

## On the Mineral Composition and Strontium Content of Molluscan Shells from Japanese Waters

By

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### Abstract

The writer examined about 30 species of molluscan shells which were collected in Japanese sea (Tokyo Bay and the coast of Wakkanai City which is the northernmost of Japan) and 7 species of limnetic molluscan shells which were collected in Lake Biwa, Shiga Pref. He investigated the mineral composition by x-ray powder diffraction method, and quantitatively analysed Sr by x-ray fluorescent spectrographic analysis and also analysed Ca by cheletometric titration method. From the results obtained, he compared the mineral composition of the specimens from Wakkanai (the coldest sea in Japan) with that of those from warm waters (mainly collected in Tokyo Bay), and examined the difference in the strontium content between marine shells and limnetic shells, and also examined this difference between calcite and aragonite in shells.

According to the mineral composition, the specimens are classified into three groups: a) those consisting of aragonite, b) those consisting of calcite, and c) those consisting of both aragonite and calcite. In the specimens which were used in this research, those consisting of aragonite are the most and those consisting of calcite are the least. Those which consist of both aragonite and calcite, are composed of two layers of aragonite and calcite, and it is observed in them that aragonite composed of the inner layer and calcite the outer layer. Comparing the specimens composed of two layers from Wakkanai with those from Takeoka (Tokyo Bay), the inner aragonite layer in the former is thinner than that in the latter. But the remarkable difference of mineral composition in the specimens from various localities could not be found in this research.

When the Sr/Ca ratios obtained from the results of analysis are compared, those of specimens from Lake Biwa are remarkably smaller than those of marine specimens, i.e. ca. 1/10 of marine specimens. Also, the Sr/Ca ratios of marine molluscan shells is remarkably smaller than that of sea water, i.e. ca. 1/10 of sea water. And in marine specimens, this ratio in aragonite is larger than that in calcite. The difference of this ratio between the specimens from Lake Biwa and marine molluscan shells may be a distinctive feature of limnetic molluscan shells and a good help to distinguish fossil calcium carbonate of marine shells from that of limnetic shells.

### Introduction

Geochemical studies of calcareous fossils, limestones and molluscan shell

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materials have recently attracted larger attention with increasing of the interest on paleoecology and paleotemperature. An excellent study was performed by Heinz A. LOWENSTAM (1954) on the effect of temperature on skeletal carbonate minerals of mollusca. He found that the aragonite: calcite ratios in calcareous materials of some kinds of calcium carbonate-secreting marine organisms marked by a large increase in aragonite over calcite with increase in temperature were widely distributed. In our country, chemical and mineralogical studies on pearls and pearl oysters were performed in details by the members of National Pearl Research Laboratory and others, and K. WADA, a member of the above mentioned laboratory, investigated mineral composition of many marine molluscan shells. He described that there are three types in the mineral composition: a) shells which consist of aragonite, b) those consist of calcite, and c) those consist of both aragonite and calcite. But the difference in mineral and chemical compositions in molluscan shells from various places have scarcely been examined in Japan. In order to make clear the mineral composition of such biogenetic materials and compare the mineral composition of shells from the coast of Wakkanai City and those from other relatively warmer waters, and also to investigate the geochemical behavior of strontium in hydrosphere, the writer studied mineralogical composition and strontium content of molluscan shells which were mainly collected from Tokyo Bay, northernmost seashore of Hokkaido (Wakkanai) and Lake Biwa. The followings are the results obtained up to the present.

## Experimental

### 1. Specimens

The specimens used for this study are all Recent species, and the majority of them were drifted ashore, except those collected in Lake Biwa. They were collected at following localities:

Wakkanai City, Hokkaido Pref. (Okhotsk Sea)

Takeoka, Amaha-cho, Kimitsu-gun, Chiba Pref. (Tokyo Bay)

Miyazu City, Kyoto Pref. (Wakasa Bay)

Kobe City, Hyogo Pref. (Osaka Bay)

Otsu City, Shiga Pref. (Lake Biwa)

The specimens were marine except those from Lake Biwa. Wakkanai City is located in the northernmost of Japan, and its eastern part faces Okhotsk Sea. So, the specimens collected there were shells of mollusca which lived in the coldest zone of Japanese waters. Specimens from Takeoka (Tokyo Bay) were those lived in warm water, and they may represent the group lived in warm waters. Lake Biwa is the largest lake in Japan and it is located nearly in the center of Japan.

Therefore, specimens from there are considered to represent the limnetic molluscan shells in Japan.

## 2. Methods of Experiment

For determination of mineral composition, x-ray powder diffraction method, microscopic observation and Meigen reaction method were adopted. All the specimens were examined by x-ray powder method using a Philips Geiger Counter X-ray Spectrometer. The reflection of calcite d-spacing of  $3.03\text{\AA}$  is very intensive, and so even a small amount of calcite such as 1% or less which was contained in aragonite could be detected. However, sometimes it was difficult to detect 2 or 3% of aragonite in calcite, because the reflection of d-spacing of  $3.39\text{\AA}$  which was the principal reflection of aragonite, was not so intensive. Therefore, observation by a polarizing microscope and Meigen reaction method were used on some specimens, especially when no more than calcite was detected by x-ray examination.

Chemical analysis was performed to determine the quantities of Ca and Sr. Ca was determined by cheletometric titration. First, specimens were dissolved with hydrochloric acid. Next, they were slightly alkalified with ammonium hydroxide and ammonium chloride, and then boiled. After insoluble materials and precipitates were removed by filtering, titration was performed on filtrates. The quantity of Sr was determined by x-ray fluorescent spectrographic analysis using a Philips Geiger Counter X-ray Spectrometer. In this examination, tungsten radiation was used, and the analysing crystal was LiF. Powdered specimens were used for analysis, but before examination, 1.5 mg of  $\text{Rb}_2\text{CO}_3$  dissolved in pure water was added to 1 g powdered specimen as a standard on a water-repellent coated watch glass using a pipette, and specimen was mixed after it was dried. Strontium content was calculated from the ratio of the intensity of principal reflection of  $\text{SrK}\alpha$  at  $25.09^\circ$  to that of  $\text{RbK}\alpha$  at  $26.58^\circ$ , using the calibration curve which was prepared preliminary. The calibration curve was made by the ratio of the intensity of reflection at  $25.09^\circ$  to that at  $26.58^\circ$  in x-ray fluorescent spectra of many samples which were artificially made by adding 1.5 mg of  $\text{Rb}_2\text{CO}_3$  and various amount of strontium to 1 g of  $\text{CaCO}_3$ .

## Results

The results obtained are listed in Tables 1 and 2. According to the mineral composition, the specimens can be divided into three groups: a) those which consist of aragonite, b) those consist of calcite, and c) those of both aragonite and

calcite. In the tables, the mineral composition was shown by symbols A, C, and A C respectively. Some specimens were examined only on the mineral composition and were not analysed, and therefore they were not shown in Tables 1 and 2. They are as follows: (Localities were shown in parentheses.)

- a) Specimens which consist of aragonite:
- |   |                   |
|---|-------------------|
| <i>Anodonta woodiana lauta</i> (v. MARTENS) | (Otsu, Lake Biwa) |
| <i>Inversidens brandti</i> (KOBELT)         | (Otsu, Lake Biwa) |
| <i>Umbonium giganteum</i> (LESSON)          | (Takeoka)         |
| <i>Glycymeris yessoensis</i> (SOWERBY)      | (Wakkanai)        |
| <i>Tectonatica janthostoma</i> (DESHAYES)   | (Wakkanai)        |
- b) Specimens which consist of calcite:
- |                                    |             |
|------------------------------------|-------------|
| <i>Crassostrea gigas</i> (THUBERG) | (Wakkanai)  |
| <i>Ostrea gigas</i> (THUNBERG)     | (Hiroshima) |
- c) Specimens which consist of both aragonite and calcite:
- |   |            |
|---|------------|
| <i>Omphalius pfeifferi</i> (PHILIPPI)       | (Takeoka)  |
| <i>Rapana thomasi</i> CROSSE                | (Takeoka)  |
| <i>Siphonalia cassidariaeformis</i> (REEVE) | (Wakkanai) |
| <i>Patinopecten yessoensis</i> (JAY)        | (Wakkanai) |
| <i>Mytilus coruscum</i> (GOULD)             | (Kobe)     |
| <i>Mytilus coruscum</i> (GOULD)             | (Miyazu)   |

Calcite could not be detected in any of specimens which were collected in Lake Biwa. This is noteworthy, but this does not show that all the shells of limnetic mollusca consist of aragonite. The majority of the specimens from Takeoka and the half of the specimens from Wakkanai consist of aragonite. Comparing the specimens from Wakkanai with those from Takeoka, specimens which consist of both calcite and aragonite are more abundant in the former. As for *Crassostrea gigas* (THUNBERG), three specimens from three localities were used, and every one of them consists of calcite. The specimens which belong to family Pectinidae, consist of calcite, or both calcite and aragonite. *Pecten albicans* (SCHRÖTER) and *Chlamys farreri nipponensis* KURODA from Takeoka consist of calcite. The specimens which consist of both aragonite and calcite are interesting. Such specimens used in this research are composed of two layers, outer calcite layer and inner aragonite layer. *Spondylus cruentus* LISCHKE, *Mytilus grayanus* DUNKER, *Mytilus coruscum* (GOULD) and *Chlamys swifti* (BERNARDI) have a two layers structure. In the former three, the pink or purple outer layer consists of calcite and the white inner layer consists of aragonite, and in *Chlamys swifti* (BERNARDI) from Wakkanai, the inner aragonite layer is very thin. The hitherto mentioned was observed in bivalves, but a similar structure was also observed in roll-shells. In *Omphalius pfeifferi* (PHILIPPI), *Rapana thomasi* ROSSE, *Turbo cornutus* SOLANDER, and *Nucella freycineti* (DESHAYES),

Table 1. Constituent Minerals and Chemical Analysis of Marine Molluscan Shells.

Name of specimen	Location	Constitute Mineral*	CaO (%)	SrO (%)	Sr/Ca × 1000
<i>Turbo cornutus</i> SOLANDER	Takeoka	AC	54.30	0.15	3.3
<i>Galeostraea modesta</i> (REEVE)	Takeoka	A	53.06	0.18	4.2
<i>Neverita didyma</i> (RÖDING)	Takeoka	A	54.71	0.18	4.1
<i>Tonna luteostoma</i> (KÜSTER)	Takeoka	A	54.32	0.15	3.3
<i>Cancellaria spengleriana</i> (DESHAYES)	Takeoka	A	53.72	0.27	6.0
<i>Anadara subcrenata</i> (LISCHKE)	Takeoka	A	53.57	0.15	3.2
<i>Glycymeris vestita</i> (DUNKER)	Takeoka	A	54.52	0.41	9.0
<i>Chlamys farreri nipponensis</i> KURODA	Takeoka	C	54.19	0.09	1.7
<i>Pecten albicans</i> (SCHRÖTER)	Takeoka	C	53.82	0.14	3.1
<i>Spondylus cruentus</i> LISCHKE	Takeoka	{outer layer C	53.82	0.13	2.9
		{inner layer A	54.45	0.23	5.1
<i>Ostrea gigas</i> (THUNBERG)	Takeoka	C	54.24	0.10	2.4
<i>Nucella freycineti</i> (DESHAYES)	Wakkanai	AC	54.20	0.15	3.3
<i>Mytilus grayanus</i> DUNKER	Wakkanai	AC	54.63	0.11	2.6
<i>Chlamys swifti</i> (BERNARDI)	Wakkanai	AC	54.69	0.08	1.6
<i>Callista brevisiphonata</i> (CARPENTER)	Wakkanai	A	54.05	0.17	4.0
<i>Macra chinensis</i> PHILIPPI	Wakkanai	A	54.38	0.17	4.0
<i>Fabulina hokkaidoensis</i> HABE	Wakkanai	A	54.92	0.14	3.0
<i>Solen krusensternei</i> SCHRENCK	Wakkanai	A	54.41	0.18	4.1
<i>Solen strictus</i> (GOULD)	Kobe	A	53.88	0.17	4.1

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

Table 2. Chemical Analysis of Molluscan Shells from Lake Biwa.

Name of Specimen	CaO (%)	SrO (%)	Sr/Ca × 1000
<i>Semisulcospira bensoni</i> (PHILIPPI)	53.98	0.02	0.5
<i>Cipangopa'udina longispira</i> (SMITH)	54.78	0.01	0.3
<i>Lanceolaria oxyrhyncha</i> (v. MARTENS)	53.18	0.01	0.3
<i>Corbicula sandai</i> REINHARDT	54.45	0.01	0.3
<i>Unio douglasiae nipponensis</i> (v. MARTENS)	53.55	0.02	0.5
<i>Unio biwae</i> KOBELT	53.46	0.01	0.3
<i>Cristaria plicata spatiosa</i> (CLESSIN)	53.01	0.01	0.3

Note: These specimens consist of aragonite.

the outer layer consists of calcite and the inner layer consists of aragonite. But the structure in roll-shells is more complicated than that in bivalves.

From the results of chemical analysis, the ratio of Sr to Ca was calculated, and it was shown in Sr/Ca × 1000 in the tables. These values of the specimens from Lake Biwa are much smaller than those of marine specimens. So, it can be

considered that it results from the striking difference of ratio of Sr to Ca between lake water and sea water, and this small value may be an outstanding feature of limnetic molluscan shells. In marine specimens, this ratio of shells which consist of calcite is smaller than the ratio of those consist of aragonite. And such a difference can be found in calcite and aragonite layers in the same shells, such as *Spondylus cruentus* LISCHKE. Accordingly, in shells which consist of both calcite and aragonite, the ratio usually takes an intermediate value between those of calcite and aragonite shells.

### Consideration and Conclusion

The marine specimens which were used in this research were collected in seashores of central and northern parts of Japan. As many specimens were revealed to consist of aragonite, in Japanese waters shells consisting of aragonite may be the most abundant in three types of mineral composition. It is interesting that all the specimens from Lake Biwa consist of aragonite, and the writer thinks it necessary to investigate the limnetic molluscan shells from other localities in Japan. From the mineral composition, the specimens which are composed of two layers of aragonite and calcite are noticeable. According to the results hitherto obtained, calcite always builds up the outer layer and aragonite dose the inner layer. Three specimens belonging to family Ostreidae from three localities were used, and every one of them consists of calcite. And also three specimens of family Mytilidae from three localities were all composed of two layers of aragonite and calcite. Comparing the specimens from Wakkanai with those from Takeoka (Tokyo Bay), they are not so different in mineral composition. Although the specimens used in this research were not so much, it is suggested that there is no remarkable difference in mineral composition in connection with localities in Japanese sea. But in specimens which were composed of two layers of aragonite and calcite, the inner aragonite layer in specimens from Wakkanai is generally thinner than that in those from Takeoka. Data are not so sufficient to say the relation between the ratio of calcite to aragonite and temperature of sea water as shown by H.A. LOWENSTAM, but it is probable to say that growth of the inner aragonite layer and that of the outer calcite layer may be diversely affected by the temperature of sea water in shells which are composed of two layers.

Strontium content is remarkably small in specimens from Lake Biwa. This is considered to be a distinctive feature proper to limnetic molluscan shells. Also, it will be a great help to distinguish fossil calcium carbonate of marine shells from that of limnetic shells. It is well known that Sr coexists with Ca in carbonate and  $\text{SrCO}_3$  crystallizes in a aragonite structure. Therefore, Sr is found more abundant

in aragonite than in calcite. A similar relation is also known in organogenetic calcium carbonate, i.e. strontium content of shells consisting of aragonite differs from that of shells consisting of calcite. And this difference is known between the inner aragonite layer and the outer calcite layer in the same shell.

According to K. RANKAMA and Th. G. SAHAMA, in sea water Sr is contained 13 g/ton and Ca 400 g/ton, and therefore  $Sr/Ca \times 1000$  is 32.5, which comes to about ten times as much as the value obtained from marine shells in this research. If it is assumed that Ca and Sr in sea water were lost mainly by physiological action of organisms, Sr:Ca ratio might have gradually increased through the long geological ages in sea water and attained such values as mentioned above.

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### References

- HABE, T., 1965, Coloured illustration of the shells of Japan, (2): Hoikusha.
- HAMADA, T., 1964, Note on the drifted Nautilus in Thailand: *Scientific papers of the College of General Education, University of Tokyo*, Vol. 14, No. 2, pp. 255-283.
- HARADA, J., HARITANI, Yu, and NAGAI, T., 1957, Fluorescent x-ray spectrographic method: *Journal of the mineralogical society of Japan*, Vol. 3, No. 4, pp. 338-357.
- KOBAYASHI, I., 1964, Introduction to the shell structure of bivalvian mollusca: *Earth science*, No. 73, pp. 1-12.
- KIRA, T., 1964, Coloured illustration of the shells of Japan: Hoikusha.
- KULP, J.L., TUREKIAN, K.K., and BOYD, D.W., 1952, Strontium content of limestones and fossils: *Geol. Soc. America Bull.*, Vol. 83, pp. 701-716.
- LOWENSTAM, Heinz A., 1954, Factors affecting the aragonite: calcite ratio in carbonate-secreting marine organisms: *The journal of geology*, Vol. 62, No. 3, pp. 283-332.
- RANKAMA, K., and SAHAMA, Th. G., 1949, *Geochemistry*.
- SIEGEL, F.R., 1958, Effect of strontium on the aragonite-calcite ratios of Pleistocene corals: *Geol. Soc. America Bull.*, Vol. 69, p. 1643.
- TUREKIAN, K.K., 1955, Paleoecological significance of the strontium-calcium ratio in fossils and sediments: *Geol. Soc. America Bull.*, Vol. 66, pp. 155-158.
- TUREKIAN, K.K., and ARMSTRONG, R.L., 1961, Chemical and mineralogical composition of fossil molluscan shells from the Fox Hills Formation, South Dakota: *Geol. Soc. America Bull.*, Vol. 72,

II, pp.

- WADA, K., 1961, Crystal growth of molluscan shells: *Bulletin of the National Pearl Research Laboratory*, No. 7, pp. 715-828.
- WADA, K., 1962, Biomineralogical studies on the mechanism of pearl formation: *Bull. National Pearl Research Laboratory*, No. 8, pp. 948-1059.
- WADA, K., 1964, Studies on the mineralization of the calcified tissue in molluscas-VII: *Bull. National Pearl Research Laboratory*, No. 9, pp. 1078-1085.
- WADA, K., 1964, Studies on the mineralization of the calcified tissue in molluscas-VIII: *Bull. National Pearl Reserach Laboratory*, No. 9, pp. 1087-1098.