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STRONTIUM, CALCIUM AND MAGNESIUM CONTENTS OF SOME MARINE ALGAE FROM THE WEST COAST OF INDIA*

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ABSTRACT

As a part of programme of work on marine radioactivity in aquatic environment a few samples of algae were collected from the west coast of India and analysed for strontium, calcium and magnesium contents. Strontium to calcium atom ratio in brown algae was found to vary from 21.6×10^{-3} to 29.5×10^{-3} while in green and red algae it varied from 5.1×10^{-3} to 9.1×10^{-3} and 4.9×10^{-3} to 5.6×10^{-3} respectively. Brown algae accumulated strontium in preference to calcium from sea water.

INTRODUCTION

MARINE algae are economically important as sources of iodine, potash (Sverdrup *et al.*, 1957) in addition to their utilization as supplementary food, fodder and manure (Chidambaram and Unni, 1947; Dawson, 1966). Brown and red algae found all along the Indian Coast are valuable raw material for industrial products like 'agar' and 'alginate' (Thivy, 1958; Srinivasan and Santhanaraj, 1965). The coastal environment from where the algae are collected is likely to be contaminated because of the discharge from the nuclear plants and pollutants from the industrial establishments. As some marine organisms and plants selectively concentrate many elements from the aquatic environment (Vinogradov, 1953; Sverdrup *et al.*, 1957; Mauchline and Templeton, 1964) the pollutants discharged into the sea may reach human being through the sea food. It is therefore, necessary to know the chemical composition of algae to study the environmental contamination.

A few samples of algae of different groups–Chlorophyceae, Phaeophyceae and Rhodophyceae collected from the west coast of India were analysed for the contents of strontium, calcium and magnesium. The behaviour of stable strontium can be used to predict the fate of strontium-90 which forms consideable part of the fallout and discharge from the nuclear plants. Calcium and magnesium are important as the former is chemically similar to strontium and the latter forms an essential constituent of chlorophyll molecule.

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EXPERIMENT

Processing

Algae samples were collected from Bombay, Ratnagiri and Kovalum (near Trivandrum) on the west coast of India. After washing with sea water, the samples were initially dried in the folds of filter paper. They were then dried in an electric oven at 105°C. The dried material was ashed in a muffle furnace at a temperature of 500°C. The ash was dissolved in conc. HCl (100 mg ash/ml) and used for the various estimations.

Analytical technique

For the estimation of calcium and magnesium one ml of the stock solution was taken and diluted to 50 ml. 10 ml of this diluted solution were taken and the pH was adjusted to 5 with dilute ammonia using bromocresol green as indicator. At this stage iron if present, precipitates as Fe $(OH)_3$. The precipitate was centrifuged and discarded. The supernatant was transferred to a volumetric flask and the volume was made to 25 ml.

Calcium: Calcium in 1-2 ml of this diluted solution was precipitated as oxalate and determined titrimetrically using EDTA and standard Magnesium solution according to Henley and Saunders (1958).

Total Calcium and Magnesium: Total calcium and magnesium content was determined by directly adding excess of EDTA to 1-2 ml of the diluted solution and titrating excess of EDTA with standard magnesium solution. Magnesium content was calculated from the difference between the first and second determination.

Strontium: Viswanathan *et al.* (1969) have studied the interference due to the presence of oxalate on strontium determination by atomic absorption spectrophotometry and found that oxalate does not have significant interfering effect. Oxalate precipitation separates calcium and strontium from the bulk of the cations and anions present in the sample.

10 ml of the stock solution was taken and diluted to 50 ml. pH was adjusted to 5 with bromocresol green indicator and dilute ammonia. Iron precipitated as Fe $(OH)_3$ was centrifuged and discarded. The supernatant was made acidic (pH-1) with HCl, and 20 ml of saturated ammonium oxalate solution was added. The pH was readjusted to 5 with dilute ammonia. The precipitate was allowed to settle overnight. The oxalate precipitate was then centrifuged and dissolved in minimum quantity of dil. HCl (6N). Strontium was estimated by atomic absorption spectrophotometry using the method of addition.

As the phosphate content of algae samples is high the coprecipitation of phosphate with oxalate precipitation of calcium and strontium at pH 5 was studied. To 10 ml aliquots of solution containing calcium and strontium, 1000 to 10,000 μg of phosphate was added and calcium and strontium were precipitated as oxalate. The precipitate was centrifuged and the supernatant and the precipitate were analysed separately for phosphate by the molybdenum blue method according to Hansen and Robinson (1953). The results are given below:

Coprecipitation of phosphate with strontium and calcium oxalate

Phosphate in μg added to solution containing Ca and Sr	*Phosphate recovered in precipitate μg*	*Phosphate recovered in filtrate μg*
1000	Below detectable level	1000
2000	,,	2000
4000	,,	3800
10000	,,	9500

From the values given above, it is seen that no detectable amount of phosphate coprecipitates with calcium and strontium oxalate precipitate.

RESULTS AND DISCUSSION

Table 1 represents the details of the samples collected and the species analysed. Table 2 gives the values of strontium, calcium, magnesium and Sr/Ca atom ratios in different species of algae. In Table 3 are given the mean accumulation and discrimination factors for different groups of algae.

TABLE 1. *Details of collection and species analysed*

SAMPLE No.	SPECIES	DATE	LOCATION
Chlorophyceae			
1	*Enteromorpha intestinalis*	30-7-64	Trombay (Bombay)
2	,,	14-9-64	,,
3	,,	,,	,,
4	,,	1-10-64	Afghan church (Bombay)
5	,,	25-11-64	,,
6	,,	28-1-65	,,
7	*Ulva lactuca*	19-12-64	,,
8	*Caulerpa sertularioides*	,,	,,
9	*Caulerpa racemosa* v. *uvifera*	31-1-65	,,
Phaeophyceae			
10	*Sargassum* sp.	4-3-64	Ratnagiri
11	,,	8-12-64	,,
12	,, (near to s. *cintum*)	9-3-65	Kovalum
13	*Padina tetrastromatica*	22-12-64	Afghan church
14	*Padina* sp.	26-2-64	Ratnagiri
15	*Spathoglossum asperum*	2-2-65	Afghan church
Rhodophyceae			
16	*Catenella repens*	1-10-64	,,
17	,,	19-10-64	,,
18	*Gracilaria corticata*	31-1-65	,,
19	,,	9-3-65	Kovalum

From Table 2 it is seen that calcium content in algae ranged from 1856 to 25000 ppm dry wt. Variations in calcium content among the same species, *Enteromorpha intestinalis* collected during different months may be attributed to the age and different growth stages of algae in different seasons. Molisch (1895) and Pringsheim (1926) have demonstrated that different algae require very different quantities of calcium. Pillai (1956), while studying the seasonal changes in the chemical composition of different species of algae collected from Palk Bay near Mandapam found that there is increased absorption of elements during early stages of growth after rainy season, with limited growth during latter part of summer by which time algae attain maturity and disappear. Hass *et al.* (1935) studied calcium and magnesium metabolism in calcareous algae such as *corralina squamata* and found seasonal changes in amounts of these elements on a dry weight basis. In our analysis, it was observed that accumulation factor for calcium was higher than that for magnesium in all the species examined. Rao and Tipnis (1965) in their studies on the chemical composition of algae collected from the Gujarat Coast reported high calcium content in phaeophyceae compared to chlorophyceae. This was not observed in the present investigation.

TABLE 2. *Strontium, Calcium and Magnesium contents and Sr/Ca atom ratios in different species of algae*

Sample No.	Strontium ppm dry wt	Calcium ppm dry wt	Magnesium ppm dry wt	Sr/Ca $x10^3$
1	78	8744	74500	4.08
2	307	17280	16430	8.13
3	123	10990	28650	5.12
4	119	5980	10540	9.10
5	107	7403	14150	6.70
6	63	4688	17500	6.15
7	42	9813	31670	1.96
8	48	7814	7464	2.81
9	224	21370	118410	4.80
10	445	9456	2954	21.53
11	1458	19070	8790	34.97
12	646	10030	7440	29.47
13	228	4189	12930	24.90
14	380	6549	9155	26.55
15	—	16870	3784	—
16	19	1856	7874	4.68
17	29	3446	11200	3.85
18	139	13160	4237	4.83
19	304	25000	8375	5.56

Magnesium content in the species examined varied between 2954 and 1,18410 ppm dry wt. Magnesium content was found more in chlorophyceae compared to phaeophyceae and rhodophyceae. Rao and Tipnis (1965) have also reported high magnesium content in chlorophyceae. Very high magnesium content (1,18410 ppm dry wt.) was observed in one of the species of chlorophyceae — *Caulerpa racemosa* Among the species analysed *Enteromorpha intestinalis* showed consistently high values of magnesium. Thivy (1958) in her article on "Economic Seaweeds" emphasized that *Enteromorpha intestinalis* is rich in magnesium content. Strauss (1967) investigated the metabolism of alkali and alkali earth metals in algae collected from different media of varying composition and arrived at the conclusion that magnesium content is greater than calcium in chlorophyceae.

Strontium content in the samples investigated ranged from 19 to 1458 ppm dry wt. Among the groups of algae studied, both the strontium content and Sr/Ca atom ratios have been observed higher in phaeophyceae than chlorophyceae or rhodophyceae. Sr/Ca atom ratios varied between 1.96 and 9.10 x 10^{-3} in green algae, 3.85 and 5.56 x 10^{-3} in red algae and 21.53 and 34.97 x 10^{-3} in brown algae. Odum (1957) has reported Sr/Ca ratios of about 11-13 x 10^{-3} in aragonatic green algae and 3-4 x 10^{-3} in cases of red algae, while Goldsmith *et al.* (1955) have found some what higher ratios of 3.9 to 7.6 x 10^{-3} for corralines. Spooner (1949) studied the uptake of carrier free mixture of Sr^{89} and Sr^{90} added to seawater, by marine algae. He concluded that radioactive strontium was extracted from sea water by the brown seaweeds, in particularly by *Fucus serratus*. By contrast red and green algae extract 'active' strontium only to a small or negligible extent.

TABLE 3. *Mean accumulation and discrimination factors for Marine Algae*

GROUP	NO. OF SAMPLES	A (Sr)	A (Ca)	A (Mg)	D (Sr-Ca)
Chlorophyceae	9	15.3	24.8	24.5	0.6
Phaeophyceae	5	78.8	26.3	5.2	3.2
Rhodophyceae	4	15.3	25.9	5.5	0.5

Average concentrations of Calcium, Strontium and Magnesium in sea water taken for calculating accumulation and discrimination factors are 420, 8 and 1450 ppm respectively.

Concepts of Accumulation (A) and Discrimination (D) as defined by Bowen (1956) have been used in this paper to calculate accumulation and discrimination factors. Bowen defined an accumulation factor "A" as

$$A = \frac{\text{ppm element in dry organism}}{\text{ppm element in sea water}}$$

He has further, defined a discrimination factor "D" for the uptake of a pair of related elements X and Y as

$$D = \frac{X/Y \text{ in dry organism}}{X/Y \text{ in sea water}}$$

From Table 3 it can be inferred that the various species of algae concentrate strontium, calcium and magnesium from sea water. Marked discrimination for strontium in preference to calcium was shown by brown algae which is in agreement with that reported by Bowen.

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