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On the Apparent Distribution Coefficient of Uranyl between Sea Water and Skeletal Calcium Carbonates

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Abstract Some hermatypic corals, molluscs, and their inhabiting sea water were collected from the tropical (Malay Peninsula) and subtropical (Ryukyu Islands) localities, and the $m_{UO_2^{2+}}/m_{Ca^{2+}}$ of them were determined in order to evaluate the apparent distribution coefficient of uranyl between biogenic carbonate and sea water, which can be an aid to understand the factors controlling uranium concentration in skeletal calcium carbonates.

The result suggests that the compositional factor such as mineral phases and organic matrices and the physiological factor such as chemistry of the body fluid and extrapallial fluid become of major causes to control uranium concentration in skeletal carbonates. Moreover, a little difference in distribution coefficient of uranyl in coralline aragonite between Malay Peninsula and Ryukyu Islands may be attributed to the difference in water temperature. The difference in uranium concentration between two shell layers of an individual specimens of Tridacnid may be interpreted as the result of a subtle control over physiological process during shell formation, rather than compositional and environmental causes.

Introductory Notes

Since ODUM (1951) reported that Sr/Ca ratio in skeletal carbonates of some organisms was propotional to the ratio in sea water where the organisms had grown, CHAVE (1954a, 1954b), DODD (1965, 1966), LOWENSTAM (1961, 1964), and others have investigated the factors controlling the concentration of minor elements in skeletal calcium carbonates. It has been known from their keen observations that the concentrations of minor elements such as Sr and Mg are controlled by (1) crystal form of calcium carbonate, (2) species of the organism which secreted carbonate skeleton, (3) temperature in the environment where the skeleton was formed, and (4) chemistry of sea water, salinity.

On the other hand, in order to clarify thermodynamically the controlling factors, the distribution coefficients of Mn, Sr, and Zn between solution and calcium carbonate precipitates have been measured in laboratory experiments by BORDIN *et al.* (1965),

HOLLAND *et al.* (1963, 1964), TSUSUE and HOLLAND (1966), and CROCKET and WINCHESTER (1966). Their results, however, cannot be applied directly to skeletal carbonates, because their experiments were carried out in high temperature region, where the carbonate-secreting organisms could not live by any possibility. KITANO and his co-workers succeeded in precipitating low Mg calcite, high Mg calcite and aragonite separately at low temperature and pressure from the solution the properties of which are close to those of media for biological calcification (KITANO and HOOD, 1965; KITANO and KANAMORI, 1966). Their success widely opened a new approach to attack the above--mentioned problem by measuring the distribution coefficients of minor elements between the carbonate crystals and the parent solutions. As a result, they came to the conclusion that, when carbonate precipitation was carried out in a state of equilibrium, the controlling factors of minor element concentrations were (1) the crystal form of calcium carbonate precipitated, (2) the ratio of activity of Ca to that of Me (metalic ion) dissolved in the parent solution, (3) the ratio of solubility product of calcium carbonate to that of $MeCO_3$ in distilled water, (4) the activity coefficient of $MeCO_3$ in carbonate precipitate phase, and (5) temperature in the field where calcium carbonate precipitate was formed. KINSMAN (1969, KINSMAN and HOLLAND, 1969) also precipitated the aragonitic calcium carbonate inorganically from sea water in the temperature range (16 to 96 °C) the part of which was low enough for the marine organisms, and measured the distribution coefficient of Sr between the aragonite and sea water. He showed that the distribution coefficient for Sr co-precipitated with aragonite from sea water decrease linearly with temperature, and then emphasized its temperature dependence.

Thus, the factors controlling the concentration of minor elements in the biogenic carbonates seem to be clearly worked out. However, the papers which measured the distribution coefficient of uranyl between a mineral of calcium carbonate and the solution and discussed on the factors controlling U concentration can be counted on the fingers of both hands (*e. g.* TATSUMOTO and GOLDBERG, 1959; BLANCHARD and OAKES, 1965; VEEH and TUREKIAN, 1968; KITANO and OOMORI, 1971; KITANO *et al.*, 1971).

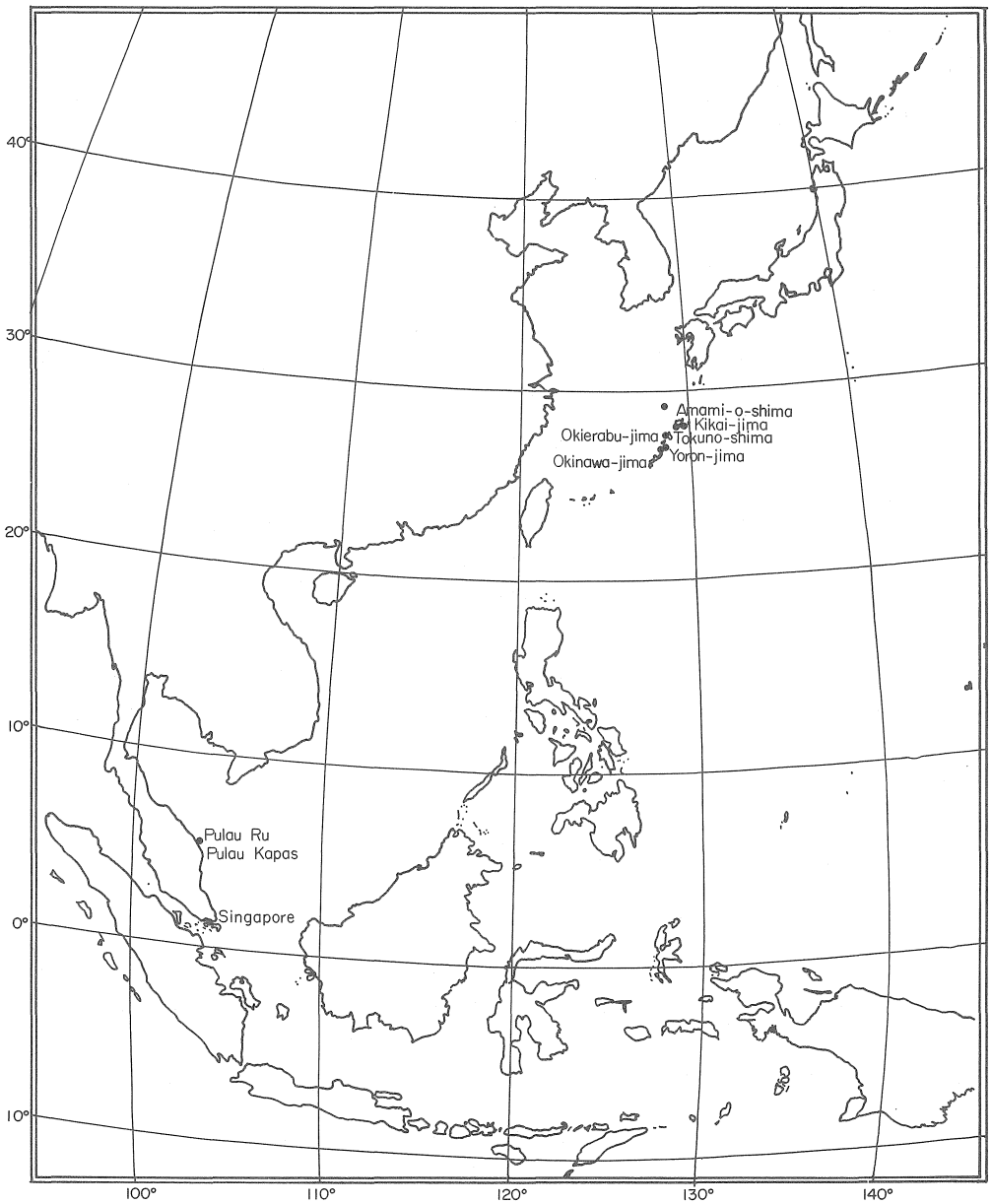
In this paper, the apparent distribution coefficients of UO_2 between sea water and aragonite and calcite of hermatypic corals and molluscs are calculated and discussed as an aid to understand the factors controlling U concentration in the skeletal calcium carbonates.

Samples and Methods

Sampling sites are shown in Text-fig. 1. Table 1 lists the sites and dates of collection of sea water samples used in this study. Samples of both sea water and benthic organisms were collected at the same time in four locations, Singapore, Pulau Ru, Aka-zaki, and Chabana. The organisms analyzed here are zooxanthellae-bearing hermatypic corals and molluscs.

Before the chemical analysis, all skeletal samples were examined their calcium

carbonate mineralogy by X-ray diffraction method. The α-spectrometry and fission track techniques as the same as I described before (OMURA, 1976) were employed for quantitative analysis of U. Ca concentration in both sea water and skeletal carbonate samples was analyzed by flame photometry, and chlorinity by Mohr's method.



Text-fig. 1 Map showing the localities of sea water and skeletal carbonate samples along the western part of the Pacific Ocean.

Table 1 The sites and dates of collection of sea water samples.

Sample	Location	Latitude•Longitude	Collection Date
WA-1	South of Kuji, Amami-o-shima	28°12′N•129°16′E	Aug. 1, 1971
WA-2	Station No. 17, KT-71-11	29°14.6′N•128°30.1′E	July 31, 1971
WA-3	Southwest of Kikai-jima	28°15′N•129°42′E	Aug. 5, 1971
WTk-1*	Hedono, Tokuno-shima	27°48.4′N•128°53.5′E	May 4, 1971
WY-1*	Chichibina-banare, Yoron-jima	27°02.8′N•128°24.2′E	Apr. 28, 1971
WY-2*	South of Aka-zaki, Yoron-jima	27°01.1′N•128°27.3′E	Apr. 30, 1971
WP-1*	Pulau Ru, Eastern Malaya	05°50′N•102°30′E	Aug. 10, 1969
W-1*	Singapore	01°15′N•103°50′E	Aug. 15, 1969

* coastal water.

Results

Table 2 gives a summary of the analyses of sea water samples. The standard error cited is based on the counting statistics of the samples and background, and does not include any systematic errors.

Since the water samples were collected from the locations without any distinct influx of land drainages, it was expected that chlorinity values would show only a small variation and all samples would be normal sea water. This was confirmed by the data which ranged from 17.30 to 19.30%. Ca/Cl ratios of the samples examined were found to vary only from 0.020 to 0.0245. These values agree with those reported previously by HARVEY (1960) and BLANCHARD and OAKES (1965).

^{238}U concentration ranges from (2.45 ± 0.12) to $(3.76 \pm 0.17) \times 10^{-6}$ g/l, and ^{238}U in the samples of the Ryukyu Islands indicate no local variation in concentration. $^{234}U/^{238}U$ activity ratio is not unity and shows that the activity of ^{234}U is several percent or more higher than that of ^{238}U. In the samples examined, however, this ratio is not necessarily constant, as expected by previous workers (THURBER, 1962; VEEH, 1966).

The measured values of the apparent distribution coefficient are listed in Table 3.

It is necessary, in actual fact, to determine U and Ca concentrations both in a skeleton and its inhabiting sea water in order to obtain the apparent distribution coefficient from the following equation:

$$K^{A}_{UO_2} \text{ (or } K^{C}_{UO_2}) = \frac{(m^{A}_{UO_2}/m^{A}_{Ca}) \text{ or } (m^{C}_{UO_2}/m^{C}_{Ca})}{(m^{S}_{UO_2}/m^{S}_{Ca})}$$

where K, $m^{A}_{UO_2}$, $m^{C}_{UO_2}$, $m^{S}_{UO_2}$, m^{A}_{Ca}, m^{C}_{Ca}, and m^{S}_{Ca} denote the apparent distribution coefficient ($K^{A}_{UO_2}$, for aragonite; $K^{C}_{UO_2}$, for calcite), and the molar concentrations of UO_2

Table 2 Chlorinity, Ca and ^{238}U concentrations, Ca/Cl ratio, and $^{234}U/^{238}U$ activity ratio of sea water samples.

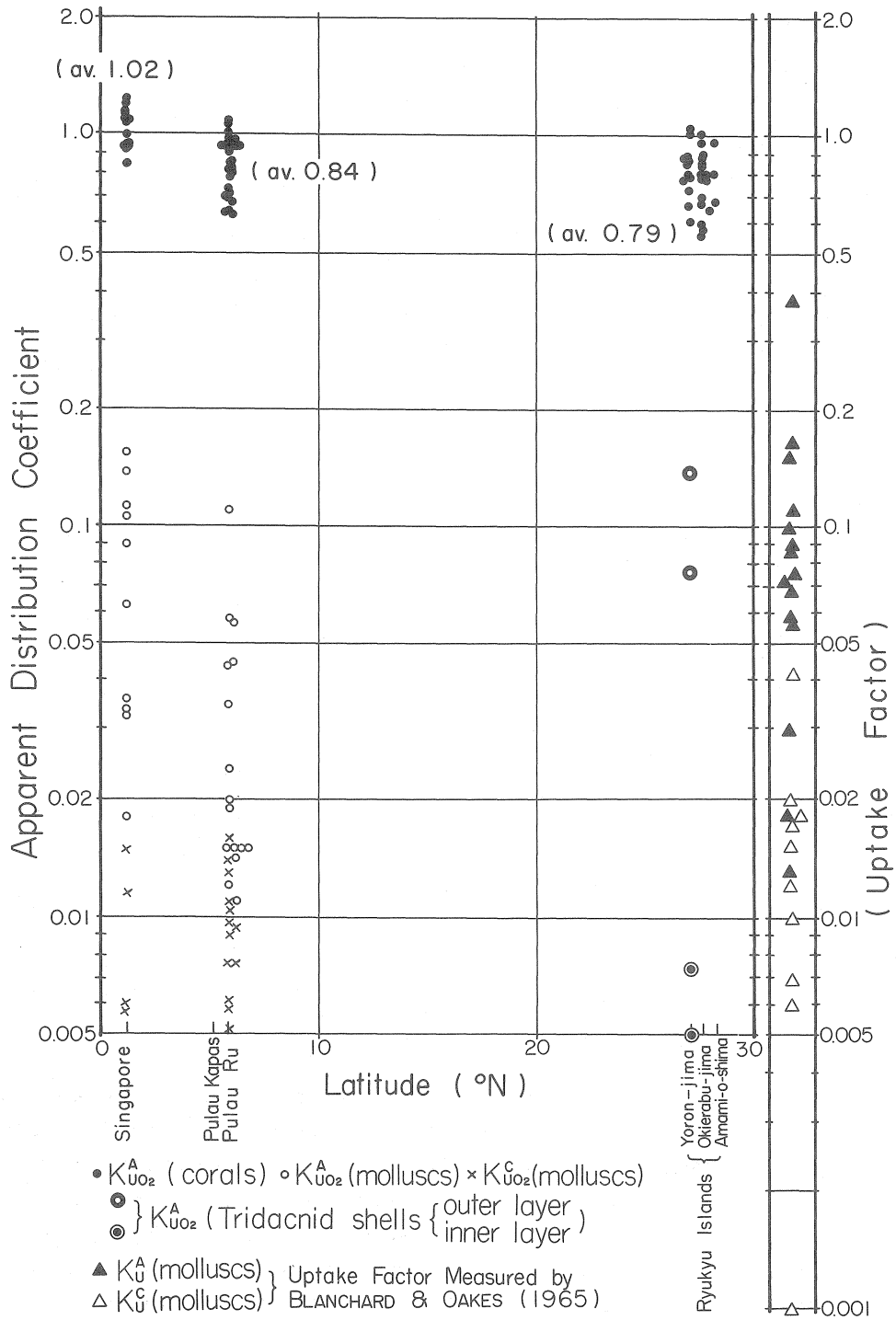
Sample	Chlorinity (‰)	Ca (mg-atom/l)	Ca/Cl (‰)	^{238}U ($\times 10^{-6}$ g/l)	$^{234}U/^{238}U$ (activity ratio)
WA-1	18.88	10.0	0.0212	3.60±0.11	1.15±0.05
WA-2	19.00	9.5	0.020	3.68±0.15	1.14±0.06
WA-3	19.00	10.5	0.0221	3.52±0.10	1.15±0.04
WTK-1	—	—	—	3.76±0.17	1.15±0.07
WY-1	19.21	9.5	0.020	3.41±0.16	1.08±0.07
WY-2	19.25	9.5	0.020	3.63±0.09	1.14±0.04
WP-1	18.29	10.5	0.0230	3.60±0.10	1.06±0.04
W-1	17.30	10.0	0.0245	2.45±0.12	1.18±0.08

Table 3 Ca and U concentration, and apparent distribution coefficient of UO_2 between some skeletal carbonates and sea water.

Sample	Materials		Location	^{238}U (ppm)	Ca (mg/g)	U/Ca ($\times 10^{-6}$)	K_{UO_2} or K_{UO_2}
	Genus	Class					
CEM-1	*Favia*	Anthozoa	Okierabu-jima	2.70±0.07	384	1.18	0.774
CYM-1	*Acropora*		Yoron-jima	2.75±0.06	377	1.23	0.788
CYM-7	*Goniastrea*		Yoron-jima	2.10±0.03	382	0.926	0.598
CP-1	*Pocillopora*		Pulau Kapas	3.23±0.05	380	1.43	0.994
PR-1		Pelecypoda	Pulau Ru	0.0469±0.0012	388	0.0203	0.0141
PS-1*	*Ostrea*		Singapore	0.0331±0.0010	368	0.0152	0.0105
GR-1		Gastropoda	Pulau Ru	0.0491±0.0014	382	0.0216	0.0150
MR-1		Cepharopoda	Pulau Ru	0.0247±0.0010	380	0.0109	0.0076

* calcite; the others, aragonite.

and Ca in aragonite, calcite, and sea water, respectively. Ca concentrations in all skeletal carbonates, however, were not determined in this study, because they can be adequately approximated by the analytical data (Table 3) of a part of the samples and of those by the previous workers (*e. g.* BLANCHARD and OAKES, 1965). As many data gave a mean value of about 38 % for Ca in a whole skeleton, the value of 380 mg/g was used as mean Ca concentration. The apparent distribution coefficients calculated by the approximation are summarized in Text-fig. 2. It is a plot of these values versus the latitude of sampling sites, spreading from the Ryukyu Islands to Malay Peninsula. U in present-day molluscs was critically studied in terms of the uptake factor in great extent



Text-fig. 2 The measured apparent distribution coefficient of UO_2 between skeletal carbonates and sea water of the samples from Ryukyu Islands and Malayan region.

by BLANCHARD and OAKES (1965), and their results are incorporated in Text-fig. 2 together with those calculated by the present study.

The analytical results obtained in this study can be summarized into the following four points:

(1) The aragonitic molluscan shells have somewhat higher K values than the calcitic ones from the same location.

(2) Both Table 3 and Text-fig. 2 ascertain that the $K^{A}_{UO_2}$ values of corals are much higher than those of molluscs both of which were collected at the same location, and composed of the same aragonitic hard tissues.

(3) Although still insufficient in number of analytical data for inhabiting sea water, corals collected in Malayan region appear to show a slightly higher $K^{A}_{UO_2}$ values (1.02 in Singapore and 0.84 in Pulau Ru and Pulau Kapas, respectively, in average) than those (0.79) from Ryukyu Islands.

(4) The remarkable difference in apparent distribution coefficient can be recognized between the inner and outer structural layers of the same Tridacnid shell.

Discussions

U concentrations in the present-day samples were measured as a total amount of U in the carbonate hard tissues with their organic matrices. Even if the concentrations in the crystal of calcium carbonate predominate over those in other origins, it still remains unexplained whether they substitute Ca ions in the crystal lattice, occur in other mineral phases, or are adsorped on the crystal surfaces.

Biogenic carbonates are precipitated not directly from sea water, but from "body fluid" specific to each organism; and hence the concentrations of both Ca and UO_2 in the body fluid may have to be determined together with those in skeletal carbonates for the critical discussion. In this study, instead, the apparent distribution coefficient of UO_2 between skeletal carbonate and sea water was calculated from the equation shown above.

The thermodynamic distribution coefficient of UO_2 ($K^{T,A}_{UO_2}$) between aragonite and solution was given by KITANO and OOMORI (1971) as follows:

$$K^{T,A}_{UO_2} = (a^{L}_{Ca} \cdot a^{S}_{UO_2CO_3})/(a^{L}_{UO_2} \cdot a^{S}_{CaCO_3})$$

$$= S^{O}_{CaCO_3(aragonite)}/S^{O}_{UO_2CO_3(rutherfordine)}$$

where a^{L}_{Ca}, $a^{L}_{UO_2}$, $a^{S}_{UO_2CO_3}$, and $a^{S}_{CaCO_3}$ denote the activities of Ca and UO_2 dissolved in solution, UO_2CO_3 and $CaCO_3$ in carbonate crystalline phase, and $S^{O}_{CaCO_3(aragonite)}$ and $S^{O}_{UO_2CO_3(rutherfordine)}$ in distilled water, respectively. They precipitated inorganically aragonite from a parent solution at room temperature (20 ± 1 °C) and determined the thermodynamic distribution coefficients of UO_2 between the aragonitic precipitate and the solution. According to their work, the $K^{T,A}_{UO_2}$ value thus measured in the solution

Table 4 U concentrations reported previously and apparent distribution coefficients of UO_2 between various skeletal carbonates and sea water.

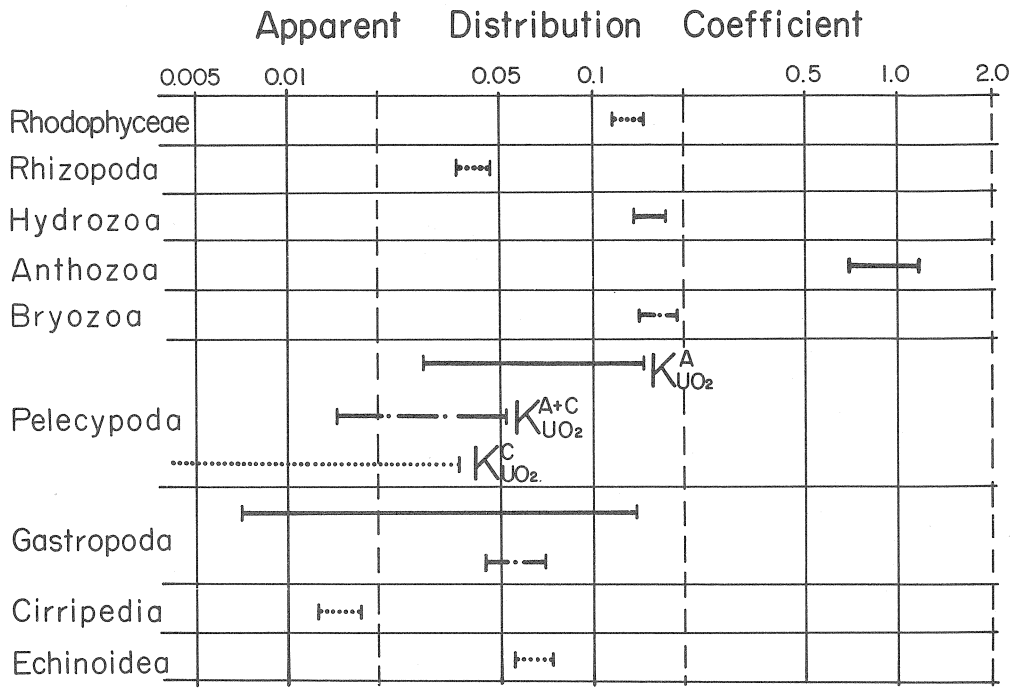
Class	Crystal Form	^{238}U (ppm)	Apparent Distribution Coefficient	Reference
Rhodophyceae	Calcite	0.37	0.13	SACKETT & POTRATZ, 1963
Rhizopoda	Calcite	0.11–0.13	0.039–0.046	HOLMES *et al.*, 1968
Hydrozoa	Aragonite	0.42	0.15	SACKETT & POTRATZ, 1963
Anthozoa	Aragonite	2.0–3.5	0.70–1.2	THURBER, 1962 ; BROECKER & THURBER, 1965 ; OSMOND*et al.*, 1965 ; KU, 1968 ; and others
Bryozoa*	Aragonite+Calcite	0.47	0.17	TATSUMOTO & GOLDBERG, 1959
Pelecypoda	Aragonite	0.008–0.433	0.028–0.15	BROECKER, 1963 ; BLANCHARD, 1963 ; and others
	Aragonite+Calcite	0.004–0.160	0.014–0.056	BROECKER, 1963 ; BLANCHARD, 1963 ; and others
	Calcite	0.001–0.140	0.001–0.042**	BLANCHARD & OAKES, 1965
Gastropoda	Aragonite	0.002–0.389	0.007–0.14	BROECKER, 1963 ; BLANCHARD, 1963 ; and others
	Calcite	0.013–0.180	0.046–0.063	BROECKER, 1963 ; BLANCHARD, 1963 ; and others
Cirripedia	Calcite	0.041	0.014	TATSUMOTO & GOLDBERG, 1959
Echinoidea	Calcite	0.17–0.18	0.060–0.063	TATSUMOTO & GOLDBERG, 1959

* contained detrital sand and/or silt particles (TATSUMOTO and GOLDBERG, 1959).
** were measured values by BLANCHARD and OAKES (1965).

system "$Ca(HCO_3)_2 + MgCl_2 + UO_2(NO_3)_2 \longrightarrow$ aragonite" ranges from 1.0 to 0.3. They expected the apparent distribution coefficient of UO_2 between marine calcareous skeletons and sea water as 1.2 to 0.3 for aragonite and 0.2 to 0.0n for calcite.

In spite of the existence of many carbonate-secreting organisms, only a limited number of organisms has been examined for U concentration, and the previous investigations seem to be biassed on corals and molluscs (Table 4).The apparent distribution coefficients in Table 4 and Text-fig. 3 are the values calculated from the approximation that U and Ca concentrations in sea water are 3×10^{-6} and 0.4 g/l, respectively and Ca concentration in the carbonate skeletons, 380 mg/g.

So far, only molluscan shells have provided numerous data regarding the relationship between U concentration and mineralogy. Text-figs. 2, 3, and Table 4 show that the aragonitic shells have somewhat higher K values than the calcitic ones have. Hence, it may be suggested that U concentration in molluscan shells is primarily dependent



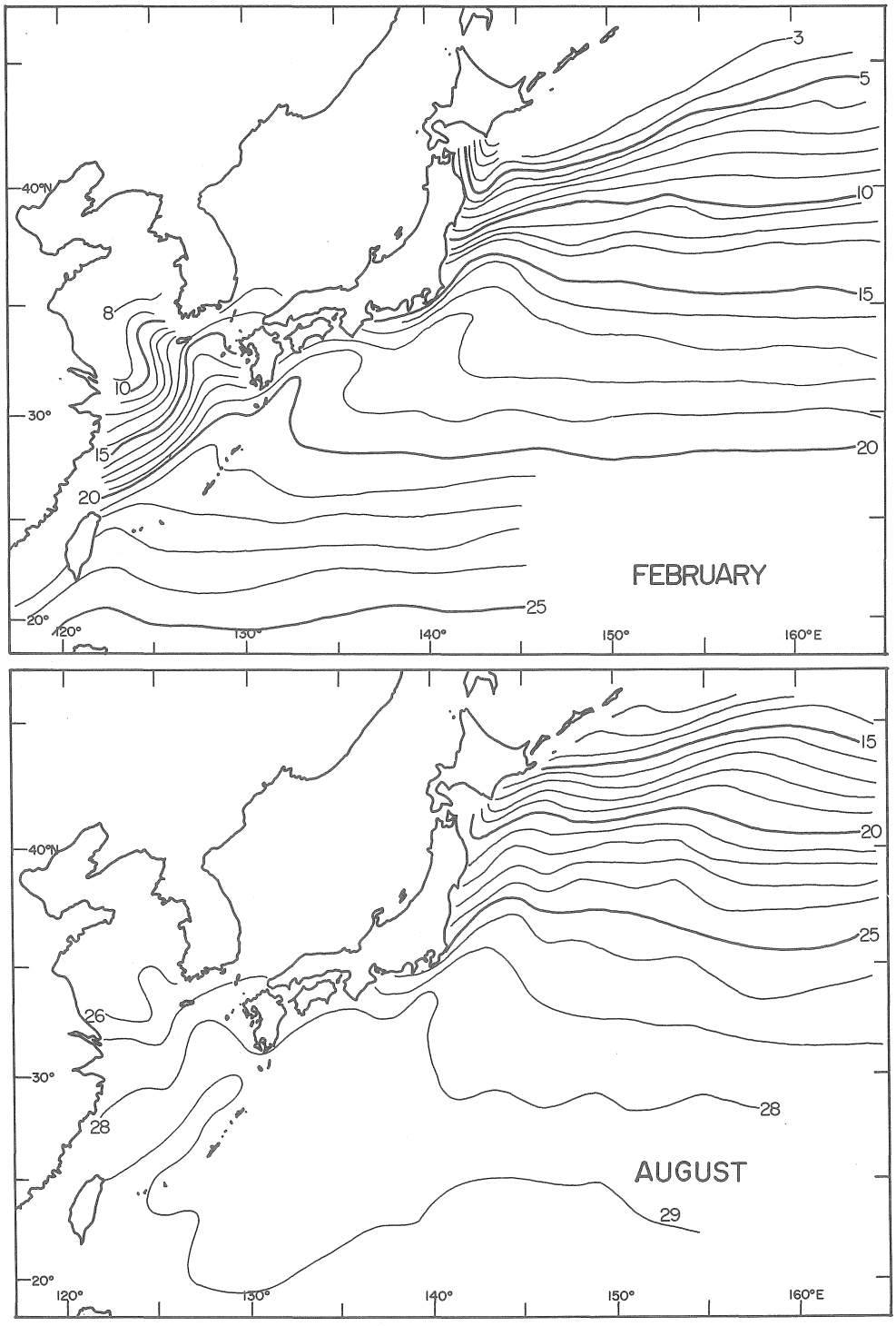
Text-fig. 3 Summary of the estimated apparent distribution coefficients of UO_2 between various skeletal carbonates and sea water. (Drawn from the data of Table 4)

upon the crystal form of calcium carbonate.

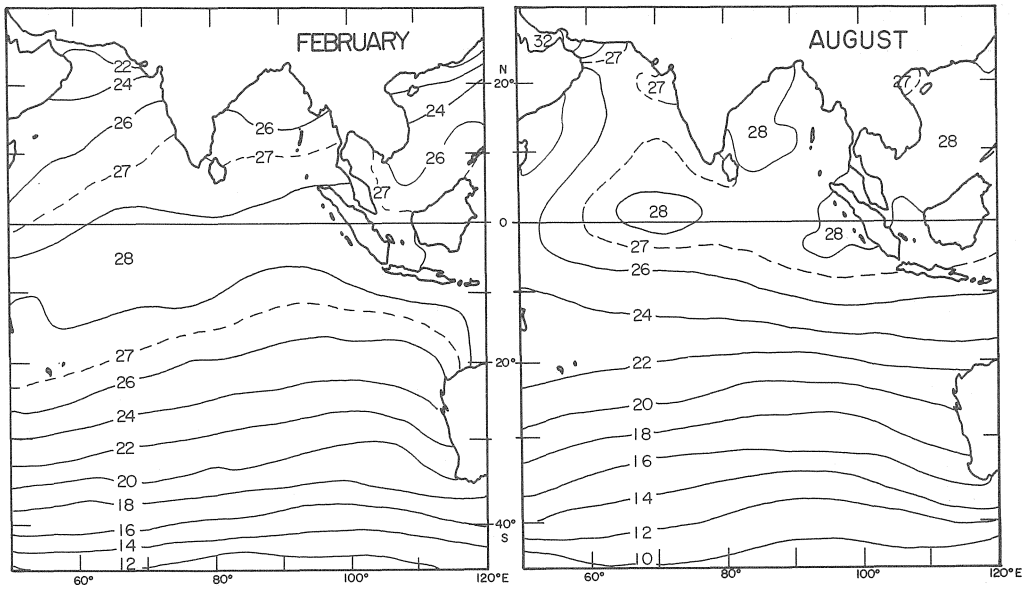
Much higher K values of corals than those of the aragonitic molluscan shells from the same locations suggest that the difference in species of the carbonate-secreting organisms has the major pronounced influence on U concentration, as well as the crystal form of skeletal carbonate. Moreover, Table 4 and Text-fig. 3 in which U concentrations in various organisms are summarized in terms of the apparent distribution coefficient also supported the pronounced effect of taxonomic difference. Next we must add special attention to the coincidence between the observed values of corals and the values estimated experimentally in laboratory by KITANO and OOMORI (1971). Such agreement may suggest that corals uptake U without any recognizable physiological discrimination, during the secretion process of aragonite through the body fluid which keeps a similar concentration in U of sea water.

The difference in K values measured from coralline aragonite of Malayan region and Ryukyu Islands may be attributed to the difference of any ecological condition between two regions, because the physiology of hermatypic corals may not vary essentially among various localities. Among the ecological factors under consideration, temperature of sea water may be the most significant, as compared with other factors such as supply of food, salinity and other natures of sea water.

Meteological reports show that the temperature of the surface water in Malayan



Text-fig. 4 The monthly mean temperature of the surface water in February and August of the Western Pacific Ocean.



Text-fig. 5 The monthly mean temperature of the surface water in February and August of the Indian Ocean. (Ramage *et al.*, 1972)

region is almost constant (28 to 29°C) through a year, while that in the Ryukyu Islands is relatively low and varies considerably with respect to season; the minimum, 19 to 20 °C in January, the maximum, about 29°C in August (Text-figs. 4 and 5). Therefore, it is strongly suggested that U concentration in aragonitic skeletons of coral may be governed by the temperature of sea water, like Sr concentration as reported by KINSMAN and HOLLAND (1969). The apparent distribution coefficient of UO_2 between the aragonitic skeletons of coral and sea water, however, appears to increase with temperature rise under such temperature region, a conclusion being opposite to the case of Sr.

On the other hand, it is clear that the K values of aragonite-secreting organisms other than coral are less than 0.2, which is lower than the value suggested for aragonitic skeletons by KITANO and OOMORI (1971). Such low K values imply the physiological discrimination displayed by these organisms against U. Although it is very important to determine the magnitude of the discrimination against U for each group of organisms taxonomically defined, this problem cannot be discussed any further, because of too scanty nature of the informations as to U concentration.

As reported before (OMURA *et al.*, 1973), it is also confirmed that the significant difference in K value between the inner and outer structural layers of the same specimen. As both layers are to be secreted simultaneously with the same mineral, aragonite, from the same extrapallial fluid, the observed difference may be interpreted as the result of a subtle control over physiological processes during shell formation, rather than any environmental causes. Shell ultrastructures might also have some control on the heterogeneities in U distribution, as certain molluscan shell layers may

differ from the others in crystal size and fabric, and relative abundance of the associated conchiolin matrix even in the same mineralogy.

Conclusions

The α-spectrometry coupled with fission track analysis was performed to determine U concentration in the present-day hermatypic corals, molluscan shells, and sea water from Malay Peninsula and Ryukyu Islands. Then the apparent distribution coefficient of UO_2 between skeletal carbonates and sea water was calculated in order to evaluate the factors controlling U concentration in the skeletal calcium carbonate of marine organisms.

When the environmental factors can be eliminated, the compositional and physiological factors become of major interest. The compositional factors such as mineral phases of the skeletal carbonates and composition of organic matrices appear to be important. The effect of mineral phase is clearly shown as the distinct difference of the apparent distribution coefficient of UO_2 between aragonitic and calcitic shells of molluscs at the same locality. Shell ultrastructures may also have some control on U concentration in molluscs.

The physiological factors include the chemistry of the body fluid and extrapallial fluid, the physiology of the mantle of the organism and of zooxanthellae known to be symbiotic in hermatypic corals and molluscs such as Tridacnids. The phyletic differences in U concentration depend upon these first three factors, and the effect of zooxanthellae seems to be relatively small compared to the others as guessed from the sharp distinction of U concentrations between corals and Tridacnid shells. The difference in U concentration between two shell layers of an individual specimens of Tridacnid may be interpreted as the result of a subtle control over physiological process during shell formation, rather than compositional and environmental causes.

Moreover, a little difference in distribution coefficient of UO_2 in coralline aragonite between Malayan region and Ryukyu Islands may be attributed to the difference in any ecological factors such as water temperature.

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