

# ALKALINE EARTH ELEMENTS IN MARINE SEDIMENTS OFF TARAPUR COAST

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WITH the release of radioactive materials to the sea, there is very marked uptake of radioactivity by bottom sediments and marine organisms. Organic material produced by the detrital material resulting from the disintegration of marine organisms and also from influx of terrestrial materials, etc., concentrate at the bottom. Bottom organic detritus is considered the source of nourishment for benthic invertebrates<sup>1</sup> and these benthos are utilised as food for human consumption. The larger benthic forms ingest the sediment, causing mechanical abrasion of the solid particles and acceleration of the solution of such materials as calcium carbonate by their stomach fluids which are somewhat acidic.

Even though the water concentration may be below maximum permissible level, some bottom living organisms may accumulate considerable amount of radioactivity through their food habits. Crozier<sup>2</sup> has calculated that *Stichopus* (Sea cucumbers), in certain shallow coastal areas of Bermuda, pass 6 to 7 kg. (dry wt.) of mud per square metre per year through their digestive tracts; in a certain enclosed area of 1.7 mi<sup>2</sup> the mud eaten annually may be from 500 to 1,000 tons.

Different isotopes of the same element generally behave identically, the degrees at which a given radio-isotope is taken up and retained by an organism depends to a large extent on the amount of the stable isotope of the same element present in the environment. Also, elements closely related to each other in their ionic properties will tend to behave similarly and thus simulate isotope dilution. Thus, the uptake of strontium-90 which is an important fission product having a high fission yield is guided both by the stable strontium and calcium present in the environment which is utilised by the organisms, i.e., the leachable portion present in the sediment. Thus, it is very important to study the leachable part of strontium and calcium present in the sediment in order to study the uptake of Sr-90 by benthic organisms.

As regards Ra-226, it contributes a significant part of our environmental alpha activity

and is important as it is closely in equilibrium with animal body.<sup>3</sup>

Sarma *et al.*<sup>4</sup> have extensively analysed sediments, sea-water and biomaterial samples off Tarapur coast for content of major and trace elements and natural radioactivities. They have given the values for the various elemental contents in the marine sediments after leaching with N/20 HCl, 5% EDTA, 1 N ammonium citrate and 1 N ammonium acetate but values for the different elements in sediments are not given after total decomposition in order to find out the leaching capacities of the leaching reagents used.

In the present work, premonsoon sediment samples collected off Tarapur coast were decomposed completely and analysed for Ra-226, calcium and strontium contents and the data obtained are compared with those reported for different leaches.

## METHOD

Sediment samples were oven-dried at 100–110° C. and 10 gm. of the sample were taken in a platinum dish (150 ml. capacity) and heated to 400° C. in an electric muffle furnace to destroy the organic matter present. After cooling the dish, it was treated with 80 ml. of nitric acid (3 N) and boiled. The leachate was centrifuged off and transferred to a 250 ml. pyrex beaker. The residue was transferred back to the platinum dish and dried. To the dried residue, 25 ml. of perchloric acid (60%) and 50 ml. of hydrofluoric acid (40%) were added and the acids evaporated to dryness. The treatment with perchloric acid and hydrofluoric acid was repeated twice. The perchlorates of elements left after the above treatment were dissolved in 2 N hydrochloric acid and filtered through Whatman No. 42 filter-paper. In order to decompose any residue left after the above treatment, the paper and the residue were placed in the platinum dish and heated to dull redness to destroy the paper. Residue in the platinum dish was treated with about 4 times its weight of sodium carbonate and fused at 900° C. in the muffle furnace. After cooling the dish, the solid was washed five times with 10 ml.

portions of distilled water and washings were discarded. Insoluble fraction was treated with nitric acid (3 N) and extract transferred to the original beaker.

Any insoluble portion that still remained was given hydrofluoric-perchloric acid treatment followed by sodium carbonate fusion. The final solution was made up to 250 ml. and aliquots of this solution were taken for the determination of Ra-226, strontium and calcium.

**Radium-226.**—Radium was determined after coprecipitation with barium sulphate.<sup>5</sup>

**Strontium.**—Strontium was precipitated as oxalate and determined by atomic absorption spectrophotometry using method of addition.<sup>6</sup>

**Calcium.**—Calcium was precipitated as oxalate and determined titrimetrically using standard EDTA-Mg solutions.<sup>7</sup>

#### RESULTS AND DISCUSSION

The values for radium-226, strontium and calcium after total decomposition of the sediments are given in Table I. Table II represents the values of the elements in sediments obtained by various leaching agents. From these data, it is seen that calcium is leached 89–100% by HCl, 56–100% by EDTA, 55–97% by citrate and 23–56% by acetate leach. For strontium, the corresponding values are 70–100% by HCl, 35–75% by EDTA, 12–83% by citrate and 23–79% by acetate.

TABLE I

Radium-226, strontium and calcium content in sediment after total decomposition

Sample No.	Location		Ra-226 $\mu\text{g. atom} \times 10^{-9}/\text{g.}$	Sr $\mu\text{g. atom/g.}$	Ca $\mu\text{g. atom/g.}$
6T	19° 55.4' N	72° 28.3' E	2.89	1.23	430
10T	19° 47.2' N	72° 37.9' E	3.37	1.29	428
11T	19° 44.9' N	72° 36.4' E	2.95	0.93	420
12T	19° 42.2' N	72° 34.9' E	4.10	1.39	525
13T	19° 39.4' N	72° 33.4' E	3.31	1.55	436
14T	19° 43.8' N	72° 28.5' E	..	1.39	440
16T	19° 46.9' N	72° 34.0' E	4.17	1.24	560
18T	19° 50.0' N	72° 34.2' E	4.37	..	488

As regards radium, the values obtained are 23–80% for HCl, 12–31% for EDTA, 5–17% for citrate and 2–8% for acetate leach.

Goldberg and Arrhenius<sup>8</sup> have used a technique which involves the preferential EDTA chelative dissolution of the sediment. This pro-

TABLE II

Ra-226, Sr and Ca contents in various leachates and % leached of the total

Sample	Leach	Ra-226		Sr		Ca	
		$\mu\text{g. atom} \times 10^{-9}/\text{gm.}$	% leached	$\mu\text{g. atom/g.}$	% leached	$\mu\text{g. atom/g.}$	% leached
6T	HCl	0.81	28	1.28	104	434	101
	EDTA	0.82	28	0.91	74	430	100
	Amm. citrate	0.50	17	0.60	49	235	55
	Amm. acetate	0.09	3	0.34	28	200	47
10T	HCl	0.78	23	1.28	99	434	101
	EDTA	0.59	18	0.81	63	312	71
	Amm. citrate	0.28	8	0.60	47	409	96
	Amm. acetate	0.16	5	0.38	29	200	47
11T	HCl	2.36	80	0.91	98	371	89
	EDTA	0.41	14	..	..	430	102
	Amm. citrate	0.50	17	0.77	83	409	97
	Amm. acetate	0.09	3	0.21	23	235	56
12T	HCl	2.25	55	1.28	92	557	106
	EDTA	0.82	20	1.04	75	441	84
	Amm. citrate	0.23	7	..	..	476	91
	Amm. acetate	0.31	8	1.10	79	235	45
13T	HCl	1.99	60	1.45	94	434	100
	EDTA	1.04	31	0.54	35	416	95
	Amm. citrate	0.34	10	0.30	19	409	94
	Amm. acetate	0.09	3	0.45	29	225	52
14T	HCl	..	..	1.10	79	434	99
	EDTA	..	..	0.57	41	457	104
	Amm. citrate	..	..	0.17	12	..	..
	Amm. acetate	..	..	0.41	29	102	23
16T	HCl	1.67	40	1.10	89	559	100
	EDTA	1.06	25	0.46	37	312	56
	Amm. citrate	0.32	8	..	..	447	80
	Amm. acetate	0.15	4	0.38	31	211	37
18T	HCl	1.98	45	..	..	499	102
	EDTA	0.53	12	..	..	462	95
	Amm. citrate	0.23	5	..	..	409	84
	Amm. acetate	0.10	2	..	..	172	35

cess was designed to remove the readily soluble phases of the sediment leaving the minerals as intact as possible. According to these authors, such a treatment would be expected to attack trace elements adsorbed onto the surface of the clay minerals but would leave the lattice structure of clay minerals of igneous rocks intact. In the present investigation, it is observed in case of radium, that EDTA removes only 12–31% of radium from the sediments. This indicates that most of the radium is firmly held in the crystal lattice of these sediment particles.



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## PREPARATION OF BIXIN AND METHYL BIXIN FROM INDIAN SEEDS OF *BIXA ORELLANA*

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**BIXA ORELLANA** is a shrub in Central and South America, and in India it grows into a tree. The plant is commonly associated with the Annatto dye obtained from the seeds; its earlier use for dyeing of fabrics has ceased with the development of synthetic dyes. Bixin is the main component and this is at present in considerable demand as a non-toxic fat-soluble food colour.

In the earlier method of isolation of Bixin,<sup>1</sup> the seeds were stirred with water for a few hours and filtered through a sieve in order to obtain crude annatto preparation which was later purified. The extraction is not efficient because the outer red coating of colouring matter is not detached fully even after shaking with water for six hours in a machine. Boiling the seeds with water brings in many impurities. Direct extraction of the seeds seemed to offer better possibilities and we have examined the use of various solvents. Further, a careful physical examination of the seeds showed that the seed-coat is quite hard and non-porous, that the kernel is also hard and the pigment is entirely on the seedcoat. Therefore, it is most convenient to extract the entire seeds without powdering; this reduces the difficulty of filtration of the extracts, and the extraction of other components present in the kernel. Petroleum ether and ether are not satisfactory as solvents; the best extraction could be carried out by means of acetone or ethyl acetate. Extraction in a Soxhlet apparatus is slow; direct boiling in a flask and decanting the extract through cotton is found to be most convenient. A typical experiment is given below:

The seeds of *Bixa orellana* (200 g.) were directly boiled with ethyl acetate (2 × 500 ml.), the solution decanted and concentrated. It deposited about 2.2 g. of pure crystalline labile bixin which was filtered off. The filtrate was poured into excess of petroleum ether with vigorous stirring, when 1.8 g. of a deep red solid was precipitated; it was filtered and mother liquor marked (A). On TLC, using silica gel as the adsorbent and employing the solvent (CHCl<sub>3</sub>-MeOH, 94:6) for developing the chromatogram, the solid was found to be mainly bixin with a small amount of deep orange impurity that did not move. Purification could be effected by taking the ethyl acetate solution of the solid and diluting it with petroleum ether, when pure bixin (1.5 g.) was precipitated. The mother liquor (A) obtained earlier was concentrated. The solid residue (5.2 g.) obtained was taken up in ether and separated into alkali-soluble and neutral portions. The alkali-soluble portion, after acidification followed by column chromatography over silica gel yielded some more of bixin (0.8 g.).

Thus, labile bixin was obtained as red prismatic needles, m.p. 197-99°,  $\lambda_{\text{max}}^{\text{CHCl}_3}$  502 (log  $\epsilon$ , 4.49), 471 (4.46) and 446 (4.35) nm.;  $\nu_{\text{max}}^{\text{KBr}}$  3300 (broad), 1725 (s), 1660 (w), 1615 (m), 1575 (s), 1430 (w), 1290 (m), 1260 (m), 1210 (m), 1165 (s), 1010 (w) and 965 (s) cm<sup>-1</sup>. It gave cornflower blue colour when treated with concentrated H<sub>2</sub>SO<sub>4</sub>.

Following the earlier procedure,<sup>2</sup> labile bixin has been converted into its methyl ester by shaking its solution in methanolic potassium