

ANOMALOUS BEHAVIOUR OF RADIO-ISOTOPES OF THORIUM IN THE COASTAL SURFACE SEDIMENTS OF THE ARABIAN SEA

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ABSTRACT

Geochemical behaviour of Thorium isotopes and their activity ratios have been studied in the surface layers of coastal sediments collected from the Arabian Sea. These coastal areas offer an unique advantage for geochemical study and transport of natural radioactivity which can be correlated with the transport and deposition of artificially introduced radioisotopes or terrestrial run offs as pollutants in these areas. It is known that Southern region of the west coast of India is concentrated with large amounts of placer deposits containing thorium while the northern region is relatively free from such deposits.

The surface layers of the coastal sediments are leached with 5% ethylene diamine tetra-acetic acid (EDTA) for the extraction of Thorium isotopes. The leaching agent is so chosen that it has a high efficiency for leaching thorium and at the same time it does not attack the core of the sediment particles. The Th^{232}/Th^{232} activity ratios in the Kerala belt (8° - 77° E) have been found to be in the range of 0.65 to 0.67, while this ratio is in the range of 2.00 to 2.18 in the northern region (19° - 13° E, 73° - 75° E). The Th^{230} and Th^{232} activities also show anomalous behaviour in these areas. The Th^{230}/Th^{232} activity ratio lies in the range of 0.95 to 1.07.

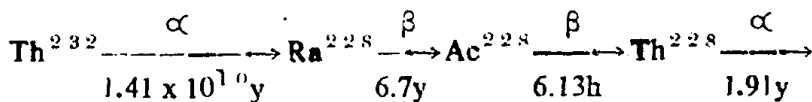
Key-words: Thorium, isotopes, radioactivity, sediments, Arabian sea.

INTRODUCTION

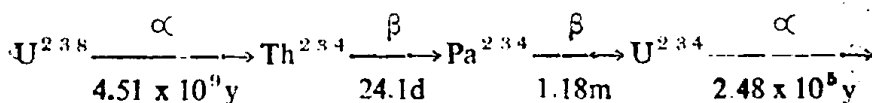
Th^{232} , Th^{230} and Th^{228} are the three long-lived, natural isotopes of thorium. The thorium isotopes, Th^{232} and Th^{228} which belong to thorium series are separated by Ra^{228} and Ac^{228} , while Th^{230} belongs to uranium series.

The parts of the radioactive decay chains of thorium and uranium are shown below :-

Thorium series :



Uranium series :



Coastal sediments largely include terrestrial run off. The radioactivity content within the mineral body of the sediments is 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 investigations 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 a dominant role and the physico-chemical equilibrium is expected to exist only between the labile chemical species present on the particle surface and the chemical species in the ambient medium.

During the last few years, a number of workers have studied the anomalous behaviour between Th^{232} and Th^{228} in the deep sea sediments, waters etc. as part of their investigations on geochemical processes of the oceans. Goldberg (1968), Bernat and Goldberg (1969) have studied the anomaly between Th^{232} and Th^{228} in the deep sea sediments and waters at various depths in the Pacific and Atlantic Oceans. In their study of the radioactive disequilibrium of Thorium, the three isolates of Thorium from the sediment core were obtained by them after (a) completely dissolving the phillipsite, (b) leaching the sediment sample with hot 6N hydrochloric acid and (c) dissolving the total sediment sample having particle size of less than 2 μm .

Analyses of Thorium isotopes obtained from fractions of the North Pacific core has indicated that there were movements of Ra^{228} within the sedimentary column; Thorium comes to the deposit primarily from the sea water and there is no evidence for the migration of Thorium isotopes within the sedimentary column.

Goldberg and Koide (1962) and Goldberg (1968) in their studies on the rates of sedimentation determined $\text{Th}^{230}/\text{Th}$ activity ratios in the deep sea sediments of the Pacific and Indian Oceans. Noakes, Supernaw and Akers (1967) have carried out a geochemical study of the coastal Mississippi river sediment at Greenville in order to investigate the occurrence and distribution of natural Thorium isotopes. In their analytical procedures, the coastal river sediments were destroyed in concentrated hydrochloric acid and the activity ratios of $\text{Th}^{230}/\text{Th}^{232}$ were determined. The sediment samples treated with hot 6N of concentrated hydrochloric acid do attack the mineral core of the sediment particle 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.

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

In the present investigations, the ratios of $\text{Th}^{228}/\text{Th}^{232}$ and Th^{230} on the surface of the sediments have been carried out. The procedure adopted

is to avoid attacking the mineral body of the sediments while extracting the materials.

SAMPLE COLLECTION

The sediment samples used in this study are the top layers (< 15cm deep) of sediments representing fresh sediments at different locations along the west coast of India. These samples were air-dried in aluminium trays and then used for the separation of Thorium isotopes. The sediment samples had particle size 2-4 μm (75%) and 4-10 μm (16%).

EXPERIMENTAL METHODS

(a) Surface leaching of Thorium :

Ethylene diamine tetra-acetic acid (EDTA) has been found to be the most efficient leaching agent as thorium in the ionic form is best complexed with EDTA at pH 3.00.

In the surface leaching processes, 500g of the uncrushed, air-dried sediment was shaken at the room temperature with 800ml of 5% EDTA adjusted to pH 3.00 for about 8 hours. The sediment was allowed to settle and the supernate was filtered through 0.22 μm membrane filter. The procedure was repeated eight times. The EDTA filtrate was acidified to pH 2.00 and then evaporated to dryness. To the dried extract, 15ml of distilled water and 1 ml of 2 N nitric acid were added. The solution was stirred and 200 mg instalments of ammonium persulphate were added and the solution was warmed till all the EDTA was destroyed. After destruction of EDTA, 30 mg of Fe (III) was added, Fe was precipitated as ferric hydroxide. The precipitate was dissolved in 10 ml of 8N nitric acid.

(b) Ion exchange method for separation of Thorium :

Anion-exchange resin, Dowex-1 x 8% (50-100 mesh) was washed with running distilled water to remove fine particles. 5g of the resin was then loaded in pyrex glass column (1x15cm).

Column operations :

(i) Dowex-1 resin was converted into nitrate form by passing 50 ml of 8N nitric acid at a flow rate of 1.0 ml/min.

(ii) The 8N nitric acid solution was passed through anion — exchange resin column at a flow rate of 0.5 ml/min. Thorium was adsorbed on the column. The effluent was rejected.

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

(iv) The adsorbed Thorium from the column was first washed with 10 ml of 0.1N nitric acid at a flow rate of 0.5 ml/min and then it was desorbed

with 50 ml of 1.0 N hydrochloric acid at a flow rate of 0.5 ml/min. The two effluents of nitric and hydrochloric acids containing thorium were pooled together and evaporated to dryness.

The Thorium present in the nitrate form in the residue was converted to chloride form by evaporating it to dryness with 1.0 ml instalments of concentrated hydrochloric acid.

Purification of Thorium :

The residue containing Thorium was dissolved in 10 ml of 8N hydrochloric acid and passed through another similar pyrex glass column (1 x 15 cm) containing Dowex-1 X 8% (50-100 mesh) in chloride form and the effluent was collected. The effluent was evaporated to dryness and the residue was converted into nitrate form by repeated evaporation to dryness with 1.0 ml instalments of concentrated nitric acid.

(c) Molecular plating of Thorium :

The purified Thorium nitrate residue was dissolved in 1.0 ml of 0.001 N nitric acid and then transferred to a plating cell. 20 ml of iso-propyl ether was added to the solution and a current of 5 ma was passed keeping the voltage to 400 volts. The plating was carried out at room temperature for one hour. A thin adherent film of Thorium was obtained on the stainless steel disc.

COUNTING OF THORIUM

The alpha spectrum of the plated Thorium sample was obtained using partially depleted silicon surface barrier detector, a low noise amplifier, a pre-amplifier and 400 channel analyser. The diameter of the detector was 16mm and it was mounted inside a brass vacuum chamber. The plated Thorium source was placed 5mm below the silicon detector. The resolution of the detector was 43 KeV full width at half-maximum at 5.108 MeV alphas. The counting efficiency was 30% for weightless samples plated on stainless steel discs (Joshi and Mishra, 1980). Thorium samples were counted for 1000 minutes because of the low Th^{232} , Th^{230} and Th^{228} activities in order to get satisfactory counting statistics.

RESULTS AND DISCUSSION

(a) $\text{Th}^{228}/\text{Th}^{232}$ and $\text{Th}^{230}/\text{Th}^{232}$ activity ratios on the surface of the coastal sediments collected from the Arabian Sea :

Fig. 1 shows a typical anomaly between the activities of Th^{232} and Th^{228} in the sediment sample collected from Goa. Table I gives the activity ratios of $\text{Th}^{228}/\text{Th}^{232}$ and $\text{Th}^{230}/\text{Th}^{232}$ from the surface layers of the coastal sediment samples collected from the west coast of India.

Large variations in the activity ratios of $\text{Th}^{228}/\text{Th}^{232}$ were observed from the surface sediment samples collected from the west coast of India.

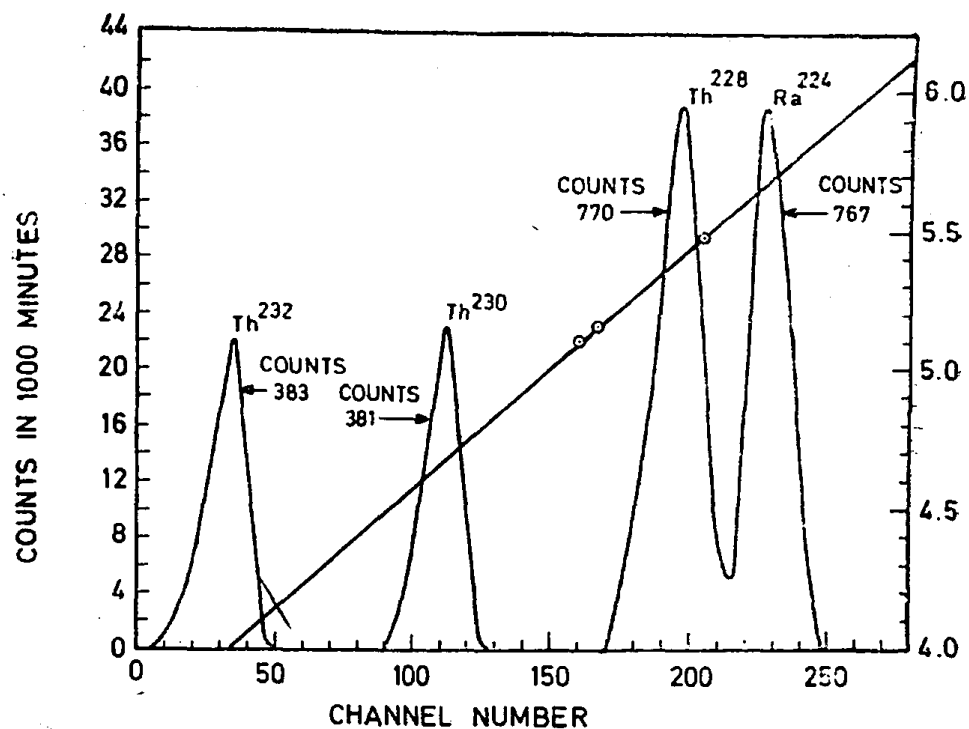


Fig. 1. Disequilibrium between Th²³² and Th²²⁸ in sediment sample from Goa.

Table I. Th²²⁸/Th²³² and Th²³⁰/Th²³² activity ratios on the surface labile layers of the coastal sediments of the Arabian Sea.

Place of Collection	Th ²²⁸ /Th ²³²	Th ²³⁰ /Th ²³²
Janjira	2.11	0.98
Suvandurg	2.13	0.97
Dabhol	2.14	0.99
Ratnagiri	2.06	0.99
Vijayadurg	2.16	0.96
Malwan	2.13	0.95
Vengurla	2.18	1.05
Goa	2.01	0.99
Karwar	2.04	1.07
Kumta	2.05	1.01
Honawar	2.02	1.00
Coondapur	2.03	0.98
Mangalore	2.00	0.99
Shertally	0.67	0.23
Alleppey	0.65	0.24
Chavara	0.64	0.24
Quilon	0.66	0.24

However, these variations in the ratios existing on the surface of the sediments get masked when special care is not taken in the analytical (chemical) procedure to avoid attacking the mineral core of the sediment. The ratios are

observed as 1.00 for sediments from monazite bearing areas of the Kerala coast, and for the sediments of the northern Arabian Sea, the ratios get distorted whenever these are completely destroyed before analysing for the Thorium isotopes.

The area between Mangalore and Janjira invariably shows the activity ratio of $\text{Th}^{228}/\text{Th}^{232}$ about 2.00 indicating a preferential accumulation (deposition) of Th^{228} in this region. The excess of Th^{228} over Th^{232} in the coastal sediments observed in the present work can be due to one or all of the following reasons:

- (i) Dissolution and transport of Ra^{228} from the surface of the sediments depending upon the coastal currents.
- (ii) Flow into the sea of the river waters and other types of land run offs with high values of $\text{Th}^{228}/\text{Th}^{232}$ and $\text{Ra}^{228}/\text{Th}$ ratios.
- (iii) Progressive weathering and leaching of the Thorium bearing minerals deposited in the coastal waters.

The circulation in the near shore region off the Kerala coast indicates a northerly drift in this region. The high ratios of $\text{Th}^{228}/\text{Th}^{232}$ in the surface sediments off Mangalore to Janjira are thus due to the net transport of Ra^{228} leached out of sediments of the Kerala region and because of the decay of Ra^{228} to Th^{228} during its northerly transport and its depositions in this region.

The ratio of $\text{Th}^{230}/\text{Th}^{232}$ in the monazite bearing areas of the Kerala region is found to be constant i.e. 0.24 for the sediments while this activity ratio is about 1.0 for the sediment samples collected from Mangalore to Janjira. The significance of these values is to be understood on the basis of dissolved Ra^{226} in the sea water and the relative abundance of Thorium and Uranium in the mineral core of the sediments.

- (b). **Cleansing surface labile layer of coastal sediments free of organic matter by phosphate-free hydrogen peroxide in the presence of 0.05N hydrochloric acid:**

Some sediment samples were treated with phosphate free hydrogen peroxide in the presence of 0.05N hydrochloric acid in order to obtain the activity ratio $\text{Th}^{228}/\text{Th}^{232}$ (leachable and organic forms). The supernate obtained after the hydrogen peroxide treatment and centrifugation was filtered. The filtrate was processed for column treatment and plated for Thorium as described earlier. The residue was also processed in a similar way to obtain the activity ratio of $\text{Th}^{228}/\text{Th}^{232}$ and $\text{Th}^{230}/\text{Th}^{232}$. Table II gives the activity ratios of $\text{Th}^{228}/\text{Th}^{232}$ and $\text{Th}^{230}/\text{Th}^{232}$ in the supernates and the sediment cores. Fig. 2 shows disequilibrium between Th^{232} and Th^{228} in the supernate after the hydrogen peroxide treatment of Chavara sediment from the Kerala region. Fig. 3 gives the equilibrium between Th^{232}

Table II. $\text{Th}^{228}/\text{Th}^{232}$ and $\text{Th}^{230}/\text{Th}^{232}$ activity ratios in supernates and core of the particles after 0.05N HCl + H_2O_2 treatment of the coastal sediments.

Place of collection	Remarks	$\text{Th}^{228}/\text{Th}^{232}$	$\text{Th}^{230}/\text{Th}^{232}$
Shertallay	Supernate	0.67	0.23
—do—	Organic matter free sediment.	1.00	0.23
Alleppey	Supernate	0.65	0.24
—do—	Organic matter free sediment.	1.01	0.24
Chavara	Supernate	0.64	0.24
—do—	Organic matter free sediment.	1.00	0.24
Quilon	Supernate	0.66	0.24
—do—	Organic matter free sediment.	1.00	0.24

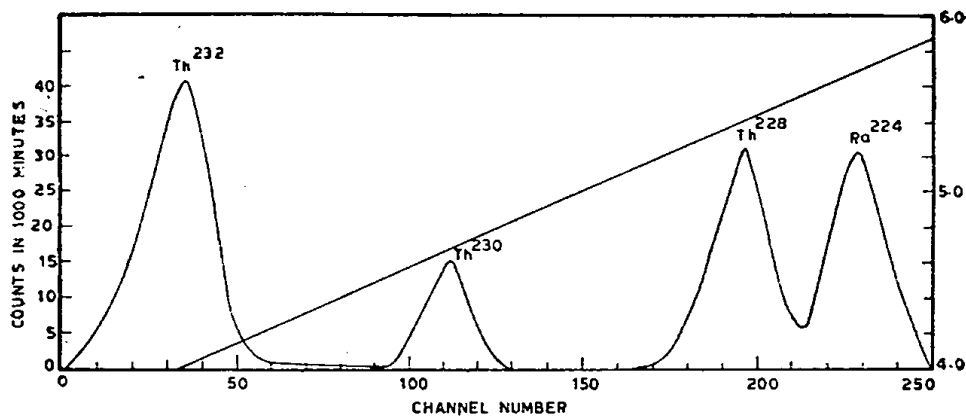


Fig. 2. Disequilibrium between Th^{232} and Th^{228} in supernate after H_2O_2 treatment of Chavara sediment.

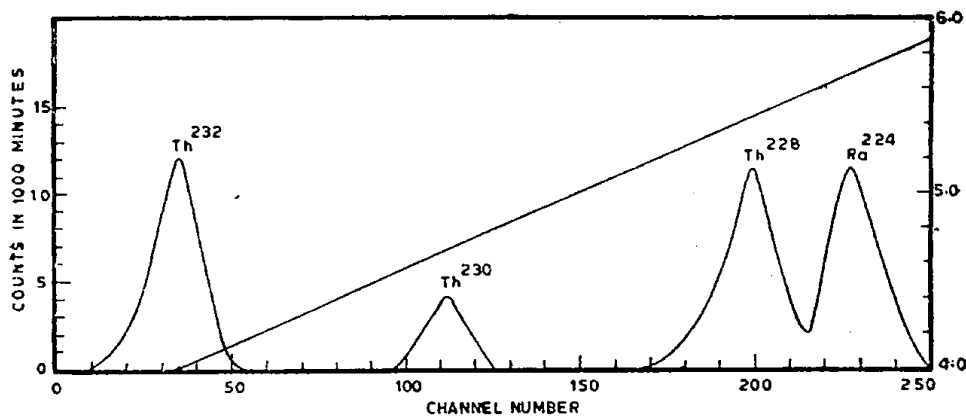


Fig. 3. Equilibrium between Th^{232} and Th^{228} in sediment sample from Chavara in Kerala State, after destroying organic matter.

and Th^{228} in the core of the sediment sample from Chavara after destroying the organic matter. It is seen from these experiments that disequilibrium between Th^{232} and Th^{228} thus exists only on the surface organic layer of the particles.

The agreement in the activity ratio 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 can be attributed to the immobility of Thorium from the sediments. The high activity ratios for $\text{Th}^{230}/\text{Th}^{232}$ between Mangalore and Janjira can be understood on the basis of transport and decay of U^{234} .

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