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CONDITIONS CONTROLLING THE CRYSTAL FORM OF CALCIUM CARBONATE MINERALS (2)

(Mineralogical Study of Mollusca)

By

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Introduction

As it has been touched upon in the writers' preceding report¹⁾, there are four crystal forms in calcium carbonate minerals. Among them calcite and aragonite are the forms that are able to be formed at the temperatures and pressures encountered near the surface of the earth. Among the factors controlling the form of calcium carbonate minerals under the condition, that the influences of the temperature and the presence of magnesium ion etc. have been discussed in the same report and the others²⁾.

In the present report the writers discuss the results of experiments upon more than ten kinds of mollusca, which are representative samples of creatures producing calcium carbonate minerals under the conditions of temperature and pressure mentioned above.

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Species of mollusc	Environment of habitation
<i>Ostrea gigas</i> THUNBERG	To a depth of 20m below sea level, on rocks where fresh water are pouring in, never in highly saltish water.
<i>Patinopecten yessoensis</i> (JAY)	Between 20m and 200m below sea level, in sandy mud in saltish cold sea water.
<i>Neptunea arthritica</i> (BERNARDI)	Between 20m and 200m below sea level, though sometimes peeps over the level at low tide, on rocks in the sea water of a cold current.
<i>Tectura pallida</i> (GOULD)	On a rocks.
<i>Corbicula japonica</i> (PRIME)	Only in a low saltish (S=0.8–1.8‰) water, where fresh water is pouring in.
<i>Arca navicularis</i> BROGUIERE	In the sands of a rather northern shallow sea, where no fresh water is pouring in.
<i>Mya japonica</i> JAY	Co-exists with genus <i>Ostrea</i> , but even in fresh water at a beach and never in deep sea.
<i>Tellina</i> sp.	To a depth of 20m below sea-level. From Hoku-riku district to Sakhalin.
<i>Gomphina melanaegis</i> RÖMER	To a depth of 20m below sea-level, in sandy mud, in rather northern sea.
<i>Protothaca euglypta</i> (SOWERBY)	In sandy mud of a very shallow sea. Only northern district from Iwate prefecture.
<i>Glycymeris yessoensis</i> (SOWERBY)	To a depth of 200m below sea-level, in the sea water of a cold current.
<i>Mactra sulcataria</i> REEVE	Between 20m and 30m below sea-level, in sandy mud in the sea-water of a cold current, never in low saltish water.
<i>Panope japonica</i> ADAMS	Between 20m and 200m below sea level, in silt, never in Honshu.

Samples and their environments

The samples used in this experiment are all recent species which can be collected along the coast of Hokaido, namely in the Japan Sea at Oshoro, Shioya Village and Zenibako, Otaru City (on Ishikari Bay); in the Okhotsk Sea at Esashi, Kitami Province; in the Pacific Ocean at Atkkeshi Town.

Various and complete data about the sea waters near every one of these places are well known through the observations by marine laborato-

ries or by observation ships. The details about the samples are tabulated as follows:

Microscopic observations

The general microscopic aspect of a thin cross section of mollusca is shown in Fig. 1. It is well known that the shell of a mollusc consists of three layers. But the finer structures through crossed nicols are found to be more interesting as follows:

In every layer many fine crystals of calcium carbonate minerals, calcite or aragonite, lie side by side in a definite direction. In lamellar layer (inner layer) they lie almost parallel to the inside wall of a shell, in prismatic layer (middle one) obliquely to the wall and in periostracum (outer one) almost at right angles to the wall, though in the last two layers they change their directions nearly to parallel to the wall as they draw nearer to each outer side.

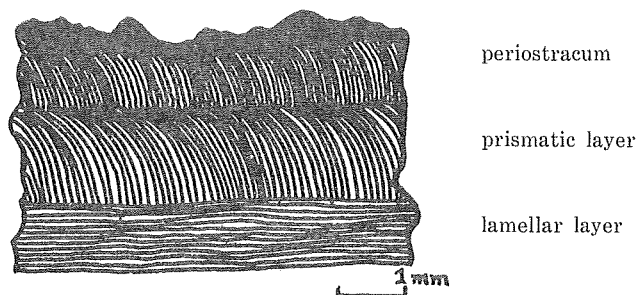


Fig. 1. The structure of cross section (*Patinopecten yessoensis* (JAY).

At the growing front part of a shell only the inner layer develops itself and in some cases, where the development of the outer two layers is observed, the development of the inner layer is far better than that of the other. In some species the middle layer is missing. In all these cases the fine structure in every layer is almost analogous to that mentioned above.

In etching the section with dilute hydrochloric acid and taking its electron-microscopic photograph, a pattern of many blending lines is observed. This pattern of the part impreviuous to etching seems to consist mainly of organic substances, which spread into a three dimensional network containing the crystals of calcite or aragonite in each mesh. To

ascertain this assumption Laue photographs of genus *Glycymeris* of various geological ages were taken along the layers. In genus *Glycymeris*, as reported by TSUBOI¹⁾, calcium carbonate exists only in aragonite state and its crystals lie side by side almost along the C-axis, though the disorder in the direction of the crystal arrangement is more remarkable as the age of the specimen is older. This may perhaps be caused by disappearance of organic substances by decomposition, which sustain the arrangement of the crystals. By the way these genus *Glycymeris* specimens contain from 10 to 30% of organic substances according to the results of a chemical analysis.

Differential thermal analyses

Differential thermal analysis is applied to *Corbicula japonica* (PRIME), which consists mainly of aragonite and partially of calcite. The results are shown in Fig. 2.

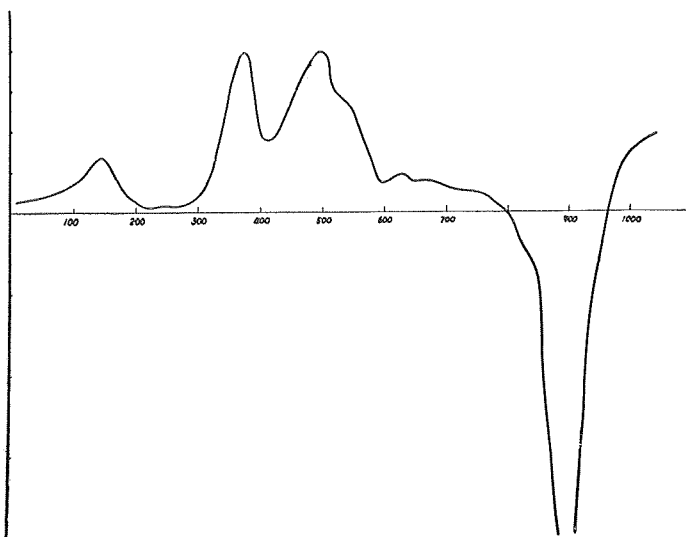


Fig. 2. The differential thermal analysis curve of *Corbicula japonica* (PRIME).

There is an exothermic peak as about 400°C, and another one beyond 500°C. Then some trifling changes are observed until 900°C and beyond it a remarkable endothermic peak is observed.

Examining these results, the first peak as about 400°C is assumed to

depend upon the thermal decomposition of organic substances in the sample, the second peak beyond 500°C upon the transition from aragonite into calcite and the last great endothermic peak upon the decomposition of calcite into calcium oxide and carbondioxide.

In the analyses of some other samples, a second peak beyond 500°C is obviously observed in every case excepting the samples that contain no aragonite, such as *patinopecten yessoensis* (JAY). The last endothermic peak is so large in every case that the curve goes out of scale. When one determines not to let the curve go out of scale, the other peaks become too small in his graph to be observed, obviously. As for the first peak, various types are observed in their situations and degrees. This seems to correspond to the fact that the quantity of the organic substances in the molluscs ranges from 10 to 30% and the kind also differs respectively.

X-Ray examinations

The Norelco-Geiger-X-ray spectrometer was also applied to all samples. Especially as for *Patinopecten yessoensis* (JAY), in which three layers are distinctly observable and separable respectively due to its

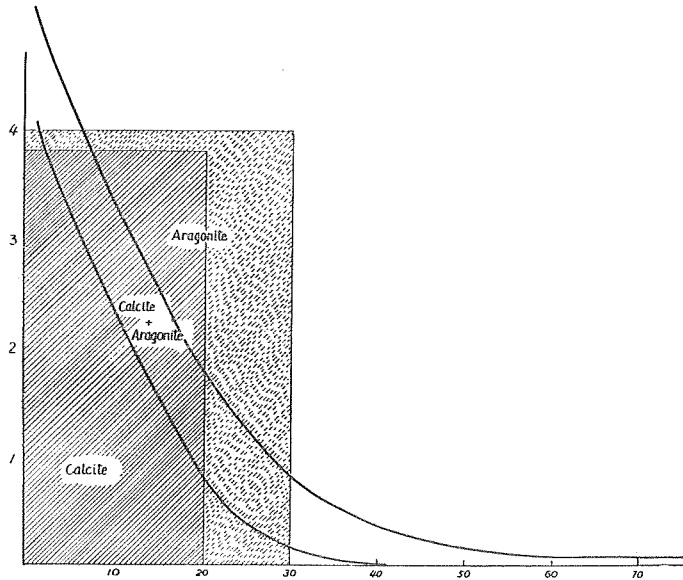


Fig. 3. Diagram of conditions crystallizing calcite and aragonite in mollusca.

TABLE 1. X-ray diffraction patterns of mollusca.

Index	Sample		<i>Patinopecten yessoensis</i> (JAY)		" lamellar layer		" prismatic layer	
	Calcite <i>d</i>	Aragonite <i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
3.86			3.87	13	3.87	14	3.87	17
		3.40						
		3.25						
3.03			3.04	83	3.04	86	3.04	99
		2.85	2.85	9	2.85	9	2.85	12
		2.72						
2.49			2.50	13	2.50	14	2.50	16
		2.48						
		2.41						
		2.37						
		2.34						
2.28			2.29	17	2.29	18	2.29	20
		2.26						
		2.24						
		2.19						
		2.11						
2.09			2.09	15	2.09	16	2.09	18
		1.99						
1.91			1.90	29	1.90	30	1.90	34
		1.89						
1.87			1.87	23	1.87	24	1.87	27
		1.82						
		1.75						
		1.73						
1.62								
1.61								
		1.56						

structure, it is applied to every layer. As for *Neptunea arthritica* (BERNARDI) in which two layers, namely an outer brown layer and an inner white one, are distinct and separable, the spectrometer was applied not only to those layers but also to every layer. The results are given in Table 1.

It is evident from the results shown in the table, that *Ostrea gigas* THUNBERG and *Patinopecten yessoensis* (JAY) consist only of calcite. Especially in the latter, each of three layers consists of the same state calcite. *Neptunea arthritica* (BERNARDI), *Tectura pallida* (GOULD), *Corbicula japonica* (PRIME) and *Protothaca euglypta* (SOWERBY) consist of aragonite and calcite, amongst which *Neptunea arthritica* (BERNARDI) the lamellar layer consists of calcite and its periostracum of calcite and aragonite. All the other specimens consist of aragonite only.

Oceanographical consideration

Figure 3 shows the results published in the writer's first report

" periostracum		<i>Ostrea gigas</i> THUNBERG		<i>Neptunea arthritica</i> (BERNARDI)		" lamellar layer		" periostracum	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
3.87		3.87	12	3.87	9	3.87	17	3.87	8
				3.40	18			3.40	28
				3.28	9			3.28	14
3.04	76	3.04	98	3.04	52	3.04	100	3.04	46
2.85		2.86	10						
				2.70	11			2.70	17
2.50		2.49	14	2.50	12	2.50	23	2.50	11
				2.48	7				
				2.41	6				
				2.38	8			2.38	12
				2.35	8			2.35	12
2.29		2.28	18	2.29	12	2.29	23	2.29	11
2.09		2.09	16	2.10	12	2.10	23	2.10	11
				1.98	11	1.98	21	1.98	17
1.90		1.92	30	1.91	11	1.91	21	1.91	10
				1.88	12	1.88	23	1.88	18
1.87		1.87	24	1.87	13	1.87	25	1.87	12
				1.82	5	1.82	10	1.82	16
				1.75	5	1.75	10	1.75	16
		1.63	8						
		1.61	10	1.61	6	1.61	12	1.61	5

with annexed data on the magnesium chloride consistency and the temperature of sea-water well known in the field of oceanography.

It is an established fact, that in any places on the earth the kinds and quantities of ions in sea-water are almost constant, especially their relative quantities are practically definite so long as there is no dilution by pouring-in of water from large rivers or a lake. Also it is acknowledged that the salinity of sea-water (S%) is proportional to its chlorine ion (Cl-%) consistency. M. Kundsén has given an equation as follows:

$$S\% = 1.8050 \text{ Cl}^{-}\% + 0.03$$

In as much as the percentage of magnesium chloride in the salinity is 10.878, and the salinity along the coast of Hokkaido ranges from 32 to 34³⁾, it follows that magnesium chloride consistency is about 3% there. In general the salinity becomes gradually smaller, the measurements are more, but it does not become smaller than 33, so far as this report is concerned.

<i>Tectura pallida</i> (GOULD)		<i>Corbicula japonica</i> (PRIME)		<i>Protothaca euglypta</i> (SOWERBY)		<i>Tellina</i> sp.		<i>Arca navicularis</i> BRUGUIERE	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
3.85	10								
3.38	23	3.40	31	3.40	32	3.40	42	3.40	34
3.28	13	3.28	20	3.28	19	3.28	26	3.28	20
3.04	41	3.01	11	3.04	9				
						2.87	8	2.88	9
2.71	16	2.70	23	2.71	20	2.70	33	2.70	26
2.49	13					2.49	21		
		2.48	17	2.48	17	2.48	20	2.48	17
2.42	9	2.41	10	2.41	9	2.41	11	2.41	12
2.38	13	2.38	17	2.37	17	2.38	23	2.38	19
2.37	10	2.34	14	2.34	13	2.34	19	2.35	15
2.28	10								
		2.19	10	2.19	9	2.20	9	2.24	7
2.11	9	2.11	10	2.11	10	2.11	7	2.20	8
2.09	11							2.11	10
1.98	16	1.98	23	1.98	21	1.98	28	1.98	23
1.91	13								
1.88	12	1.88	16	1.88	12	1.88	17	1.88	15
1.87	13								
1.31	8	1.82	12	1.82	11	1.82	14	1.81	11
1.75	10	1.75	13	1.75	11	1.75	18	1.75	15
1.73	7	1.73	11	1.73	8	1.73	13	1.73	10
1.61	7								

The temperature of sea-water is generally under 20°C⁴⁾, though it sometimes partially goes up to about 30°C in summer, and down to about 0°C⁵⁾⁶⁾ in winter. The greater the depth, the smaller the temperature change by seasons becomes.⁷⁾⁸⁾

Judging from the considerations mentioned above, the environment in which mollusca live, comes ordinarily in the oblique-lined domain in Fig. 3, and in special cases in the broken-lined one.

By the way, in the environment where the sea-water is extremely diluted by the pouring-in of river water, certain mollusca form only calcite in their shells. These are *Ostrea gigas* THUNBERG, *Patinopecten yessoensis* (JAY), *Neptunea arthritica* (BERNARDI), *Tectura pallida* (GOULD) and *Corbicula japonica* (PRIME).

Conclusions

Putting together the results of the various experiments briefly men-

<i>Mya japonica</i> JAY		<i>Gomphina melanaegis</i> RÖMER		<i>Glycymeris yessoensis</i> (SOWERBY)		<i>Mactra sulcataria</i> REEVE		<i>Panope japonica</i> ADAMS	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
3.40	37	3.40	30	3.40	36	3.40	28	3.38	35
3.28	22	3.28	19	3.28	19	3.28	19	3.28	22
2.88	9			2.88	8			2.88	10
2.71	24	2.71	23	2.70	21	2.70	17	2.70	35
2.48	18	2.48	15	2.48	14	2.48	14	2.48	21
2.41	11	2.41	12	2.41	9			2.41	10
2.38	21	2.38	18	2.38	16	2.38	15	2.38	22
2.35	27	2.34	14	2.34	13	2.34	14	2.37	17
						2.26	6		
2.19	9	2.24	6	2.20	9	2.20	7	2.19	9
2.11	12	2.19	9	2.11	11	2.11	9	2.11	10
		2.11	10						
1.98	24	1.98	23	1.99	23	1.99	21	1.98	22
1.88	17	1.88	15	1.88	14	1.88	12	1.88	18
1.81	14	1.82	12	1.82	11	1.82	10	1.82	14
1.75	14	1.75	12	1.75	13	1.75	12	1.75	17
1.73	11	1.73	9	1.73	10	1.73	9	1.73	12

tioned above, the established oceanographical data, and the results of their preceding report, the writers attain to the conclusions as follows:

(1) In the mollusca, which always inhabit sea-water not diluted with river water, the crystals of calcium carbonate are apt to take the aragonite form.

(2) In the mollusca, which either sometimes live above the surface of sea or inhabit sea-water diluted with river water, calcite or a mixture of calcite and aragonite is apt to be formed. Among them in those mollusca which inhabit either low temperature sea-water or extremely diluted sea-water, only calcite is formed.

By the way, as for a mollusc, which inhabits near the border line in the conditions mentioned above, no definite inclination can be easily discovered.

(3) The afore-mentioned conclusions are practically satisfactory in the case where the outer causes are far in the lead, but, on some occasions

the inner factors, which perhaps depend upon the organic substances in the mollusca, predominate over the outer. For instance in *Anodonta* sp., that is one of the fresh-water mollusca, the crystal form of calcium carbonate is only aragonite.

(4) A study on the influences of pH values of sea-water, of a co-existing small quantity of a substance, and of the organic substances in mollusca still remains to be performed.

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