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Natural Radioactivity and Geochemical Processes in the Marine Environment of the West Coast of India

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ABSTRACT

In studies related to the geochemistry of thorium and uranium, it was observed that the disequilibrium between Th^{232} and Th^{228} and between U^{238} and U^{234} exists on the surface of the labile organic layer of the sediment particles and as the surface organic matter is removed the core of the particles show equilibrium activities. The studies related to sedimentation and geochemistry of elements in coastal waters, it is important to recognise the physico-chemical equilibrium between labile chemical species present on the particle surface and the chemical species in the ambient medium.

The thickness of the labile organic layer on the sediment particles has been calculated and found to be in the range of 2.5×10^{-6} cm to 10.0×10^{-6} cm. The values are comparable to the values obtained by Electron Microscopy Method.

1. INTRODUCTION

1. NATURAL RADIOACTIVITY

MEASUREMENT of natural radioactivity due to thorium and uranium isotopes and their daughter products have been carried out in the marine organisms, deep sea sediments and sea water in the Pacific and Atlantic Oceans and Japan Sea. There is no systematic investigation available on coastal marine sediments, particularly for the sediments from the Indian Ocean area.

The coastal sediments mainly comprised of terrestrial run off and the radioactivity content within the mineral body of the sediments are more representative of the content in the terrestrial clay and silt carried into the sea than of the radioactivity picked up or retained by the sediments through

marine geochemical processes. In the studies related to sedimentation and geochemistry of thorium and uranium in the coastal waters, it is important to recognise that in the dynamic processes of the marine environment the sediment and water interface play the most important part and physico-chemical equilibrium is expected to exist or be established only between the labile chemical species present on the particle surface and the chemical species in the ambient medium.

Figures 1, 2 and 3 show the disintegration schemes of thorium, uranium and actinium series.

2. PRESENT INVESTIGATIONS

The present investigations are carried out with a view to understand the distribution of the labile component of natural radioactivity in the marine sediments and waters along the West Coast of India.

The different aspects of the investigations are divided as follows:

Th 90	Th-232 $1.41 \times 10^{10} \text{y}$		Th-228 1.91 Y		
Ac 89		Ac-228 6.13 h			
Ra 88	Ra-228 6.7 Y		Ra-224 3.64 d		
Fr 87					
Rn 86			Rn-220 55.3 S		
At 85				At-216 $3 \times 10^4 \text{S}$	
Po 84			Po-216 0.145 S		Po-212 $3.04 \times 10^7 \text{S}$
Bi 83				Bi-212 60.6 m	
Pb 82			Pb-212 10.64 h		Pb-208 (STABLE)
Tl 81				Tl-208 3.1 m	

Figure 1. Disintegration scheme of Th^{232} (Thorium series).

U 92	U-238 4.51 × 10 ⁹ y		U-234 2.48 × 10 ⁵ y			
Pa 91	↙ α	Pa-234 1.18 m	↘ β			
Th 90	Th-234 24.1 d		Th-230 8.0 × 10 ⁴ y			
Ac 89			↙ α			
Ra 88			Ra-226 1620 y			
Fr 87			↙ α			
Rn 86			Rn-222 3.82 d			
At 85			↙ α	At-218 2 s		
Po 84			Po-218 3.05 m	↘ β	Po-214 1.64 × 10 ⁻⁴ s	Po-210 138.4 d
Bi 83			↙ α	Bi-214 19.7 m	↘ β	Bi-210 5.0 d
Pb 82			Pb-214 26.8 m	↘ β	Pb-210 20.4 y	Pb-206 (STABLE)
Tl 81				Tl-210 1.32 m	↘ β	Tl-206 4.19 m

Figure 2. Disintegration scheme of U²³⁸ (Uranium series).

SECTION II.—The collection of representative samples from top layers of the sediments from different coastal and backwater locations along the West Coast of India is discussed. These samples include those from Bombay (19° N, 73° E), the low background radioactivity area to Kottlppad (8° N, 77° E) and the high radioactivity background monazite bearing area.

SECTION III.—Deals with the surface leaching of the coastal sediments with ethylene diamine tetra-acetic acid (EDTA) to leach thorium from the surface of the sediments. Th²²⁸/Th²³² and Th²³⁰/Th²³² activity ratios are then determined in these leachates. Th²²⁸/Th²³² activity ratios lie in the range of 0.55 to 0.67 in the Bombay and monazite region while this ratio is in the range of 2.00 to 2.19 in areas between Ratnagiri and Honawar. Th²³⁰/Th²³² activity ratios are in the range of 0.13 to 0.15 in the Bombay region 0.23 to 0.25 in the monazite region and 0.95 to 1.07 in areas between Ratnagiri and Honawar.

U 92	U-235 7.1×10^8 Y			
Pa 91	α	Pa-231 3.25×10^4 Y		
Th 90	Th-231 25.52 h	β	Th-227 18.21 d	
Ac 89		Ac-227 21.6 Y	α	
Ra 88		α	Ra-223 11.44 d	
Fr 87		Fr-223 22.0 m	β	
Rn 86		α	Rn-219 4.0 S	
At 85		At-219 0.9 m	β	
Po 84		α	Po-215 1.78×10^{-3} S	Po-211 0.52 S
Bi 83		Bi-215 7.5 m	α	Bi-211 2.16 m
Pb 82			Pb-211 36.1 m	Pb-207 STABLE
Tl 81				Tl-207 4.79 m

Figure 3. Disintegration scheme of U^{235} (Actinium series).

Removal of the labile surface component of thorium by destroying the organic matter with phosphate-free hydrogen peroxide and 0.05 M hydrochloric acid has been carried out and the thorium isotopic ratios are obtained in the leachates and the sediment mineral core residues.

It has been found that the disequilibrium between Th^{232} and Th^{228} exists only on the surface of the labile layer and as the surface organic layer is removed the core shows equilibrium activities.

This section also gives the concentrations of Ra^{228} activity obtained in coastal sediments and water.

SECTION IV.—Deals with the leaching of uranium isotopes from the sediments. Uranium is leached with saturated solution of ammonium carbonate and U^{234}/U^{238} and U^{235}/U^{238} activity ratios are determined in these leachates. U^{234}/U^{238} activity ratios lie in the range of 1.12 to 1.14, while U^{235}/U^{238} activity ratio is 0.046 which is the same as that for natural uranium.

Removal of the surface labile component of uranium by destroying the organic matter with phosphate-free hydrogen peroxide and 0.05 M hydrochloric acid has been carried out and uranium isotopic activity ratios are obtained in the leachates and the sediment residues.

It has been observed that disequilibrium between U^{238} and U^{234} exists only on the surface of the labile layer and as the surface organic layer is removed the core shows equilibrium activities.

This section also deals with the interaction of protactinium with humic and fulvic acids obtained from coastal marine water and sediments.

SECTION V.—Deals with the methods for estimating the thickness of the surface layer containing the labile component of thorium and uranium which can be removed by leaching with suitable leaching agents that removed thorium and uranium from the surface of the particles without chemically attacking the mineral body of the sediments.

The thickness of the labile organic layer lie in the range of 2.5×10^{-6} cm to 10.0×10^{-6} cm. These values are comparable to the values obtained by electron microscopy method.

SECTION VI.—Deals with the total amount of thorium and uranium and leachable fractions of thorium and uranium in the sediment samples. Significance of these results in understanding the physico-chemical processes in the coastal marine environment is discussed.

The geochemical disequilibrium between Th^{230} and U^{234} is discussed in the section. The Th^{230}/U^{234} activity ratios lie in the range of 0.12 to 2.06 from Bombay to Kottilppad. Pa^{231} activities are determined on the surface of these sediments and the activity ratios of Pa^{231}/U^{235} are calculated. These ratios lie in the range of 6.0 to 21.7. The significance of this ratio is discussed.

II. SAMPLE COLLECTION

The samples used in this study are the top layer (< 15 cm deep) of sediments representing fresh sediments and surface water samples collected from different locations along the West Coast of India.

1. SEDIMENTS

In the sampling procedure, number of samples are collected from nearby places at each sampling station. These sediments are pooled together (~ 5 kgs) and then used as representative sample of the respective stations.

Figure 4 gives the location of the sampling stations from Bombay (19° N, 73° E) to Kottilppad (8° N, 77° E). Figure 5 gives sample collection sites in the Bombay region. Details of sampling stations are given in table 1.

The samples after collection are spread in aluminium trays ($4' \times 3'$), air-dried and stored in polythene bottles as stock of samples.

2. SEA WATER

30 litres of coastal sea water samples are collected at a number of locations in the Bombay region. The samples collected are usually clear and contain little suspended matter.

Table 1. Sampling stations along the West Coast of India.

Sampling station	Location
Bombay	19° N, 73° E
Dabhol	$17^{\circ} 36'$ N, $73^{\circ} 15'$ E
Jaygad	$17^{\circ} 30'$ N, $73^{\circ} 30'$ E
Ratnagiri	17° N, $73^{\circ} 30'$ E
Deogad	$16^{\circ} 30'$ N, $73^{\circ} 30'$ E
Malwan	16° N, $73^{\circ} 45'$ E
Vengurla	$15^{\circ} 45'$ N, $73^{\circ} 48'$ E
Goa	$15^{\circ} 30'$ N, 74° E
Karwar	$14^{\circ} 48'$ N, $74^{\circ} 30'$ E
Honawar	$14^{\circ} 12'$ N, $74^{\circ} 45'$ E
Shertallay	$9^{\circ} 36'$ N, $76^{\circ} 30'$ E
Alleppey	$9^{\circ} 30'$ N, $76^{\circ} 30'$ E
Thottapally	$9^{\circ} 24'$ N, $76^{\circ} 30'$ E
Kayamkulam	$9^{\circ} 12'$ N, $76^{\circ} 45'$ E
Karunagapally	$9^{\circ} 06'$ N, $76^{\circ} 45'$ E
Chavara	9° N, $76^{\circ} 45'$ E
Kottilppad	8° N, 77° E

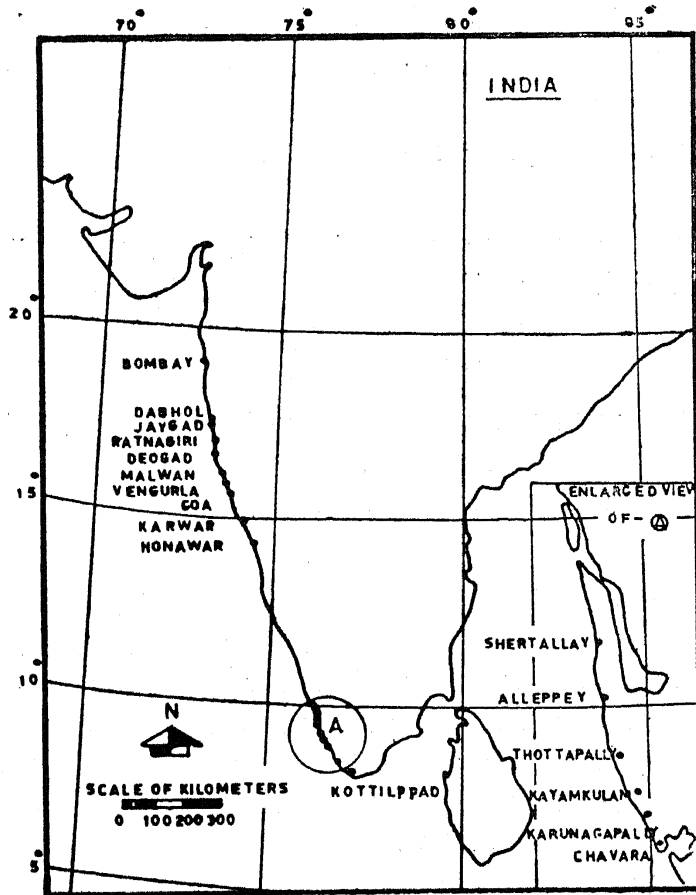


Figure 4. Map of the West Coast of India showing the sampling points.

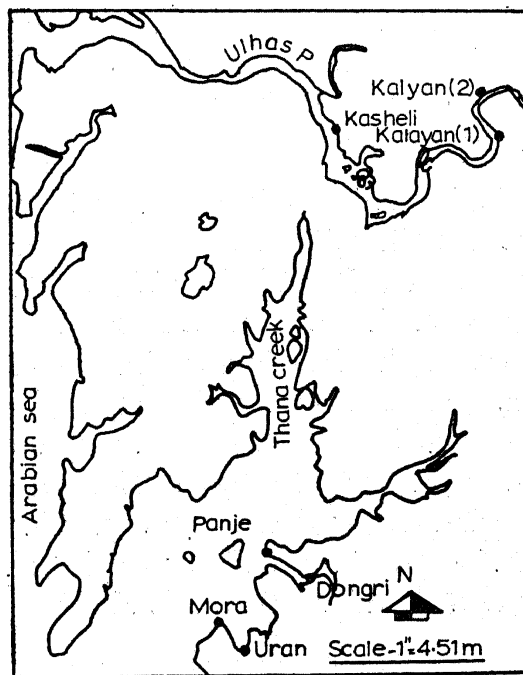


Figure 5. Map of Bombay region showing the sampling points.

In all cases, sea water samples are filtered through 0.22μ membrane filters. The clear filtrates thus obtained are used for the determination of the isotopes of radium, uranium and protactinium.

Measurements of radium are carried out using 3 litres of sea water, while U^{234}/U^{238} and U^{235}/U^{238} activity ratios are determined using 20 litres of sea water.

III. DISEQUILIBRIUM STUDIES IN Th^{228}/Th^{232} ACTIVITY RATIOS AND Th^{230}/Th^{232} ACTIVITY RATIOS IN COASTAL SEDIMENT SURFACES

1. INTRODUCTION

DURING the last few years, a number of workers have studied the disequilibrium between Th^{232} and Th^{228} in various marine organisms, deep sea sediments and waters in their investigations on geochemical processes of the oceans.

Goldberg,¹ Bernat and Goldberg² have determined disequilibrium between Th^{232} and Th^{228} in deep sea sediments and waters at various depths in the Pacific and Atlantic Oceans. In their study of radioactive disequilibrium of thorium, the three isolates of thorium from the sediment core were obtained after: (i) completely dissolving the phillipsite, (ii) leaching the sample with hot 6 N hydrochloric acid and (iii) dissolving total sample having particle size less than 2 μ .

Table 2 reproduces the activity ratios of Th^{228}/Th^{232} and Th^{230}/Th^{232} obtained by them at different depths.

Analyses of thorium isotopes obtained from fractions of North Pacific core ($17^{\circ} 10' N$ and $132^{\circ} 50' W$) indicated that there were movements of Ra^{228} within sedimentary column, thorium comes to the deposit primarily from sea water and there is no evidence for the migration of thorium isotopes within the sedimentary column.

Goldberg and Koide³ and Goldberg¹ in their studies on the rates of sedimentation determined Th^{230}/Th activity ratios in the deep sea sediments of the Pacific Ocean ($15^{\circ} S-50^{\circ} S$), ($15^{\circ} N-50^{\circ} N$) and of the Indian Ocean. Similar studies on the rates of sedimentation using Th^{230}/Th ratio have been carried out in the Pacific for the region $> 50^{\circ} S$ by Holmes.⁴ Neakes *et al.*,⁵ have carried out a geochemical study of the coastal Mississippi River sediments at Greenville in order to investigate the occurrence and distribution of natural thorium isotopes. In their analytical procedure these coastal river sediments were destroyed in concentrated hydrochloric acid and then the ratios of Th^{230}/Th^{232} were determined. The results of their studies in Pacific and Indian Oceans and Mississippi River are given in table 3.

Table 2. $\text{Th}^{228}/\text{Th}^{232}$ and $\text{Th}^{230}/\text{Th}^{232}$ activity ratios at different depths in sedimentary phases ($17^{\circ} 10' \text{ N}$, $132^{\circ} 50' \text{ W}$).

Depth in the core (cm)	$\text{Th}^{228}/\text{Th}^{232}$			$\text{Th}^{230}/\text{Th}^{232}$		
	Phillipsite	Hot 6 N HCl leachate	< 2 u	Phillipsite	Hot 6 N HCl leachate	< 2 u
0-4	5.6	1.02	0.94	29.7	31.8	24.2
4-8	7.1	1.07	0.93	15.3	24.7	17.5
8-12	7.9	1.08	0.90	12.4	11.4	12.6
12-16	9.9	1.05	0.92	5.0	6.7	6.4
16-20	9.8	1.10	0.88	2.15	1.9	2.5
30-34	9.6	1.18	0.75	0.95	0.65	0.64
40-44	9.6	1.03	..	0.95	0.43	..
50-54	7.4	1.10	0.86	0.94	0.49	0.51
100-105	9.8	0.48
290-295	7.0
324-331	7.6	0.66
470-475	8.2	0.78

Table 3. $\text{Th}^{230}/\text{Th}$ Ratios in Sediments.

Place of collection	Latitude	$\text{Th}^{230}/\text{Th}$	Reference
Pacific Ocean	$15^{\circ} \text{ S} - 50^{\circ} \text{ S}$	0.2-0.7	Goldberg and Koide (1962) Goldberg (1968)
do.	$15^{\circ} \text{ N} - 50^{\circ} \text{ N}$	0.4-6.0	do.
Indian Ocean	..	0.5-1.1	do.
Pacific Ocean	$> 50^{\circ} \text{ S}$	1.0-12.0	Holmes (1965)
Mississippi River	Greenville	1.0-4.0	Noakes <i>et al.</i> (1967)

Sediment samples treated with hot 6 N or concentrated hydrochloric acid do attack the mineral core of the sediment particles and the results cannot be taken to represent the physico-chemical equilibrium existing between the chemical species present in the sediment particles and in the ambient medium.

Miyake *et al*⁶ have determined $\text{Th}^{228}/\text{Th}^{232}$ and $\text{Th}^{230}/\text{Th}^{232}$ activity ratios in sea water collected from Western North Pacific, Japan and China Seas. They have also measured the above activity ratios in suspended matter from sea waters of Western North Pacific. They have suggested that the excess of Th^{228} in sea water may be due to the migration of Ra^{228} through the water sediment interface. Table 4 gives $\text{Th}^{228}/\text{Th}^{232}$ and $\text{Th}^{230}/\text{Th}^{232}$ activity ratios obtained in waters and suspended matter.

Recently, the importance of thorium isotopes in the marine geochemical studies has been recognised not only in the geochronological investigations of the deep sea deposits but also in the investigations of geochemical balance of the isotopes in the oceans.

In the present work, we investigate the ratios of $\text{Th}^{228}/\text{Th}^{232}$ and $\text{Th}^{230}/\text{Th}^{232}$ on the surface of the sediments. The chemical used for leaching has been chosen to avoid attacking the mineral body of the sediments.⁷

2. EXPERIMENTAL PROCEDURES

2.1. SURFACE LEACHING OF THORIUM

For the surface leaching of thorium trial experiments were carried out with two leaching reagents, viz: (i) saturated solution of ammonium acetate and (ii) 5% ethylene diamine tetra-acetic acid solution (EDTA).

Ethylene diamine tetra-acetic acid (EDTA) has been found to be the preferred one because thorium in ionic form is best complexed with EDTA at pH 3.0.⁸

Table 4. $\text{Th}^{228}/\text{Th}^{232}$ and $\text{Th}^{230}/\text{Th}^{232}$ Activity ratios in waters and suspended matter Miyake *et al*⁶ (1970).

Place of collection	Location	$\text{Th}^{228}/\text{Th}^{232}$	$\text{Th}^{230}/\text{Th}^{232}$
Western North Pacific surface waters	24° 58' N, 151° 00' E to 44° 00' N, 150° 58' E	2.7-36.0	0.9-5.4
Western North Pacific Coastal waters	33° 27' N, 139° 20' E to 35° 05' N, 135° 25' E	8.5- 9.1	0.8-2.4
Japan Sea surface waters	40° 36' N, 131° 01' E to 41° 12' N, 132° 15' E	10.0-15.0	0.6-1.3
East China Sea surface waters	31° 00' N, 126° 40' E to 31° 51' N, 129° 33' E	2.5-22.5	0.9-3.3
Western North Pacific suspended matter	33° 27' N, 139° 20' E to 41° 01' N, 143° 31' E	1.2- 3.2	1.4-1.5

2.1.1 LEACHING WITH 5% EDTA: 500 gms of air dried sediment are shaken with 800 ml instalment of 5% EDTA solution (pH 3.0) at room temperature for eight hr in a mechanical shaker. The sediment is allowed to settle overnight. The supernate is filtered through 0.22 μ membrane filter. The sediment is again shaken with another aliquot of 800 ml of 5% EDTA. The procedure is repeated eight times. The filtrate (\sim six litres) thus obtained is acidified to pH 2.0 with dilute nitric acid and then evaporated to dryness. The EDTA (and other organic) residue is destroyed as follows:

2.2. DESTRUCTION OF EDTA

Trial experiments have been carried out for the destruction of EDTA by the following methods: (i) destruction with nitric acid and hydrogen peroxide and (ii) destruction with ammonium persulphate. The rate of destruction of EDTA by nitric acid and hydrogen peroxide has been found to be slow and hence ammonium persulphate has been used.

2.2.1 AMMONIUM PERSULPHATE METHOD FOR EDTA DESTRUCTION: 10 ml of 2 N nitric acid are added to the dried residue. The solution is stirred. 200 mg of ammonium persulphate are added and the solution is warmed and evaporated to dryness. The process is repeated several times till all EDTA is destroyed. The entire procedure requires about an hour.⁹

2.2.2 DISCUSSION: 10 ml of 8 M nitric acid are added to the residue and the solution is shaken. No suspended solid matter could be discerned in the solution. This is taken as indicative of the absence of any dissolution of the silicate mineral body of the sediment in the leaching procedure.

The destruction of EDTA when tried with nitric acid and hydrogen peroxide as an alternate procedure, a trace of residue was obtained which did not dissolve in 10 ml of 8 M nitric acid. However the quantity of the white residue is in the range of one to two mgs. Since the leaching is done with 500 gms of sediment, the appearance of a mg or so as residue cannot be taken as an indication of the absence of any significant dissolution of the siliceous mineral body of the sediment.

2.3. ION-EXCHANGE METHOD FOR THE SEPARATION OF THORIUM

2.3.1 ION-EXCHANGE COLUMNS: The anion-exchange resin, Dowex — 1 \times 8% (50–100 mesh) is washed with running distilled water to remove the fine particles. 5 gms of the resin is then loaded in pyrex glass column (1 \times 15 cms.).

2.3.2 COLUMN OPERATIONS: (i) The column is converted into nitrate form by passing 50 ml of 8 M nitric acid at a flow rate of 1.0 ml/min. (ii) The 8 M nitric acid extract is treated with 10 mg of Fe^{3+} carrier and thorium is co-precipitated with ferric hydroxide by 1:1 ammonium hydroxide. The solution is centrifuged and residue is redissolved in nitric acid, hydroxide reprecipitated and separated by centrifugation. This procedure removes the sulphate ions introduced during ammonium persulphate treatment.

The hydroxide precipitate is taken in 10 ml of 8 M nitric acid and the solution is passed through the column at a flow rate of 0.5 ml/min. Thorium is adsorbed on the column. The effluent is rejected.

(iii) The column is washed with 50 ml of 8 M nitric acid at a flow rate of 1.0 ml/min and the washings are rejected.

(iv) The adsorbed thorium from the column is first washed with 10 ml of 0.1 M nitric acid at a flow rate of 0.5 ml/min, and then it is desorbed with 50 ml of 1.0 M hydrochloric acid at a flow rate of 0.5 ml/min. The two effluents of nitric and hydrochloric acids containing thorium are pooled together and evaporated to dryness.

The thorium present in the nitrate form in the residue is converted to the chloride form by repeated evaporation to dryness with 1.0 ml instalments of concentrated hydrochloric acid.

2.4. PURIFICATION OF THORIUM

(i) The residue of thorium chloride is dissolved in 10 ml of 8 M hydrochloric acid.

(ii) Dowex-1 \times 8% (50-100 mesh) column similar to the above one is prepared and then it is washed with 50 ml of 8 M hydrochloric acid at a flow rate of 1.0 ml/min.

(iii) The thorium chloride solution obtained above is passed through the column at a flow rate of 0.5 ml/min. The column is then washed with 50 ml of 8 M hydrochloric acid at a flow rate of 1.0 ml/min. The effluents are pooled together and evaporated to dryness. The residue is converted to the nitrate form by repeated evaporation to dryness with 1.0 ml instalments of concentrated nitric acid.

2.5. MOLECULAR PLATING OF THORIUM

The plating cell used for the purpose has a stainless steel base to which is screwed a thick perspex tube of one inch internal diameter. The stainless

steel base acts as a cathode and a platinum rod (1.0 mm dia.) as the anode. The platinum rod is also attached to a motor for stirring the solution during plating.

Buffed stainless steel planchet (one inch in dia.) is washed several times with ethylene trichloride, dipped in dilute nitric acid and warmed for few minutes. The planchet is then washed with distilled water and mounted on the plating cell. Figure 6 shows the arrangement of the plating cell.

The purified thorium nitrate residue is dissolved in 1.0 ml of 0.001 M nitric acid and transferred into the plating cell. 20 ml of isopropyl alcohol is added to the solution, stirred for 5 min. slowly increasing the current to 5 ma and voltage to 350 volts. The plating is carried out at room temperature for an hour¹⁰. A 100% plating efficiency for thorium could be obtained but the deposit has been observed to be thick and non-adherent. Hence a compromise of 40–45% plating of thorium activity is allowed to get a very thin adherent film of thorium on the planchet. The planchet is removed, washed clean of the adhering solution in running distilled water and dried at room temperature.

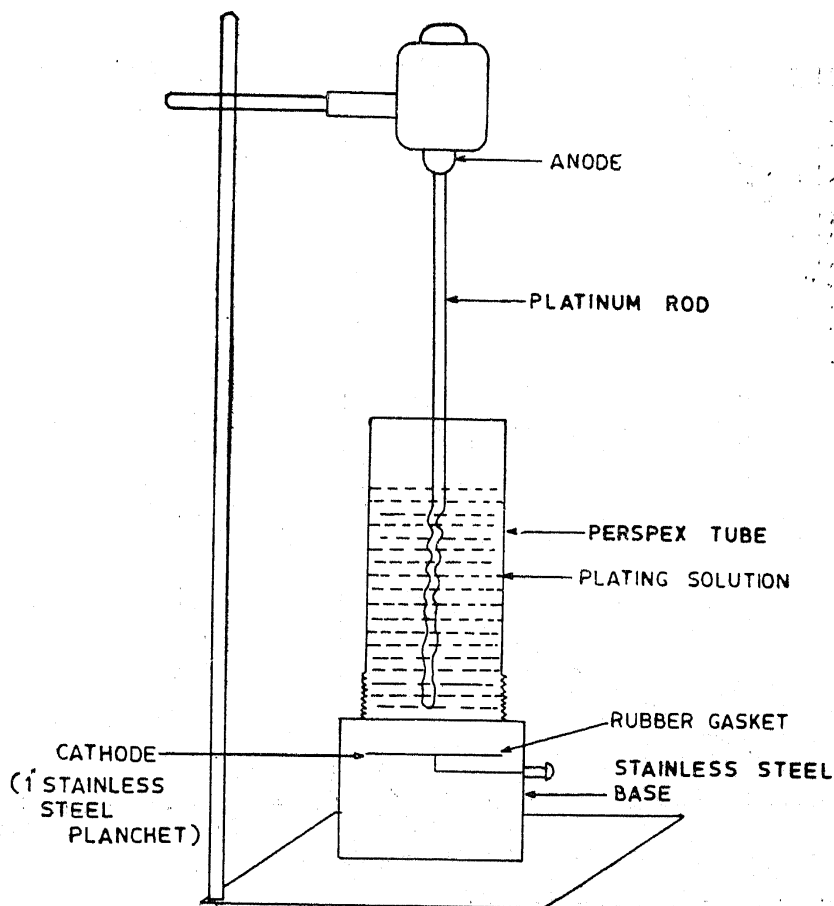


Figure 6. Diagrammatic representation of plating cell and stirrer used in molecular plating.

3. COUNTING OF THORIUM

The alpha spectrum of the plated thorium sample is obtained using a partially depleted silicon surface barrier detector (active area 200 mm^2 and a depletion depth of 700μ), a low noise amplifier, a pre-amplifier and 256 channel analyser. The diameter of the detector is 15.96 mm and it is mounted inside a brass vacuum chamber. The plated source (15 mm in dia.) is mounted in the vacuum chamber 5 mm below the silicon detector. Resolution of the detector is 43.4 KeV full width at half-maximum (FWHM) at 5.108 MeV and 5.477 MeV alphas of Po^{208} and Am^{241} respectively (figure 7). The counting efficiency is 24% for weightless samples plated on stainless steel planchets.

The instrument stability is checked by counting standard source of Po^{208} , U^{238} , Pu^{239} and Am^{241} before and after the sample counting. The alpha particle background is essentially negligible over long periods of time.

Thorium samples are counted for 1000 min because of the low Th^{232} , Th^{230} and Th^{228} activities in order to get satisfactory counting statistics.

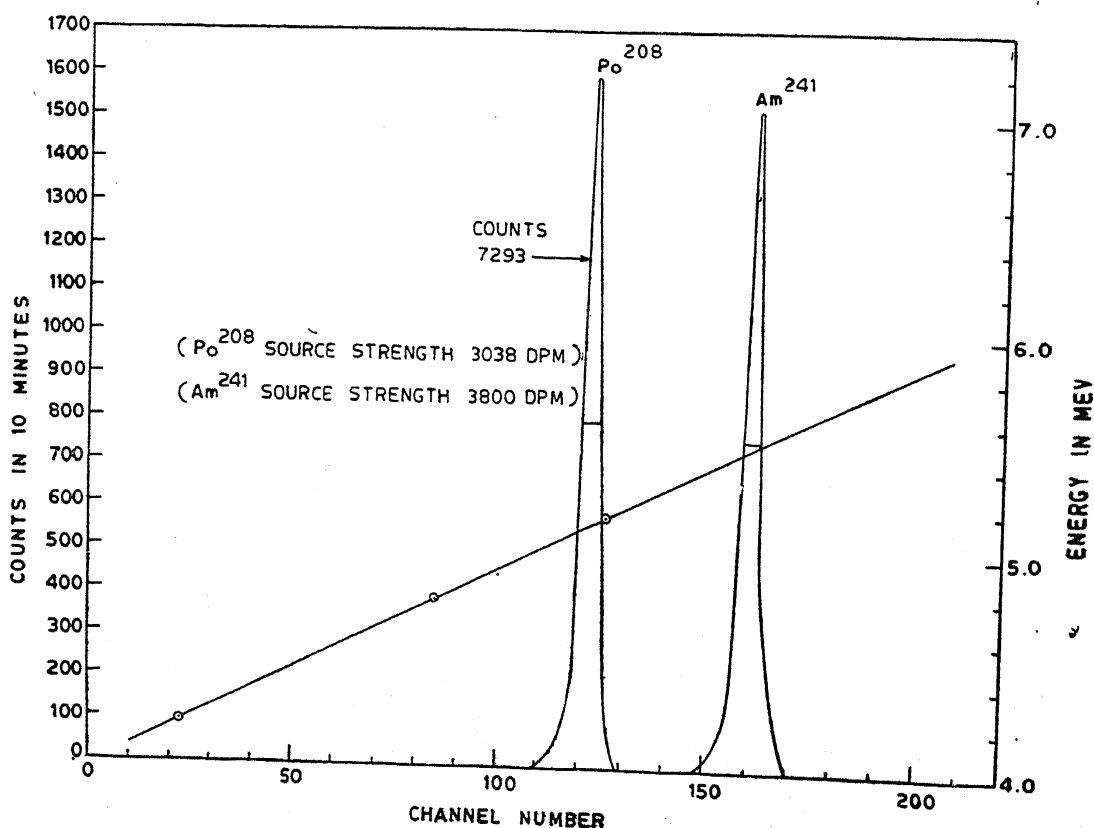


Figure 7. Alpha Spectra of Po^{208} and Am^{241} sources in Alpha Spectrometer (the resolution is indicated in the figure).

These samples accumulate counts under Th^{232} and Th^{228} peaks giving standard deviation of 5 to 10%. Standard deviation obtained for the counts under Th^{230} peak usually lies in the 10% range.

4. RESULTS AND DISCUSSION

Figures 8 to 22 show the disequilibrium between Th^{232} and Th^{228} in coastal sediment samples collected from Bombay harbour to Kottilppad.

Table 5 gives the activities of Th^{232} , Th^{230} and Th^{228} in 5% EDTA leachates of the coastal sediments collected from the Bombay harbour region (19°N , 73°E).

Table 6 gives the corresponding activities in the latitude band ($17^\circ - 14^\circ 12' \text{N}$, $73^\circ 30' - 74^\circ 45' \text{E}$) from Ratnagiri to Honawar, while table 7 gives the activities of thorium isotopes in the monazite bearing areas ($8^\circ - 10^\circ \text{N}$, $76^\circ - 77^\circ \text{E}$).

4.1. $\text{Th}^{228}/\text{Th}^{232}$ ACTIVITY RATIOS IN THE COASTAL SEDIMENTS

$\text{Th}^{228}/\text{Th}^{232}$ activity ratios in Bombay harbour region and in the monazite bearing areas are obtained in the range of 0.55 to 0.67 while this ratio is in the range of 2.00 to 2.19 in areas between Ratnagiri and Honawar.

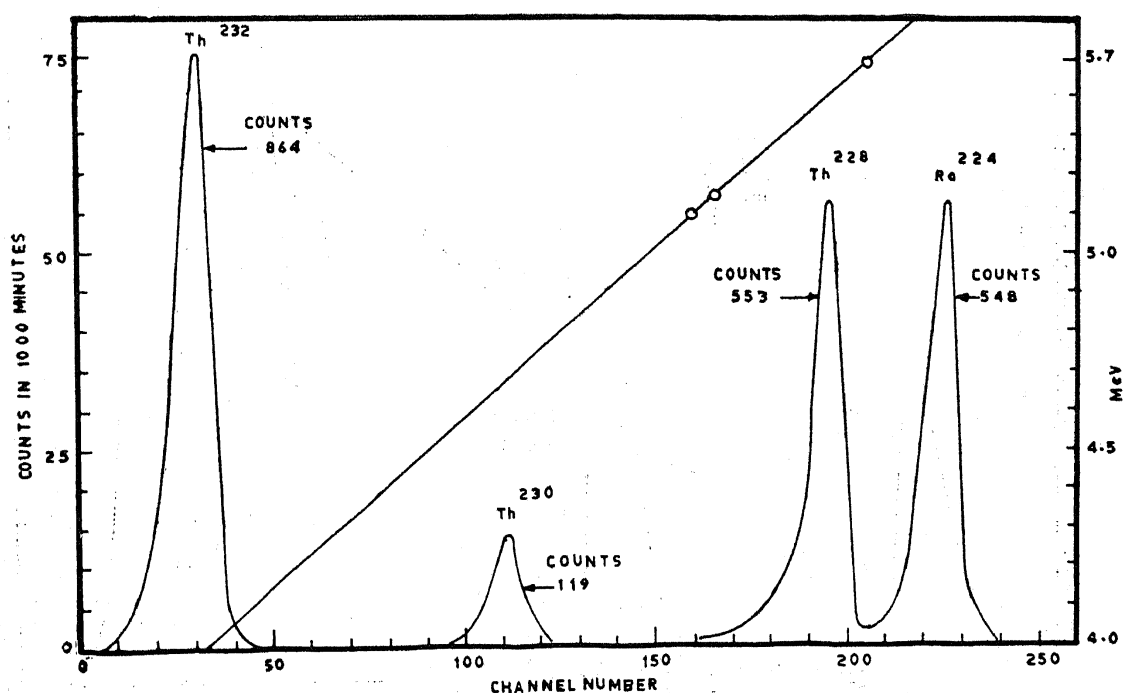


Figure 8. Disequilibrium between Th^{232} and Th^{228} in sediment sample from Bombay Region.

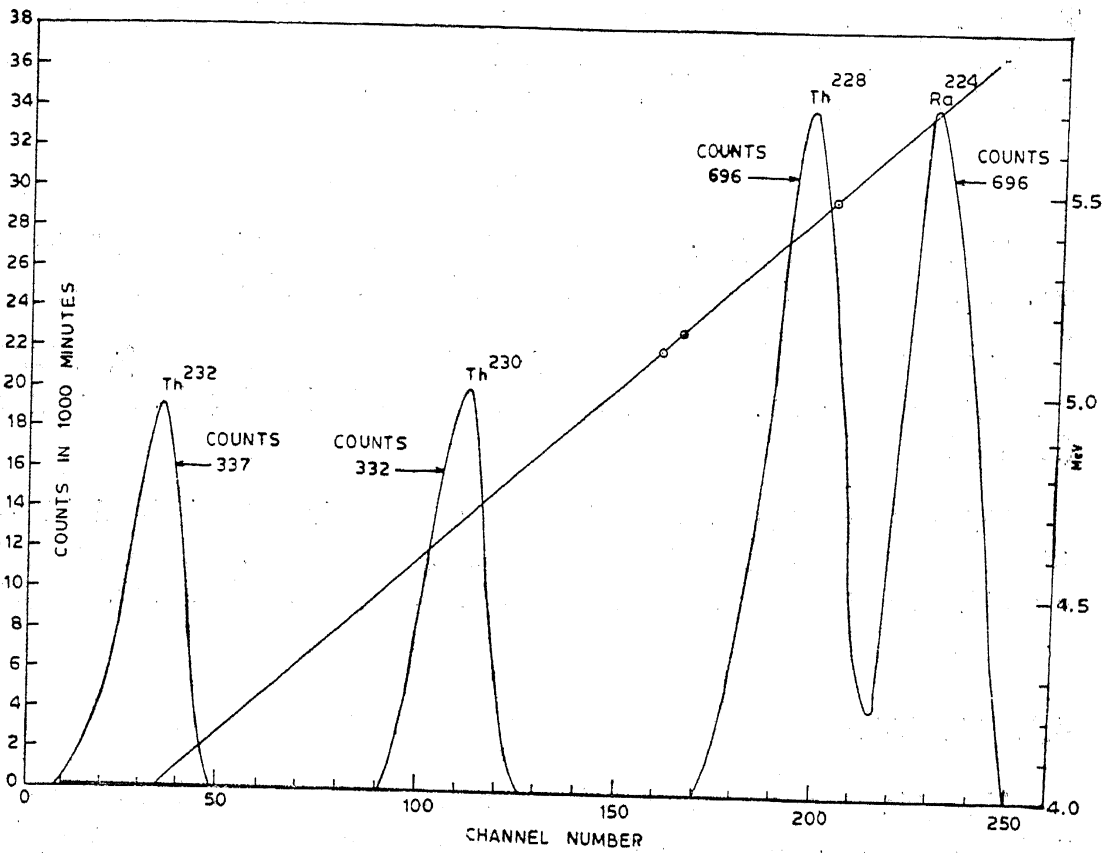


Figure 9. Disequilibrium between Th^{232} and Th^{228} in sediment sample from Ratnagiri.

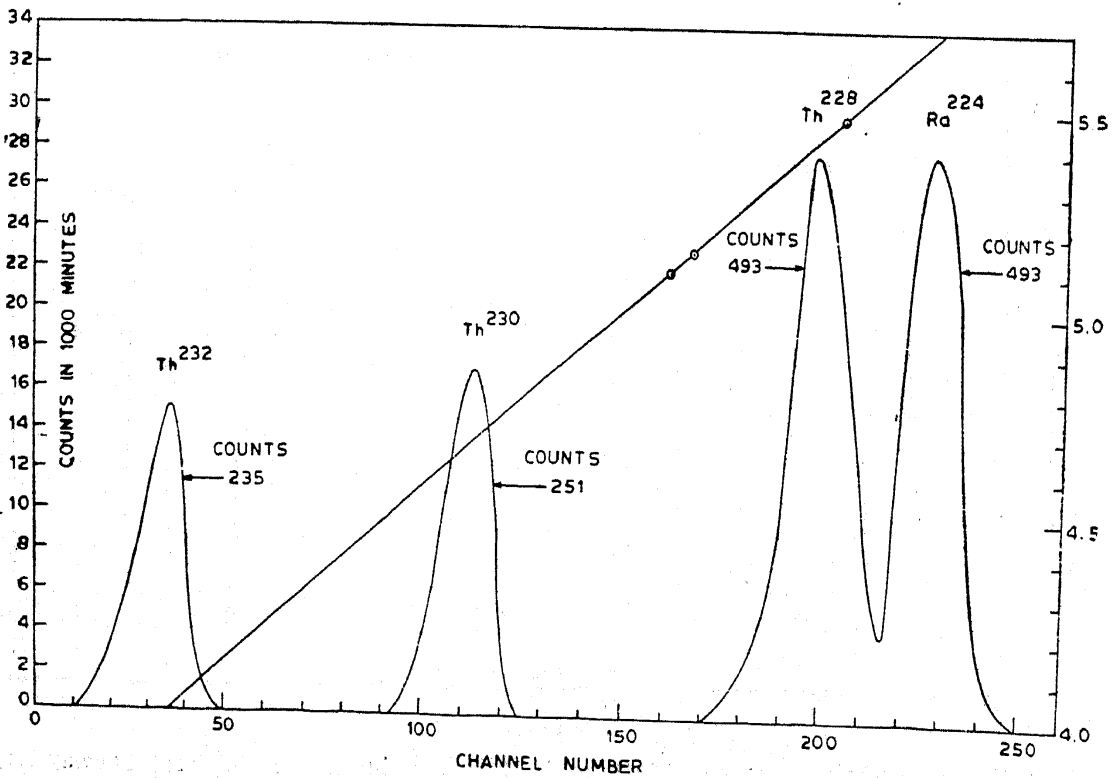


Figure 10. Disequilibrium between Th^{232} and Th^{228} in sediment sample from Deogad.

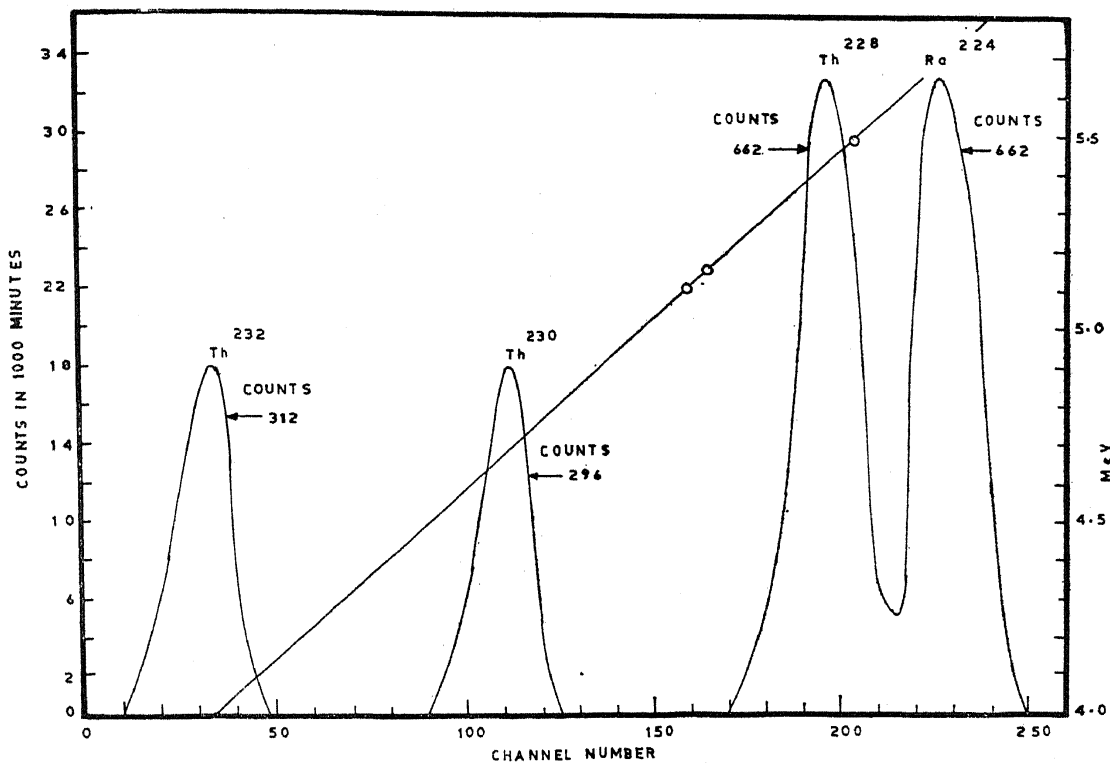


Figure 11. Disequilibrium between Th²³² and Th²²⁸ in sediment sample from Malwan.

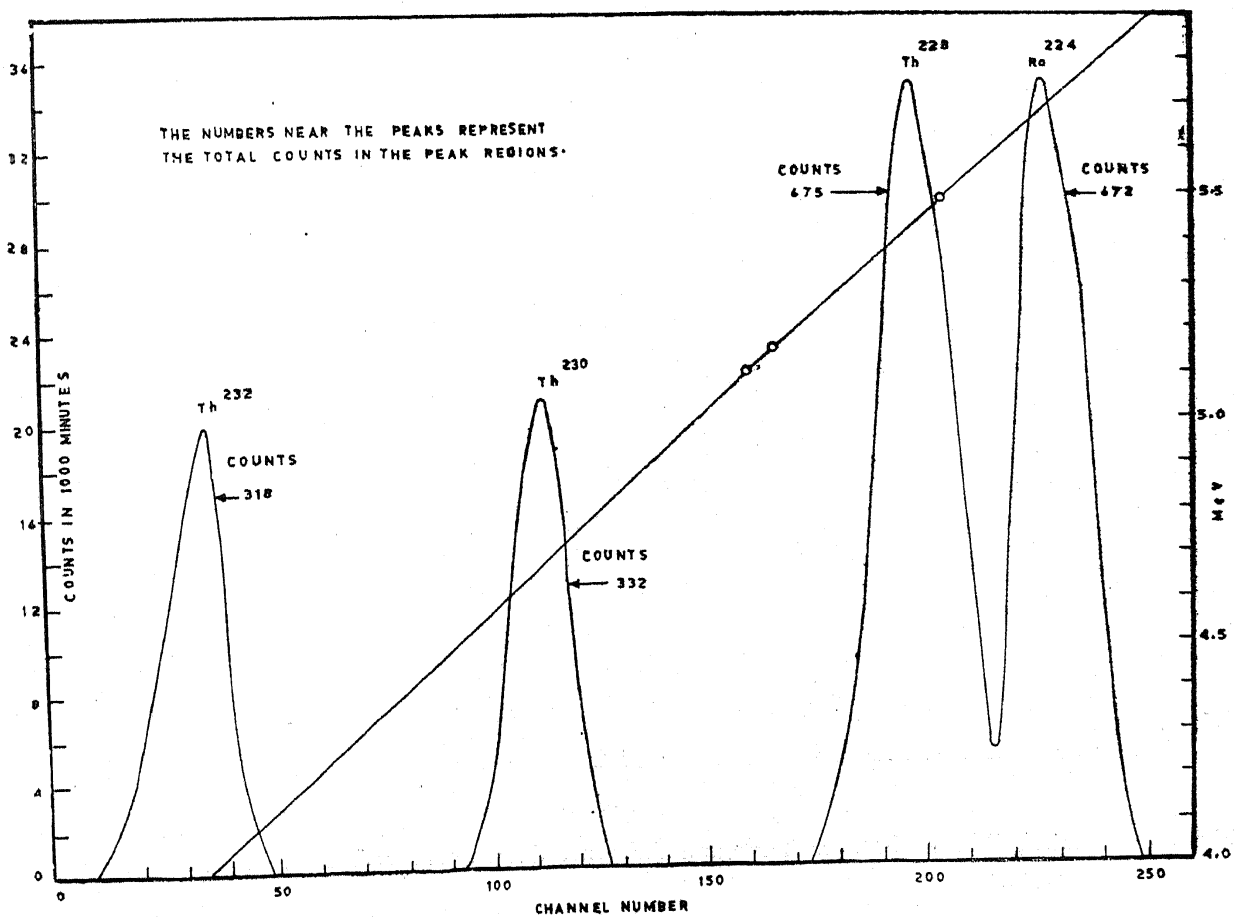


Figure 12. Disequilibrium between Th²³² and Th²²⁸ in sediment sample from Vengurla.

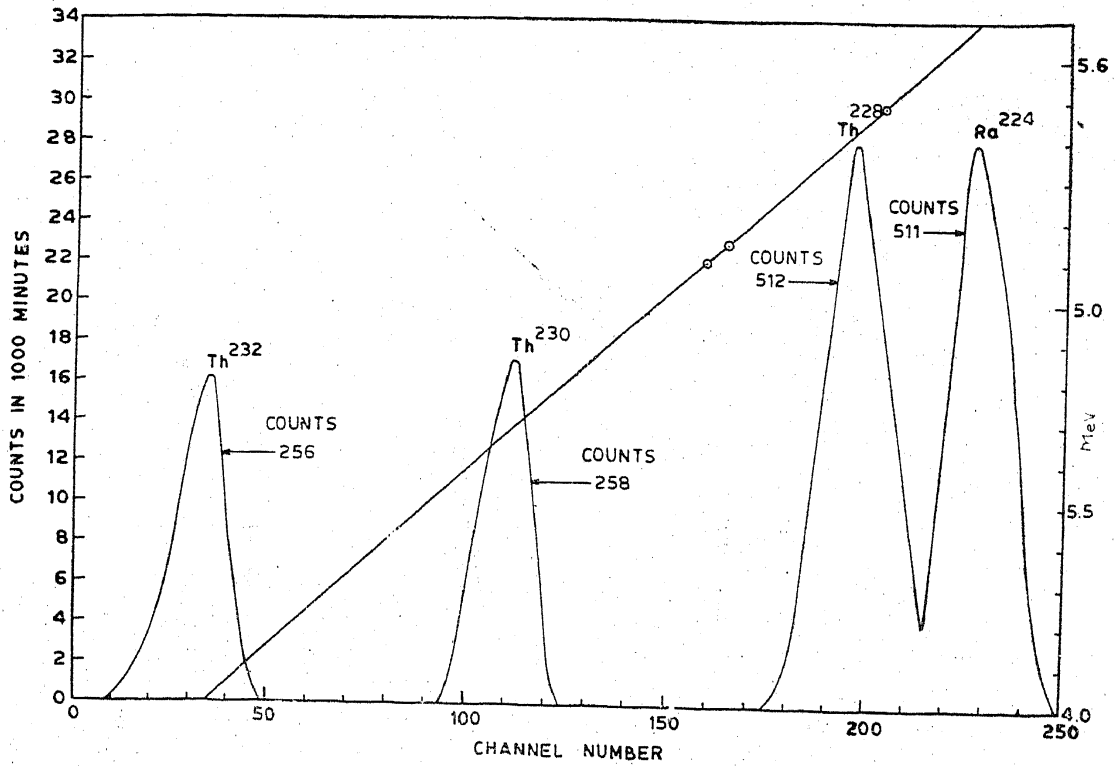


Figure 13. Disequilibrium between Th²³² and Th²²⁸ in sediment sample from Goa.

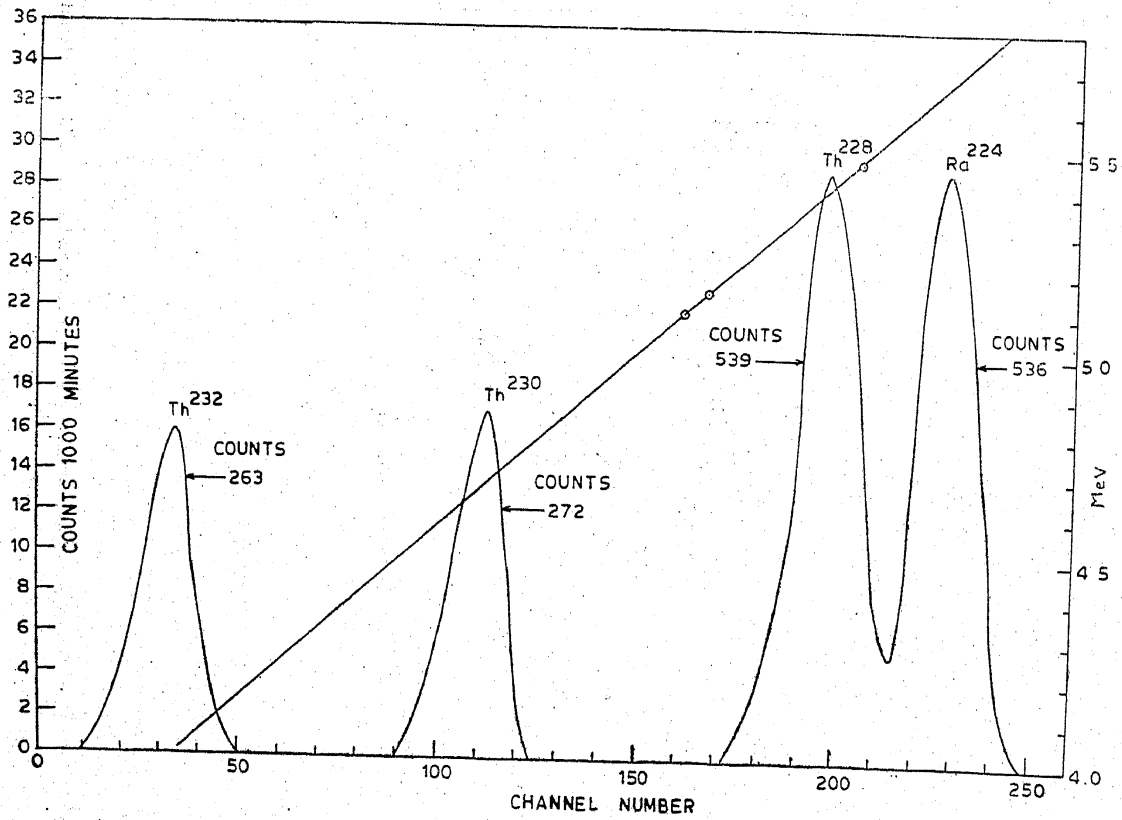


Figure 14. Disequilibrium between Th²³² and Th²²⁸ in sediment sample from Karwar.

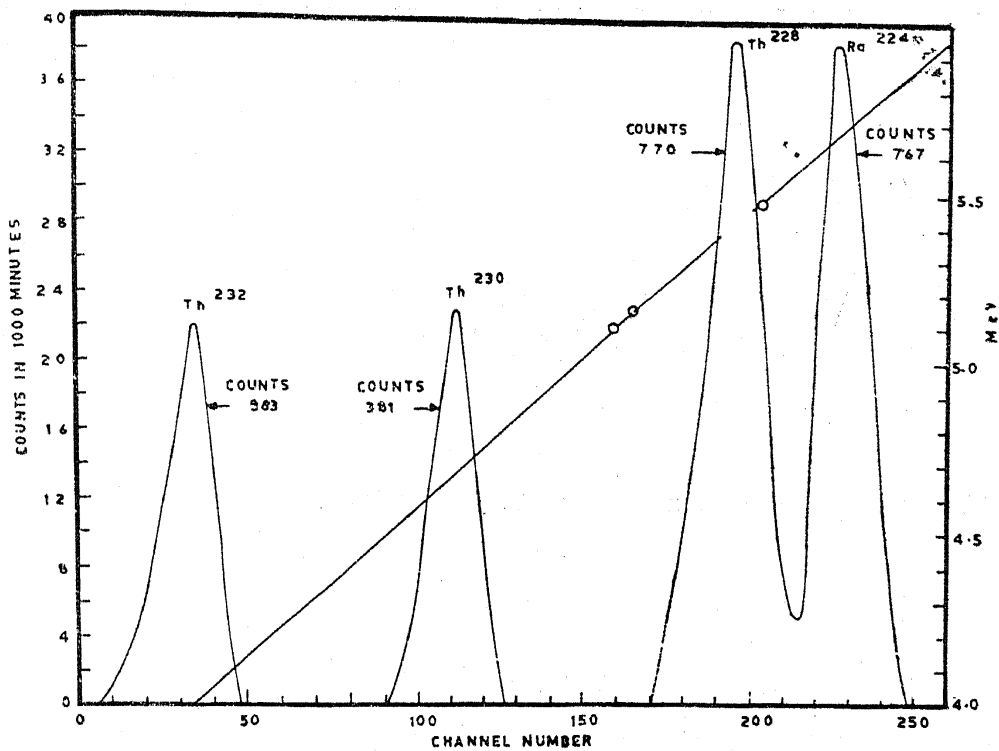


Figure 15. Disequilibrium between Th^{232} and Th^{228} in sediment sample from Honawar.

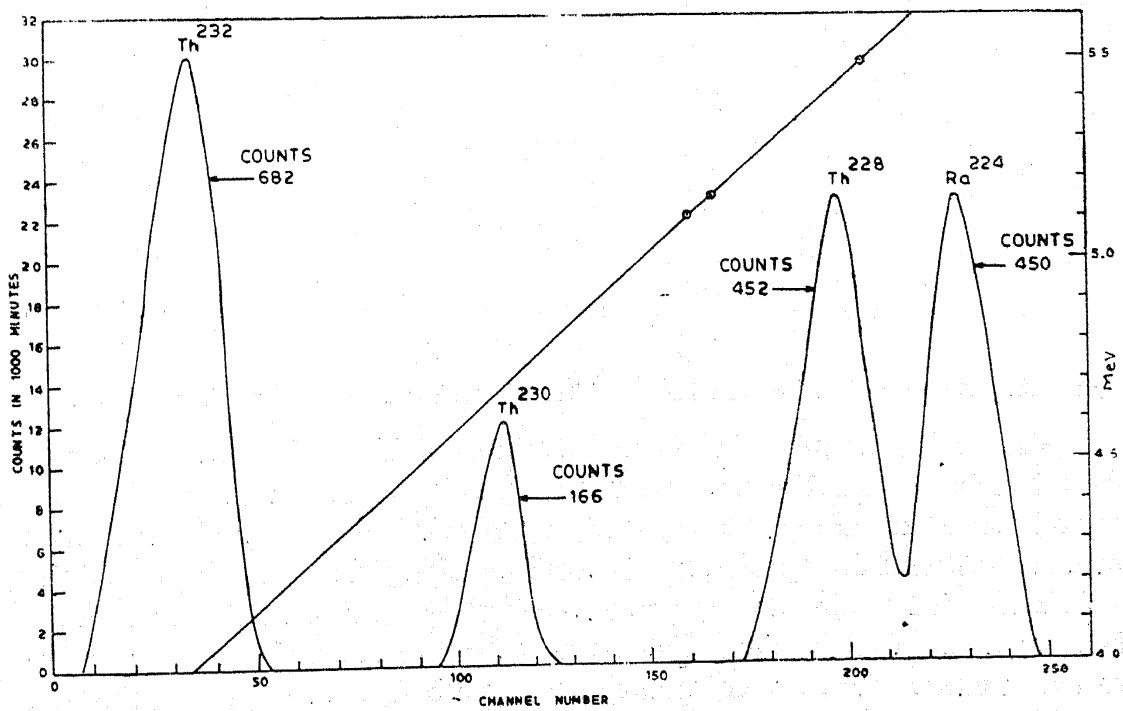


Figure 16. Disequilibrium between Th^{232} and Th^{228} in sediment sample from Shertally.

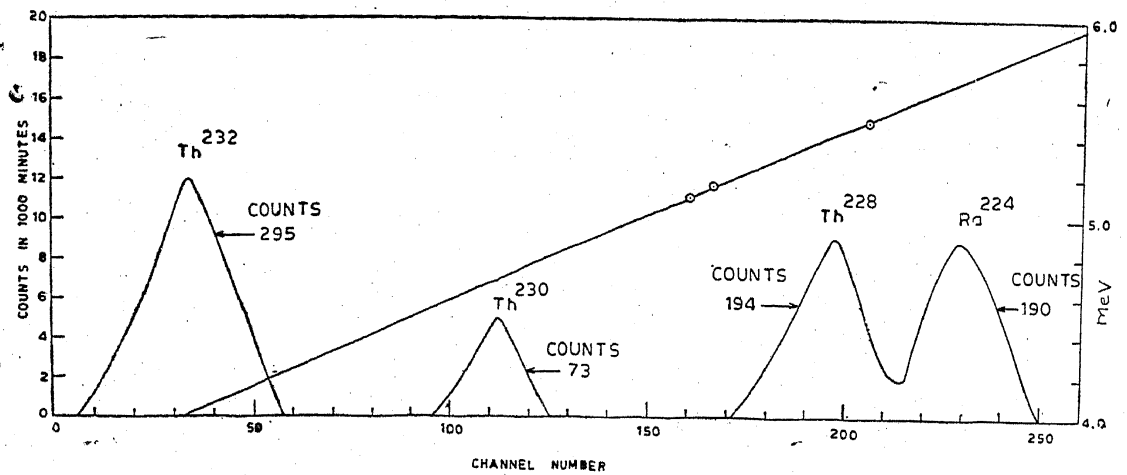


Figure 17. Disequilibrium between Th^{232} and Th^{228} in sediment sample from Alleppey.

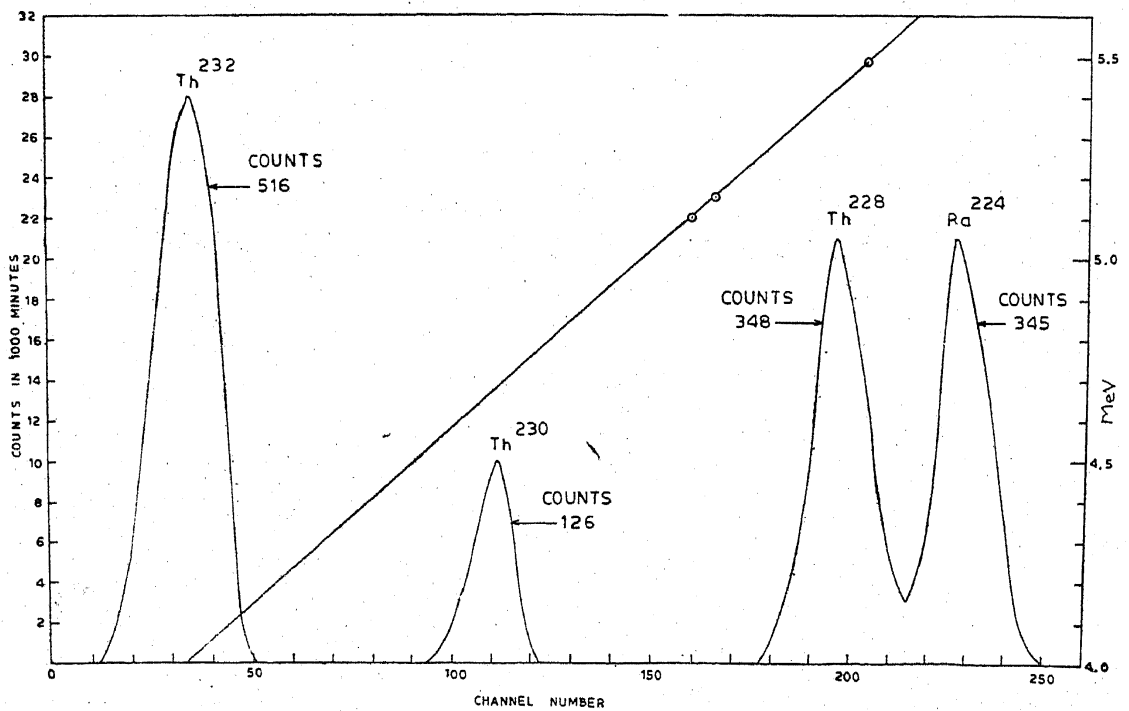


Figure 18. Disequilibrium between Th^{232} and Th^{228} in sediment sample from Thottapally.

Significant variations in the activity ratios of $\text{Th}^{228}/\text{Th}^{232}$ are observed from Bombay to Kottilppad. However, these variations in the ratios existing on the surface of the sediments get masked when special care is not taken in analytical chemical procedure to avoid attacking the mineral core of the sediments. The ratios are observed as ~ 1.0 for sediments from monazite bearing areas and for the sediments of tables 5 and 6 the ratios get distorted whenever these are completely destroyed before analysing for thorium isotopes.

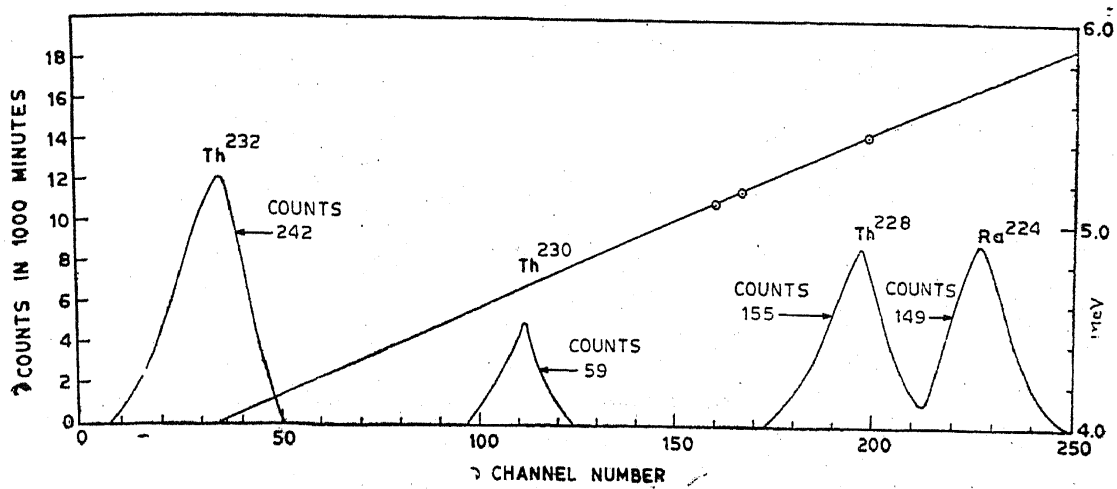


Figure 19. Disequilibrium between Th^{232} and Th^{228} in sediment sample from Kayamkulam.

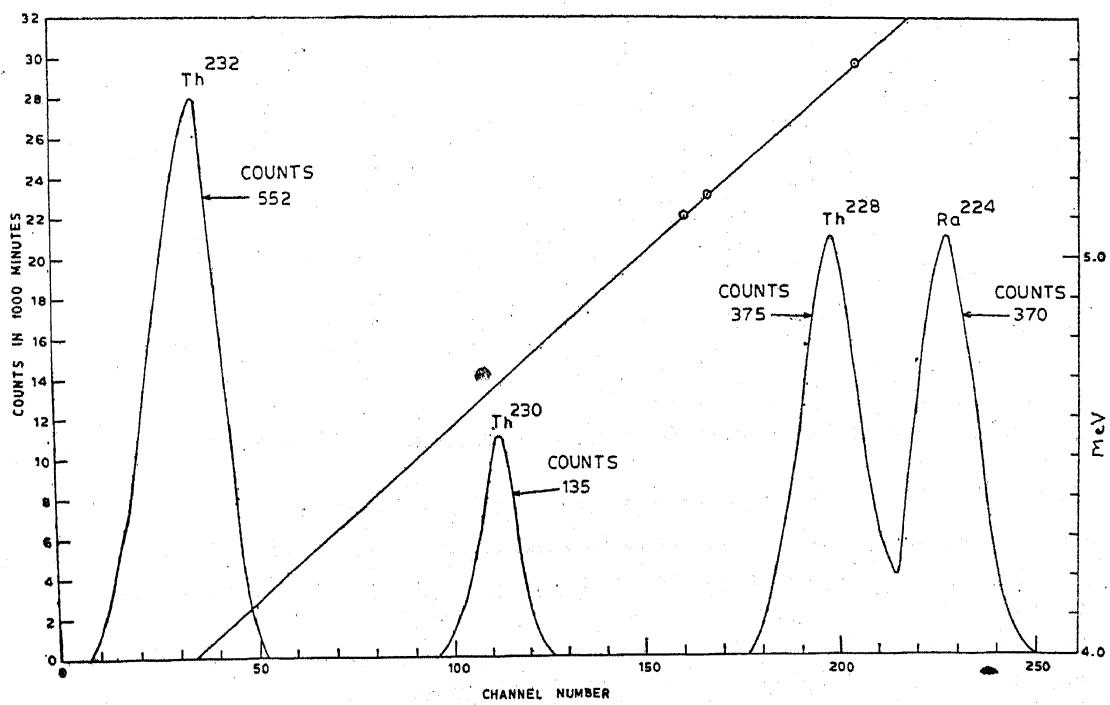


Figure 20. Disequilibrium between Th^{232} and Th^{228} in sediment sample from Karunagapally.

Earlier workers estimated thorium in deep sea cores and observed disequilibrium between Th^{232} and Th^{228} . Bernat and Goldberg² obtained values of the ratio of $\text{Th}^{228}/\text{Th}^{232}$ in the range of 1.03 to 1.18 in the hot 6 N hydrochloric acid leachate of the entire sample of a deep sea sediment and the ratio in the range of 0.75 to 0.94 on total dissolution of less than 2 μ size fraction of the sample,

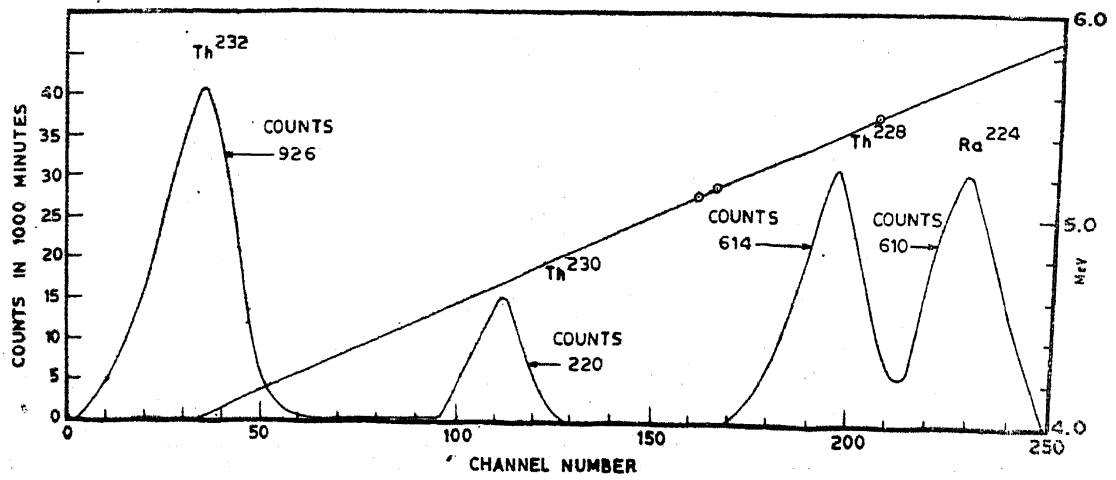


Figure 21. Disequilibrium between Th^{232} and Th^{228} in sediment sample from Chavara.

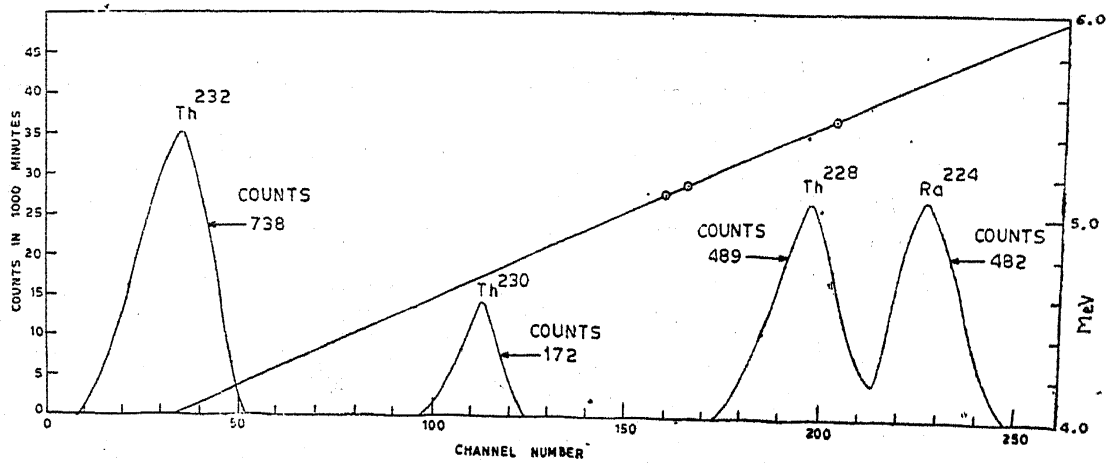


Figure 22. Disequilibrium between Th^{232} and Th^{228} in sediment sample from Kottilppad.

Table 5. $\text{Th}^{228}/\text{Th}^{232}$ and $\text{Th}^{230}/\text{Th}^{232}$ Activity ratios in sediments of Bombay (19°N , 73°E).

Place of collection	Th^{232} (dpm)	Th^{230} (dpm)	Th^{228} (dpm)	$\text{Th}^{228}/\text{Th}^{232}$	$\text{Th}^{230}/\text{Th}^{232}$
Dongri	0.88	0.13	0.50	0.57	0.15
Mora	2.10	0.29	1.15	0.55	0.14
Uran	4.71	0.62	2.68	0.57	0.13
Panje	6.25	0.96	3.63	0.57	0.15
Kasheli	3.13	0.44	1.74	0.56	0.14
Kalyan (1)	9.20	1.27	6.13	0.66	0.14
Kalyan (2)	3.58	0.50	2.29	0.64	0.14

The dpm in the columns indicate count rates obtained with the plated sample.

Table 6. $\text{Th}^{228}/\text{Th}^{232}$ and $\text{Th}^{230}/\text{Th}^{232}$ Activity ratios in sediments from Ratnagiri to Honawar.

Place of collection	Th^{232} (dpm)	Th^{230} (dpm)	Th^{228} (dpm)	$\text{Th}^{228}/\text{Th}^{232}$	$\text{Th}^{230}/\text{Th}^{232}$
Ratnagiri	0.97	0.96	2.01	2.07	0.99
Ratnagiri	1.32	1.30	2.72	2.06	0.98
Ratnagiri	1.40	1.38	2.90	2.07	0.99
Deogad	0.98	1.05	2.05	2.09	1.07
Malwan	1.30	1.23	2.76	2.12	0.95
Vengurla	1.08	1.12	2.37	2.19	1.04
Vengurla	1.33	1.38	2.81	2.11	1.04
Goa	1.42	1.37	2.84	2.00	0.97
Goa	1.29	1.24	2.58	2.00	0.96
Goa	1.07	1.07	2.13	2.00	1.00
Goa	1.17	1.25	2.35	2.00	1.06
Karwar	1.00	1.07	2.05	2.05	1.07
Karwar	1.09	1.13	2.25	2.06	1.04
Honawar	1.59	1.59	3.21	2.01	1.00

The dpm in the columns indicate count rates obtained with the plated sample.

 Table 7. $\text{Th}^{228}/\text{Th}^{232}$ and $\text{Th}^{230}/\text{Th}^{232}$ Activity ratios in sediments of monazite bearing areas.

Place of collection	Th^{232} (dpm)	Th^{230} (dpm)	Th^{228} (dpm)	$\text{Th}^{228}/\text{Th}^{232}$	$\text{Th}^{230}/\text{Th}^{232}$
Shertallay	2.84	0.69	1.88	0.66	0.24
Alleppey	1.23	0.30	0.81	0.66	0.24
Thottapally	2.15	0.52	1.45	0.67	0.24
Kayamkulam	1.01	0.25	0.65	0.64	0.24
Karunagapally	2.30	0.56	1.56	0.67	0.24
Chavara	3.87	0.92	2.50	0.64	0.24
Kottilppad	3.08	0.72	2.04	0.66	0.23

The dpm in the columns indicate count rates obtained with the plated samples.

Miyake *et al*¹¹ have determined the activity ratios of $\text{Th}^{228}/\text{Th}^{232}$ in Western North Pacific surface waters. The activity ratio in this region varies from 2.7 to 36.0. In Japan sea surface waters the ratio varies from 10.0 to 15.0. In the coastal waters ($33^{\circ} 27' - 35^{\circ} 05' \text{ N}$, $139^{\circ} 20' - 135^{\circ} 25' \text{ E}$), the $\text{Th}^{228}/\text{Th}^{232}$ activity ratio lies in the range of 8.5 to 9.1. Such high values of the ratio are not obtained in sediments due to the fact that Th^{232} can only appear in the sea water from the primary mineral. The solubility being extremely low whereas Th^{228} in water appears from the decay of dissolved Ra^{228} which is significantly higher than thorium. The ratio obtained for the suspended matter from Western North Pacific waters lies in the range of 1.2 to 3.2. In our view, if the sediments or suspended

matter are leached under such conditions that the core of the particles is not attacked, they would have obtained equal ratios for the sediments and suspended matter.

The circulation in the near shore region off the Kerala Coast¹² indicated northerly drift of surface water in this region. The high ratios of $\text{Th}^{228}/\text{Th}^{232}$ in Ratnagiri to Honawar samples are then due to the net transport of Ra^{228} leached out of the sediments of monazite bearing areas of Kerala region and decay of Ra^{228} to Th^{228} during its northerly transport and the deposition in these regions. ^{7,13,14}

4.2. $\text{Ra}^{228}/\text{Th}$ ACTIVITY RATIO IN WATERS

4.2.1 $\text{Ra}^{228}/\text{Th}$ ACTIVITY RATIO IN DOUBLE DISTILLED WATER SHAKEN WITH MONAZITE (THAT HAS BEEN IN STORAGE FOR MORE THAN A DECADE): 25 gms of monazite are shaken with 800 ml instalment of double distilled water for 8 hr. The supernate is filtered through 0.22 u membrane filter. The procedure is repeated five times. The filtrate (about four litres) are pooled together for the determination of Ra^{228} and thorium. Ra^{228} is determined after precipitating it with barium as sulphate.¹⁵ The precipitate is allowed to age for 72 days for the decay of Ra^{228} ($T_{1/2} = 11.44$ d) and Ra^{224} ($T_{1/2} = 3.64$ d) and then counted for Ac^{228} betas ($T_{1/2} = 6.13$ h). Chemical yield of radium is obtained from the recovery of Ba^{140} tracer. Thorium is chemically separated from the supernate and then estimated by thorium-thorin spectrophotometric method.¹⁶

4.2.1.1 DISCUSSION: $\text{Ra}^{228}/\text{Th}$ activity ratio is found to be -387 instead of the equilibrium ratio of 1.0 , indicating that considerable amount of Ra^{228} is preferentially leached out from the surface by distilled water.

4.2.2 $\text{Ra}^{228}/\text{Th}$ ACTIVITY RATIO IN NATURAL SEA WATER SHAKEN WITH MONAZITE (THAT HAS BEEN IN STORAGE FOR MORE THAN A DECADE): 4 litres of Bombay sea water is filtered through 0.22 u membrane filter. Barium (10 mg) and lead (200 mg) carriers are added to precipitate out radium and lead from the sea water. The supernate is filtered through 0.22 u membrane filter. To the filtrate free from radium, a few mg of sodium sulphate are added (equivalent to sulphate ions removed due to precipitation of barium as sulphate). The sea water, thus treated, is shaken with 25 gms of monazite as in para 4.2.1, filtered through 0.22 u membrane filters and Ra^{228} and thorium are determined as given in para 4.2.1.

4.2.2.1 DISCUSSION: $\text{Ra}^{228}/\text{Th}$ activity ratio is found to be -425 instead of the equilibrium value of 1.0 , indicating that considerable amount of Ra^{228} is preferentially leached out from the surface by natural sea water

Recently, Moore¹⁷ and Kaufman¹⁸ have reported the ratio upto 600 of unsupported Ra²²⁸ in sea water to the parent nuclide Th²³².

Ra²²⁸ preferentially dissolved in sea water is the main source of the excess of Th²²⁸ as compared to equilibrium value.

These results suggest long distance transport of Ra²²⁸ before it decays to Th²²⁸ which then gets deposited on the settling suspended matter.

The excess of Th²²⁸ over Th²³² in the sediments observed in the present work can then be due to any or all of the following reasons: (i) Dissolution and transport of Ra²²⁸ from the surface of the sediments depending upon the coastal currents. (ii) Flow into the sea of river waters and other land run offs with high values of Th²²⁸/Th²³² and Ra²²⁸/Th ratios. (iii) Progressive weathering and leaching of thorium bearing minerals deposited in the coastal waters.

4.3. Ra²²⁸ IN SEDIMENTS

4.3.1 LEACHING WITH EDTA: 15 gms of sediment sample is shaken with 500 ml of 5% EDTA at pH 8.0¹⁹ for 8 hr each. The sediment is allowed to settle and the supernate is filtered through 0.22 μ membrane filter. The procedure is repeated three times. The pooled filtrates (about 1.5 litre) are evaporated to dryness. The dried mass is transferred to a platinum dish and heated in a muffle furnace at 500° C for 2 hr. The residue is taken in dilute nitric acid (a clear solution is obtained leaving no part of the residue undissolved) and radium is co-precipitated with barium as sulphate.¹⁵ This precipitate of radium is allowed to age for 72 days (*cf.* para 4.2.1) and counted for Ac²²⁸ betas.

4.3.1.1 DISCUSSION: Table 8 gives the results obtained. It is seen that there is more Ra²²⁸ concentrations on the surface of the sediments of Ratnagiri and Goa as compared to the sediments from monazite bearing areas. This may be understood as a further corroboration of the observation on the coastal currents made by Sastry and D'Souza.¹²

The Th²³² activity on the surface of the sediments in the monazite bearing areas is always high and there is always some depletion of equilibrium Ra²²⁸ activity because of the leaching processes in the environment. This accounts for the lower than 1.0 ratio of Th²²⁸/Th²³². In fact we feel that this ratio should appear always less than 1.0 on the surface of the sediment where one cannot visualise transport of Ra²²⁸ into the area from higher Ra²²⁸ activity regions. Th²²⁸/Th²³² ratio obtained by the surface leaching of soil samples from areas of high rainfall has also been reported to be less than 1.0 by Bhat,²⁰

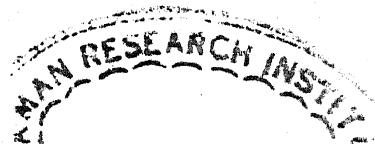


Table 8. Activities of Ra²²⁸ in coastal sediments.

Place of collection	Ra ²²⁸ uuc/gm
Bombay	0.22
Ratnagiri	0.54
Ratnagiri	0.54
Goa	0.53
Goa	0.54
Shertallay	0.21
Alleppey	0.27
Thottapally	0.21
Karunagapally	0.20
Chavara	0.32
Kottilppad	0.30

4.4. Ra²²⁸ IN COASTAL SEA WATER SAMPLES

3 litres of sea water sample from each location is filtered through 0.22 μ membrane filter. Radium is separated by the method given.¹⁵ The precipitate is allowed to age for 72 days (*cf.* para 4.2.1) and counted for Ac²²⁸ betas.

4.4.1. DISCUSSION: Table 9 gives the results obtained. The concentrations of Ra²²⁸ is somewhat fluctuating. However, it is discernible that the concentration in the Bombay region is systematically lower than the concentration obtained in the sea waters south of Bombay.

Joshi and Ganguly^{14,21} interpret this on the basis of preferential leaching of Ra²²⁸ as explained earlier.

4.5. Th²³⁰/Th²³² ACTIVITY RATIOS ON THE SURFACE OF THE COASTAL SEDIMENT

4.5.i. DISCUSSION: Th²³⁰/Th²³² activity ratios in the Bombay region has been found to be in the range of 0.13 to 0.15 (table 5). The corresponding activity ratios lie in the range of 0.95 to 1.07 in sediment samples from Ratnagiri to Honawar (table 6), while these ratios are in the range of 0.23 to 0.25 (table 7) in the monazite bearing areas.

Earlier workers have determined Th²³⁰/Th²³² activity ratios in deep sea cores and waters. Miyake *et al*^{6,11} have determined the activity ratio of Th²³⁰/Th²³² in sea water from Western North Pacific. In the coastal waters the ratio lies in the range of 0.8 to 2.4. Th²³⁰/Th²³² activity ratios in surface waters off the coast of Japan are also determined. It is important to note that Th²³⁰/Th²³² ratios in Pacific waters and the Japan sea waters (very low according to investigators) lie in the range of 0.5 to 5.4 with an average of 2.5.²²⁻²⁵

Table 9. Activities of Ra²²⁸ in coastal sea water samples.

Place of collection	Ra ²²⁸ uuc/litre
Bombay	0.77
Bombay	0.57
Bombay	0.37
Ratnagiri	0.75
Ratnagiri	0.98
Ratnagiri	0.61
Ratnagiri	1.03
Goa	0.78
Goa	0.90
Goa	0.82
Goa	0.71

Experiments performed by Sackett *et al*²⁶ have shown that ocean water collected from the Pacific, one from the surface, near the coast outside San Diego Bay in 1956 and the other taken at a depth of 3500 meters from 33° 54.5' N, 124° 40' W have been analysed for total thorium alpha activity. The Th²²⁷ concentration in both the surface water and deep water samples is below its equilibrium concentration with respect to U²³⁵, indicating that not only Th²³⁰ but apparently also Pa²³¹ or Ac²²⁷ or both, are precipitated with the sediments.

In our experiments, we have observed ratios of Th²³⁰/Th²³² varying from 0.13 in Bombay region to 1.07 in some areas along the West Coast of India (tables 5-7). The primary source of Th²³⁰ is the uranium content of monazite in this coastal region. Uranium content as U₃O₈ in the monazite averages to 0.37% and thorium as ThO₂ averages to 9.6%. The activity ratio of Th²³⁰/Th²³² in the mineral body of monazite under equilibrium conditions calculate to 0.11.²⁷ The values for the ratios obtained for the surface activity of the sediments in the Bombay region is somewhat close (though a little higher) to the calculated value for monazite. The values for the regions between Ratnagiri to Honawar is about ten times higher. The high values for the Ratnagiri-Honawar region can be understood on the basis of the decay of the precursor U²³⁴ in the sea water of Th²³⁰ and the northerly transport of the same.

4.6. CLEANSING SURFACE LAYER OF SEDIMENTS FREE OF ORGANIC MATTER BY PHOSPHATE-FREE HYDROGEN PEROXIDE IN PRESENCE OF 0.05 M HYDROCHLORIC ACID

Some sediment samples have been treated with phosphate-free hydrogen peroxide in presence of 0.05 M hydrochloric acid in order to obtain the ratio of Th²²⁸/Th²³² (leachable and organic forms). The supernate obtained after hydrogen peroxide treatment and centrifugation is filtered. The filtrate is processed for column treatment and plated for thorium as described earlier,

4.6.1 DISCUSSION: Figure 23 shows disequilibrium between Th^{232} and Th^{228} in the supernate of Chavara sediment. The sediment that remained after cleansing the surface free of organic matter is treated the same way as the original sediment for leaching of thorium. The ratio of $\text{Th}^{228}/\text{Th}^{232}$ in the monazite bearing areas lies in the range of 0.64 to 0.67. This ratio is obtained as 1.00 when sediment surface is cleansed of organic matter and then leached with EDTA (pH 3.0). Figure 24 shows the equilibrium activities of Th^{232} and Th^{228} leached from the surface of the sediments cleansed of organic matter. Table 10 gives the activity ratios of some of the samples from monazite bearing areas. $\text{Th}^{230}/\text{Th}^{232}$ activity ratio is in the range of 0.23 to 0.25 for the original sediment as well as for the sediments cleansed of organic matter. The disequilibrium between Th^{232} and Th^{228} thus exists only on the surface organic layer of the particles. However, the equalities in the values obtained in the ratios of $\text{Th}^{230}/\text{Th}^{232}$ for the original sediment as well as for the organic matter cleansed sediments point to the fact that the relative proportion of uranium thorium in the mineral body is more than a factor of two higher than the average indicated earlier.

Table 10. $\text{Th}^{228}/\text{Th}^{232}$ and $\text{Th}^{230}/\text{Th}^{232}$ Activity ratios in supernates and residues after 0.05 M HCl + H_2O_2 treatment of coastal sediments.

Place of collection	Remarks	Th^{232} (dpm)	Th^{230} (dpm)	Th^{228} (dpm)	$\text{Th}^{228}/\text{Th}^{232}$	$\text{Th}^{230}/\text{Th}^{232}$
Shertallay	Supernate	0.85	0.20	0.56	0.66	0.24
Shertallay	Organic matter free sediment	2.49	0.59	2.48	1.004	0.23
Alleppey	Supernate	1.10	0.26	0.73	0.66	0.24
Alleppey	Organic matter free sediment	0.83	0.21	0.82	1.01	0.25
Thottapally	Supernate	1.41	0.34	0.94	0.67	0.24
Thottapally	Organic matter free sediment	2.48	0.61	2.46	1.008	0.25
Kayamkulam	Supernate	0.95	0.22	0.61	0.64	0.23
Kayamkulam	Organic matter free sediment	0.83	0.21	0.83	1.00	0.25
Karunagapally	Supernate	1.11	0.25	0.74	0.67	0.23
Karunagapally	Organic matter free sediment	2.41	0.59	2.39	1.008	0.24
Chavara	Supernate	2.17	0.52	1.42	0.65	0.24
Chavara	Organic matter free sediment	0.83	0.20	0.83	1.00	0.24
Kottilppad	Supernate	2.12	0.48	1.40	0.66	0.23
Kottilppad	Organic matter free sediment	2.54	0.60	2.53	1.003	0.24

The dpm in the columns indicate count rates obtained with the plated sample.

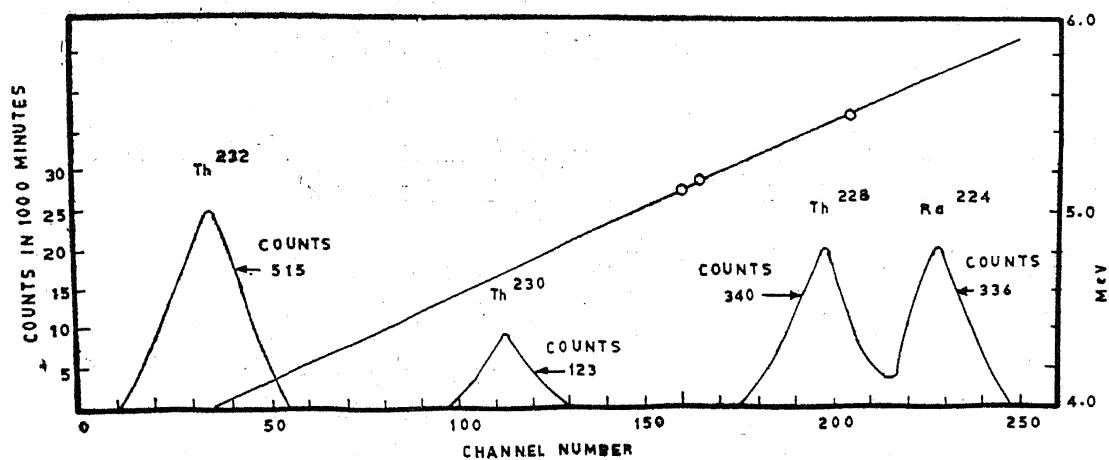


Figure 23. Disequilibrium between Th^{232} and Th^{228} in supernate obtained after Hydrogen peroxide treatment of the sediment from Chavara.

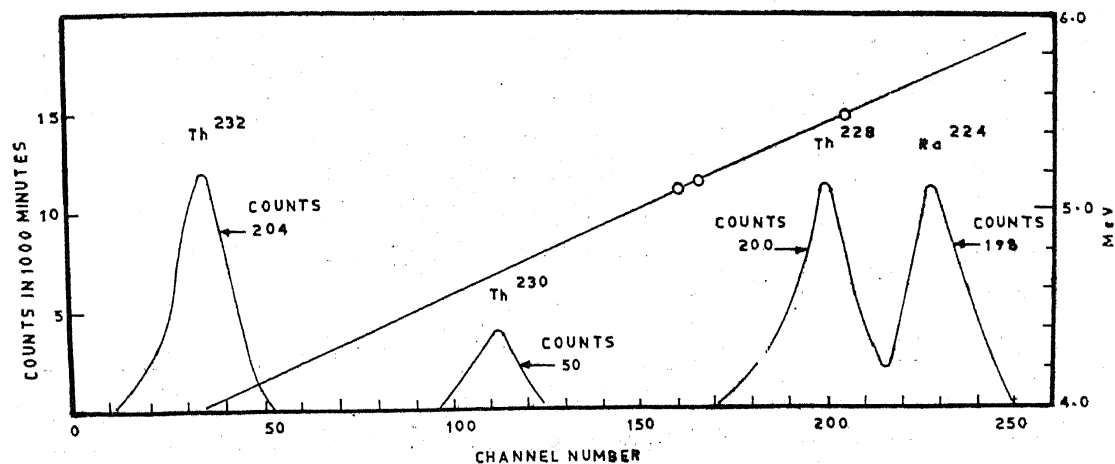


Figure 24. Equilibrium between Th^{232} and Th^{228} in sediment sample from Chavara after destroying organic matter.

Chemical analysis of the mineral core of the sediments (*cf.* table 36) also supports a similar higher uranium to thorium activity ratios. We may conclude then that the equality of activity ratios of $\text{Th}^{230}/\text{Th}^{232}$ in the sediment surface as well as in the mineral core of the samples from monazite bearing areas is attributable to the immobility of thorium from the sediments. The higher ratios for $\text{Th}^{230}/\text{Th}^{232}$ between Ratnagiri to Honawar can only be understood on the basis of the transport and decay of U^{234} .

4.7. SURFACE LEACHING OF OLD MONAZITE WITH 5% EDTA

25 gms of old monazite sample is shaken with four instalments of 800 ml of 5% EDTA at pH 3.0 for 8 hr each. The supernate is centrifuged and filtered through 0.22 μ membrane filter. The leachate is treated for thorium as detailed earlier (*cf.* Section III, paras 2.1.1., 2.2.1, 2.3.2, 2.4 and 2.5). The plated sample is counted for alphas (*cf.* para 3).

4.7.1 DISCUSSION: Figure 25 shows the spectrum obtained. The alpha spectrum of the sample showed as expected equilibrium activity between Th^{232} and Th^{228} .

IV. DISEQUILIBRIUM STUDIES IN $\text{U}^{234}/\text{U}^{238}$ ACTIVITY RATIOS AND $\text{U}^{235}/\text{U}^{238}$ ACTIVITY RATIOS IN COASTAL SEDIMENT SURFACES

1. INTRODUCTION

Uranium can exist in a number of oxidation states from +2 to +6. The two important stable states of uranium are +4 and +6. The +4 state has two 5f electrons and resembles thorium in the outer electron configuration and hence in chemical behaviour.

Uranium in the pentavalent state is most unstable in normal conditions, while the hexavalent state is most stable. In hexavalent state uranium coordinates with two oxygen ions forming a uranyl ion $(\text{UO}_2)^{+2}$. Uranyl ion thus obtained behaves in a different way as compared to uranium in tetravalent state. UO_2^{++} ion has a tendency to form complexes²⁸ with anions such as CO_3^{-2} , PO_4^{-3} and SO_4^{-2} . Because of this complexing property uranium is more soluble in the hexavalent state than in the tetravalent state and this property plays a dominant role in the geochemistry of uranium in sediments, rocks and waters.

Uranium in hexavalent state is found in large number of uranium minerals. This state exists on the surface of the mineral particles in the areas of oxidation and weathering. Uranium is found in the tetravalent state

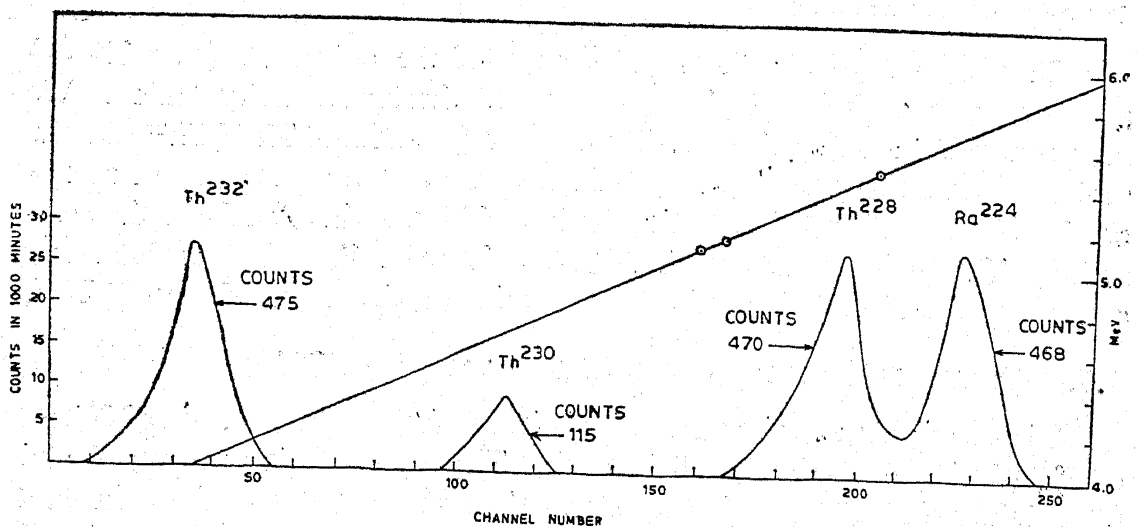


Figure 25. Equilibrium between Th^{232} and Th^{228} in sample of old Monazite.

in igneous rocks below the surface.²⁹ The oxidation of tetravalent uranium to the hexavalent state in a medium depends on the oxidation potential, which in turn depends on thermodynamical parameters such as pressure, temperature, etc.

During the last decade, workers in this field studied the disequilibrium between U^{238} and U^{234} in sea and river waters, corals, reefs and deep sea sediments but very little investigations are carried out with coastal sediments.

Chalov *et al*³⁰ and Cherdyntsev *et al*³¹⁻³⁴ and Kazachevaskii *et al*³⁵ have studied isotopic ratios of U^{234}/U^{238} in Russian Rivers and natural waters.

Thurber,³⁶ Koide and Goldberg³⁷ also determined uranium content and activity ratios of U^{234}/U^{238} in Pacific Ocean waters. Umemoto³⁸ determined U^{234}/U^{238} activity ratios in sea water from a depth of 20 meters collected at Sagami Bay in the Pacific Ocean. Blanchard³⁹ also analysed coastal water samples off North America for U^{234}/U^{238} activity ratios. These samples include those from the East Coast, the Gulf Coast, the West Coast and Alaska. Blanchard found that regardless of salinity and uranium content, the activity ratio is 1.15. Miyake *et al*^{6,11,40} have analysed the water samples from Kuroshio region in Western North Pacific and suggested that the biological activity as a possible cause for the variation in U^{234}/U^{238} activity ratios. Sarma *et al*¹⁹ have determined activity ratios of U^{234}/U^{238} in coastal waters of Bombay and Tarapur. The results of these activity ratios of U^{234}/U^{238} in waters at various locations in the world are given in table 11.

Table 11. U^{234}/U^{238} Activity ratios in waters.

Place of collection	U^{234}/U^{238}
Russian River and Natural water ³⁰	>1.0
do. ³¹⁻³⁴	>1.0
Black Sea water ³⁵	1.15
Water from the Sea of Azov ³⁵	1.20
Pacific water ³⁶	1.15
do. ³⁷	1.15
Sagami Bay Pacific water ³⁸	1.17-1.18
Coastal Waters of North America ³⁹	1.15
Western North Pacific water ^{6,11,40}	1.07-1.18
Bombay Sea water ¹⁹	1.15
Tarapur Sea water ¹⁹	1.15

U^{234}/U^{238} activity ratios in various marine organisms and deep sea sediment cores were determined by number of workers. Thurber³⁶ determined U^{234}/U^{238} activity ratios in marine carbonate samples, colites from Bahamas and living and fossil corals from Eniwetok. According to Thurber, the disequilibrium is significant for several reasons. The anomaly may be used as a geochemical tool in the study of behaviour of uranium in rocks and natural waters. Blanchard³⁹ analysed live molluscan shells from different parts of United States. Shells and sediments from Merrimack Estuary have also been analysed by Blanchard for U^{234}/U^{238} activity ratios. Ku⁴¹ determined U^{234}/U^{238} activity ratios in deep sea sediments of the Atlantic and Pacific Oceans in order to determine the age of the deep sea cores. The core samples are destroyed by acids and U^{234}/U^{238} activity ratios obtained. Veeh⁴² found the activity ratios of U^{234}/U^{238} in fossil corals occurring in their growth positions between 2 and 9 meters above sea level at many places in the Pacific. The results are used for the determination of age of the fossil corals. Veeh⁴³ also analysed anaerobic sediments from the upper continental slope in the Eastern Pacific, the Gulf of California and Norwegian Fiord for total uranium content and U^{234}/U^{238} activity ratios in order to investigate the total amount of uranium removed from the ocean. Moore⁴⁴ reported U^{234}/U^{238} activity ratios in suspended matter in Amazon River. Scott⁴⁵ has also observed U^{234}/U^{238} activity ratios in the stream sediments,⁴⁶ Miyake *et al*^{6,11} have determined uranium content and the activity ratios of U^{234}/U^{238} in marine organisms such as plankton and algae from the Western North Pacific. Table 12 gives the activity ratios of U^{234}/U^{238} in marine organisms and sediments obtained from various parts of the world. Ratios are usually greater than unity except for some sediments where values significantly less than unity have been observed.

Table 12. U^{234}/U^{238} Activity ratios in marine forms and sediments.

Sample	Place of collection	U^{234}/U^{238}
Marine carbonates ³⁶	Bahamas	1.16
Oolites ²⁶	Bahamas	1.15
Living coral ³⁶	Eniwetok	1.13
Fossil coral ³⁶	Eniwetok	1.17
Molluscan shells (Live pelecypods) ³⁹	United States (East Coast, Gulf coast, West coast, Alaska)	1.08-1.16
Shells (<i>Mya drendria</i>) ³⁹	Merrimack Estuary	1.10-1.11
Sediments ³⁹	Merrimack Estuary	0.93-0.96
Deep sea sediments ⁴¹	Atlantic and Pacific Oceans	0.95-1.04
Fossil corals ⁴²	Pacific	1.11
Anaerobic sediments ⁴³	Eastern Pacific, Gulf of California and Norwegian Fiord	0.99-1.15
Suspended matter ⁴⁴	Amazon River	0.94
Stream sediments ⁴⁵	United States	0.89-1.30
Plankton ^{6,11}	Western North Pacific	1.10-1.18
Algae ^{6,11}	Western North Pacific	1.07-1.17

There have not been such data on the ratio of activities of U^{234}/U^{238} and U^{235}/U^{238} on the labile surface fractions of the coastal marine sediments. Earlier workers obtained ratios of these activities by chemical methods which involved chemical attack of the mineral body of the deep sea sediments. We find it extremely difficult to correlate the ratios of the activity obtained in sea water and the ratios obtained with the sediment by earlier workers on the basis of the geochemical equilibrium processes between the sediments and the ambient media.

In the present investigation, U^{238} , U^{235} and U^{234} activities are determined by leaching the coastal sediments with a mild leaching solution of ammonium carbonate.

2. EXPERIMENTAL PROCEDURES

2.1. SURFACE LEACHING OF URANIUM

Uranium has a great tendency to form two stable anionic complexes with carbonate ions, the dicarbonate, $[UO_2(CO_3)_2(H_2O)_2]^{-2}$ and the tricarbonate, $[UO_2(CO_3)_3]^{-4}$. In the presence of excess of carbonate ions, the tricarbonate complex of uranium is the more stable one.⁴⁷

2.1.1 LEACHING THE SEDIMENTS WITH SATURATED SOLUTION OF AMMONIUM CARBONATE: 300 gms of air-dried sediment are shaken with four instalments of 800 ml of saturated solution of ammonium carbonate for 8 hr, using a mechanical shaker. The sediment is allowed to settle overnight. The supernate is filtered through 0.22 μ membrane filter. The filtrate (about 3 litres) thus obtained is evaporated to dryness.

2.2. DESTRUCTION OF AMMONIUM CARBONATE

To the dried mass, 5 ml of concentrated hydrochloric acid and 10 ml of distilled water are added and the mass is gently heated to drive off ammonium salts. After the white fumes are driven off, the residue is cooled and treated with 2 ml of concentrated hydrochloric acid and evaporated to dryness. The procedure is repeated four times. The residue is then heated in a muffle furnace at 450°C. It is taken in 10 ml of 8 M hydrochloric acid. A clear solution is obtained leaving no visible residue indicative of no dissolution of silica of the sediment.

2.3. REMOVAL OF IRON BY SOLVENT EXTRACTION

The solution in 8 M hydrochloric acid is shaken with 10 ml of diisopropyl ether for 4 min in a separating funnel. The organic and aqueous layers are allowed to separate and the organic layer containing iron is

removed. The aqueous layer is shaken again with equal volume of di-isopropyl ether and the procedure is repeated four times to remove the last traces of iron. The aqueous layer is evaporated to dryness and the dried mass is dissolved in 10 ml of 8 M hydrochloric acid.

2.4. ION-EXCHANGE METHOD FOR THE SEPARATION OF URANIUM

2.4.1 ION-EXCHANGE COLUMNS: The anion-exchange resin, Dowex-1 \times 8% (50-100 mesh) is washed with running distilled water to remove the fine particles. 5 gms of the resin are then loaded in pyrex glass column (1 \times 15 cms).

2.4.2 COLUMN OPERATIONS: (i) The column is converted into chloride form by passing 50 ml of 8 M hydrochloric acid at a flow rate of 1.0 ml/min. (ii) The uranium solution in 8 M hydrochloric acid is passed through the column at a flow rate of 0.5 ml/min. Uranium and protactinium are adsorbed on the column and the effluent is rejected, (iii) The column is washed with 50 ml of 8 M hydrochloric acid at a flow rate of 1.0 ml/min. and the washings are rejected, (iv) Protactinium is eluted from the column by passing 10 ml of 3.8 M hydrochloric acid at a flow rate of 1.0 ml/min. and the effluent is rejected, (v) Finally, the adsorbed uranium is eluted from the column by passing 50 ml of 1.0 M hydrochloric acid at a flow rate of 0.5 ml/min. The effluent is evaporated to dryness.

The purified uranium obtained in chloride form is converted into the nitrate form by heating the dried mass with 1.0 ml instalments of concentrated nitric acid and evaporation to dryness.⁴⁸

2.5. ELECTROPLATING OF URANIUM

The dried residue is taken in 1.2 ml of 0.001 M nitric acid and transferred into the plating cell (*cf.* Section III, figure 6). 1.2 ml of saturated ammonium oxalate solution and 2.6 ml of double distilled water are added to it and after stirring the solution with the platinum anode rod, a current of 150 ma is passed at 6 volts for about an hour at 78° C. The plating efficiency obtained by this method is about 70%.

3. COUNTING OF URANIUM

The alpha counting set up used in the study has been described earlier (*cf.* Section III, para 3).

The counting time is set at 1000 min. for each of the samples in order to obtain satisfactory counting statistics. The samples generally accumulate 3×10^3 to 10×10^3 counts under the U^{238} and U^{234} peak regions giving

a standard deviation of 1-2%. The total counts under U^{235} peak have been reckoned from the accumulated counts in the channels 40 to 60 in the figures to follow. Under these conditions the statistics for counts under U^{235} peak is no better than standard deviations of 5-7% (Joshi and Ganguly, 1976).

4. RESULTS AND DISCUSSION

4.1. U^{234}/U^{238} AND U^{235}/U^{238} ACTIVITY RATIOS IN THE COASTAL SEDIMENTS

Figures 26 to 42 show the disequilibrium between U^{238} and U^{234} activities in coastal sediments.

Table 13 gives the activity ratios of U^{234}/U^{238} and U^{235}/U^{238} in the coastal sediments from Bombay to Honawar while table 14 gives the corresponding activity ratios in the monazite bearing areas.

The range of values for U^{234}/U^{238} in these areas lie between 1.12 to 1.14. The ratio of U^{235}/U^{238} is about 0.046, which is the same as that for natural uranium (U^{235}/U^{238} activity ratio in natural uranium is 0.04657).

U^{234}/U^{238} ratios obtained by earlier workers in the different regions of the world are given earlier in table 12. Values obtained for deep sea sediments range from 0.93 to 1.15. The half-life of U^{234} being considerably shorter than that of U^{238} , the age of formation of a sediment from the

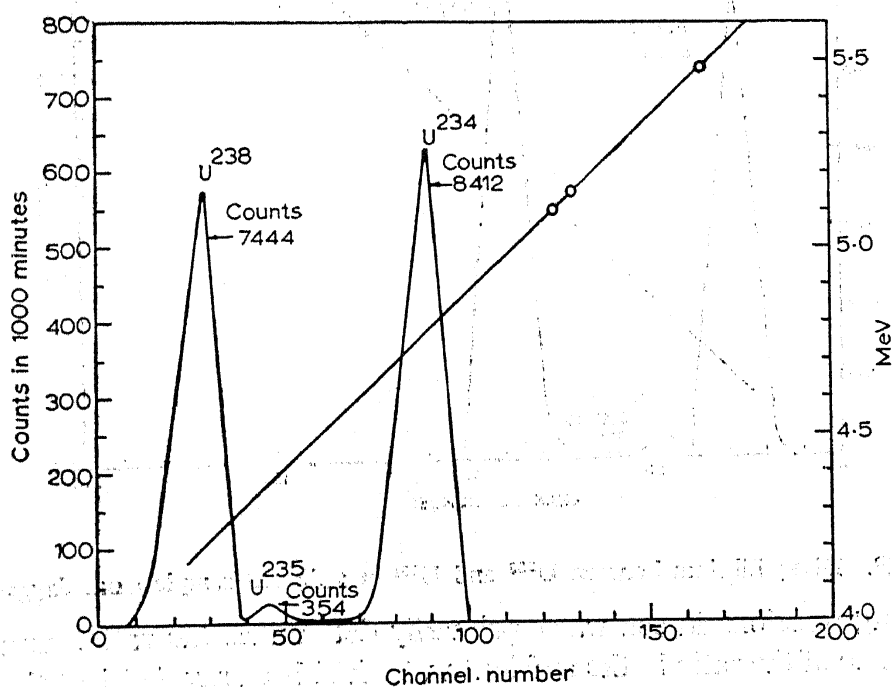


Figure 26. Disequilibrium between U^{238} and U^{234} in sediment sample from Bombay Harbour.

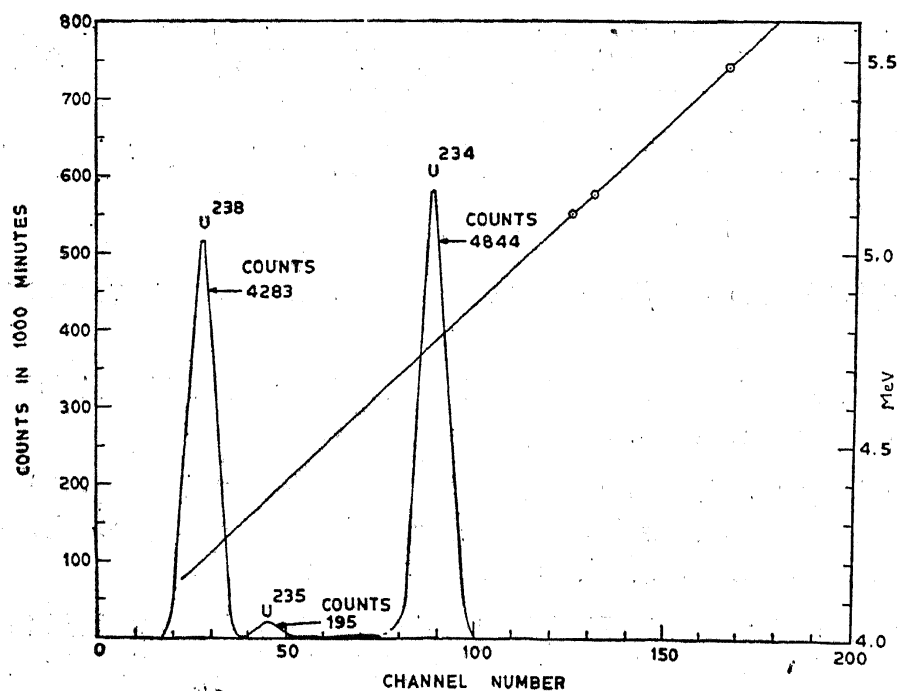


Figure 27. Disequilibrium between U^{238} and U^{234} in sediment sample from Dabhol.

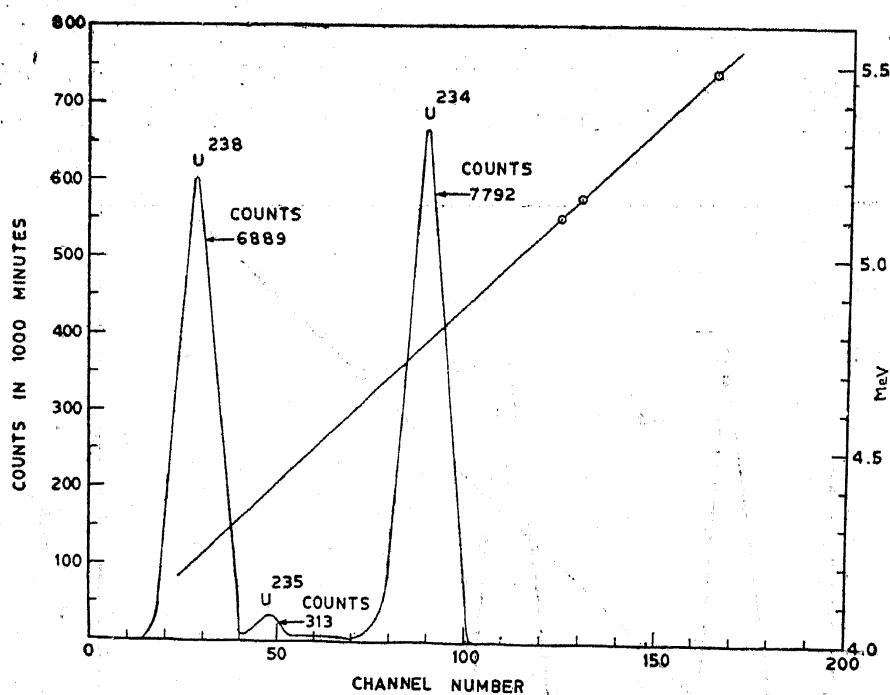


Figure 28. Disequilibrium between U^{238} and U^{234} in sediment sample from Jaygad.

precipitating reactions in sea water primarily determines the ratio, assuming that the value of the ratio in the ambient water had been say 1.15 at the time of sedimentation. From the published procedures of chemical analysis

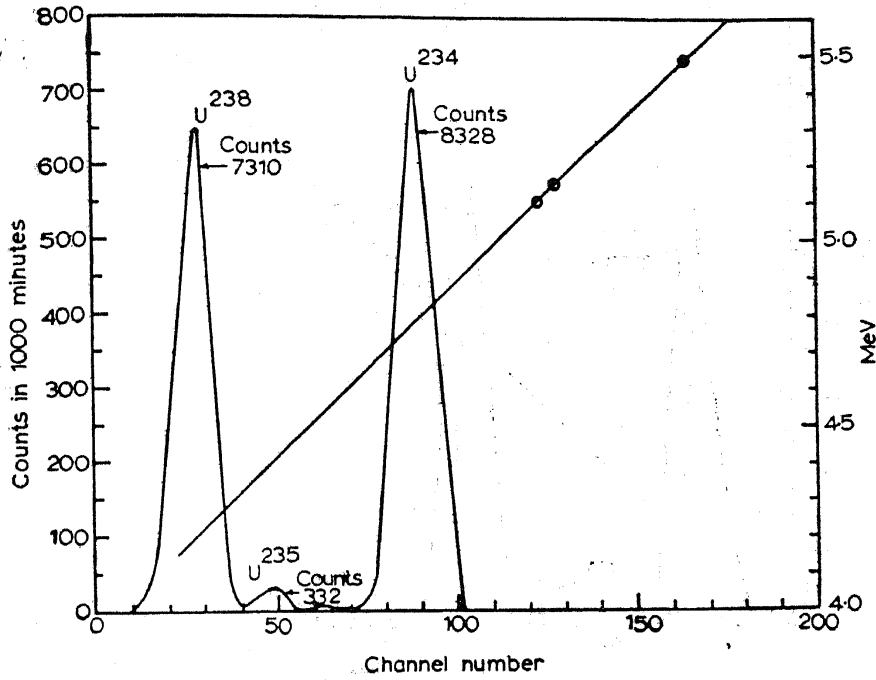


Figure 29. Disequilibrium between U²³⁸ and U²³⁴ in sediment sample from Ratnagiri.

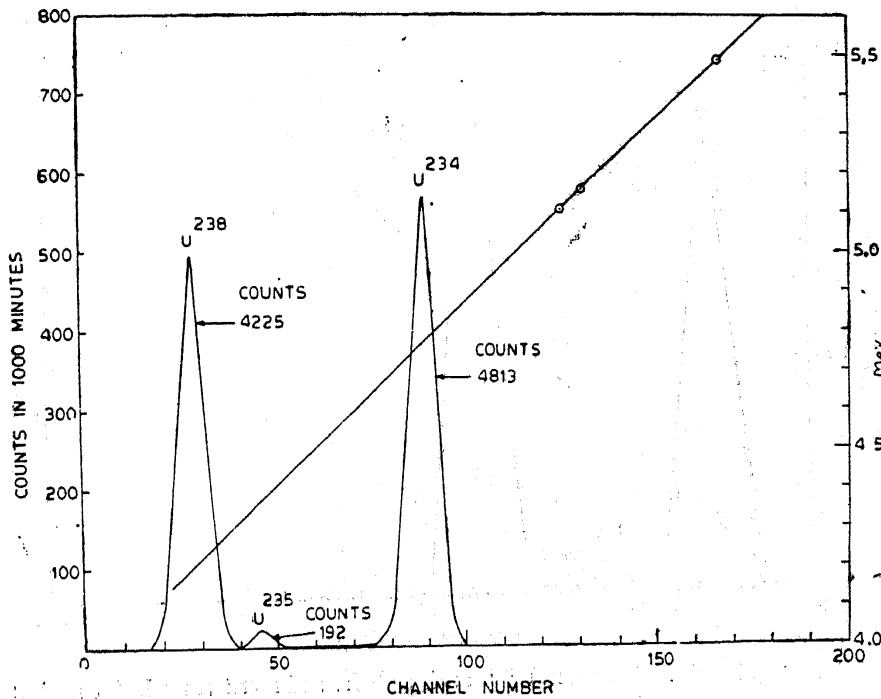


Figure 30. Disequilibrium between U²³⁸ and U²³⁴ in sediment sample from Deogad.

and results it is not always discernible the exchanges in recent time of uranium between sediments and sea waters. Values obtained for the different life forms are similar to the usual values obtained for sea water. Values

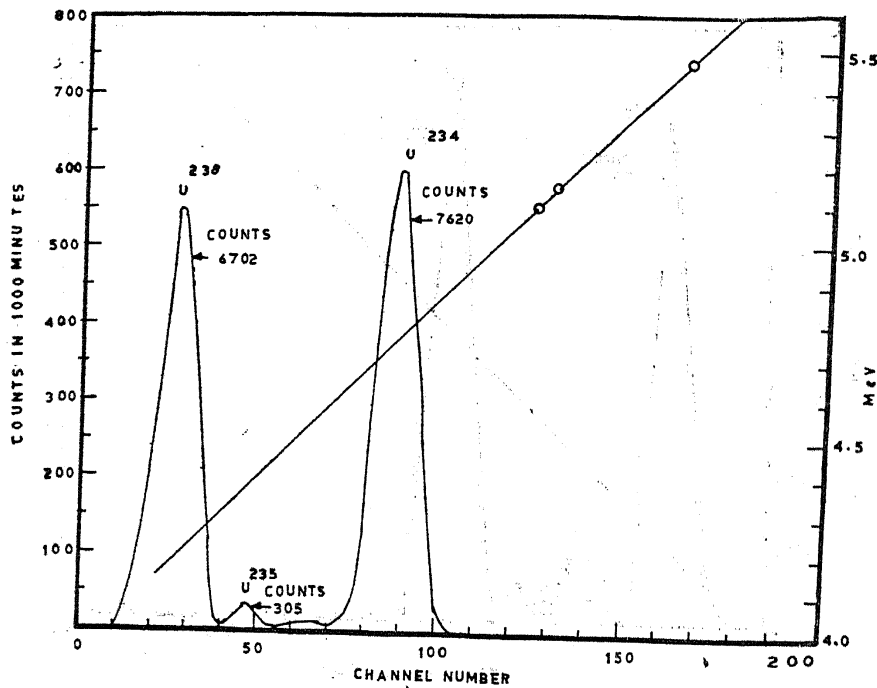


Figure 31. Dis-equilibrium between U^{238} and U^{234} in sediment sample from Malwan.

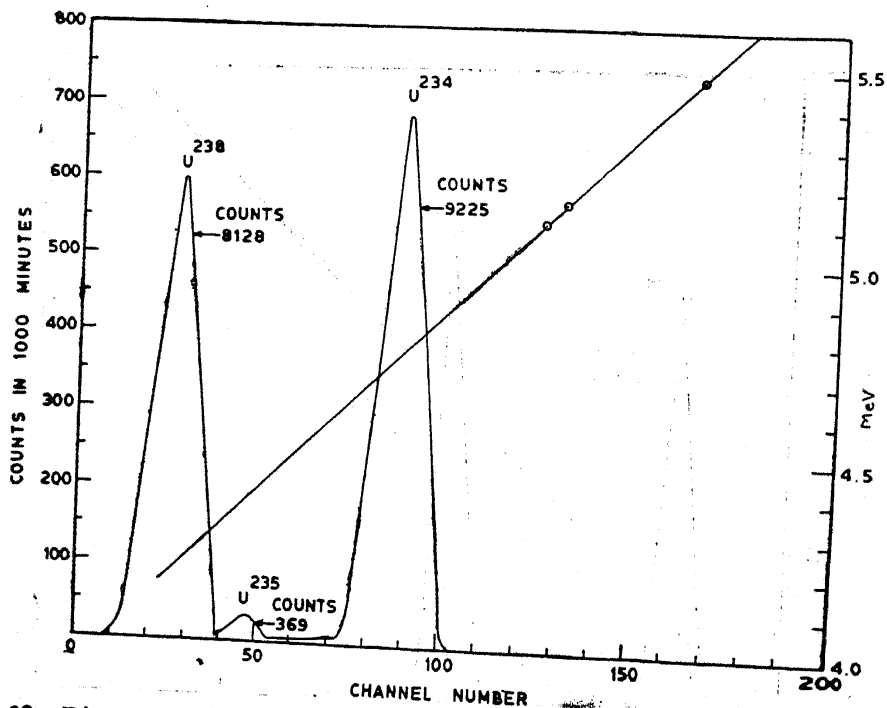


Figure 32. Dis-equilibrium between U^{238} and U^{234} in sediment sample from Vengurla.

less than unity obtained in suspended matter or sediments of flowing rivers, reflect the situation that developed with the preferential leaching of U^{234} compared to U^{238} by river waters. From these ratios, however, the activity ratio in the water could not be obtained.

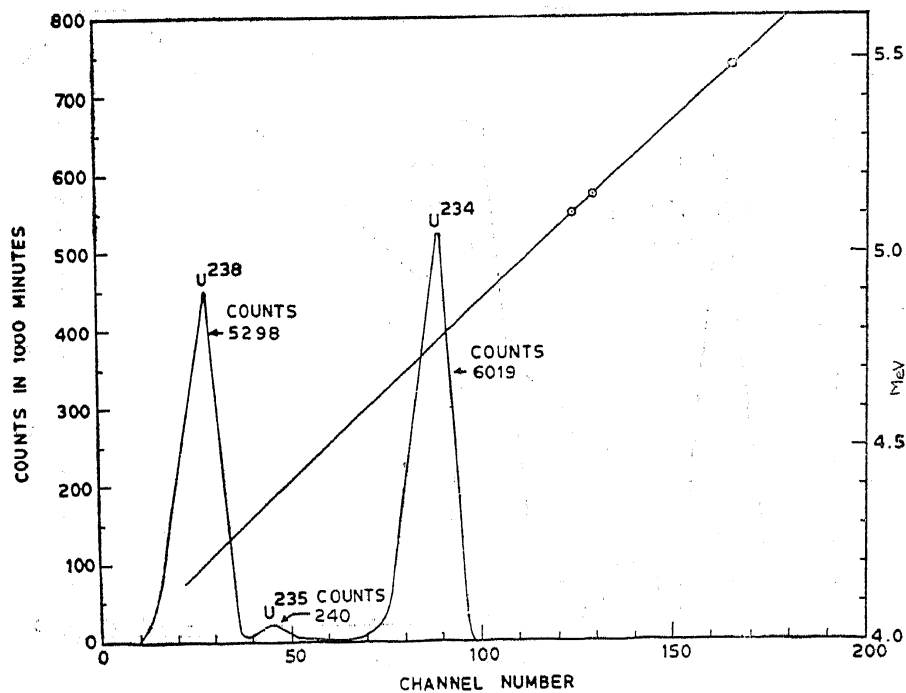


Figure 33. Disequilibrium between U²³⁸ and U²³⁴ in sediment sample from Goa.

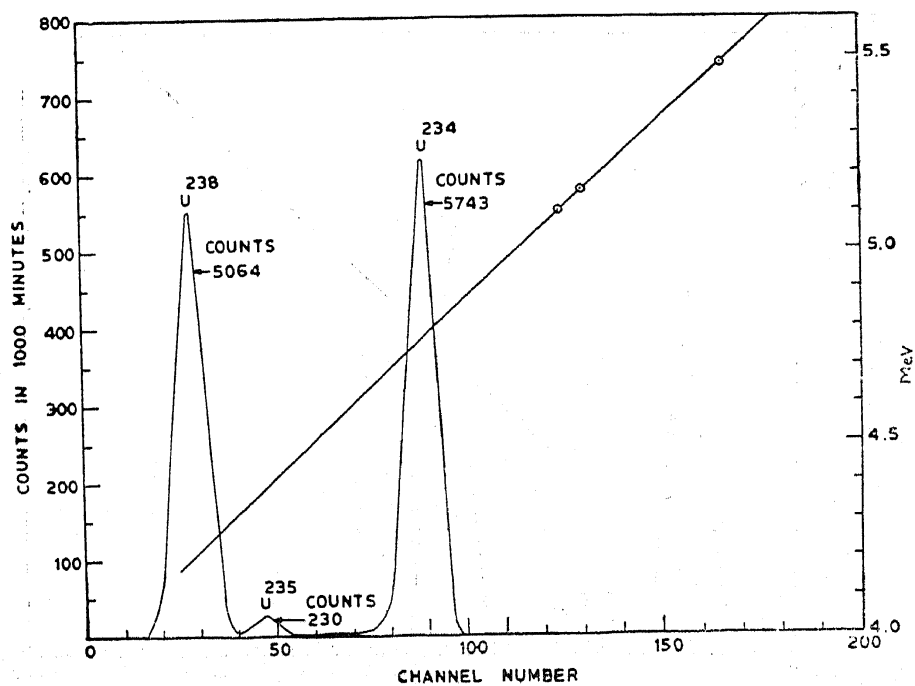


Figure 34. Disequilibrium between U²³⁸ and U²³⁴ in sediment sample from Karwar.

4.2. U²³⁴/U²³⁸ AND U²³⁵/U²³⁸ ACTIVITY RATIOS IN THE COASTAL WATERS OF BOMBAY

To obtain the activity ratios of U²³⁴/U²³⁸ and U²³⁵/U²³⁸ in coastal waters, 20 litres of sea water samples from different locations from Bombay

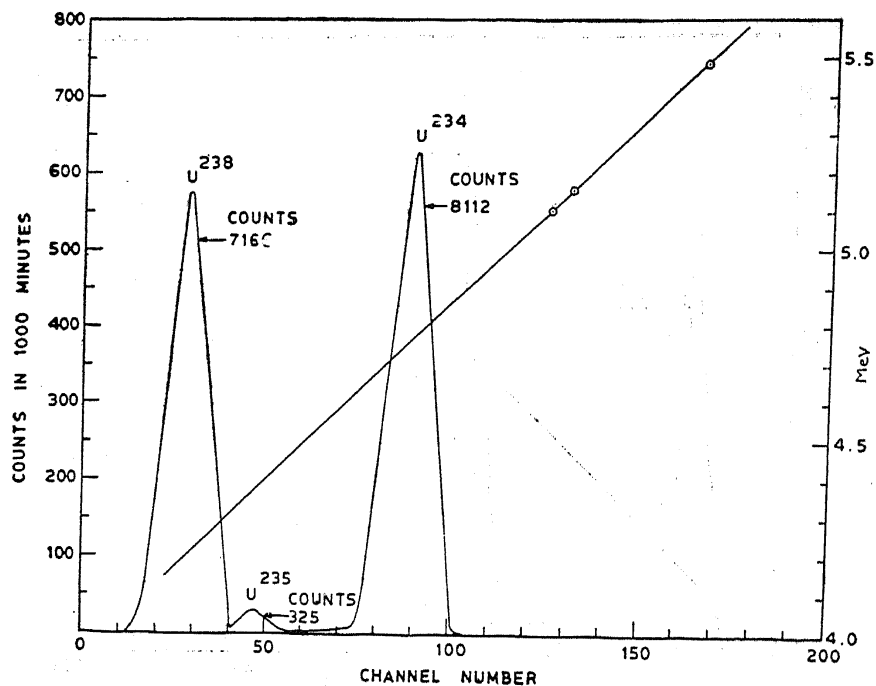


Figure 35. Disequilibrium between U^{238} and U^{234} in sediment sample from Honawar.

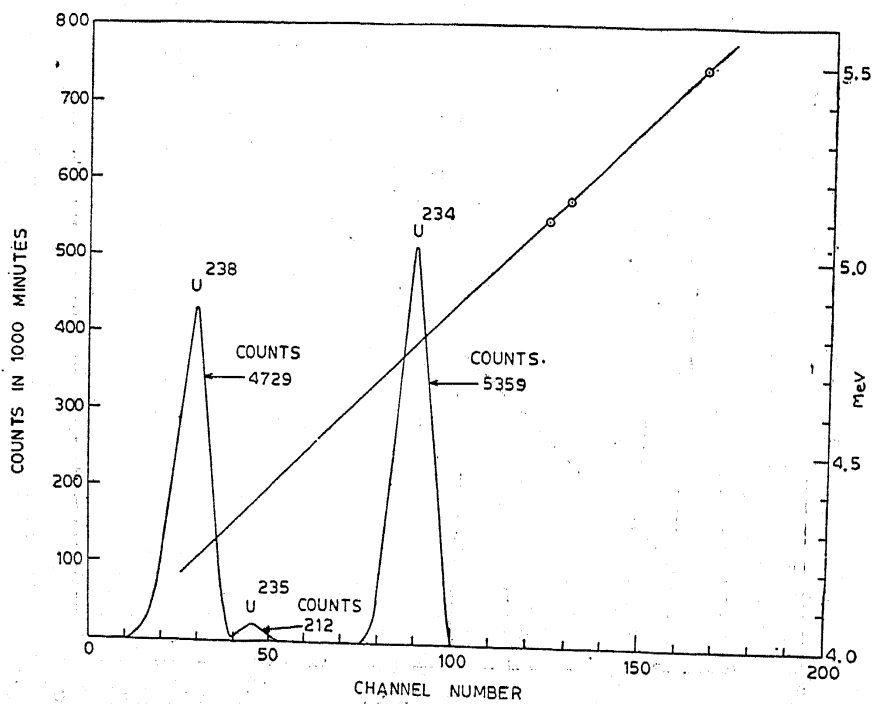


Figure 36. Disequilibrium between U^{238} and U^{234} in sediment sample from Shertallay. region have been collected. The sea water samples are filtered through 0.22 μ membrane filter and to these filtrates 20 mg of Fe^{3+} carrier is added. Iron is precipitated as ferric hydroxide, which carries down with it the

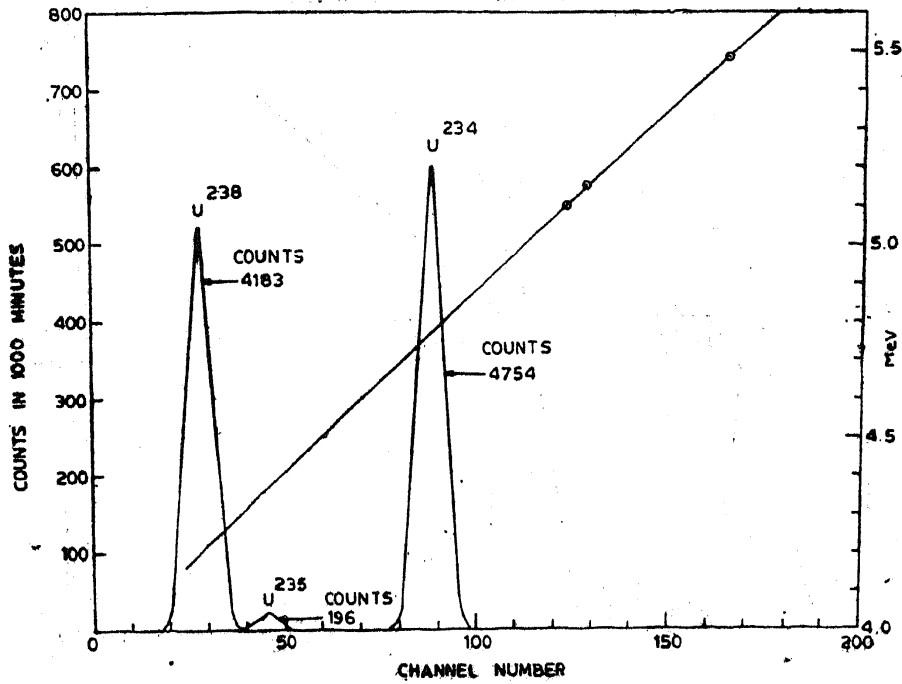


Figure 37. Disequilibrium between U^{238} and U^{234} in sediment sample from Alleppey.

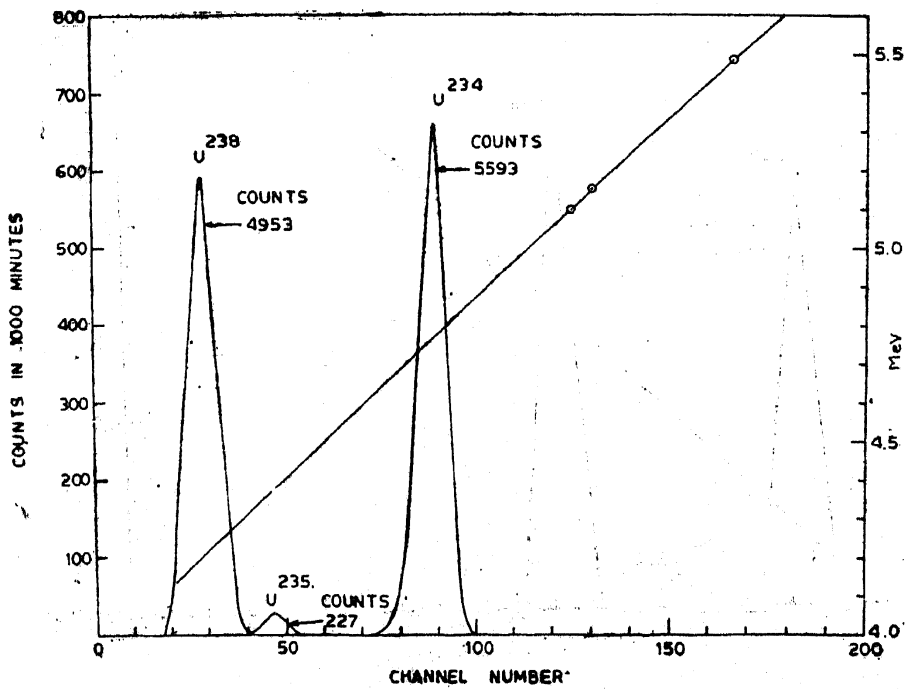


Figure 38. Disequilibrium between U^{238} and U^{234} in sediment sample from Thottapally.

uranium activity. From the resulting precipitate, iron is removed by solvent extraction retaining uranium in the aqueous layer. Uranium is then separated by ion-exchange method as detailed earlier.

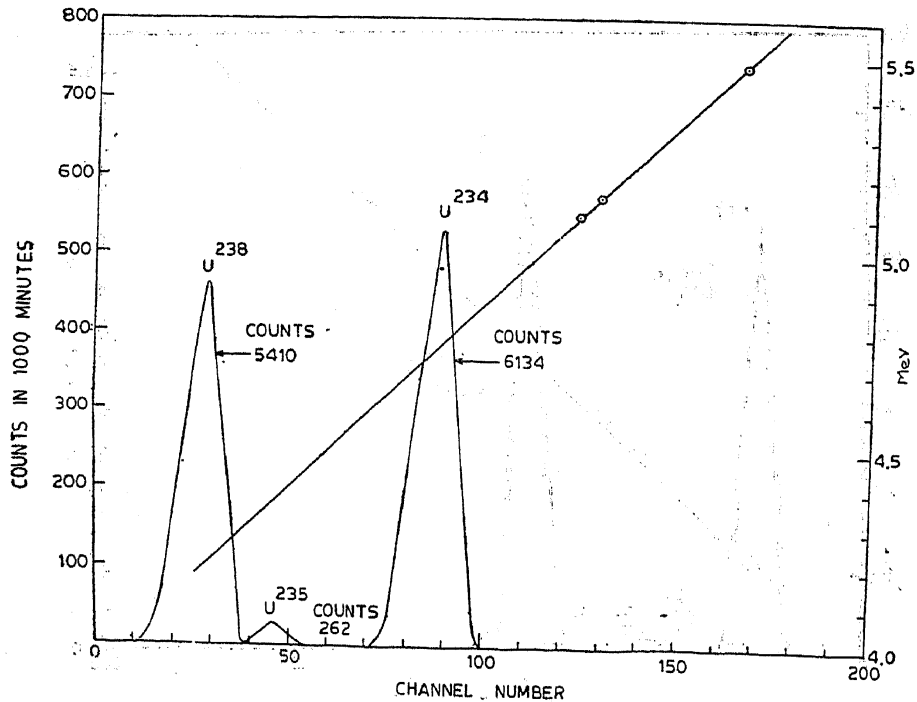


Figure 39. Disequilibrium between U^{238} and U^{234} in sediment sample from Kayamkulam.

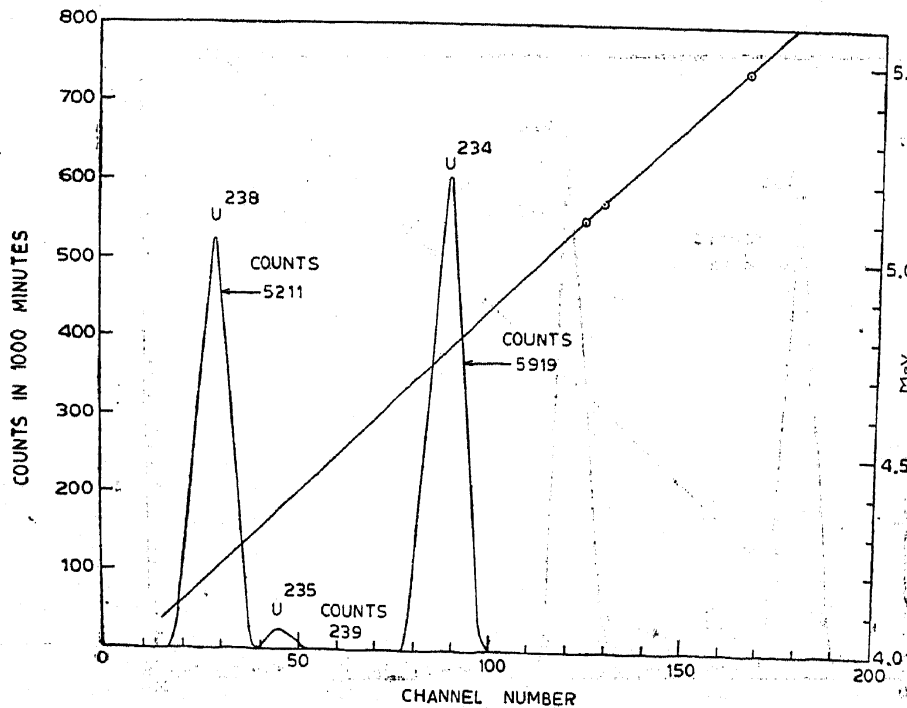


Figure 40. Disequilibrium between U^{238} and U^{234} in sediment sample from Karunagapally.

4.2.1 DISCUSSION : Table 15 gives the activity ratios of U^{234}/U^{238} and U^{235}/U^{238} in coastal waters of Bombay. The U^{234}/U^{238} activity ratios lie in the range of 1.15

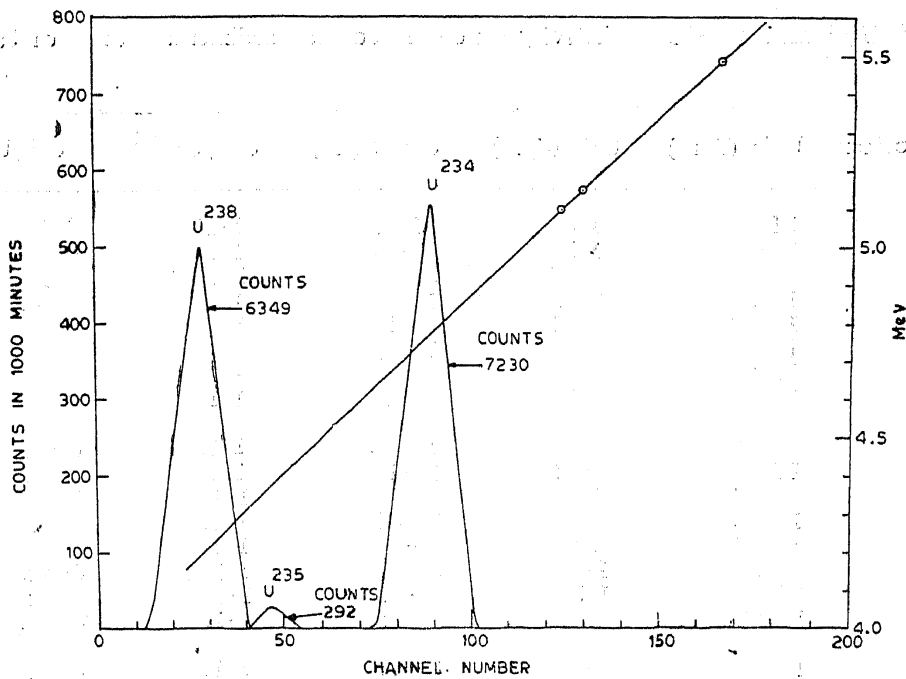


Figure 41. Disequilibrium between U^{238} and U^{234} in sediment sample from Chavara.

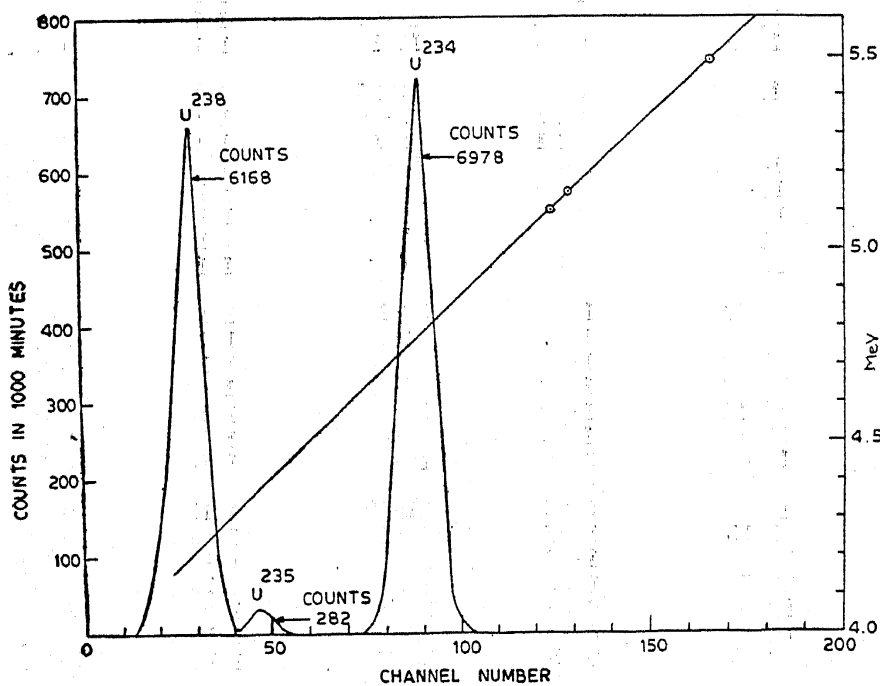


Figure 42. Disequilibrium between U^{238} and U^{234} in sediment sample from Kottilppad.

to 1.16 while U^{235}/U^{238} ratio is 0.046 which is close to the theoretical value of 0.046 for natural uranium,

Table 13. U^{234}/U^{238} and U^{235}/U^{238} Activity ratios in coastal sediments from Bombay to Honawar.

Place of collection	U^{238} (dpm)	U^{235} (dpm)	U^{234} (dpm)	U^{234}/U^{238}	U^{235}/U^{238}
Bombay	31.02	1.48	35.05	1.13	0.048
Bombay	29.97	1.36	33.87	1.13	0.045
Bombay	29.98	1.37	33.88	1.13	0.046
Bombay	16.58	0.75	18.74	1.13	0.045
Bombay	17.87	0.81	20.19	1.13	0.045
Bombay	16.67	0.75	18.83	1.13	0.045
Bombay	20.56	0.93	23.23	1.13	0.045
Bombay	18.00	0.83	20.17	1.12	0.046
Dabhol	13.78	0.62	15.56	1.13	0.045
Dabhol	17.85	0.81	20.18	1.13	0.045
Dabhol	8.37	0.39	9.46	1.13	0.047
Dabhol	18.06	0.82	20.41	1.13	0.045
Dabhol	18.38	0.84	20.62	1.12	0.046
Jaygad	35.36	1.60	39.99	1.13	0.045
Jaygad	28.70	1.30	32.47	1.13	0.045
Jaygad	17.81	0.81	20.15	1.13	0.046
Jaygad	19.60	0.89	22.17	1.13	0.045
Jaygad	20.62	0.94	23.30	1.13	0.046
Jaygad	25.73	1.22	29.07	1.13	0.047
Ratnagiri	21.05	0.95	23.93	1.14	0.045
Ratnagiri	18.36	0.83	20.86	1.14	0.045
Ratnagiri	30.46	1.38	34.70	1.14	0.045
Ratnagiri	15.78	0.72	17.97	1.14	0.046
Ratnagiri	15.06	0.68	17.16	1.14	0.045
Ratnagiri	15.99	0.72	18.21	1.14	0.045
Ratnagiri	4.99	0.23	5.70	1.14	0.046
Ratnagiri	4.53	0.21	5.18	1.14	0.046
Deogad	13.61	0.62	15.49	1.14	0.046
Deogad	17.60	0.80	20.05	1.14	0.046
Deogad	19.95	0.90	22.73	1.14	0.045
Malwan	21.69	0.98	24.66	1.14	0.045
Malwan	18.88	0.86	21.49	1.14	0.046
Malwan	26.47	1.20	30.12	1.14	0.045
Malwan	27.92	1.27	31.75	1.14	0.046
Vengurla	35.60	1.62	40.44	1.14	0.045
Vengurla	35.37	1.60	40.14	1.14	0.045
Vengurla	33.16	1.50	37.67	1.14	0.045
Vengurla	33.87	1.54	38.44	1.14	0.045
Vengurla	17.42	0.79	19.80	1.14	0.045
Vengurla	18.67	0.85	21.20	1.13	0.046
Goa	23.13	1.05	26.26	1.13	0.045
Goa	22.08	1.00	25.08	1.14	0.045
Goa	22.50	1.02	25.54	1.13	0.045
Goa	19.68	0.89	22.39	1.14	0.045
Goa	19.70	0.89	22.36	1.13	0.045
Goa	20.43	0.93	23.20	1.14	0.045
Goa	14.92	0.67	16.95	1.14	0.045
Goa	8.98	0.42	10.20	1.14	0.047
Goa	15.26	0.71	17.33	1.14	0.047
Karwar	26.59	1.21	30.15	1.13	0.045
Karwar	16.39	0.75	18.60	1.13	0.046
Karwar	16.10	0.73	18.27	1.13	0.045
Karwar	21.10	0.96	23.93	1.13	0.046

Table 13. (Contd.)

Place of collection	U ²³⁸ (dpm)	U ²³⁵ (dpm)	U ²³⁴ (dpm)	U ²³⁴ /U ²³⁸	U ²³⁵ /U ²³⁸
Honawar	28.56	1.29	32.36	1.13	0.045
Honawar	21.58	0.98	24.66	1.14	0.045
Honawar	29.86	1.35	33.80	1.13	0.045

The dpm in the columns indicate count rates obtained with the plated sample.

 Table 14. U²³⁴/U²³⁸ and U²³⁵/U²³⁸ Activity ratios in coastal sediments from monazite bearing areas.

Place of collection	U ²³⁸ (dpm)	U ²³⁵ (dpm)	U ²³⁴ (dpm)	U ²³⁴ /U ²³⁸	U ²³⁵ /U ²³⁸
Shertallay	19.71	0.88	22.50	1.14	0.045
Alleppey	17.42	0.82	19.79	1.14	0.047
Thottapally	20.63	0.95	23.29	1.13	0.046
Kayamkulam	22.54	1.09	25.54	1.13	0.048
Karunagapally	21.71	0.99	24.67	1.14	0.045
Chavara	26.46	1.22	30.13	1.14	0.046
Kottilppad	25.71	1.18	29.08	1.13	0.045

The dpm in the columns indicate count rates obtained with the plated sample.

 Table 15. U²³⁴/U²³⁸ and U²³⁵/U²³⁸ Activity ratios in Sea water from Bombay region (19° N, 73° E).

Place of collection	U ²³⁸ (dpm)	U ²³⁵ (dpm)	U ²³⁴ (dpm)	U ²³⁴ /U ²³⁸	U ²³⁵ /U ²³⁸
Sewree	9.00	0.42	10.43	1.16	0.047
Colaba	15.08	0.69	17.35	1.15	0.046
Nariman Point	13.79	0.63	15.86	1.15	0.046
Worli	16.42	0.75	18.88	1.15	0.046
Haji Alc.	13.50	0.63	15.53	1.15	0.047
Gateway	14.30	0.67	16.45	1.15	0.047

The dpm in the columns indicate count rates obtained with the plated sample.

Earlier workers in the field have determined U²³⁴/U²³⁸ activity ratios in waters of various parts of the world. Thurber,^{36,50} assumed that the activity ratios of U²³⁴/U²³⁸ in sea water near the different coasts are approximately the same and are close to the value of 1.15 obtained by him. The values obtained in the present investigation bears out the conclusion of Thurber.

The U²³⁴/U²³⁸ activity ratios have been used not only for geochronological purposes but also as an indicator of various geochemical processes in uranium deposits.⁵¹

The behaviour of U^{234} relative to its parent U^{238} should be understood in order to evaluate the significance of determination of the subsequent daughter nuclides. This applies particularly to the use of Th^{230} for dating^{3,5,2,53} U^{234} can be used for dating geological events provided it meets certain requirements. The initial ratio of U^{234}/U^{238} in the sample to be dated must be known. This ratio must change with time by radioactive decay or growth.

An important factor in the geochemical balance of uranium is the rate of its removal and dissolution in the ocean. The varying amount of uranium carried into the different regions of the oceans by streams and oceanic current and at the same time maintaining a somewhat constant ratio of U^{234}/U^{238} points towards a little understood universal geochemical mechanism in the uranium dissolution processes in the marine environment.

4.3. CLEANSING SURFACE LAYER OF SEDIMENTS FREE OF ORGANIC MATTER BY PHOSPHATE-FREE HYDROGEN PEROXIDE IN PRESENCE OF 0.05 M HYDROCHLORIC ACID

To cleanse the particles of surface organic matter and to obtain an extract of the uranium from the surface layer of the sediments, 300 gms each of the samples from Ratnagiri, Goa, etc., having been treated with 800 ml of 0.05 hydrochloric acid and phosphate-free hydrogen peroxide. The hydrochloric acid extract after this treatment is filtered through 0.22 μ membrane filter and the filtrate is processed for column treatment and plated for uranium as described in paras 2.4.2 and 2.5 of this section. The organic matter cleansed sediment is then treated with saturated solution of ammonium carbonate to extract uranium for plating and counting as detailed earlier.

4.3.1 DISCUSSION: Figures 43 to 46 give the results obtained. The ratio of U^{235}/U^{238} in the cleansed residue is 0.046 which is the same as the theoretical value for this ratio. In the acid-hydrogen peroxide extract of the sediment, the disequilibrium is observed between U^{238} and U^{234} while U^{235}/U^{238} ratio exhibits theoretical value of 0.046.

Table 16 gives U^{234}/U^{238} and U^{235}/U^{238} activity ratios obtained in these experiments.

The results are in conformity with the results obtained with thorium (*cf.* section III). Further, the disequilibrium exist only on the surface of the sediment particles and have the same ratio as in the ambient sea water. We did not carry out any estimation of thorium isotopes in sea water, however, in the light of our observations with uranium ratios, we conclude that the activity ratios in coastal sea water are also same as obtained on leaching the sediments.

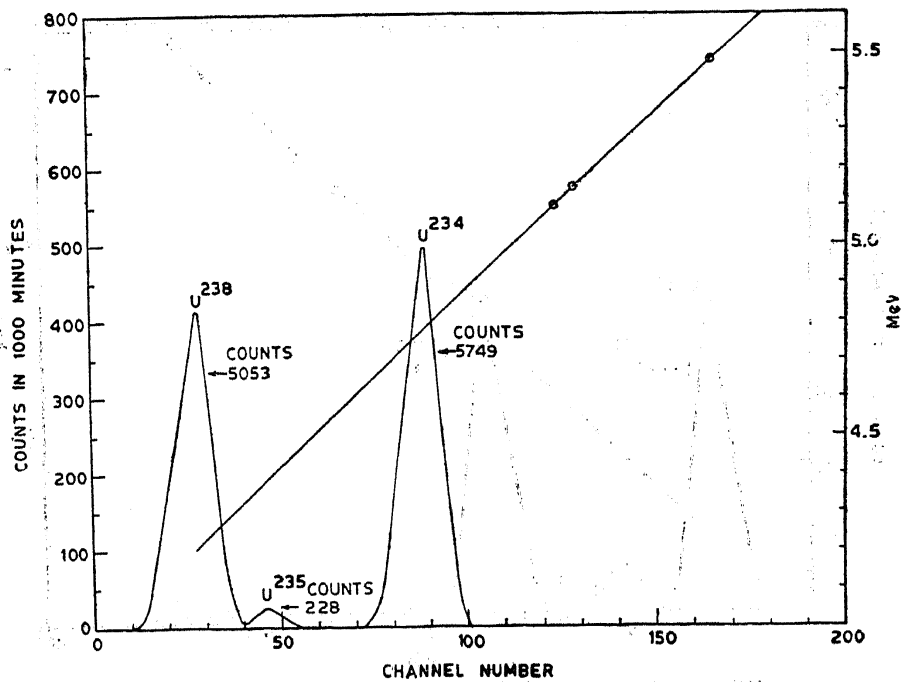


Figure 43. Disequilibrium between U²³⁸ and U²³⁴ in supernate after H₂O₂ + 0.05 M HCl treatment of Ratnagiri sediment.

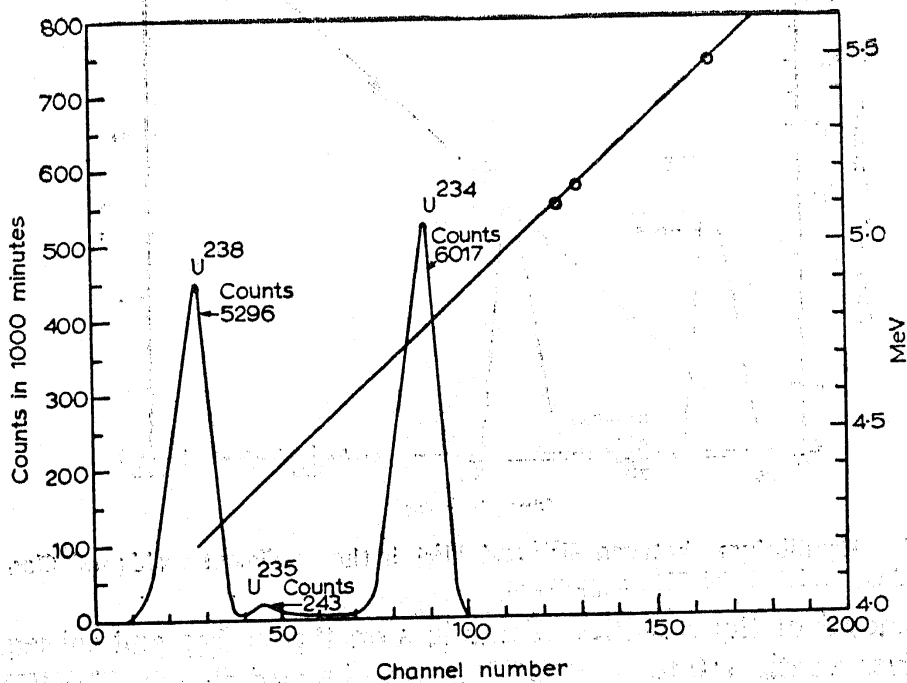


Figure 44. Disequilibrium between U²³⁸ and U²³⁴ in the supernate obtained after H₂O₂ + 0.05 M HCl treatment of the sediment from Goa.

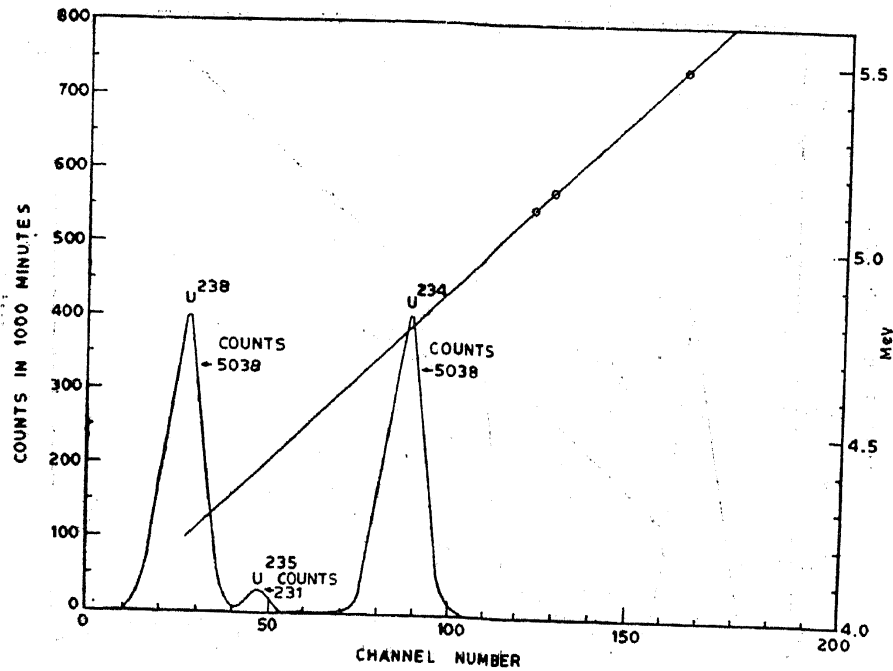


Figure 45. Equilibrium between U^{238} and U^{234} in the sediment residue of Ratnagiri after removal of H_2O_2 and 0.05 M HCl supernate.

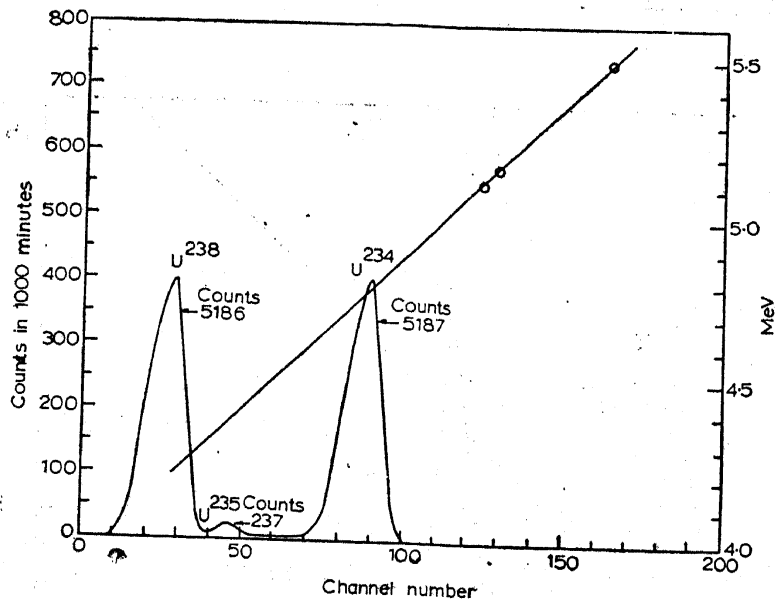


Figure 46. Equilibrium between U^{238} and U^{234} in the sediment residue of Goa after removal of H_2O_2 and 0.05 M HCl supernate.

On removal of the activities of uranium on the surface and subsequent leaching gives a ratio 1.0 for U^{234}/U^{238} as was obtained also for Th^{232}/Th^{232} .

4.4. MECHANISM FOR THE DISEQUILIBRIUM BETWEEN U^{238} and U^{234} .

It has been suggested that during the decay of U^{238} , the daughter U^{234} atoms are more likely to be oxidised to hexavalent state forming the more

Table 16. U^{234}/U^{238} and U^{235}/U^{238} Activity ratios in supernates and organic matter free sediment after 0.05 M HCl + H_2O_2 treatment.

Place of collection	Remarks	U^{238} (dpm)	U^{235} (dpm)	U^{234} (dpm)	U^{234}/U^{238}	U^{235}/U^{238}
Bombay	Supernate	29.90	1.35	33.79	1.13	0.045
Bombay	Organic matter free sediment	29.61	1.36	29.62	1.00	0.046
Dabhol	Supernate	18.50	0.85	20.72	1.12	0.046
Dabhol	Organic matter free sediment	18.12	0.83	18.18	1.00	0.046
Ratnagiri	Supernate	21.05	0.95	23.95	1.14	0.045
Ratnagiri	Organic matter free sediment	20.99	0.96	20.99	1.00	0.046
Vengurla	Supernate	18.80	0.86	21.24	1.13	0.046
Vengurla	Organic matter free sediment	18.23	0.85	18.12	0.99	0.047
Goa	Supernate	22.07	1.01	25.07	1.14	0.046
Goa	Organic matter free sediment	21.60	0.99	21.59	0.99	0.046

The dpm in the columns indicate count rates obtained with the plated sample.

soluble $(UO_2)^{+2}$ ions than parent U^{238} atoms. It is assumed that U (VI) is somewhat more loosely bound in structure than U (IV), the former being able to exchange with dissolved form in water. This exchange is negligible, although some escape of U^{234} into sea water does occur.

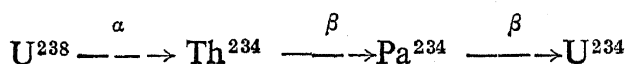
There are two mechanisms suggested for this type of exchange. Crardintsev,³¹ and co-workers suggested that U^{234} is relocated by recoil at crystal defects and micro-cracks, where it becomes more labile and more accessible to oxidation. This view has also been supported by Starik *et al.*,⁵⁴ Chalov⁵⁵ and Thurber.⁵⁶

A somewhat different mechanism has been suggested by Rosholt *et al.*^{57,58} and Dooley *et al.*⁵¹ They point out that recoil energy during the radioactive transformation is more than sufficient to break the chemical bonds and that U^{234} is stripped of two of its electrons as a result of the recoil. Thus, U^{234} ends up preferentially as hexavalent uranium. A third possibility of increasing the oxidation state of uranium from IV to VI state during the radioactive transformation from U^{238} to U^{234} is by increase in the positive charge of the ions due to beta decay. In the series, $Th^{234} \xrightarrow{\beta} Pa^{234} \xrightarrow{\beta} U^{234}$, we move from a element which is tetravalent (Th) to pentavalent (Pa) to hexavalent uranium.

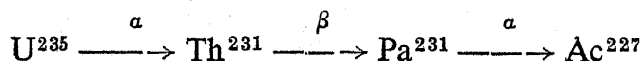
The difference between the two explanations is that whereas in the first model, the daughter U^{234} is more rapidly oxidised than the parent U^{238}

due to selective exposure, the second model assumes that the daughter U^{234} is actually more oxidised from the time of its formation. Thus, to obtain significant fractionation would require an oxidising agent, if the first approach is valid and no such agent is necessary if electron-stripping is recognised as the mechanism.

4.4.1 DISCUSSION: We would like to re-examine these suggested mechanisms for the appearance of U^{234} in sea water in excess of the equilibrium values. In the two decay series of uranium, *viz.*,



and



The recoil due to alpha decay is first felt by Th^{234} ($T_{\frac{1}{2}} = 24.1 d$) and Th^{231} ($T_{\frac{1}{2}} = 25.52 h$).

If the recoil hypothesis of Cherdynstsev is to be followed, the availability of Th^{234} and Th^{231} in the crystal defects and micro-cracks need to be established.

In the U^{235} series, Pa^{231} ($T_{\frac{1}{2}} = 3.25 \times 10^4 y$) suffers another alpha disintegration recoil to be displaced and relocated in the crystal. The authors of the recoil hypothesis have not produced evidence either in respect of Th^{234} (half-life reasonably *long* for experimental purposes) or in respect of long-lived Pa^{231} .

As has been discussed earlier a disequilibrated ratio of U^{234}/U^{238} in the oceanic waters has usually a value of 1.15 ± 0.02 . The organic surface layer of the coastal sediments also gave similar values.

On removal of the surface layer of organic matter and leaching uranium from cleansed sediment, the equilibrium ratio of 1.0 for U^{234}/U^{238} is obtained. If it is assumed that there exists a somewhat universal enrichment of U^{234} by about 15% of equilibrium value in sea water and in the surface layers of the sediments, one should come across weathered mineral particles in which a ratio less than 1.00 exists on the surface of the mineral core of the particles.³⁹

Earlier workers reported values of the ratio for some river sediments as significantly less than 1.0.^{44,45} But these values are always greater than 0.85.

Since the chemical procedure adopted by them most probably gave the value for the ratio for the entire bulk of the particles, it might be argued as possible that there existed a ratio much less than 1.0 (say 0.85 or less) for the surface layer and 1.0 for the core of the particles giving a mean value higher than 0.85. We are looking for such a situation in the coastal sediments which are essentially the sediments of terrestrial origin and still retains in many cases the original mineralogical character. As stated earlier, we failed to observe any significant deficit from the value of 1.0 for the ratio on the surface of the sediment cleansed of organic matter.

Thus, in the present investigation, we could not obtain data in support of the mechanism for the enrichment of U^{234} in the leachates as proposed by earlier workers. It is possible that in some specific minerals, the transformation of U (IV) to U (VI) takes place during the process of transmutation of U^{238} to U^{234} and U (VI) stays stable in the mineral.

4.5. INTERACTION OF PROTACTINIUM AND HUMIC ACID IN PRESENCE OF ARTIFICIAL SEA WATER

The following experiments are performed to examine the solubilisation of protactinium by sea water.

Experiments have been conducted using artificial sea water at pH 7.5 and humic acid spiked with Pa^{233} ($T_{1/2} = 27 d$).

4.5.1 PRECIPITATED HUMIC ACID CARRYING Pa^{233} ACTIVITY IN ARTIFICIAL SEA WATER MEDIUM: As Pa^{234} (1.18 min. half-life) is short-lived, the gamma-active Pa^{233} is used for the experiments. 51 ml of double distilled water is taken in 150 ml polythene bottle. In another polythene bottle 50 ml of artificial sea water⁵⁹ and 1.0 ml double distilled water are added and in the third polythene bottle, 50 ml of artificial sea water, 1.0 ml of humic acid (0.45 mg) are added. To each of these bottles 250 λ Pa^{233} source is added. The solutions are stirred and then immediately counted for Pa^{233} gamma activities. Table 17 gives the initial counts of Pa^{233} in these bottles. The polythene bottles containing the solutions are shaken for six days and then filtered through 0.22 μ membrane filters. The filtrates are taken in new polythene bottles of same dimensions and the residues are also taken in similar polythene bottles together with the membrane filter and shaken with distilled water to keep the geometry same in all the cases. The filtrates and the residues are counted for Pa^{233} gamma activities.

4.5.1.1 DISCUSSION: Table 18 gives the counts obtained with these bottles. It is seen from tables 17 and 18 that 70% of Pa^{233} is precipitated due to hydrolysis in the medium (pH 7.5);⁶⁰ gave the precipitates

an empirical chemical composition $\text{Pa}_2\text{O}_5 \times \text{H}_2\text{O}$. However, in the presence of 1.0 ml (0.45 mg) of humic acid and artificial sea water, Pa^{233} is precipitated to the extent of 93%.

4.5.2. BEHAVIOUR OF PROTACTINIUM IN EXCESS OF AMMONIACAL MEDIUM IN PRESENCE OF HUMIC ACID: The polythene bottles containing the solutions in table 18 are shaken each with 5 ml of liquor ammonia and then the solutions are filtered through 0.22 μ membrane filters. The residue retained on the filter is again dispersed as before in polythene bottles and the filtrates and the residues are taken for separate counting.

Table 17. Interaction of Pa^{233} with humic acid.

Polythene bottle No.	Contents in the bottle	Set 1 counts in 10 min.	Set 2 counts in 10 min.
1.	Pa^{233} (250 λ) + double distilled water (51 ml)	51254	51348
2.	Pa^{233} (250 λ) + double distilled water (1 ml) + Artificial sea water (50 ml)	51309	51209
3.	Pa^{233} (250 λ) + humic acid (1 ml) + Artificial sea water (50 ml)	51163	51405

The samples in the polythene bottles are counted on 19-7-1972 for Pa^{233} gammas.

Table 18. Interaction of Pa^{233} with humic acid.

Poly-thene bottle No.	Contents in the bottle	Set 1 counts in 10 min	Total counts	Set 2 counts in 10 min.	Total counts
1.	Pa^{233} (250 λ) + double distilled water (51 ml)	44102		44134	
2.	Filtrate (51 ml) from Polythene bottle No. 2 of table 17	13478	+ } 44266	13520	+ } 44119
3.	Residue from polythene bottle No. 2 of table 17. + 51 ml double distilled water.	30788		30599	
4.	Filtrate (51 ml) from polythene bottle No. 3 of table 17	3032	+ } 44218	3207	+ } 44209
5.	Humic acid residue from polythene bottle No. 3 of table 17 + 51 ml double distilled water.	41186		41002	

The samples in the polythene bottles are counted on 25-7-1972 for Pa^{233} gammas.

Table 19. Solubilisation of Pa²³³ and humic acid with excess of ammonia solution.

Polythene bottle No.	Contents in the bottle	Set 1 counts in 10 min	Total counts	Set 2 counts in 10 min	Total counts
1.	Filtrate (51 ml) from polythene bottle No. 1 of table 18 containing excess ammonia	4180	31750	4169	31772
2.	Residue from polythene bottle No. 1 of table 18 + 51 ml double distilled water.	27570		27603	
3.	Filtrate (51 ml) from polythene bottle No. 2 of table 18 containing excess ammonia	699	31868	703	31749
4.	Residue from polythene bottle No. 2 of table 18 + 51 ml double distilled water	9001		9015	
5.	Filtrate (51 ml) from polythene bottle No. 3 of table 18 containing excess ammonia	3130	31795	3040	31813
6.	Residue from polythene bottle No. 3 of table 18 + 51 ml double distilled water	19038		18991	
7.	Filtrate (51 ml) from polythene bottle No. 4 of table 18 containing excess ammonia	21	31795	17	31813
8.	Residue from polythene bottle No. 4 of table 18 + 51 ml double distilled water	2159		2291	
9.	Filtrate (51 ml) from polythene bottle No. 5 of table 18 containing excess ammonia	10539	31795	10504	31813
10.	Humic acid residue from polythene bottle No. 5 of table 18 + 51 double distilled water	19076		19001	

The samples in the polythene bottles are counted on 7-8-1972 for Pa²³³ gammas.

4.5.2.1 DISCUSSION: Table 19 gives the counts of Pa²³³ in each of the bottles. On addition of 5 ml of liquor ammonia (pH 10.0) to the humic acid residue in 51 ml of double distilled water, much of the humic acid goes in solution and solubilises Pa²³³ activity. About 36% of Pa²³³ activity goes in solution with humic acid, while 64% of Pa²³³ activity remains on the residue. However, the filtrates of the humic acid in table 18 on addition of 5 ml of liquor ammonia carried down 99% of Pa²³³ activity.

It is of interest to note in the results of these experiments that protactinium has a significant tendency to follow humous material. Precipitated protactinium pentoxide can be solubilised by humic acid. Further, precipitating humic acid can carry with it solubilised protactinium.

4.6. INTERACTION OF PROTACTINIUM AND FULVIC ACID IN PRESENCE OF ARTIFICIAL SEA WATER

Similar study as above has been carried out with fulvic acid.*⁶¹ Pa²³³ activity is added to fulvic acid in artificial sea water.

4.6.1 FULVIC ACID SOLUBILISING Pa²³³ ACTIVITY IN ARTIFICIAL SEA WATER MEDIUM: 51 ml of double distilled water is added to one polythene bottle. To the second polythene bottle, 50 ml of artificial sea water and 1.0 ml of double distilled water are added and in the third polythene bottle, 50 ml of artificial sea water and 1.0 ml of fulvic acid (0.6 mg) are added. To each of the bottles, 250 λ Pa²³³ source is added. The solutions are stirred well and immediately counted for Pa²³³. Table 20 gives the initial counts of protactinium. The polythene bottles containing the solutions are shaken for 7 days and then filtered through 0.22 μ membrane filters. The filtrates and the residues are counted for Pa²³³ as described earlier.

4.6.1.1 DISCUSSION: Table 21 gives the counts of Pa²³³ in these bottles. It is observed from tables 20 and 21 that 70% of Pa²³³ is precipitated due to hydrolysis of protactinium in the medium (pH 7.5) and in the presence of 0.6 mg of fulvic acid in artificial sea water, Pa²³³ is precipitated to the extent of 91% (table 21).

4.6.2 BEHAVIOUR OF PROTACTINIUM IN EXCESS OF AMMONIACAL MEDIUM IN PRESENCE OF FULVIC ACID: In order to know the behaviour of protactinium with fulvic acid in excess of ammonia, the polythene bottles containing these solutions are shaken, each with 5 ml of liquor ammonia and then filtered through 0.22 μ membrane filters. The filtrates and the residues are counted separately.

Table 20. Interaction of Pa²³³ with fulvic acid.

Polythene bottle No.	Contents in the bottle	Set 1 counts in 10 min.	Set 2 counts in 10 min.
1.	Pa ²³³ (250 λ) + Double distilled water (51 ml)	15598	15600
2.	Pa ²³³ (250 λ) + Double distilled water (1 ml) + Artificial sea water (50 ml)	15564	15506
3.	Pa ²³³ (250 λ) + Fulvic acid (1 ml) + Artificial sea water (50 ml)	15541	15572

The samples in the polythene bottles are counted on 26-10-1972 for Pa²³³ gammas.

* Alkali extract of sediment, when treated with acid, precipitate humic acid, leaving a straw yellow coloured organic matter in solution. This fraction of humous material which does not precipitate with acid is named as fulvic acid. The acidic fulvic solution is filtered through 0.22 μ membrane filter and dialysed till free of electrolytes, evaporated to a small bulk and filtered. The filtrate has been taken for the experiments.

Table 21. Interaction of Pa²³³ with fulvic acid.

Polythene bottle No.	Contents in the bottle	Set 1 counts in 10 min	Total counts	Set 2 counts in 10 min	Total counts
1.	Pa ²³³ (250 λ) + Double distilled water (51 ml)	14050		13001	
2.	Filtrate (51 ml) from polythene bottle No. 2 of table 20	3901	} 13026	3885	} 12988
3.	Residue from polythene bottle No. 2 of table 20 + 51 ml double distilled water	9125		9103	
4.	Filtrate (51 ml) from polythene bottle No. 3 of table 20	1074	} 12999	1068	} 12970
5.	Fulvic acid residue from polythene bottle No. 3 of table 20 + 51 ml double distilled water.	11925		11902	

The samples in the polythene bottles are counted on 2-11-1972 for Pa²³³ gammas.

4.6.2.1 DISCUSSION: Table 22 gives Pa²³³ counts in each of the bottles. It is seen from the table that on addition of 5 ml of liquor ammonia, only 11% of Pa²³³ activity goes in solution while 89% of Pa²³³ activity remains on the residue. However, the filtrates of the fulvic acid as shown in table 22, on addition of 5 ml of liquor ammonia, carried down 60% of Pa²³³ activity while 40% of Pa²³³ activity goes in solution in presence of fulvic acid.

Thus, it is observed from the data of tables 17 to 22 that humic and fulvic acids solubilise and carry with them protactinium activity and protactinium activity follows the organic matter significantly.

4.7. THE EFFECTS OF THE ORGANIC CONSTITUENTS OF NATURAL SEA WATER ON Pa²³³

The experiments have been conducted using:

- (i) Natural sea water,
- (ii) Natural sea water after removing humic acid and fulvic acid,
- (iii) Natural sea water after removing humic, fulvic acids and other dissolved organic constituents in sea water.

Natural sea water from Bombay harbour is filtered through 0.22 μ membrane filter,

Table 22. Solubilisation of Pa²³³ and fulvic acid with excess of ammonia solution.

Polythene bottle No.	Contents in the bottle	Set 1 counts in 10 min	Total counts	Set 2 counts in 10 min	Total counts
1.	Filtrate (51 ml) from polythene bottle No. 1 of table 21 containing excess ammonia	928 +	7358	917 +	7335
2.	Residue from polythene bottle No. 1 of table 21 + 51 ml double distilled water	6430		6418	
3.	Filtrate (51 ml) from polythene bottle No. 2 of table 21 containing excess ammonia	181 +	7391	187 +	7390
4.	Residue from polythene bottle No. 2 of table 21 + 51 ml double distilled water	2100 +		2112 +	
5.	Filtrate (51 ml) from polythene bottle No. 3 of table 21 containing excess ammonia	720 +		710 +	
6.	Residue from polythene bottle No. 3 of table 21 + 51 ml double distilled water	4390		4381	
7.	Filtrate (51 ml) from polythene bottle No. 4 of table 21 containing excess ammonia	749 +	7253	754 +	7289
8.	Residue from polythene bottle No. 4 of table 21 + 51 ml double distilled water	1102 +		1110 +	
9.	Filtrate (51 ml) from polythene bottle No. 5 of table 21 containing excess ammonia	597 +		608 +	
10.	Fulvic acid residue from polythene bottle No. 5 of table 21 + 51 ml double distilled water	4805		4817	

The samples in the polythene bottles are counted on 23-11-1972 for Pa²³³ gammas.

In the second case, 1.0 litre of filtered sea water is shaken with 50 mgs of Al as aluminium nitrate. The pH is adjusted to 7.5 by a drop of sodium hydroxide solution and kept overnight. The supernate is filtered through 0.22 μ membrane filter. The filtrate is free from humic and fulvic acids.⁶²

In the third case, 1.0 litre of sea water is shaken with 5 gms of charcoal powder free from phosphates for six hours and the solution is filtered through 0.22 μ membrane filter. The filtrate is about 90% free from organic matter.

4.7.1. EFFECT ON Pa²³³: In one polythene bottle, 51 ml of filtered sea water is taken. In the second polythene bottle, 51 ml of sea water free from humic and fulvic acids is taken and in the third polythene bottle 51 ml of sea water free from organic matter is taken for the experiments. In all the three cases, 250 λ of Pa²³³ are added and the pH of the solution is adjusted to 7.5 by adding a drop of sodium hydroxide solution. The solutions are shaken and the bottles are counted immediately for initial Pa²³³ counts. Table 23 gives the results. The solutions in the bottles are shaken for 7 days and filtered through 0.22 μ membrane filters. The filtrates and the residues are counted separately as detailed earlier.

4.7.1.1 DISCUSSION: Table 24 gives the results obtained. It is seen from tables 23 and 24 that the residue in the bottle containing natural sea water (in the first case) carried 70% of the Pa²³³ activity.

The residue in the bottle containing natural sea water free from humic and fulvic acids (in the second case) carried 75% of Pa²³³ activity.

The residue in the bottle containing natural sea water free from organic matter (in the third case) carried 80% of Pa²³³ activity.

4.7.2 BEHAVIOUR OF PROTACTINIUM IN EXCESS OF AMMONIACAL MEDIUM IN THE ABOVE THREE CASES AS GIVEN IN PARA 4.7: In order to know the behaviour of protactinium with the natural sea water of the three cases as in para 4.7.1 in excess ammoniacal medium, 5 ml of liquor ammonia is added to each of the three polythene bottles and they are shaken for 11 days. The solutions are filtered through 0.22 μ membrane filters and the filtrates and the residues are counted for Pa²³³ as detailed earlier.

Table 23. Interaction of Pa²³³ with natural sea water sample from Bombay Harbour.

Polythene bottle No.	Contents in the bottle	Set 1 counts in 10 min	Set 2 counts in 10 min
1.	Pa ²³³ (250 λ) + Natural sea water (51 ml)	5408	5398
2.	Pa ²³³ (250 λ) + Natural sea water free from humic and fulvic acids (51 ml)	5415	5401
3.	Pa ²³³ (250 λ) + Natural sea water free from organic matter (51 ml)	5405	5414

The samples in the polythene bottles are counted on 29-11-1972 for Pa²³³ gammas.

4.7.2.1. DISCUSSION: Table 25 gives the results obtained. It is observed from the table that on addition of liquor ammonia, the residue in the bottle containing natural sea water (in the first case) carried 63% of Pa²³³ activity.

The residue from the polythene bottle containing natural sea water free from humic and fulvic acids (in the second case) carried 80% of Pa²³³ activity.

And the residue from the polythene bottle containing natural sea water free from organic matter (in the third case) carried 79% of Pa²³³ activity.

Natural sea water because of the presence of dissolved organic matter is capable of solubilising protactinium. Protactinium organic complex is apparently a very stable one and the activity remains associated with the organic matter either in the dissolved or in the precipitated state in the marine environment.

Table 24. Interaction of Pa²³³ with natural sea water.

Polythene bottle No.	Contents in the bottle	Set 1 counts in 10 min	Total counts	Set 2 counts in 10 min	Total counts
1.	Pa ²³³ (250 λ) + Natural sea water (51 ml)	4400		4412	
2.	Filtrate (51 ml) from polythene bottle No. 1 of table 23	1320	} 4405	1311	} 4389
3.	Residue from polythene bottle No. 1 of table 23 + 51 ml double distilled water	3085		3078	
4.	Filtrate (51 ml) from polythene bottle No. 2 of table 23	1060	} 4361	1100	} 4380
5.	Residue from polythene bottle No. 2 of table 23 + 51 ml double distilled water	3301		3280	
6.	Filtrate from polythene bottle No. 3 of table 23	865	} 4385	836	} 4396
7.	Residue from polythene bottle No. 3 of table 23 + 51 ml double distilled water	3520		3560	

The samples in the polythene bottles are counted on 7-12-1972 for Pa²³³ gammas.

Table 25. Solubilisation of Pa²³³ in excess ammonia.

Polythene bottle No.	Contents in the bottle	Set 1 counts in 10 min	Total counts	Set 2 counts in 10 min	Total count
1.	Pa ²³³ (250 A) ² + Natural sea water containing excess ammonia (51 ml)	3218		3209	
2.	Filtrate (51 ml) from polythene bottle No. 2 of table 23	435	3204	421	3189
3.	Residue from polythene bottle No. 2 of table 23 + 51 ml double distilled water	460		454	
4.	Filtrate (51 ml) from polythene bottle No. 3 of table 23	859		853	
5.	Residue from polythene bottle No. 3 of table 23 + 51 ml double distilled water	1450		1461	
6.	Filtrate (51 ml) from polythene bottle No. 4 of table 23	361		370	
7.	Residue from polythene bottle No. 4 of table 23 + 51 ml double distilled water	440	3274	449	3307
8.	Filtrate (51 ml) from polythene bottle No. 5 of table 23	478	482		
9.	Residue from polythene bottle No. 5 of table 23 + 51 ml double distilled water	1995	2006		
10.	Filtrate (51 ml) from polythene bottle No. 6 of table 23	314	3295	321	3323
11.	Residue from polythene bottle No. 6 of table 23 + 51 ml double distilled water	345		351	
12.	Filtrate (51 ml) from polythene bottle No. 7 of table 23	551		560	
13.	Residue from polythene bottle No. 7 of table 23 + 51 ml double distilled water	2085		2091	

The samples in the polythene bottles are counted on 18-12-1972 for Pa²³³ gammas.

V. MEASUREMENT OF THE THICKNESS OF THE SURFACE LAYER OF SEDIMENTS PARTICIPATING IN THE LEACHING PROCESS OR EQUILIBRIUM PROCESS IN THE ENVIRONMENT

I. INTRODUCTION

It has been observed from the results of the experiments performed on sediments after leaching with 0.05 M hydrochloric acid and phosphate-free hydrogen peroxide, that radioactive disequilibrium exists only on the surface

of the sediment particles and that as the surface organic matter is removed the leached activity from organic matter free particles show equilibrium, both in respect of thorium, *i.e.*, between Th^{232} and Th^{228} and uranium, *i.e.*, between U^{238} and U^{234} (*cf.* Section III and IV).

Attempts have been made to find out the thickness of surface layer wherein the disequilibrium of activity is observed. The thickness t of leachable surface layer has been found experimentally using monazite particles of the Kerala beach in one set of experiments and using the sediment samples from Bombay to Kottilpad, in another set of experiments.

2. DETERMINATION OF THE THICKNESS OF THE SURFACE LAYER OF MONAZITE

2.1. SAMPLE COLLECTION

Monazite sand is initially crushed in a clean, dry mortar and pestle. The particles are collected and used as "monazite sample" for experimental purpose. The density of the sample as determined pycnometrically, is found to be — 5.2 gms/c.c.

The value given for monazite⁶³ range from 4.9 to 5.3. The value obtained in the present investigation agrees with the density of pure monazite.

Figure 47 gives the X-ray diffraction powder pattern of the sample and standard monazite. No significant lines other than those lines seen in standard monazite spectrum are discernible. The purity of the sample is estimated to be better than 95% monazite.*

2.2. DETERMINATION OF PARTICLE SIZE DISTRIBUTION OF THE MONAZITE SAMPLE

Monazite particles are suspended in (pH 9.0) distilled water and allowed to settle on a glass plate and the plate dried slowly. The size of the particles and the number frequency are determined microscopically.

We assume that the particles are of spherical shape and are of density 5.2 gram/c.c., as determined above, to calculate the weight, surface area of each of the particles and the total surface area of these particles. Table 26 gives the results obtained. Figure 48 gives particle size distribution curve of the sample. The curve shows a maximum at 9.0 μm .

* The percentage of various oxides in the monazite are as follows: Rare Earth oxides = 59.76%; ThO_2 = 8.70%; P_2O_5 = 27.41%; SiO_2 = 0.93%; TiO_2 = 1.36%; ZrO_2 = 1.43%; U_3O_8 = 0.41%; PbO = 0.28%; Fe_2O_3 = 1.1%

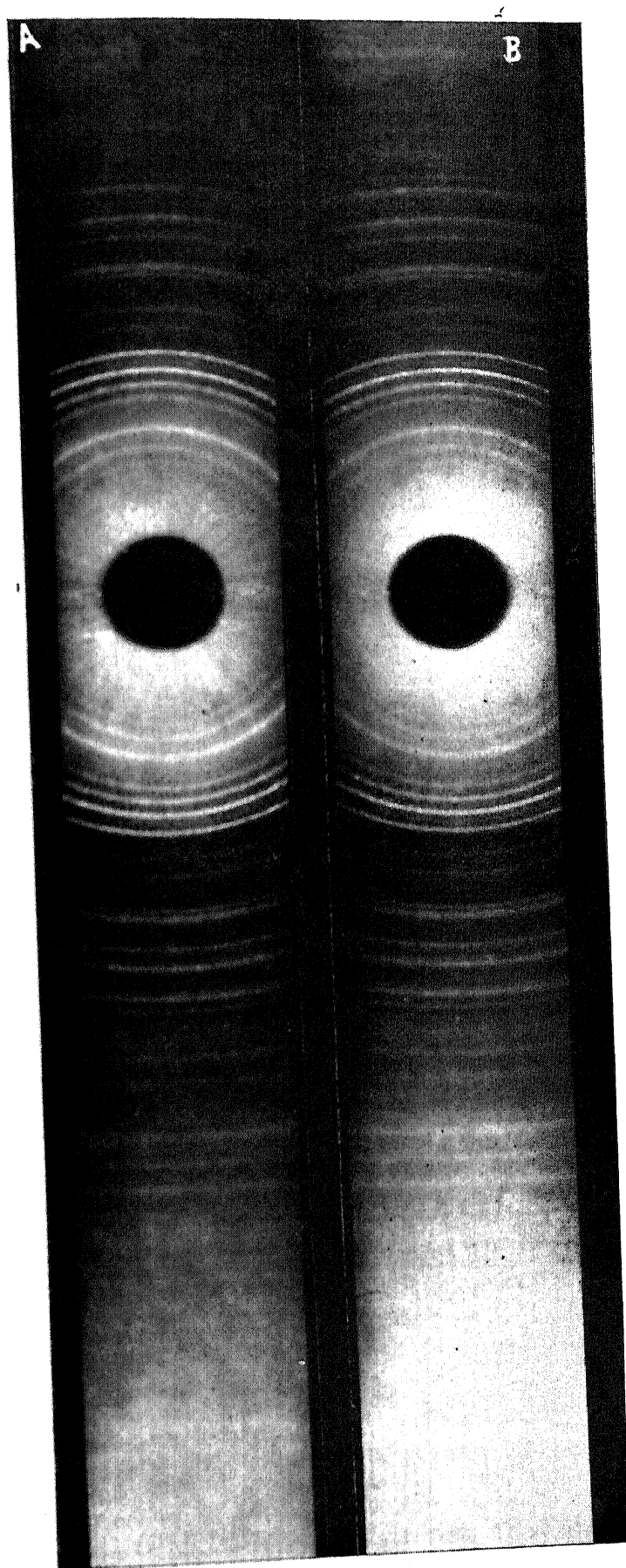


Figure 47. X-ray diffraction power pattern, A: Monazite sample, B: Standard Monazite
(facing page 232)

2.3. THORIUM AND URANIUM CONTENT AND LEACHING OF MONAZITE SAMPLE

1.0 gram of the monazite sample is decomposed by digesting the sample with concentrated sulphuric acid and a drop of hydrofluoric acid. The resulting solution is used for the determination of thorium by gravimetric method⁶⁴ and uranium by fluorimetric method.⁶⁵

In order to determine leachable thorium and uranium, 1.0 gram each of monazite sample is leached separately with 5% EDTA at pH 3.0 for the extraction of leachable thorium and saturated solution of ammonium carbonate for the extraction of leachable uranium. Thorium and uranium are then chemically separated (*cf.* Sections III and IV). Thorium is estimated by thorium-thorin spectrophotometric method⁶⁷ while uranium is determined by fluorimetric method.⁶⁵

Table 27 gives total and leachable thorium from monazite sample and table 28 gives total and leachable uranium from monazite sample.

2.4. CALCULATION OF THE THICKNESS OF THE SURFACE LAYER ACCESSIBLE TO LEACHING AGENT

We assume:

- (i) that the thickness t of the surface layer is the same for particle of all sizes,

Table 26. Diameters, weights and surface areas of monazite sample particles.

Mean diameter (um)	No. of particles	Weight of each particle $\times 10^{-12}$ gm	Surface area of each particle $\times 10^{-8}$ cm ²	Total weight of n particles $\times 10^{-12}$ gm	Total surface area of n particles $\times 10^{-8}$ cm ²
3	6	73.41	28.26	440.46	169.56
5	11	339.48	78.50	3734.28	863.50
7	27	931.35	153.86	25146.45	4154.22
9	44	1979.34	254.34	87090.96	11190.96
11	31	3613.77	379.94	112026.87	11778.14
13	32	5964.56	530.66	190878.72	16981.12
15	26	9163.23	706.50	238243.98	18369.00
17	19	13338.90	507.46	253439.10	17241.74
19	17	18622.29	1133.54	316578.93	19270.18
21	16	25143.72	1384.74	402299.52	22155.84
23	12	33033.51	1661.06	396402.12	19932.72
24	6	42421.93	1962.50	254531.88	11775.00
27	8	53439.45	2289.06	427515.60	18312.48
29	9	66216.24	2640.74	595946.16	23766.66
31	7	80882.67	1017.54	566178.69	21122.78
Total	271			3.87×10^{-6} gm	2.17×10^{-3} cm ²

The number N_i of particles in the size group 'i' for one gram of the sample can be obtained from the above table by dividing the total number of particles in the size group 'i' as given in column 2 by the total weight given at the base of column 5.

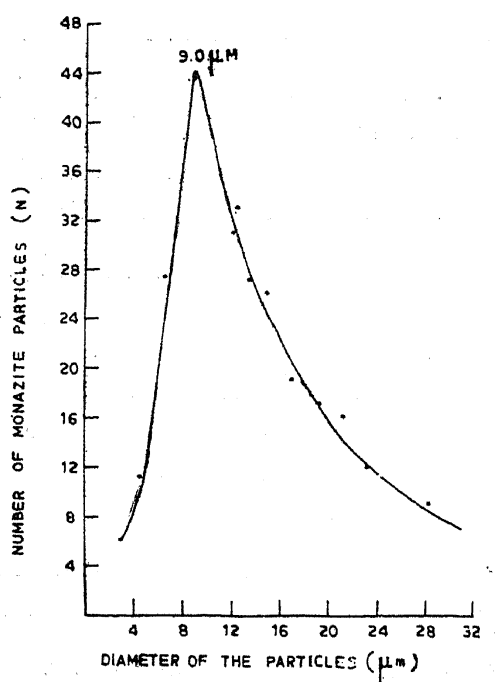


Figure 48. Particle size distribution of monazite particles.

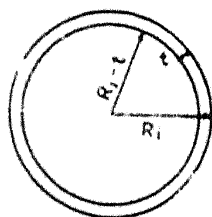
Table 27. Total and leachable thorium in monazite particles.

Weight of the sample taken (g)	Procedure	Total amount of thoria obtained	Percentage of thoria leached
1.00	Destroyed by acids	87 mg	..
1.00	Leaching with 5% EDTA	293 ug	0.34%

Table 28. Total and leachable uranium in monazite particles.

Weight of the sample taken (g)	Procedure	Total amount of uranium obtained	Percentage of uranium leached
1.00	Destroyed by acids	1.148 mg	..
1.00	Leached with saturated ammonium carbonate	5.365 ug	0.47%

- (ii) Monazite sample particles are spherical,
- (iii) Thorium and uranium are uniformly distributed in the particles,
- (iv) That thorium and uranium present in the surface layer of thickness t are quantitatively leached.



If R_i is the radius of the particles of size group i , then

$$\left(\sum_{i=1}^{\infty} \frac{4}{3} \pi \{R_i^3 - (R_i - t)^3\} N_{R_i} \cdot \rho \right) \cdot W_1 = W_2 \quad (1)$$

where ρ is the density of the monazite sample particles, N the number of particles of radius R_i in 1.0 gram of monazite sample; W_1 the weight in grams of thorium or uranium obtained by destroying 1.0 gram of monazite sample; and W_2 the weight in grams of thorium or uranium obtained by leaching 1.0 gram of monazite sample. Substituting the values for the parameters in eq. (1), the value of t is obtained as follows:

thorium, $t = 1.13 \times 10^{-6}$ cm and
 uranium, $t = 1.60 \times 10^{-6}$ cm.

2.4.1. Discussion: Agreement in the order of magnitude for the values of t is suggestive. Repeat experiments gave values in excellent agreement with the values given above for t . The differences in the absolute values when comparing t values obtained for different chemical species are to be understood principally on the basis of the limitations of the assumptions (ii) and (iv). Besides although the thickness of the leaching layer has been taken to have a sharp boundary in the calculational procedure, the layer in fact should be a diffuse one in the particles and as such the leachability of the chemical species from the surface layer would be greatly determined by the diffusion processes for the leaching agent and the chemical species that is being leached. However, the equivalent thickness of the diffuse leached layer, in well compact minerals like monazite, when the leaching agent does not chemically attack the mineral as such, is not likely to be different from the range 100 Å to 150 Å. BET measurements of the surface area of a powdered sample of monazite indicates that the surface area of the monazite sample is greater by a factor of two than the area obtained on the assumption of the spherical shape for the particles.

3. LEACHING OF COASTAL SEDIMENTS AND DETERMINATION OF THE THICKNESS OF THE LABILE SURFACE LAYER

Sediment samples are leached to different extent by the leaching agent used. Attempts are made in the following experiments to find the depth to which the labile component exists on the sediment particle surface.

3.1. DETERMINATION OF THE DENSITIES OF COASTAL SEDIMENTS

Coastal sediments are air-dried at 110° C to constant weight and then used for the pycnometric determination of the densities. Table 29 gives the densities of the coastal sediments.

3.2. DETERMINATION OF THE DENSITIES OF COASTAL SEDIMENTS AFTER REMOVAL OF ORGANIC MATTER FROM THE SURFACE

5.0 gms of air-dried coastal sediments are treated with 100 ml of 0.05 M hydrochloric acid and phosphate-free hydrogen peroxide till all organic matter from the sediments is destroyed. The organic matter free sediments are then washed with 10 ml of 0.05 M hydrochloric acid followed by a second wash with 5 c.c. of distilled water. The sediments are then dried at 110° C to constant weight and used for the pycnometric determination of the densities. The densities of organic matter free coastal sediments are also given in table 29.

Table 29. Densities of coastal sediments and of sediments after destruction of organic matter.

Place of collection (1)	Density of sediments gms/cc. (2)	Density of sediments after removal of organic matter gms/c.c. (3)	Difference in density in columns 3 and 2 (3-2) (4)
Bombay	2.350	2.382	0.032
Dabhol	2.641	2.672	0.031
Jaygad	2.461	2.494	0.033
Ratnagiri	2.750	2.781	0.031
Deogad	2.711	2.743	0.032
Malwan	2.713	2.744	0.031
Vengurla	2.601	2.634	0.033
Goa	2.262	2.296	0.034
Karwar	2.480	2.514	0.034
Honawar	2.492	2.523	0.031
Shertallay	2.580	2.611	0.031
Thottapally	2.601	2.631	0.030
Kayamkulam	2.681	2.713	0.032
Karunagapally	2.402	2.434	0.032
Chavara	3.379	3.410	0.031
Kottilppad	2.441	2.473	0.032

difference in density: 0.032 ± 0.002 .

3.2.1. DISCUSSION: It is to be noted in the results that while the densities of the sediments from different locations range from 2.262 to 3.379 gms/c.c., the difference in the densities of organic matter cleansed sediments and original sediments lie in the close range of $+ 0.032 \pm 0.002$ gms/c.c.

3.3. DETERMINATION OF THE PARTICLE SIZE DISTRIBUTION IN THE SEDIMENT

3.3.1. PARTICLE SIZE DISTRIBUTION BY DISPERSION IN DISTILLED WATER: Sediments from various locations are shaken for 4 hr in distilled water and then allowed to settle on 0.22 μ membrane filter and to the membrane dried in air is added a drop of "Emulsion oil". The size of the particles and the number frequency are determined microscopically.

3.3.2. PARTICLE SIZE DISTRIBUTION IN SEDIMENT SAMPLES: Sediments are suspended in distilled water, the pH is adjusted to 9.0 using sodium hydroxide solution and then shaken for 4 hr. The particle suspension is transferred to 0.22 μ membrane filter and to the membrane dried in air is added a drop of Emulsion oil. The size of the particles and the number frequency are then determined microscopically.

3.3.3 PARTICLE SIZE DISTRIBUTION IN ORGANIC MATTER CLEANSED SEDIMENT: The organic matter in the sediment samples is destroyed by 0.05 M hydrochloric acid and phosphate-free hydrogen peroxide. The sediment particles are then washed with 10 ml of 0.05 M hydrochloric acid, followed by a wash with 5 ml of distilled water. The washed particles are taken in water, pH is adjusted to 9.0 and are shaken for 4 hr. The particle suspension is transferred to 0.22 μ membrane filter, dried and added to it a drop of Emulsion oil. The particle size and the number frequency are determined microscopically.

3.3.3.1 DISCUSSION: In figure 49 is plotted the number frequency of particles as obtained by these procedures. The difference in the distribution is indicative of the agglomerates that are present in the particles, which do not get dispersed in neutral medium.

Figures 50 and 51 give the particle size distribution curves for coastal sediments from Bombay to Honawar and for the monazite bearing areas.

The distribution curves of the organic matter destroyed sediments are very slightly shifted towards the smaller particle size region in each case. However, the total surface area calculated for the same total number of sediment particles and their corresponding organic matter free particles do not show significant differences.

The maxima in the distributions for each of the sixteen samples are at 7.0 μ M.

3.4. CALCULATION OF THE THICKNESS OF THE SURFACE LAYER OF LABILE COMPONENT

From the data obtained above, the total weight and the total surface area of the particles are calculated. Knowing the densities of sediment particles, with and without the organic surface layer, the volume of the

surface layer of the labile component is calculated. From these then the thickness of the surface layer of the labile component is obtained as follows :

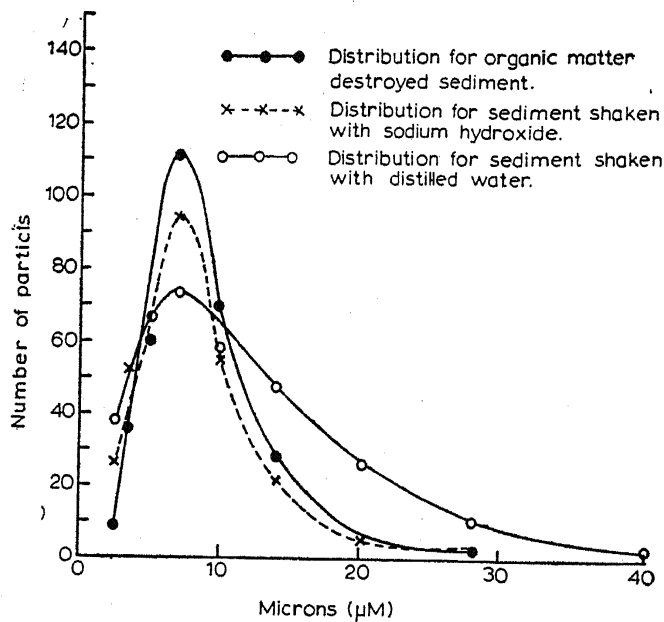
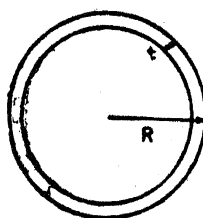


Figure 49. Particle size distribution for the coastal sediment from Ratnagiri.

Quantitative formulation on the basis of assumptions as given earlier is as follows :



Let, V_R be the volume of the particle of radius R ; ρ be the density of the particle; t be the thickness of the labile layer; ρ_C be the density of the mineral core of the material; ρ_L be the density of the organic (labile) layer; W_R , be the weight of the particle of radius R ; V_{RL} be the volume of the labile layer of a particle of radius R ; and N_R be the number of particles of radius R ; then $V_R = 4/3 \Pi R^3$; and $W = 4/3 \Pi R^3 \rho$.

To determine t

Weight of the particle of radius R and composed entirely of core material

$$= 4/3 \Pi R^3 \rho_C = 4/3 \Pi R^3 \rho \cdot \rho_C/\rho$$

$$= W_R \cdot \frac{\rho_C}{\rho}$$

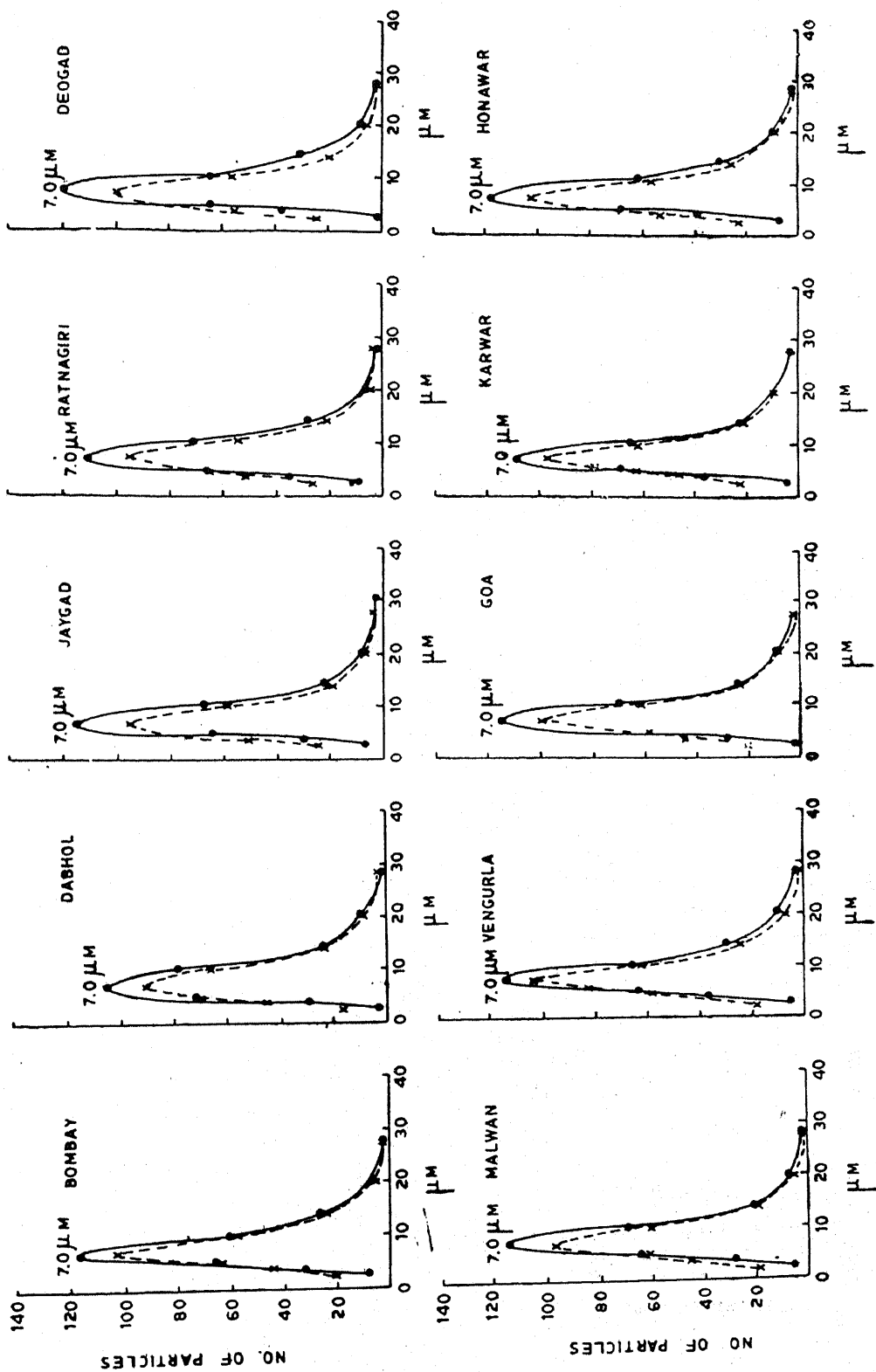


Figure 50. Particle size distribution for coastal sediments from Bombay to Honawar (Legend as in Fig. 49) (Each distribution normalised to the same total number of particles).

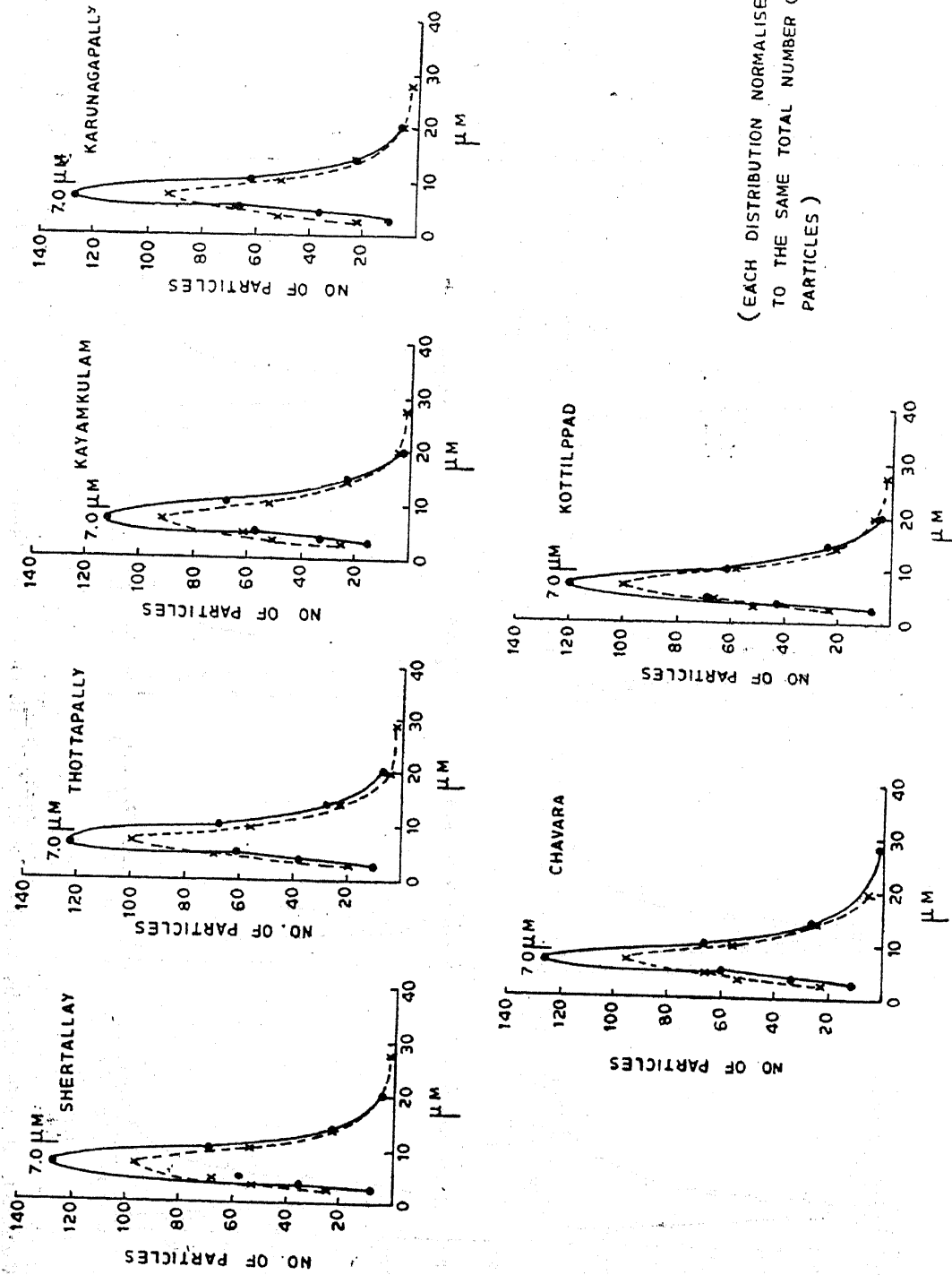


Figure 51. Particle size distribution for coastal sediments of Monazite bearing areas of South India.

$$\therefore W_R \rho_C / \rho - W_R = V_{RL} (\rho_C - \rho_L)$$

$$\text{i.e., } V_{RL} = W_R (\rho_C / \rho_L - 1) / (\rho_C - \rho_L)$$

$$\begin{aligned} \text{Total volume of organic layer} &= \sum_R V_{RL} \cdot N_R \\ &= (\rho_C - \rho) / \rho (\rho_C - \rho_L) \sum_R W_R N_R \quad (3) \end{aligned}$$

Of the parameters on the right hand side of eq. (3) only ρ_L (density of the organic layer) remains to be known.

3.4.1. DETERMINATION OF THE DENSITY OF THE ORGANIC MATTER (ρ_L) IN COASTAL SEDIMENTS: 350 gms of Ratnagiri sediment is shaken with 800 ml of alkali mixture of 0.2 N sodium hydroxide and 0.2 N sodium carbonate for six hours at 80° C. The procedure is repeated four times. The supernate is centrifuged and humic acid is precipitated by adjusting the pH of the supernate to 2.0 with hydrochloric acid. The precipitate is centrifuged, dissolved in 1:1 ammonia and again centrifuged. From the clear supernate, humic acid is precipitated by hydrochloric acid at pH 2.0. The organic matter thus obtained is washed with distilled water, dried at 110° C and the density is determined pycnometrically. The density of the organic matter is found to be 1.246 gms/c.c.

Substituting the density of the organic matter as 1.246 gms/c.c. in eq. (3), the thickness of the surface layer of the labile component is calculated.

3.4.1.1 DISCUSSION: Table 30 gives the results obtained. The thickness of the surface leachable layer range from 2.5×10^{-6} cm to 10.0×10^{-6} cm. The values fall sharply into two groups, viz., Group I ranging in values from 5.9×10^{-6} cm to 10.0×10^{-6} cm. This group is comprised of samples collected from non-monazite areas and Group II, the values range from 2.5×10^{-6} cm to 4.9×10^{-6} cm, comprised of samples collected from monazite bearing areas. This resembles the difference in disequilibrium observed for thorium isotopes in these two regions (*cf.* Section III, paras 4.1 and 4.6).

A serious limitation in the method adopted in the computation is that it does not take cognisance of the presence of organic matter trapped in calcareous deposits. The trapped organic matter has all been assumed in the computational procedure as deposited on the surface layers of the mineral core of the sediments. The total calcareous matter as determined by CO₂ evolution on treatment with 0.05 M hydrochloric acid have been observed to be < 5% by weight.⁶⁶ On dissolution of the calcareous matter, the organic matter released is extracted with dilute ammonium hydroxide. The extract is observed to be < 5% of the total organic matter present in the sediments.

Table 30. Thickness of the surface layer of the labile component of coastal sediments.

Place of collection	Thickness of the surface layer(t) $\times 10^{-5}$ cm
Bombay	0.89
Dabhol	0.65
Jaygad	0.82
Ratnagiri	0.62
Deogad	0.64
Malwan	0.59
Vengurla	0.82
Goa	1.00
Karwar	0.71
Honawar	0.65
Shertallay	0.39
Thortapally	0.36
Kayamkulam	0.39
Karunagapally	0.49
Chavara	0.25
Kottilppad	0.42

3.5. ELECTRON MICROSCOPY OF SEDIMENT SAMPLES

Electron photo-micrograph of sections of some sediment samples are taken by two stage replica technique. Figure 52 shows a particle (white) rimmed by a black layer of organic matter. Electron photo-micrograph taken for sediment dispersed in sodium hydroxide showed diffuse layers of organic matter giving rise to very uneven contour of the particles. Figure 53 shows a particle of 1.15 μ diameter with uneven contour (black portion on the right hand side). Appearance of another particle (4.3 μ) is shown in figure 54. Figure 55 gives a photo-micrograph of organic matter removed particles. The geometrical shape of the surface of the particles is discernible in figure 55. The sharpness of the edges of the particle on the left hand bottom of the figure is to be noticed.

The thickness of the organic layer has been found to vary widely, mostly within the range of 500 \AA to 1000 \AA . This may be compared with the value obtained in table 30 where it ranges from 250 \AA to 1000 \AA as mean values for sediments collected from different regions.

4. DETERMINATION OF Ra^{228} PER GRAM OF THE SURFACE ORGANIC MATTER

The surface area per unit weight of the sediment particles is obtained from the data of figures 50 and 51. Knowing, the thickness of the surface labile layer of organic matter as given in table 30, the volume of the surface organic layer is calculated. The weight of the organic layer is then calculated from the volume and density of the organic layer (*cf.* para 3.4.1).



Figure 52. Replica of the cross-section of the sediment particle (3,000 \times).



Figure 53. Electron shadowgraph of sediment particle dispersed in sodium hydroxide (30,000 \times).

(facing page 242)





Figure 54. Electron shadowgraph of sediment particle dispersed in sodium hydroxide (15,000 \times).

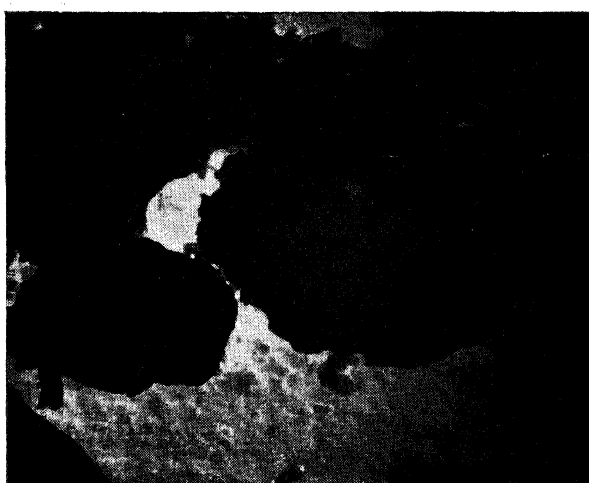


Figure 55. Electron shadowgraph of organic matter destroyed sediment particle (15,000 \times)

(facing page 243)

Ra^{228} per gram of the sediment is obtained from Section III para 4.3.2. From the concentration of Ra^{228} and the weight of the organic layer as calculated above, one can find the Ra^{228} per gm of the surface organic matter.

4.1. DISCUSSION

Table 31 gives the surface area, volume and weight of the organic layer and hence Ra^{228} per gm of the surface organic layer. The last column of this table gives Ra^{228} per gm of the sediment. Comparing the values in the last two columns, one could find that large amounts of Ra^{228} per gm of the surface organic layer are carried by the particles of sediments in coastal waters. From the leaching processes, we are more concerned with the amount of Ra^{228} per gm of the surface organic layer than Ra^{228} per gm of the sediment.

On the basis of the values obtained for Ra^{228} concentration in the waters of Ratnagiri and Goa (table 9) and the concentration of Ra^{228} in the organic layer, the calculated concentration factors range from 20,000 to 50,000 (whereas the concentration factors, if calculated on the basis of Ra^{228} per gm of the sediment appears lower by at least a factor of 100). Joshi *et al.* obtained Ra^{228} concentration in marine bivalve species in the range 0.14 to 0.97 uuc/gm which means that Ra^{228} content in the organic layer of the sediments are about 10 to 60 times the Ra^{228} content in marine bivalve species.

VI. CHEMICAL DETERMINATION OF THORIUM AND URANIUM ON THE SURFACE AND IN THE CORE OF THE SEDIMENTS AND PROTACTINIUM ON THE SURFACE OF THE SEDIMENT PARTICLES

1. INTRODUCTION

Measurements of thorium, protactinium and uranium in the coastal sediments have been carried out and the ratios of $\text{Th}^{230}/\text{U}^{234}$ and $\text{Pa}^{231}/\text{U}^{238}$ are calculated from the results. An attempt has been made to find out the distribution of the isotopes of natural radioactive elements.

The ratios of activities of $\text{Th}^{228}/\text{Th}^{232}$ and $\text{U}^{234}/\text{U}^{238}$ given in Sections III and IV have been used in determining the activities of Th^{230} , U^{234} and U^{235} in coastal sediments.

2. THORIUM IN COASTAL SEDIMENTS

2.1. TOTAL THORIUM IN THE ENTIRE SAMPLE

10 gms of air-dried sediment sample from each location are repeatedly heated with instalments of 10 ml of concentrated nitric acid, 5 ml of perchloric acid and 25 ml of 17 M hydrofluoric acid in a platinum dish till

Table 31. Surface area, weight of the surface layer and $Ra^{228}/gm.$ of the surface organic matter.

Place of collection	Total surface area $\times 10^{-3}$ cm^2 of the particles counted	Total weight 10^{-6} gm of the particles counted	Surface area per gram of the sediment $\times 10^{-3}$ cm^2	Thickness of the surface layer $\times 10^{-5}$ cm	Volume of the surface organic layer per gm of the sediment $\times 10^{-2}$ cm^3	Weight of the surface organic layer per gm of the sediment $\times 10^{-2}$ gm	Ra^{228}/gm of the sediment (uuc/gm) (Reproduced from table 8)	Ra^{228}/gm of the surface organic layer (uuc/gm)
Bombay	0.71	0.33	2.15	0.89	1.91	2.38	0.22	9
Ratnagiri	0.75	0.41	1.83	0.62	1.13	1.41	0.54	38
Ratnagiri	0.75	0.41	1.83	0.62	1.13	1.41	0.54	38
Goa	0.74	0.33	2.24	1.00	2.24	2.79	0.53	19
Goa	0.74	0.33	2.24	1.00	2.24	2.79	0.54	19
Shertalloy	0.65	0.28	2.32	0.39	0.90	1.12	0.21	19
Thottapally	0.71	0.33	2.15	0.36	0.77	0.96	0.21	22
Karunagapally	0.65	0.28	2.32	0.49	1.14	1.42	0.20	14
Chavara	0.68	0.41	1.66	0.25	0.42	0.52	0.32	62
Kottilppad	0.63	0.26	2.42	0.42	1.02	1.27	0.30	24

all the residue is decomposed and then evaporated to dryness. The dried mass is taken in 10 ml of 8 M nitric acid. Thorium is separated on the anion-exchange column as detailed in Section III, paras 2.3 and 2.4 and thorium is determined by thorium-thorin spectrophotometric method.⁶⁷

2.2. LEACHABLE THORIUM

25 gms of air-dried sediment samples are leached with EDTA and thorium is estimated from the supernate by the method given in Section III

2.3. DIRECT DETERMINATION OF THORIUM IN THE SEDIMENT CORE

For checking the results as obtained in paras 2.1 and 2.2, a few of the sediment samples are destroyed by repeatedly heating the residue with acids as given in para 2.1 and thorium is estimated as above.

3. URANIUM IN COASTAL SEDIMENTS

3.1. TOTAL URANIUM IN THE ENTIRE SAMPLE

10 gms of air-dried sediment sample from each location are destroyed by acids as given in para 2.1 and uranium is separated as detailed in Section IV, paras 2.1 to 2.4 and estimated fluorimetrically.⁶⁵

3.2. LEACHABLE URANIUM

25 gms of air-dried sediment samples are leached with saturated solution of ammonium carbonate and uranium in the leachate is estimated as detailed in para 3.1.

3.3. DIRECT DETERMINATION OF URANIUM IN THE SEDIMENT CORE

For checking the results as obtained in paras 3.1 and 3.2, a few of the sediment samples are destroyed by repeatedly heating the residue with acids as given in para 2.1 and uranium is estimated as above.

4. RESULTS AND DISCUSSION

Tables 32 to 35 give the results obtained. The results of direct determination of concentrations in the core agree very well with the results obtained as difference of columns 2 and 3 within the limits of experimental error.

Tables 32 and 33 give the total and leachable concentrations of thorium in coastal sediments collected from Bombay to Karwar and in the monazite bearing areas. Tables 34 and 35 give the concentrations of uranium in the samples from the respective regions.

Table 32. Leachable, core and total concentrations of thorium in coastal sediments from Bombay to Karwar.

Place of collection	Total thorium ug/gm	Thorium leached ug/gm	Thorium in the core of the particles ug/gm (2 — 3)	Thorium directly determined from the core ug/gm	Percentage thorium leached %
Bombay	4.18	2.89	1.29	..	69.1
Bombay	4.23	2.98	1.25	..	70.5
Jaygad	3.47	2.43	1.04	..	70.0
Ratnagiri	3.32	2.37	0.95	0.94	71.4
Ratnagiri	3.29	2.41	0.88	..	73.3
Ratnagiri	3.00	2.23	0.77	..	74.3
Ratnagiri	3.41	2.52	0.89	..	73.9
Malwan	3.19	2.15	0.96	0.94	69.5
Vengurla	3.20	2.24	0.96	0.96	70.0
Vengurla	3.35	2.48	0.87	..	74.0
Goa	3.12	2.35	0.77	0.76	75.3
Goa	3.30	2.38	0.92	..	72.1
Goa	3.46	2.57	0.89	..	74.3
Goa	3.38	2.58	0.80	..	76.3
Karwar	4.10	2.78	1.32	..	67.8
Karwar	4.00	2.76	1.24	..	69.0

Table 33. Leachable, core and total concentrations of thorium in coastal sediments from monazite bearing areas.

Place of collection	Total thorium ug/gm	Thorium leached ug/gm	Thorium in the core of the particles ug/gm (2 — 3)	Thorium directly determined ug/gm	Percentage thorium leached (%)
Shertallay	89.20	13.29	75.91	..	14.9
Thottapally	84.30	11.97	72.33	..	14.2
Kayamkulam	82.50	12.71	72.49	..	15.4
Karunagapally	87.10	13.67	73.43	..	15.7
Chavara	699.00	133.5	565.5	565.20	19.1
Kottilppad	112.00	18.48	93.52	93.41	16.5

It is to be seen that thorium concentrations both in the leached fraction and in the core are quantitatively much higher in the samples from monazite bearing areas than non-monazite areas. However, when the leached fraction is expressed as a percentage of the total, the results in the monazite bearing areas (ranging from 14 to 20%) appear much lower than the results (ranging from 68 to 76%) obtained from the non-monazite areas.

A somewhat similar situation is also observed for the distribution of uranium. The absolute values of leachable uranium are generally lower than that obtained for thorium,

Table 34. Leachable, core and total concentrations of uranium in coastal sediments from Bombay to Karwar.

Place of collection	Total uranium ug/gm	Uranium leached ug/gm	Uranium in the core of the particles ug/gm (2—3)	Uranium directly determined from the core ug/gm	Percentage uranium leached (%)
Bombay	2.13	0.98	1.15	..	45.9
Bombay	2.15	0.95	1.20	..	44.1
Jaygad	1.45	0.61	0.84	..	42.3
Ratnagiri	2.01	0.89	1.12	1.11	44.1
Ratnagiri	1.92	0.83	1.09	..	43.0
Ratnagiri	1.22	0.55	0.67	..	45.0
Ratnagiri	2.04	0.92	1.12	..	45.0
Malwan	2.00	0.89	1.11	1.10	44.4
Vengurla	1.97	0.89	1.08	1.06	45.0
Vengurla	2.04	0.86	1.18	..	42.0
Goa	1.37	0.55	0.82	0.81	40.0
Goa	1.53	0.61	0.92	..	39.8
Goa	1.94	0.86	1.08	..	44.1
Goa	1.87	0.83	1.04	..	44.1
Karwar	1.45	0.61	0.84	..	41.9
Karwar	1.45	0.61	0.84	..	42.0

Table 35. Leachable, core and total concentrations of uranium in coastal sediments from monazite bearing areas.

Place of collection	Total uranium ug/gm	Uranium leached ug/gm	Uranium in the core of the particles ug/gm (2—3)	Uranium directly determined from the core ug/gm	Percentage uranium leached (%)
Shertally	7.6	0.2	7.08	..	6.8
Thottapally	7.13	0.41	6.72	..	5.7
Kayamkulam	7.20	0.58	6.62	..	8.1
Karunagapally	7.40	0.67	6.73	..	9.0
Chavara	101.0	4.88	96.12	96.00	4.8
Kottilppad	10.3	1.01	9.29	9.15	9.8

In the non-monazite areas thorium and uranium in the core are generally close to one another in the absolute values although the percentage of the leachable fraction in the sediments are much higher for thorium than uranium. This is due to the fact that uranium is better dissolved in the ambient sea water than thorium and as such there is preferential pick up of thorium on the sediment particles than uranium.

Table 36 gives Th/U ratios by weight and by activity for sediment samples from Bombay to Kottilppad. The Th/U ratios by weight in the core of the sediments in non-monazite areas lie in the range of 0.77 to 1.57 and in the leached samples in non-monazite areas lie in the range of 2.46 to 4.56. The corresponding ratios in the monazite bearing areas are 5.89 to 10.95 in the core of the sediments while for the leachates, the ratios are in the range of 18.30 to 29.20.

These variations in the Th/U ratios by weight in the mineral core of the coastal sediments may be due to different types of igneous rocks and accessory minerals such as apatite, magnetite, zircon and monazite that are fractionated to different degrees in different regions of the West Coast. Apatite, magnetite and zircon contain Th/U ratios of the order of 1.0 or less²⁹ while monazite shows much higher values for Th/U ratios.⁶⁸

5. CALCULATION OF ABSOLUTE ACTIVITY OF LEACHABLE Th²³⁰ IN COASTAL SEDIMENTS

Absolute activity of leachable Th²³⁰ can be calculated from the expression,

$$\text{Th}^{230} \text{ (dpm)} = \frac{R \times L_{\text{Th}} \times 10^{-6} \times 6.02 \times 10^{23} \times 0.693}{232 \times 1.41 \times 10^{10} \times 5.25 \times 10^5} \quad (4)$$

$$\text{Where } R = \frac{\text{Th}^{230}}{\text{Th}^{232}} = \frac{N_{\text{Th}^{230}} \cdot \lambda_{\text{Th}^{230}}}{N_{\text{Th}^{232}} \cdot \lambda_{\text{Th}^{232}}}$$

The values of R are obtained from Section III, and tables 5 to 7.

L_{Th} = leachable thorium in ppm from sediments.

6.02×10^{23} is the Avogadro's Number,

1.41×10^{10} years is the half-life of Th²³² and

5.25×10^5 conversion factor from years to minutes.

Table 36. Th/U Ratios by weight and by activity.

Place of collection	Th/U Ratio by Weight		Th/U Ratio by activity	
	Core	leach	Core	leach
Bombay	1.12	2.95	0.40	1.03
Bombay	1.04	3.14	0.37	1.09
Jaygad	1.24	3.98	0.44	1.10
Ratnagiri	0.85	2.66	0.30	0.94
Ratnagiri	0.81	2.90	0.29	1.02
Ratnagiri	1.15	4.05	0.40	1.41
Ratnagiri	0.79	2.74	0.28	0.97
Malwan	0.93	2.46	0.32	0.87
Vengurla	0.90	2.52	0.31	0.89
Vengurla	0.74	2.88	0.25	1.02
Goa	0.94	4.27	0.33	1.49
Goa	1.00	3.90	0.36	1.37
Goa	0.82	2.99	0.29	1.05
Goa	0.77	3.11	0.27	1.10
Karwar	1.57	4.56	0.56	1.58
Karwar	1.48	4.52	0.53	1.58
Shertallay	10.72	25.56	3.76	9.08
Thottapally	10.76	29.20	3.78	10.14
Kayamkulam	10.95	21.91	3.85	7.63
Karunagapally	10.91	20.40	3.83	7.15
Chavara	5.89	27.36	2.07	9.60
Kottilppad	10.21	18.30	3.59	6.41

6. CALCULATION OF ABSOLUTE ACTIVITY OF LEACHABLE U^{234} IN COASTAL, SEDIMENTS

Absolute activity of leachable U^{234} can be calculated from the expression,

$$U = 1.0072 W_U 238 + W_U 234 \quad (5)$$

Where U is the total leachable amount by weight of uranium per unit weight of sediments; $W_U 238$ is the amount of uranium present as U^{238} , while $W_U 234$, the corresponding U^{234} amount.

As U^{238} and U^{235} are present in constant proportion in the sediments viz., 0.72% of uranium is present as U^{235} , the concentration of U^{238} and U^{235} in total leachable uranium is taken as: $1.0072 W_U 238$.

Then,

$$W_U 238 \cdot f_U 238 = W_U 238 \times 6.02 \times 10^{23} \times 0.693/238 \times T \frac{1}{2} (U^{238}) \quad (6)$$

and

$$W_U 238 \cdot f_U 238 / f_U 234 = R \cdot W_U 234 \quad (7)$$

$$\text{Where activity ratio } R = U^{238}/U^{234} \quad (8)$$

Multiplying both sides of the eq. (5) by R , we get,

$$\begin{aligned} RU &= 1.0072 W_U 238 R + R \cdot W_U 234 \\ &= 1.0072 W_U 238 R + W_U 238 \cdot f_U 238 / f_U 234 \end{aligned} \quad (9)$$

The $f_U 238$ and $f_U 234$ are given as:

$$\begin{aligned} f_U 238 &= 6.02 \times 10^{23} \times 0.693/238 \times 4.5 \times 10^9 \times 5.25 \times 10^5 \\ &= 0.742 \times 10^6 \end{aligned}$$

and

$$\begin{aligned} f_U 234 &= 6.02 \times 10^{23} \times 0.693/234 \times 2.48 \times 10^5 \\ &\quad \times 5.25 \times 10^5 = 1.369 \times 10^{10} \end{aligned}$$

Substituting these values in eq. (9), $W_U 238$ is obtained and then substituting $W_U 238$ in eq. (5), we get $W_U 234$.

$W_U 234$ is multiplied by $f_U 234$ to get U^{234} in dpm.

6.1. DISCUSSION

Table 37 gives again the total leachable thorium and uranium, Th^{230}/Th^{232} and U^{234}/U^{238} activity ratios in sediments. The calculated Th^{230} ,

U^{234} and activity ratio of Th^{230}/U^{234} are given in the last three columns of table 37 and table 38 gives the corresponding values in the monazite bearing areas.

The value of Th^{230}/U^{234} ratio is usually less than 1.0 (minimum value obtained in Bombay) in non-monazite bearing areas. In some places, we obtain values significantly greater than 1.0. Th^{230} is the immediate daughter of U^{234} and the U^{238} radioactive series and Th^{230} is easily scavenged out

Table 37. Calculated Th^{230} , U^{234} Activities and Th^{230}/U^{234} Activity ratios in coastal sediment from Bombay to Karwar.

Place of collection	Thorium (ppm)	Uranium (ppm)	Th^{230}/Th^{232}	U^{234}/U^{238}	Th^{230} (dpm/gm)	U^{234} (dpm/gm)	Th^{230}/U^{234}
Bombay	2.89	0.98	0.14	1.13	0.10	0.82	0.12
Bombay	2.98	0.95	0.13	1.13	0.10	0.79	0.13
Jaygad	2.43	0.61	0.97	1.13	0.57	0.51	1.12
Ratnagiri	2.37	0.89	0.99	1.14	0.57	0.75	0.76
Ratnagiri	2.41	0.83	0.98	1.14	0.57	0.70	0.81
Ratnagiri	2.23	0.55	0.98	1.14	0.53	0.46	1.15
Ratnagiri	2.52	0.92	0.99	1.14	0.61	0.77	0.79
Malwan	2.19	0.89	0.95	1.14	0.51	0.75	0.68
Vengurla	2.76	0.89	1.04	1.14	0.57	0.75	0.76
Vengurla	2.24	0.86	1.04	1.13	0.63	0.72	0.88
Goa	2.35	0.55	0.97	1.13	0.55	0.46	1.20
Goa	2.38	0.61	0.96	1.14	0.55	0.51	1.08
Goa	2.57	0.86	1.00	1.14	0.62	0.72	0.86
Goa	2.58	0.83	1.06	1.14	0.66	0.70	0.94
Karwar	2.78	0.61	1.07	1.13	0.72	0.51	1.41
Karwar	2.76	0.61	1.04	1.13	0.70	0.51	1.37

Table 38. Calculated Th^{230} , U^{234} Activities and Th^{230}/U^{234} activity ratios in coastal sediments from monazite bearing areas.

Place of collection	Thorium (ppm)	Uranium (ppm)	Th^{230}/Th^{232}	U^{234}/U^{238}	Th^{230} (dpm/gm)	U^{234} (dpm/gm)	Th^{230}/U^{234}
Shertalloy	13.29	0.52	0.24	1.14	0.78	0.44	1.77
Thottapally	11.97	0.41	0.24	1.13	0.70	0.34	2.06
Kayamkulam	12.71	0.58	0.24	1.13	0.74	0.48	1.54
Karunagapally	13.67	0.67	0.24	1.14	0.80	0.56	1.43
Chavara	133.5	4.88	0.24	1.14	7.79	4.10	1.90
Kottilppad	18.48	1.01	0.23	1.13	1.03	0.84	1.23

by sediment particles. Disequilibrium between these two nuclides as observed on sediments is to be understood on the basis of this preferential scavenging or precipitation action of Th^{230} . We have observed earlier that the ratio of $\text{U}^{234}/\text{U}^{238}$ is always about the same for the leachable fraction of the sediment and for the ambient sea water. Th^{230} is obtained from the decay of U^{234} in the ambient medium and as such we conclude that Th^{230} in the labile organic layer is obtained from the ambient sea water medium. In the monazite bearing areas, the ratio is always greater than 1.0.

7. DETERMINATION OF Pa^{231} IN COASTAL SEDIMENTS AND SEA WATER AND ESTIMATION OF $\text{Pa}^{231}/\text{U}^{235}$ ACTIVITY RATIOS

It is observed from the experimental data of tables 17 to 22 that the organic constituents of the marine environment, principally humic and fulvic acids solubilise and carry with them Pa^{233} activity to different extent, depending on the concentrations of the organic matter.

Pa^{231} ($T_{1/2} = 3.25 \times 10^4$ y), the immediate daughter of U^{235} is the longest-lived of the isotopes of protactinium. U^{235} occurs in constant proportion with U^{238} in sea water as well as in the sediments. It is thus of interest to examine the existence of disequilibrium in the different phases, viz., water and sediment of the marine environment.

7.1. Pa^{231} IN COASTAL SEDIMENTS

Oxalic acid⁶⁰ (1 M) has been found to be the most effective leaching agent for protactinium and at the same time it does not attack the mineral core of the sediment.

Sediment samples, 50 gms each are spiked with 250 λ of Pa^{233} tracer and shaken for four hours with four, 200 ml instalments of 1 M oxalic acid. The supernates are filtered through 0.22 μ membrane filter. The filtrates are pooled together and evaporated to dryness. The oxalates are destroyed with nitric acid. The dried mass is repeatedly heated with 2 ml instalments of concentrated hydrochloric acid and the residue is dissolved in 10 ml of 8 M hydrochloric acid. A clear solution is obtained.

7.1.1. ION-EXCHANGE SEPARATION OF PROTACTINIUM: The anion-exchange resin, Dowex-1 \times 8% (50-100 mesh) is washed with running distilled water to remove the fine particles. 5 gms of the resin is then loaded in teflon column (1 \times 15 cms).

7.1.2. COLUMN OPERATIONS: (i) The column is converted into chloride form by passing 50 ml of 8 M hydrochloric acid at a flow rate of 1.0 ml/min. (ii) The solution in 8 M hydrochloric acid containing Pa^{231} and

tracer Pa^{233} activity is passed through the column at a flow rate of 0.25 ml/min. Protactinium is adsorbed on the column; (iii) The column is then washed with 50 ml of 8 M hydrochloric acid at a flow rate of 0.5 ml/min. (iv) The adsorbed protactinium is eluted with 25 ml of 8 M hydrochloric acid and 0.1 M hydrofluoric acid at a flow rate of 0.5 ml/min.

The protactinium solution from the anion-exchange column is then evaporated to nearly dryness in a teflon beaker and transferred to a platinum planchet.

The chemical yield has been estimated by counting the platinum planchet on NaI (Fl) crystal for Pa^{233} gammas. The chemical yield varies from 40–90%.

7.2. Pa^{231} IN SEA WATER FROM BOMBAY

To 20 litres of sea water, 250 λ of Pa^{233} tracer is added and filtered through 0.22 μ membrane filter. 10 mg of iron carrier (Fe^{3+}) are added to the filtrate and the solution is made acidic by the addition of a few drops of nitric acid. Iron is precipitated as ferric hydroxide, by 1:1 ammonium hydroxide solution. The naturally occurring Pa^{231} and the added tracer Pa^{233} co-precipitate with ferric hydroxide. The solution is filtered through 0.22 μ membrane filter and ferric hydroxide precipitate is dissolved in 8 M hydrochloric acid. Iron is removed following the procedure as given in Section IV para 2.3 and protactinium is separated from the solution and plancheted as above.

Pa^{231} alpha activity is determined by counting the planchets for 1000 minutes with a silicon surface barrier detector. The chemical yield is obtained from the gamma activity of Pa^{233} recovered. Figure 56 gives a typical alpha spectrum of the separated Pa^{231} from the sediment sample collected from Goa. Table 39 gives the activities of leachable Pa^{231} in the coastal sediments and of dissolved Pa^{231} in Bombay sea water.

7.3. ESTIMATION OF U^{235} IN COASTAL SEDIMENTS

Total uranium concentrations in the leachable fraction from the sediments have been determined by fluorimetry.⁶⁵ It has also been observed there that the ratio of $\text{U}^{235}/\text{U}^{238}$ in the leached uranium remains the same as that of natural uranium. From the abundance of U^{235} in natural uranium, the concentration of U^{235} in the leachates is calculated.

7.4. $\text{Pa}^{231}/\text{U}^{235}$ ACTIVITY RATIOS IN SEDIMENTS AND BOMBAY SEA WATER

Table 39 gives Pa^{231} , calculated U^{235} activities and $\text{Pa}^{231}/\text{U}^{235}$ activity ratios in sediments and Bombay sea water.

The data in table 39 indicates that there is a deficiency of Pa²³¹ in coastal waters of the ocean and that Pa²³¹ is removed by precipitation as soon as it is formed by the radioactive decay of U²³⁵.⁶⁹

This behaviour of protactinium is similar to that of Th²³⁰. Hence, one can expect to find unsupported Pa²³¹ on the surface of the sediments from the ocean waters.

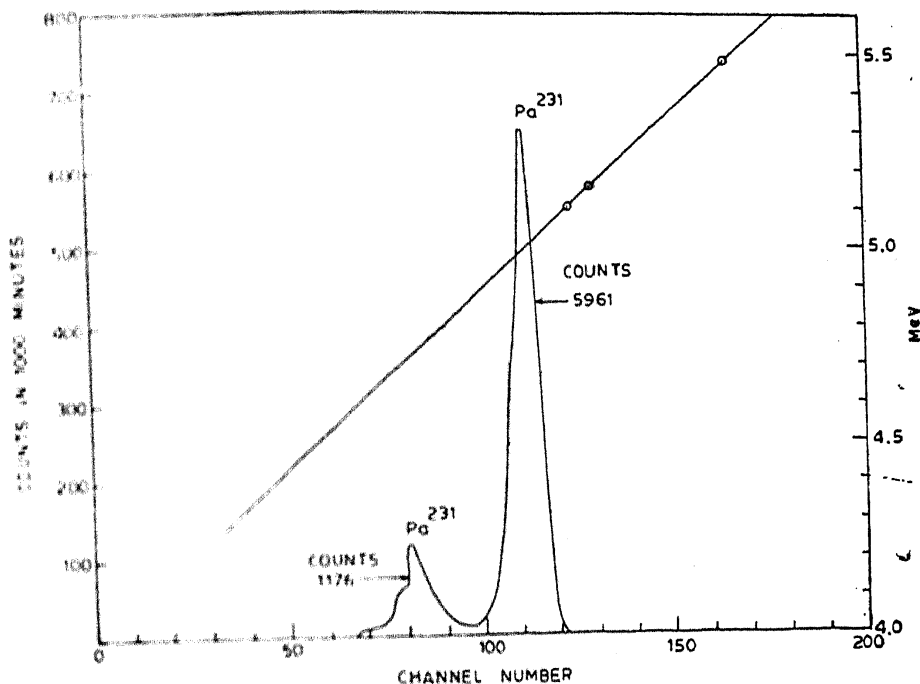


Figure 55. Alpha spectrum of Pa²³¹ from the coastal sediment sample collected from Goa.

Table 39. Activities of Pa²³¹, U²³⁵ and Pa²³¹/U²³⁵ activity ratios in coastal sediments and Sea water

Place of collection	Pa ²³¹ (dpm/gm)	U ²³⁵ (dpm/gm)	Pa ²³¹ /U ²³⁵
Bombay	0.61	0.05	12.2
Bombay	0.65	0.05	13.0
Jaygad	0.53	0.03	17.7
Ratnagiri	0.73	0.04	18.3
Ratnagiri	0.68	0.04	17.0
Malwan	0.68	0.04	17.0
Vengurla	0.65	0.04	16.3
Goa	0.60	0.03	20.0
Goa	0.66	0.04	16.5
Karwar	0.65	0.03	2.7
Kayamkulam	0.51	0.04	12.8
Karunagapally	0.51	0.04	12.8
Chavara	1.44	0.24	6.0
Kottilppad	0.57	0.05	11.4
Bombay sea water	0.000055	0.000137	0.04

On the basis of the values obtained for Pa^{231} concentration in the water from Bombay and the concentration of Pa^{231} in the sediments (table 39), the calculated concentration factor is 1.11×10^5 .

The leachable Pa^{231} comes from the organic surface layer of the sediments. Proceeding in the manner as detailed earlier in respect of the concentration factors of Ra^{228} (cf. Section V para 4) we obtained concentration factors lying in the range of 10^5 for the sediment whereas the concentration factor of the Bombay sediments for Pa^{231} in the organic layer calculates to 4.7×10^6 .

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