.

The sediment samples are leached with ammonium carbonate solution so as not to attack the mineral core of the sediment and to get the leachable uranium activities from the surface of the particles.

In all the sediment samples $U^{234}$ activity is about 12 to 14% higher than the equilibrium value indicating that there is disequilibrium between $U^{238}$ and $U^{234}$. The $U^{235}/U^{238}$ *activity ratios lie in the range of 0.045 to 0.048 thereby showing that there* is no significant fractionation between $U^{238}$ and $U^{235}$.

## INTRODUCTION

$U^{238}$ and $U^{234}$ are separated in the uranium series by $Th^{234}$ and $Pa^{234}$. The uranium series is given below:

$$_{92}U^{238} \xrightarrow[4.51 \text{ x } 10^{9}Y]{\propto} {}_{90}Th^{234} \xrightarrow[24.1d]{\beta} {}_{91}Pa^{234} \xrightarrow[1.18m]{\beta}$$

$$_{92}U^{234} \xrightarrow[2.48 \text{ x } 10^{5}Y]{\propto} {}_{90}Th^{230} \xrightarrow[8.0 \text{ x } 10^{4}Y]{\propto}$$

Masurements carried by earlier workers (Veeh, 1966) have shown radioactive disequilibrium between $U^{238}$ and $U^{234}$ in total deep sea sediment samples, corals etc. In water samples from the Pacific Ocean, Thurber (1962), Koide and Goldberg (1965) have obtained a value of 1.15 for $U^{234}/U^{238}$ activity ratio. Moore and Sackett (1964) have obtained a value of 1.14 for the above ratio in waters of North Atlantic. Miyake *et al.* (1970) have obtained values in the range of 1.07 to 1.18 at different depths in the North Pacific waters. Kazachevskii *et al.* (1964) have obtained a value of 1.15 for the Black Sea. Joshi and Ganguly (1972*a*) have obtained a value of 1.151 in the coastal waters of Bombay.

There has not been much systematic work on the ratio of the activities of $U^{234}/U^{238}$ and $U^{235}/U^{238}$ in coastal marine sediments. Blanchard (1965) obtained values of 0.93 to 0.96 for the ratio of $U^{234}/U^{238}$ in estuarine sediments, while the shells from the estuary gave ratios of 1.10 to 1.11. All the values cited above, which were obtained by the earlier workers, are by attacking the mineral body of the sediment samples. In the present work, coastal sediment samples are leached with ammonium carbonate solution, an efficient leaching agent for uranium and which does not attack the mineral core of the sediment particles. In the dynamic processes in the marine environment, the sediment and the water interface are the most important and the equilibrium is expected only to be established between the chemical occurring on the surface of the sediments and the condition in the ambient medium.

## SAMPLE COLLECTION

Fine fractions of the sediment samples were collected from the west coast of India, from Bombay (19°N, 73°E) to Kottilppad near Manavalakurichi (8°N, 77°E) in Kerala State. Figure 1 gives the location of the sampling points in the Bombay region, while Fig. 2 indicates the collection sites along the west coast of India.

## EXPERIMENTAL METHODS

The method is based on the simultaneous removal from the coastal sediments of the three isotopes of uranium, $U^{238}$, $U^{235}$ and $U^{234}$.

In the surface leaching processes, 300 gm of the uncrushed, dried sediment was taken with 800 ml of saturated ammonium carbonate solution for seven to eight hours. The sediment particles were allowed to settle down overnight and the supernate was filtered through 0.22 $\mu$ membrane filter. The procedure was repeated with two more instalments, 800 ml of ammonium carbonate solution and filtered. The pooled carbonate filtrates were evaporated to dryness and the residue was heated each time with 5 ml instalments of concentrated hydrochloric acid till all the carbonates were destroyed. The final

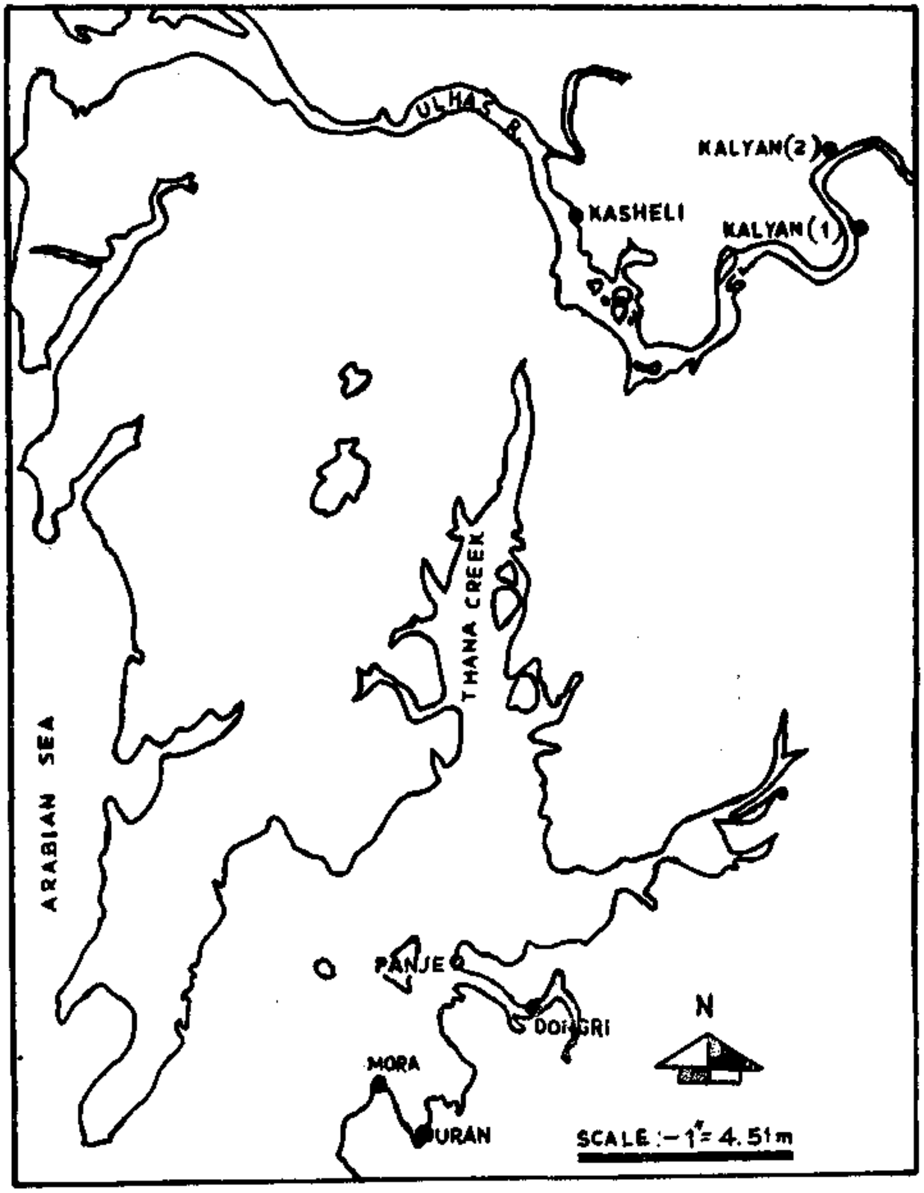

Fig. 1. Map of Bombay region showing the sampling points.

residue was ignited in a platinum dish at 450°C. The residue was then taken in 10 ml of 8 M hydrochloric acid. Removal of trace amounts of iron present in the sample was done by shaking the above hydrochloric acid solution with 10 ml of di-isopropyl ether for about five minutes.

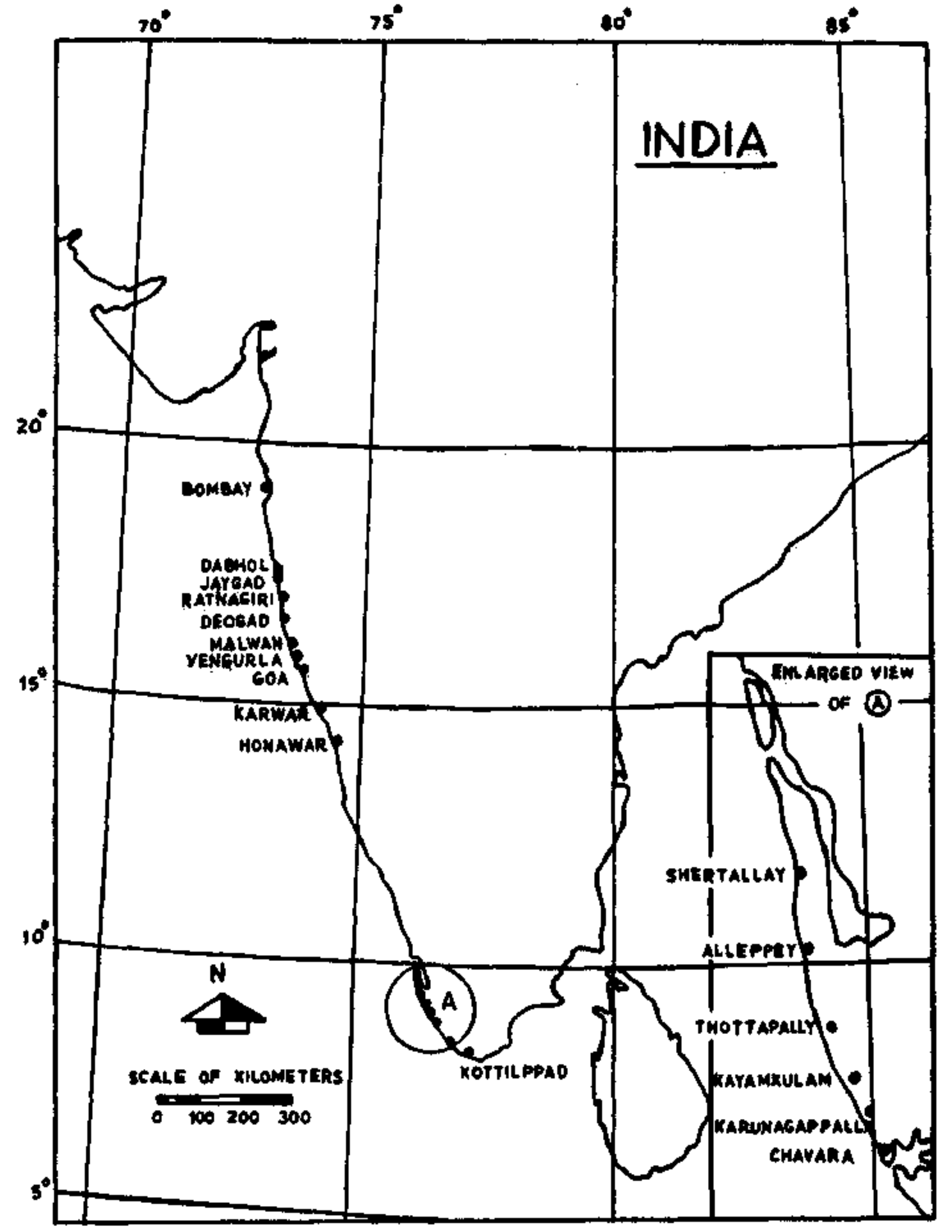

Fig. 2. Map of the west coast of India showing the sampling points.

*Ion-exchange method for the separation of uranium*

The aqueous layer after removal of iron was evaporated to dryness and then taken in 10 ml of 8 M hydrochloric acid and passed through anion-exchange column (1 x 15 cms), Dowex-1 x 8% (50-100 mesh) in chloride form. The flow-rate was adjusted to 0.5 ml/min. Uranium was adsorbed on the column. The anion-exchange column was washed with 50 ml of 8 M hydrochloric acid with a flow rate of 1.0 ml/min. Protactinium was washed from the column with 10 ml of 3.8 M hydrochloric acid (flow rate 1.0 ml/min) and then the adsorbed uranium was desorbed from the column with 50 ml of 1.0 M hydrochloric acid with a flow rate of 0.5 ml/min. The chemically pure uranium obtained by this method was converted into nitrate form and plated on stainless steel planchet following the procedure of Cohen and Hull (1944).

### *Counting*

Activities of $U^{238}$, $U^{235}$ and $U^{234}$ were obtained from the plated sample using a partially depleted silicon surface barrier detector (active area 200 mm$^2$) coupled to a well stabilised 256 channel pulse height analyser. The samples were counted for 1000 minutes to give a standard deviation ± 1.1% for $U^{238}$ and $U^{234}$ counts under the respective peaks and the standard deviation for $U^{235}$ counts was obtained as ± 5.3%. The counting efficiency was 24% and the resolution of the detector was 43.4 Kev at 5.108 Mev alphas (Joshi and Ganguly, 1970; 1972 *b* and MS).

## RESULTS AND DISCUSSIONS

No significant alpha activity has been observed for the reagent blank.

Figures 3 and 4 show typical disequilibrium between $U^{238}$ and $U^{234}$ in coastal sediment samples from Dabhol and Karwar. Table 1 gives the activities of $U^{238}$, $U^{235}$, $U^{234}$ and the activity ratios of $U^{234}$ $U^{238}$ and $U^{235}U^{238}$ From the table, it is seen that though $U^{234}/U^{238}$ activity ratio indicates the existence of disequilibrium in $U^{238}$ radioactive series, there is no significant fractionation between $U^{235}$ and $U^{238}$

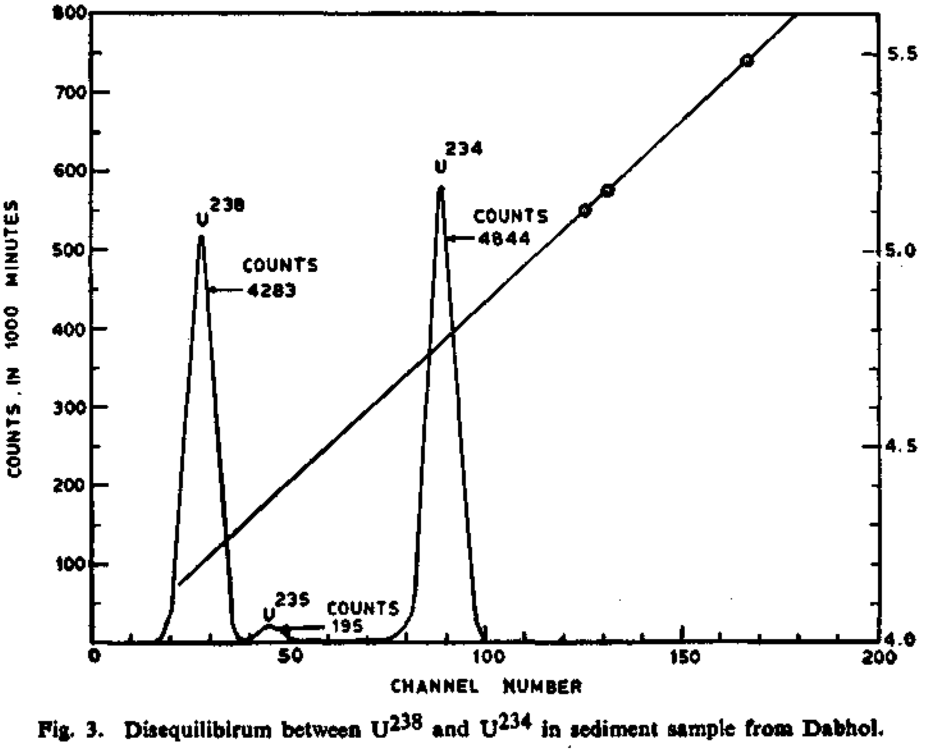

**Fig. 3. Disequilibirum between $U^{238}$ and $U^{234}$ in sediment sample from Dabhol.**

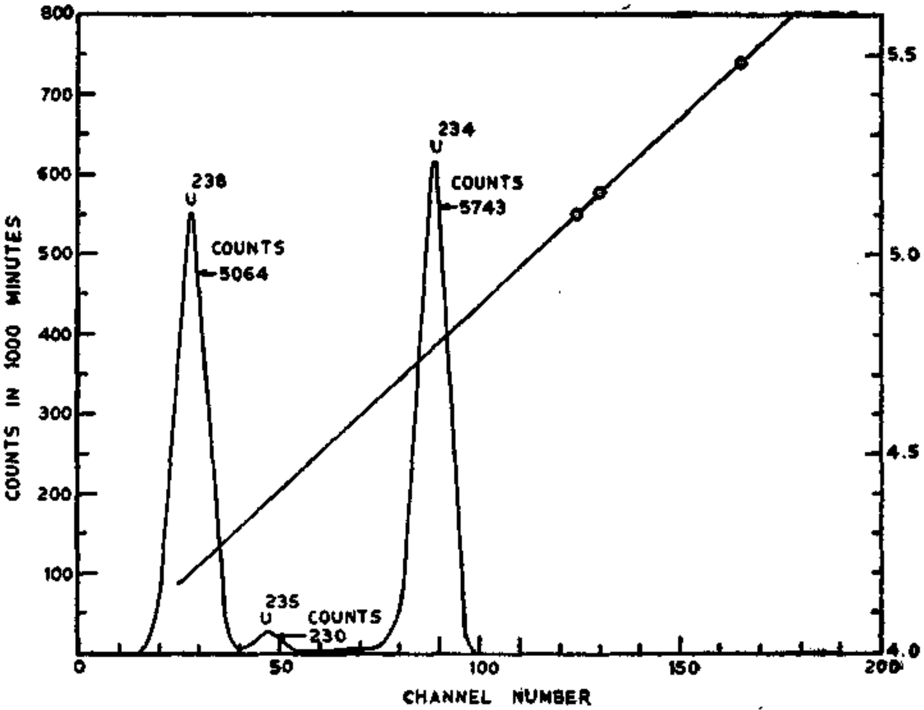

Fig. 4. Disequilibrium between $U^{238}$ and $U^{234}$ in sediment sample from Karwar.

Aliquots of Goa and Ratnagiri sediment samples were treated with 0.05 M hydrochloric acid and phosphate-free hydrogen peroxide in order to cleanse the particles of the surface organic matter and to obtain an acid extract of the uranium in the surface layer of the sediments. The acid extract after the above treatment was filtered and the filtrates were processed for column treatment for the chemical separation of uranium (Joshi and Ganguly, 1972 *a*). The remaining sediment residue was treated the same way as the original sediment.

Figure 5 gives the disequilibrium between $U^{238}$ and $U^{234}$ in the acid and hydrogen peroxide extract of the Goa sample, while Fig. 6 shows the two isotopes of uranium i.e. $U^{238}$ and $U^{234}$ are in equilibrium in the cleansed residue. Table 2 gives the activities of $U^{238}$, $U^{235}$, $U^{234}$ and the activity ratios of $U^{234}U/^{238}$ and $U^{235}/U^{238}$ in acid hydrogen peroxide extract and the corresponding leachates from the residues from Ratnagiri and Goa.

It is seen from these data that the anomaly between $U^{238}$ and $U^{234}$ exists only on the sediment particle surface and on removal of the surface activities and subsequent leaching of the residue gives the ratio of one as one would expect in the mineral core of the sediment. However, $U^{235}/U^{238}$ activity ratio exhibits, the ratio obtained for natural uranium.

TABLE 1. *Activities of uranium isotopes and their ratios in coastal sediments*

| Sr. No. | Place of collection | Location | $U^{238}$ (dpm) | $U^{235}$ (dpm) | $U^{234}$ (dpm) | $U^{234}/U^{238}$ | $U^{235}/U^{238}$ |
|---|---|---|---|---|---|---|---|
| 1. | Bombay | 19°N, 73°E | 31.02 | 1.48 | 35.05 | 1.13 | 0.048 |
| 2. | Bombay | -do- | 29.97 | 1.36 | 33.87 | 1.13 | 0.045 |
| 3. | Bombay | -do- | 29.98 | 1.37 | 33.88 | 1.13 | 0.046 |
| 4. | Bombay | -do- | 17.87 | 0.81 | 20.19 | 1.13 | 0.045 |
| 5. | Bombay | -do- | 16.58 | 0.75 | 18.74 | 1.13 | 0.045 |
| 6. | Dabhol | 17.6°N, 73.25°E | 13.78 | 0.62 | 15.56 | 1.13 | 0.045 |
| 7. | Dabhol | do- | 17.85 | 0.81 | 20.18 | 1.13 | 0.045 |
| 8. | Jaygad | 17.5°N, 73.5°E | 19.60 | 0.89 | 22.17 | 1.13 | 0.045 |
| 9. | Jaygad | -do- | 20.62 | 0.94 | 23.30 | 1.13 | 0.046 |
| 10. | Ratnagiri | 17°N, 73.5°E | 21.05 | 0.95 | 23.93 | 1.14 | 0.045 |
| 11. | Ratnagiri | -do- | 15.06 | 0.68 | 17.16 | 1.14 | 0.045 |
| 12. | Ratnagiri | -do- | 18.36 | 0.83 | 20.86 | 1.14 | 0.045 |
| 13. | Ratnagiri | -do- | 30.46 | 1.38 | 34.70 | 1.14 | 0.045 |
| 14. | Malwan | 16°N, 73.75°E | 21.69 | 0.98 | 24.66 | 1.14 | 0.045 |
| 15. | Malwan | -do- | 26.47 | 1.20 | 30.12 | 1.14 | 0.045 |
| 16. | Vengurla | 15.75°N, 73.80°E | 35.37 | 1.60 | 40.14 | 1.14 | 0.045 |
| 17. | Vengurla | -do- | 33.87 | 1.54 | 38.44 | 1.13 | 0.045 |
| 18. | Goa | 15.5°N, 74°E | 15.26 | 0.71 | 17.33 | 1.14 | 0.047 |
| 19. | Goa | -do- | 23.13 | 1.05 | 26.26 | 1.13 | 0.045 |
| 20. | Goa | -do- | 19.68 | 0.89 | 22.39 | 1.14 | 0.045 |
| 21. | Goa | -do- | 20.43 | 0.93 | 23.20 | 1.14 | 0.045 |
| 22. | Karwar | 14.2°N, 74.75°E | 29.86 | 1.35 | 33.80 | 1.13 | 0.045 |
| 23. | Karwar | -do- | 16.39 | 0.75 | 18.60 | 1.13 | 0.046 |
| 24. | Karwar | -do- | 21.10 | 0.96 | 23.93 | 1.13 | 0.046 |
| 25. | Honawar | 14.2°N, 74.75°E | 29.86 | 1.35 | 33.80 | 1.13 | 0.045 |

The inequilibrium between $U^{238}$ and $U^{234}$ is explained by Rosholt *et al.* (1963) to be due to the preferential leaching of $U^{234}$ as compared to $U^{238}$ and $U^{235}$. Rosholt and his co-workers explain that during the transition of $U^{238}$ to $U^{234}$ $U^{234}$ gets oxidised right at the time of its formation by virtue of two election-stripping. Thurber (1963), Cherdyntsev and his co-workers suggested that during the transition of $U^{238}$ to $U^{234}$, the $U^{234}$ atoms get relocated into the micro-cracks and the crystal defects, where $U^{234}$ is more likely to be oxidised compared to $U^{238}$ atoms, thus forming more soluble uranyl ions.

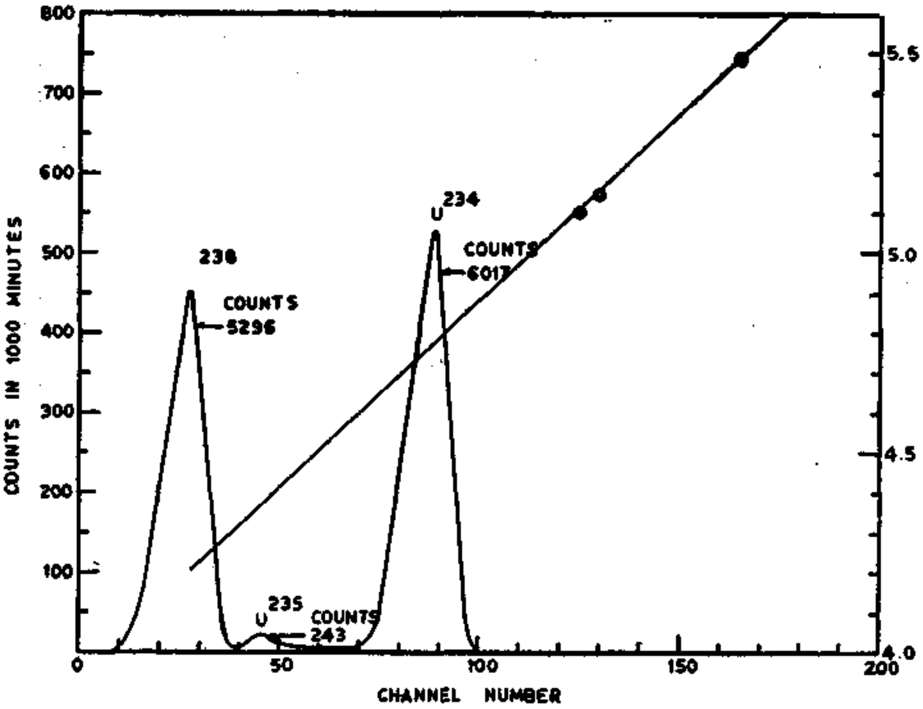

Fig. 5. Disequilibrium between $U^{238}$ and $U^{234}$ in the supernate attained after $H_2O_2$ + 0.05 M HCl treatment of the sediment from Goa.

TABLE 2. *Activities of uranium isotopes and their activity ratios in Ratnagiri and Goa sediments after hydrogen peroxide treatment*

| Sr. No. | Place of collection | Location | $U^{238}$ (dpm) | $U^{235}$ (dpm) | $U^{234}$ (dpm) | $U^{234}/U^{238}$ | $U^{235}/U^{238}$ |
|---|---|---|---|---|---|---|---|
| 1. | Ratnagiri sediment residue | 17°N, 73.5°E | 20.99 | 0.96 | 20.99 | 1.00 | 0.046 |
| 2. | Ratnagiri acid + $H_2O_2$ extract | -do- | 21.05 | 0.95 | 23.95 | 1.14 | 0.045 |
| 3. | Goa sediment residue | 15.5°N, 74°E | 21.60 | 0.99 | 21.60 | 1.00 | 0.046 |
| 4. | Goa acid+ $H_2O_2$ extract | -do- | 22.07 | 1.01 | 25.07 | 1.14 | 0.046 |

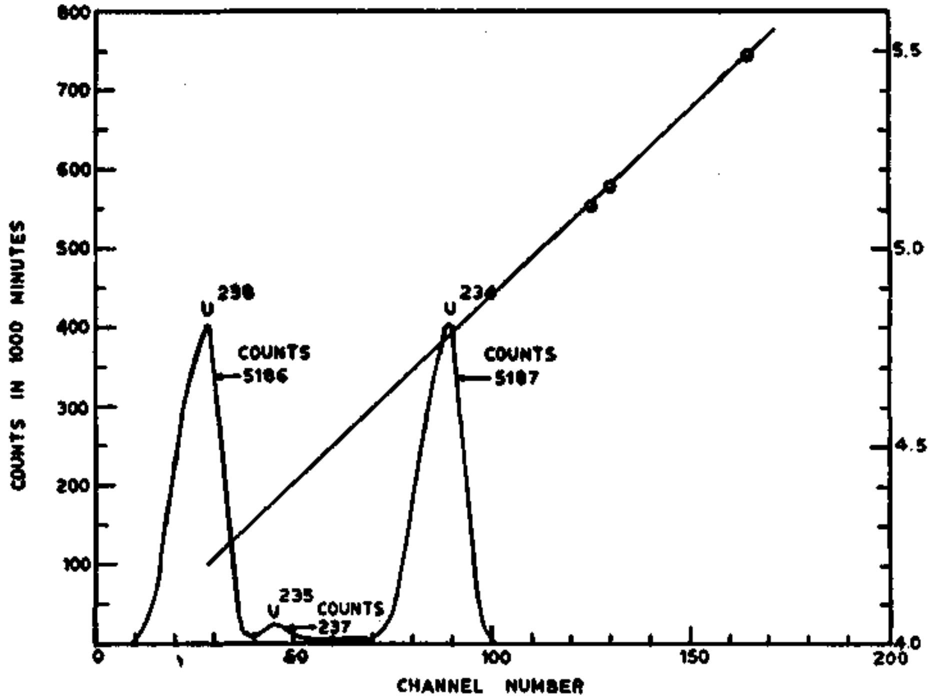

Fig. 6 Equilibrium between U238 and U234 in the sediment residue of Goa after removal of $H_2O_2$ and 0.05 M HCl Supernate.

From the above hypotheses one should get a ratio of $U^{234}/U^{238}$ less than one in the uranium leachate from the sediment cleansed of surface organic matter. In the experiment performed (Table-2 in this laboratory Joshi and Ganguly, 1972*a*) the sediments was treatment with hydrogen peroxide and 0.05 M hydrochloric acid which removed quantitatively the surface layer of organic matter uranium complex which was in equilibrium with the ambient uranium in the sea water. The carbonate leachate of this organic matter (cleansed sediment) always gives a ratio 1 which throws doubts about the validity of the above hypotheses.

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