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Mineral Composition of Seaweeds from Coral Islands of the Pacific Ocean as a Function of Environmental Conditions

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ABSTRACT: Contents of Fe, Mn, Cu, Zn and Pb were determined in Caulerpaceae seaweeds from shallows of coral islands in the south-western Pacific Ocean. Differences have been found in natural chemical properties of island environments in central and outer regions of the Ocean. Geochemical properties of island waters are shown to influence the mineral composition of the macrophytes studied.

INTRODUCTION

In a previous paper (Khristoforova et al., 1979) we investigated the heavy-metal content in the bivalve *Tridacna squamosa* from coastal waters of south-western Pacific islands as a function of ambient geochemical conditions. This investigation has ascertained that the mineral composition of the bivalve tissues depends on the chemical compositions of rocks forming the islands, those of coastal waters, and on conditions of water exchange in habitats of *T. squamosa*.

In the present paper we have studied the content of Fe, Mn, Cu, Zn and Pb in seaweeds of coral islands. Thus, a most important geochemical factor of the environment – the chemical composition of the substratum on which the seaweeds grow – remained constant throughout the study; the biogenic carbonate rock, forming the islands, was the same in all the cases.

MATERIALS AND METHODS

Common inhabitants of shallow waters of tropical coral islands, Caulerpaceae (green seaweeds) grow in places remote from intensive surfs, i.e. in calm waters (Vinogradova, 1977). We studied closely related species of seaweeds belonging to the genera *Caulerpa* and *Halimeda* (Family Caulerpaceae) collected near the Bio Island (Solomon Islands) and on Suvorov and Pukapuka (Danger) Atolls (Cook Islands). *Halimeda,* unlike *Caulerpa,* has calcareous thalli and plays a significant role in building coral reefs.

On Suvorov Atoll, samples were mainly collected near Anchorage Island situated north-east of the ring reef. The margin of the reef flat, fringing the island, faces the passage of the lagoon and drops abruptly 2–2.5 m. The vertical wall features numerous crevices, furrows and caverns and is populated by corals, bivalve molluscs and seaweeds. Over the whole height of the wall grow large- and small-sized *Halimeda: H. taenicola* Taylor and *H. micronesica* Yamada, which contribute about 50 % of all local seaweeds. At a depth of 1.5 m the prostrate-blistered alga *Caulerpa racemosa* and the fir-like *C. urvilliana* Mont. appear. From a depth of 0.7 m, among *Halimeda* and, further, *Caulerpa, Phipilia orientalis* A. et E occurred. The bottom at the foot of the wall was sandy.

Some samples were taken near the Mote-Tou Island situated at the south-western side of the atoll. *Caulerpa urvilliana* was collected from the inner reef flat and coral heads at a depth of 0.6–1.5 m. In shallow reef waters, seaweeds are rare but on the walls of the reef flat and coral heads, which occur in the lagoon, their number increases considerably.

In the Pukapuka Atoll, samples of seaweeds were collected down south, near the horseshoe-like Motu-Koe Island with its convex side facing the ocean and its concave side facing the lagoon. The sandy shore of the inlet inside the 'horseshoe' of the island gradually slops down. The benthic population is poor: on fine, easily suspended sand one can see only black holothurians. To the center of the lagoon (depth to 15 m) coral 'tables', sometimes rather expanded appear. The seaward reef flat was investigated. Here, the bottom was

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covered with coarse sand and coral debris. At about 1.5 m depth coral heads occurred, on which *Caulerpa urvilliana* was frequent; some *Halimeda micronesica* was also present.

At the small Bio Island, the shallow lagoon was investigated from the northern headland towards the reefs, beyond which was a drop-off. An exposed part of the intertidal zone consisted of weathered corallite plates. In water, these are gradually replaced by sand. The slope was very gentle. At a depth down to 1 m, *Caulerpa peltata* Lamour grew in large and dense patches accounting for 20–25 % of the total amount of local seaweeds. At depths of 0.4–0.8 m, we found abundant small and large *Halimeda*, namely *H. simulaus* and *H. discoidea* Dcne. Beginning from a depth of 1 m (about 100 m off shore), *H. discoidea* grew almost alone in the lagoon. The stony bottom was covered with white fine sand, easily suspendible.

The seaweeds collected were washed in sea water and dried in a vacuum drier at 85 °C. After hard acid mineralization, we determined (atomic-absorption spectrophotometer 'Perkin-Elmer-403') the metal content of the HCl solution. From all collected seaweeds, a herbarium was made.

In order to assess the geochemical conditions of various habitats, in areas of seaweed sampling and in some adjacent waters, water samples were taken in which – after filtration through membrane filters (0.45 μm pore size) and chemical concentration (extraction of chelates by chloroform as diethyldithiocarbaminates) – dissolved metal concentrations were determined. Using orthophenanthroline, we determined in all samples the Fe content colorimetrically: (1) the total content (from unfiltered, vaporized and mineralized samples), (2) the dissolved total (from samples mineralized by HNO_3), and (3) the dissolved free content (from untreated filtrates).

RESULTS

Table 1 lists the metal contents determined. In species of *Caulerpa* and *Halimeda* from Suvorov and Pukapuka Atolls the amounts recorded were lower in seaweeds from Bio Island. We found no Pb in seaweeds of the atolls: it is likely that Pb concentrations were very small and beyond the sensitivity of the method used for analysis. However, the Pb content in seaweeds from coastal waters of the Bio Island was considerable, approximating concentrations determined for Cu (2.46–3.69 ppm dry matter). The seaweeds studied differed significantly in Fe content. Minimal Fe content

Table 1. Metal content of seaweeds from coral islands. Values expressed as $\mu g\ g^{-1}$ dry matter

Location of station	Date of sample	Seaweed species	Fe	Mn	Zn	Pb	Cu
Suvorov Atoll Motu-Tou Is., reef flat	13. II.	*Caulerpa urvilliana*	19.40	9.45	3.73	not found	1.24
Suvorov Atoll Anchorage Is., wall of reef flat	14. II.	*Caulerpa racemosa*	15.15	4.63	9.02	not found	1.95
		Halimeda taenicola	27.62	6.43	5.95	not found	2.86
		Halimeda micronesica	25.99	7.43	6.93	not found	2.97
Pukapuka Atoll Motu-Koe Is., reef flat	17. II.	*Caulerpa urvilliana*	54.50	7.25	9.00	not found	2.25
		Halimeda micronesica	25.12	7.14	6.65	not found	3.20
Bio Island Lagoon between island and reef	22. XII.	*Caulerpa peltata*	72.66	7.64	8.87	3.69	2.22
		Halimeda discoidea	45.37	6.94	10.88	3.01	3.01
		Halimeda simulaus	41.63	6.90	9.85	2.46	3.20

(19.40 and 15.15 ppm) occurred in *Caulerpa* of Suvorov Atoll; the maximal one, in *Caulerpa* of the Bio Island (72.66 ppm). *Halimeda* from the same places also differed in Fe content: 27.62 and 25.99 ppm dry matter for Suvorov Atoll and 45.37 and 41.63 ppm dry matter for the Bio Island.

Differences in Zn content were less pronounced. For example, the Zn concentration in *Halimeda* from Suvorov Atoll was 5.95 and 6.93 ppm; in those from Bio Island, 10.88 and 9.85 ppm. Cu concentrations ranged from 1.24 to 2.22 ppm in *Caulerpa*, and from 2,86 to 3.20 ppm in *Halimeda*. No significant differences were found in Mn content of seaweeds from different areas.

Seaweeds from atolls also differed in their metal concentrations. Although such variations were less appreciable than between those of atolls and Bio Island, we succeeded in finding them within one species, *Caulerpa urvilliana*. The contents of Fe, Zn and Cu in *C. urvilliana* from Suvorov and Pukapuka Atolls were 19.40, 3.73, 1.24 and 54.50, 9.00, 2.25 ppm, respectively.

The lowest concentrations of Cu and Fe occurred in both *Caulerpa* species from Suvorov Atoll. *Caulerpa* species revealed considerable variations in Fe concentrations as a function of habitat conditions. Strongly calcareous seaweeds of the genus *Halimeda* collected in the same regions exhibited smaller variations in Fe content.

DISCUSSION

The chemical composition of rocks which form the shores of islands can noticeably influence the geochemical characteristics of near-island waters as well as the mineral composition of local organisms (Khristoforova et al., 1979). All island shores studied here consist of the same type of rock: coral lime-stone, poor in microelements. Located in the open ocean, in clear waters, the islands are neither populated nor subjected to any anthropogenic influences. Nevertheless, the seaweeds collected near these islands significantly differ in their microelement composition.

As is known, the mineral composition of seaweeds is affected by a number of factors: the time of sampling which determines both the physiological state of an organism and the hydrochemical characteristics of ambient waters; the depth of occurrence; the morphology and structure of thalli. However, of dominating influence are geochemical factors: the absolute and relative concentrations of elements in the seaweed habitat. In our opinion, the differences found in metal contents of seaweeds from coral islands, are mainly due to differences in geochemical conditions of the environment.

Suvorov and Pukapuka atolls are oceanic islands, situated in a remote region of the ocean, rather isolated from continents (Voronov et al., 1977). They are reef formations on submerged volcanic cones. In spite of the identity of rocks, forming the atolls, and the same position in the system of oceanic structures, each atoll features its own ecological peculiarities. The lagoon of Suvorov Atoll is deep (to 90 m), has a passage to and an active water exchange with the ocean. Element concentrations in water over various sites of seaweeds sampled within this atoll differed only slightly from those of water samples taken outside the outer reef flat (Table 2). It is assumed, therefore, that the microelement composition of seaweeds of the lagoon depends basically on the composition of the oceanic water entering the lagoon.

Pukapuka Atoll is formed by a closed-ring reef flat and has a shallow lagoon (to 15 m), well heated and with increasing concentrations of elements towards its center. Probably, this was the reason why the contents of metals in *Caulerpa* and *Halimeda* were greater here than in Suvorov Atoll. This difference was particularly pronounced in *Caulerpa urvilliana*. In Pukapuka Atoll, this seaweed contained Cu, Zn and Fe 1.8, 2.4 and 2.7 times more than in Suvorov Atoll.

The Bio Island is similar in its structure to the atolls studied. But it is situated in an outlying area of the ocean, within the shelf zone of the large San-Cristobal Island. Its lagoon is shallow. The reefs form an open ring, and waters of the lagoon easily mix with oceanic waters.

As can be seen from Table 2, the coastal waters of the Bio Island contain higher concentrations of dissolved Zn and Pb than the atoll waters. But the content of Cu and Fe in filtrates of these waters is small. We believe that results on the content of metals dissolved in waters do not adequately reveal the chemical factors of the environment, while sorption on suspended particles and binding of elements by metabolites of marine organisms considerably decrease the concentration of elements in a free form. This, probably, explains our data for the lagoon of the Bio Island – characterized by considerable water motion, great quantities of fine sand and abundant populations – where we found low concentrations of dissolved Cu and Fe. Beyond the reef bar, in the zone of strong wave action, no free Fe was found, though in mineralized samples (both filtered and, especially, unfiltered) concentration of this metal was the highest, when compared to that from other areas. Thus, information on total, dissolved total and dissolved free iron made it possible to assess the hydrochemical situation of the environment more adequately.

An increased amount of metals in coastal waters of Bio Island seems to be related to its location; this island

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Table 2. Contents of dissolved metals and total Fe ($\mu g\ l^{-1}$) in near-island waters of coral islands

Locality of sampling	Depth (m)	Cu	Zn	Pb	Mn	Fe	Fe_{dis}*	Fe_{total}
Suvorov Atoll Anchorage Is., wall of reef flat	2.0	3.4	24.8	4.1	8.8	4.0	8.0	23.0
Suvorov Atoll Motu-Tou Is., reef flat in front of drop-off to lagoon	0.8	3.9	5.0	2.3	7.2	6.0	14.0	16.0
Off Suvorov Atoll 1.5 km off shore	1500	5.2	26.0	3.5	11.4	not found	3.0	8.0
Pukapuka Atoll Motu-Koe Is., reef flat	1.5	4.0	16.2	1.5	13.8	9.0	17.0	21.0
Pukapuka Atoll Center of lagoon	15.0	12.0	100.0	6.8	45.0	16.0	27.0	30.0
Pukapuka Atoll Outer side of fringing reef	–	5.4	26.1	3.4	23.1	4.0	13.0	15.0
Bio Island Lagoon between island and reef, 100 m off shore	1.5	4.1	27.0	8.2	16.4	5.0	25.0	44.0
Bio Island 800 m off shore, near drop-off	6.0	3.0	32.8	12.5	23.3	not found	14.0	32.0

* Fe_{dis}: total dissolved Fe (upon acid decomposition of water filtrates)

is situated in the area of Pleistocene and recent volcanism. In this connection, we would like to mention here the geological work by Taylor and Hughes (1975) at Rennell Island (Solomon Sea, south of Guadalcanal Island). When studing the genesis of bauxites of Rennell Island, the authors concluded that bauxite deposits formed from volcanic ashes of hornblende andesites erupted by Pleistocene and recent volcanoes.

The diameter of residual grains of the ilmenite from sediments of Rennell Island leads us to believe that a volcanic source was 200 km distant. The nearest known volcano Mbano is situated south-west of the Guadalcanal Island, 180 km from Rennell Island.

Bio Island is much nearer, some 100 km south-east of this volcano. Hence we suggest that ash-falls were the main source of increased trace-metal contents in the coastal waters of that island. This assumption seems to be supported by results of pedological research undertaken during the same expedition by Drs V.O. Targuliyan and P.V. Yelpatyevsky. They found on upper terraces of the island, under an ancient tropical forest, mellow red carbonate ferrallitic soils, which seem to be a product of decomposition of ash sediments associated with lime-stones of the elevated platform.

As already mentioned, Bio Island is situated in the shelf zone of the large San-Cristobal Island. Hence abrasion of shore basalts may be an additional source of increased trace-metal amounts. Table 3 indicates that erupted basalts and andesites contain much larger amounts of elements than do sedimentary carbonate rocks. Furthermore, on the beaches of Bio Island pumice-stone fragments washed ashore occur. Finally, as Bio Island does not lie far from large populated islands-microcontinents, one can easily assume anthropogenic pollution effects, especially due to Pb from motor-car exhaust. In addition, for communication between islands, motor-boats, launches and small planes are used which run on ethyl fuel. Evidently then, suspended particles containing Pb fall on the water surface, and thus increase the content of this metal in the surface layer.

Table 3. Distribution of elements in different types of rocks. (After Turekian and Wedepohl, 1961; Vinogradov, 1962). All values expressed as % of rock weight

Element	Igneous rocks		Sedimentary rocks
	basalts	andesites	carbonates
Fe	8.56	5.85	$3.8 \cdot 10^{-1}$
Mn	$2 \cdot 10^{-1}$	$1.2 \cdot 10^{-1}$	$1.1 \cdot 10^{-1}$
Cu	$1 \cdot 10^{-2}$	$3.5 \cdot 10^{-3}$	$4.0 \cdot 10^{-4}$
Zn	$1.3 \cdot 10^{-2}$	$7.2 \cdot 10^{-3}$	$2.0 \cdot 10^{-3}$
Pb	$8.0 \cdot 10^{-4}$	$1.5 \cdot 10^{-3}$	$9.0 \cdot 10^{-4}$

CONCLUSIONS

In marine environments with a strong natural background of elements – e.g. in volcanic areas – or with addition of elements into the surrounding waters due to technogenic impact, a stable local situation can form, which, similar to that of certain land territories (Kovalsky, 1974), may be regarded as a biogeochemical situation characterized by some excess of elements in the environment and local inhabitants. The Bio Island with its shallow waters and resident organisms appears to be such an area.

Although the coral islands are formed by identical rocks, the biogenesis of coral reefs may produce an impact of chemical environmental factors, which, exercising their effect on the biota and reef-building organisms in particular, also affect the mineral composition of coral lime-stones. When decomposing and dissolving, the lime-stone, in turn, adds to the surrounding waters the microelements once abundantly accumulated. Finally, the released elements are incorporated into marine organisms. It therefore is not the environment alone which can influence the chemical composition of organisms, but the organisms themselves can modify the geochemical evolution of the environment.

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