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On Mineral Composition and Strontium Content of Calcium Carbonates secreted by Recent Marine Organisms and Fossil Calcium Carbonates: Mainly on Corals

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Abstract

The calcium carbonates secreted by recent marine organisms, mainly corals, and fossil calcium carbonates were examined concerning mineral composition and strontium content. Limestones from various districts in Japan were also examined in this study. The constituent mineral of all the recent corals which were examined, is aragonite, and the strontium content of them is nearly 0.9-1 % SrO. This figure corresponds to nearly five times amount of the strontium content of calcium carbonates by other organisms. But, as for the Mesozoic and Paleozoic specimens, there is no remarkable difference in the strontium content between fossil corals and the other fossil specimens. As to the strontium content of recent and fossil corals, there is a tendency that the strontium content gradually decreases with a lapse of time. Provided that the fossil corals originally contained nearly the same amount of strontium as recent corals, most of strontium contained in corals have been lost within a relatively short period.

Introduction

The writer (SHIGESAWA, 1967) presented the mineral composition and the strontium content of some specimens of molluscan shells from Japanese waters. Thereafter, he has continued investigation of the mineral composition and the strontium content of calcium carbonates secreted by recent organisms, fossil calcium carbonates and limestones. The skeletons of recent corals contain larger amount of strontium than the shells of recent mollusca and foraminifera. Therefore, in this paper, the results obtained from some specimens of recent and fossil corals are described, and these results are compared with those from recent and fossil molluscan and foraminiferan shells and limestones.

Experimental Procedures

The specimens examined in the present study are calcium carbonates secreted by recent marine organisms, fossil calcium carbonates and limestones. Calcium carbonates by recent organisms were mainly from Japanese waters and Southwest Pacific Ocean, and fossils and limestones examined were from Japan. But some specimens of

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recent and fossil corals from foreign countries were also examined. The following is the list of recent specimens:

Corals from Southwest Pacific Ocean, near the Caroline Islands (coll. the late Dr. M. MATUYAMA).

Corals from Tanabe Bay, Wakayama Pref., Japan (coll. Dr. S. NISHIMURA).

Coral from English Channel, near Biscay Bay (coll. Dr. E. HARADA).

Coral from Suruga Bay, Japan (coll. Dr. E. HARADA)

Foraminiferan shells from New Caledonia (coll. the members of Osaka Museum of Natural History).

Molluscan shells from western seashore of Borneo (coll. Mr. Z. IMAMURA).

Molluscan shells from Japanese waters (coll. Mr. N. SUMITOMO and the writer)

For the determination of mineral composition, x-ray powder diffraction method and microscopic observation by a polarizing microscope were adopted. Chemical analysis was carried out for the determination of calcium and strontium contents. The calcium content was determined by chelatometric titration, and strontium content was done by the method of x-ray fluorescent spectrographic analysis. As these methods are the same as those described in the previous paper (SHIGESAWA, 1967), the description in details was omitted. The error of the strontium content determined by this method was ±3% of the result obtained.

Results

The results obtained are listed in Tables 1, 2 and 3. In Table 1, are listed the results on the specimens of calcium carbonates secreted by recent marine organisms, and those on fossil specimens are contained in Table 2. In Table 3, the results on limestones are listed. Moreover, some results on molluscan shells are quoted from the previous paper.

Table 1. Constituent minerals and contents of strontium and calcium of the calcium carbonates secreted by recent marine organisms

Specimen No.	Name of specimen	Locality	Constituent mineral *	CaO (%)	SrO (%)	$\frac{Sr}{Ca}\times 1000$
1	*Deltocyathus vaughani* (YABE et EGUCHI)	Suruga Bay	A	52.90	1.01	23
2	*Acropora prostrata* (DANA)	Tanabe Bay	A	52.50	0.86	19
3	*Acropora* sp. 1	do.	A	52.54	0.90	20
4	*Acropora serealis* (DANA)	do.	A	52.95	0.91	20
5	*Acropora subulata* (DANA)	do.	A	53.27	0.96	21
6	*Acropora studeri* (BROIK)	do.	A	52.15	0.90	20
7	*Trachyphyllia geogroffi* (AUDOUIN)	do.	A	53.77	0.88	19

Table 1. Constituent minerals and contents of strontium and calcium of the calcium carbonates secreted by recent marine organisms (continued)

Specimen No.	Name of specimen	Locality	Constituent mineral*	CaO (%)	SrO (%)	$\frac{Sr}{Ca}\times 1000$
8	*Acropora* sp. 2	do.	A	53.20	0.90	20
9	*Porites* sp.	do.	A	54.27	0.95	21
10	*Dendrophyllia boschmai cyathohelioides* YABE et EGUCHI	Kinansho, Wakayama, 60-100m depth	A	52.11	0.94	21
11	*Fungia concinn* DEVVILL	Okinawa	A	51.84	0.89	20
12	*Fungia echinata* (PALLAS)	do.	A	53.45	0.87	19
13	*Keliopora corulea* (PALLAS)	Southwest Pacific Ocean	A	53.96	0.72	16
14	*Stylophora* sp.	do.	A	53.58	0.94	21
15	*Acropora* sp. 3	do.	A	53.19	0.84	19
16	*Caulastrea* sp.	do.	A	52.70	0.92	21
17	*Dendrophyllia coccinea* (EHRENBERG)	do.	A	54.12	0.87	19
18	*Acropora* sp. 4	do.	A	53.68	0.91	20
19	*Acropora* sp. 5	do.	A	53.59	0.95	21
20	*Pavona* sp.	do.	A	53.97	0.87	19
21	*Podabacia elebans lopata* (VAN DER HORST)	do.	A	54.12	0.92	20
22	*Dendrophyllia* sp.	English Channel	A	52.66	0.98	22
23	*Nucella freycineti* (DESHAYES)	Wakkanai, Japan	AC	54.20	0.15	3.3
24	*Myrilus grayanus* DUNKER	do.	AC	54.63	0.11	2.6
25	*Callista brevisiphonata* (CARPENTER)	do.	A	54.05	0.17	3.8
26	*Mactra chinesis* PHILIPPI	do.	A	54.38	0.17	3.7
27	*Fabulina hokkaidoensis* HABE	do.	A	54.92	0.14	3.0
28	*Solen krusensterni* SCHRENCK	do.	A	54.41	0.18	3.9
29	*Chlamys farreri nipponensis* KURODA	Tokyo Bay, Japan	C	54.19	0.09	1.7
30	*Pecten albicans* (SCHRÖTER)	do.	C	53.82	0.14	3.1
31	*Fusinus perplexus* (A. ADAMS)	do.	A	54.71	0.16	3.5
32	*Tonna luteostoma* (KÜSTER)	do.	A	54.32	0.15	3.3
33	*Omphalius pfeifferi* (PHILLIPPI)	do.	A	54.52	0.16	3.5
34	*Neverita didyma* (RÖDING)	do.	A	54.71	0.18	3.9
35	*Pleuroploca trapezium* (LINNE)	Shiono-misaki, Wakayama, Japan	A	55.03	0.15	3.2
36	*Barbatia lima* (REEVE)	do.	A	54.89	0.16	3.5
37	*Trochus sacellumrota* DUNKER	do.	A	54.52	0.19	4.1
38	*Vasticardium burchardi* (DUNKER)	do.	A	55.35	0.16	3.5

Table 1. Constituent minerals and contents of strontium and calcium of the calcium carbonates secreted by recent marine organisms (continued)

Specimen No.	Name of specimen	Locality	Constituent mineral*	CaO (%)	SrO (%)	$\frac{Sr}{Ca}\times 1000$
39	*Cholyconus fulmen* (REEVE)	Borneo	A	55.17	0.18	3.9
40	*Erosaria crosa* (LINNÉ)	do.	A	54.89	0.19	4.1
41	*Cypraea tigris* LINNÉ	do.	A	54.78	0.19	4.1
42	*Polinices pyriformis* (RECLUZ)	do.	A	55.40	0.25	5.3
43	*Tridachma* (*Flodacna*) *squamosa* LAMARCK	do.	A	54.32	0.18	3.8
44	*Oliva* sp.	do.	A	54.80	0.23	5.0
45	*Marginopora*	New Caledonia	A	52.11	0.19	4.3
46	*Peneroplis*	do.	A	49.02	0.13	3.1

* A: Aragonite; C: Calcite; AC: Aragonite and calcite.

Table 2. Constituent mineral and contents of strontium and calcium of fossil corals and coral limestones

Specimen No.	Name of specimen	Locality	Geological age	Constituent mineral *	CaO (%)	SrO (%)	$\frac{Sr}{Ca}\times 1000$
47	*Favosites* sp.	Miyazaki, Japan	Silurian	C	55.79	0.022	0.55
48	*Halysites gracilis* LAMBE	do.	do.	C	55.51	0.030	0.50
49	*Favosites jeffersonville* 1	Indiana, USA	Devonian	C	55.47	0.008	0.20
50	*Favosites jeffersonville* 2	do.	do.	C	55.28	0.010	0.30
51	*Syringopora niagarensis*	Alpena, Michigan, USA	do.	C	54.82	0.009	0.23
52	Coral limestone 1	Akiyoshi, Yamaguchi, Japan	Carboniferous	C	55.71	0.011	0.27
53	*Mentzelella socialis* MANSUY	Cambodia	Permian	C	55.24	0.061	1.5
54	*Michelinia multitabulata* (YABE et HAYASAKA)	Kesenuma, Miyagi, Japan	do.	C	55.12	0.076	1.9
55	Coral limestone 2	Kameoka, Kyoto, Japan	do.	C	55.23	0.015	0.38
56	Coral limestone 3	Kawachi, Shiga, Japan	do.	C	54.70	0.085	1.8
57	Coral, not identified	Itsukaichi, Tokyo, Japan	Jurassic	C	51.12	0.093	2.5
58	*Astrhelis* sp.	Kempsville, Virginia, USA	Miocene	A	51.52	0.72	20.

* C: Calcite; A: Aragonite.
Note: Some specimens contain small amount of quartz or other coloured minerals.

Table 3. Contents of strontium and calcium of limestones from Japan

Specimen No.	Locality	Geological age	CaO (%)	SrO (%)	$\frac{Sr}{Ca}\times 1000$	Remark
59	Yokokura, Kochi	Silurian	39.28	0.01	0.4	
60	Higoroichi, Iwate	do.	38.84	0.40	1.2	
61	Kamiise, Fukui	Devonian	51.68	0.26	4.1	
62	Fukuchi, Gifu	do.	49.59	0.07	1.1	
63	Akiyoshi, Yamaguchi	Permian	55.44	0.02	0.5	White
64	do.	do.	54.99	0.01	0.3	Light yellow
65	do.	do.	55.55	0.02	0.5	Gray
66	do.	do.	55.23	0.03	0.6	Dark gray
67	Akasaka, Gifu	do.	55.70	0.006	0.13	White
68	do.	do.	55.58	0.018	0.38	Dark gray
69	do.	do.	55.64	0.082	1.7	Parts of matrix
			55.49	0.11	2.3	Parts of fusuline fossil
70	do.	do.	55.63	0.11	2.3	Parts of matrix
71	do.	do.	55.86	0.048	1.0	Dark gray
72	do.	do.	55.87	0.017	0.35	Gray
73	do.	do.	53.67	0.059	1.3	Parts of fusuline fossil
			55.58	0.062	1.3	Parts of matrix, dark gray
74	Kawachi, Shiga	do.	55.34	0.11	1.7	Dark gray, contain fusuline
75	do.	do.	55.57	0.043	0.91	Gray
76	do.	do.	53.55	0.045	1.0	Dark gray
77	do.	do.	54.64	0.085	1.8	Dark gray, contain fossil
78	Fujiwara, Mie	do.	52.26	0.029	0.67	Dark gray
79	do.	do.	47.91	0.011	0.26	Dark gray
80	do.	do.	53.39	0.013	0.28	White
81	do.	do.	40.62	0.017	0.48	White
82	do.	do.	55.82	0.015	0.33	Parts of crinoid fossil
			55.71	0.014	0.33	Parts of matrix
83	Yakuno, Kyoto	do.	55.29	0.07	1.5	White
84	do.	do.	55.55	0.12	2.6	White
85	do.	do.	55.65	0.064	1.4	White
86	do.	do.	49.68	0.04	0.99	Gray
87	do.	do.	50.90	0.08	1.8	Dark gray
88	do.	do.	53.32	0.10	2.3	Dark gray
89	do.	do.	48.37	0.065	1.7	Black
90	do.	do.	55.65	0.064	1.4	Dark gray
91	Yura, Wakayama	Jurassic	53.48	0.11	2.4	Light brown
92	do.	do.	55.81	0.11	2.3	Gray
93	do.	do.	54.97	0.053	1.1	Brownish gray
94	do.	do.	53.69	0.046	1.0	Gray
95	Itsukaichi, Tokyo	do.	54.88	0.16	3.6	Fossil contained
96	do.	do.	55.55	0.048	1.2	Oolitic

Note: All of these specimens are constituted by calcite, but some of them contain small amount of quartz or other coloured minerals.

Consideration and Conclusion

Considering the mineral composition of the calcium carbonates secreted by recent marine organisms, the molluscan shells consist of calcite or / and aragonite, as generally known. The foraminiferan shells, although only two specimens were examined in this study, both consist of calcite. The specimens of corals covering more than twenty species, in which some deep-sea corals, such as *Dendrophyllia* sp. and *Deltocyathus vaughani* are involved, all consist of aragonite. It suggests that the consituent mineral of most of corals may be aragonite.

As for the strontium content in the calcium carbonates secreted by recent marine organisms, it is generally thought that the strontium content depends on the kind of organism and surroundings where they live. Every specimen of corals contains much larger amount of strontium, nearly 0.9-1% SrO, than molluscan and foraminiferan shells containing nearly 0.15-0.2% SrO, and the strontium content of recent corals corresponds to nearly five times that of molluscan and foraminiferan shells. This strontium value of 1% or nearly so is thought to be a characteristic common to corals and by which the calcium carbonates by corals may be distinguishable from those by the other organisms.

The values of strontium content of fossil corals are inconstant as shown in Table 2, but there is a tendency of the strontium content to decrease with a lapse of time. This tendency is not so well ascertained, as the fossil specimens of Mesozoic and Cenozoic Eras examined were very scanty. However, it is surely recognized that the decreasing tendency of strontium content exists among the specimens of Silurian, Devonian and Permian periods.

The constituent mineral of all the Mesozoic and Paleozoic fossil corals examined is calcite. The constituent mineral of recent corals examined is aragonite, as mentioned above. Therefore, the calcite of fossil corals, at least most of them, might be transformed from aragonite.

It is generally approved that the ratio of strontium to calcium in sea water has been stable since the later period of Paleozoic Era, as LOWENSTAM (1961) and others reported. In this study, well-preserved fossils were used as specimens, therefore the specimens of fossils are considered to be suffered neither mechanical deformation nor chemical reaction such as hydrothermal alteration. If the fossil corals consisted, at the time of their creation, of aragonite and contained the same amount of strontium as recent corals, the transformation of aragonite to calcite and loss of strontium would have gradually taken place in the geological time, and even after the transformation of aragonite to calcite, the loss of strontium would have continued.

On the other hand, considering the strontium content of limestones, it is inconstant, and there is no such specific tendency in it, as in the case of fossil corals. Accordingly, as for Mesozoic and Paleozoic specimens from Japan, remarkable differences in strontium content and constituent mineral could not be found between the fossil corals and limestones. Therefore, in fossil corals the transformation of aragonite to calcite and loss of most of strontium would have accomplished in relatively short period, perhaps in several tens of million years, and after that loss of strontium has continued.

Summarizing the above-mentioned, there is a tendency in corals that the strontium content decreases with a lapse of time. Provided that the ratio of strontium to calcium in sea water has been constant through the geological time, the fossil corals, at least most of them, were constituted of aragonite and contained nearly the same amount of strontium as that of recent corals, when they were created, and in fossil corals the transformation of aragonite to calcite and loss of most of strontium were accomplished in relatively short period, and after that loss of strontium has continued. The fact that difference between the fossil corals and the other specimens could not found as for Mesozoic and Paleozoic specimens, may be explained by the above-mentioned reasoning. The relation between the amount of loss of strontium and the lapse of time in geological time will be made clear in future.

In this paper, the hypothesis that the ratio of strontium to calcium has gradualy increased in geological time was not taken into consideration.

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