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STRONTIUM CONCENTRATIONS OF SOME RECENT PELECYPOD SHELLS

(Fig. 1—10)

Abstract: Sr concentrations of some recent pelecypods in relation to the average year temperature and salinity are discussed.

Резюме: В статье говорится о взаимоотношениях между концентрацией Sr у некоторых современных пелеципод и средней годовой температуре, а также солености воды.

Introduction

The study of recent carbonate skeletons is caused by its potencial use as an paleotemperature and paleosalinity indicator.

On the basis of the observations of previous authors the factors influencing the Sr concentrations in skeletons are as follows:

A. phylogenetic factors:

B. physic-chemical factors:

a) mineralogy of the skeletons

b) temperature of the environment

c) salinity of the environment

C. other factors.

A. It was well documented in literature (K. K. Turekian and R. L. Armstrong 1960, H. T. Odum 1957, J. R. Dodd 1963a, b, T. G. Thompson and T. J. Chow 1955, H. A. Lowenstam 1963 and others) that the differences in Sr concentrations of calcitic and aragonitic shells and in the mineralogy of recent the classes, genera and species are mainly due to phylogenetic factors. This is probably a result of metabolic processes and influence of organic compounds (N. Watabe and K. M. Wilbur 1960, H. A. Lowenstam 1963, Y. Kitano and D. W. Hood 1965 and others). However, the processes are not sufficiently known.

B. Although the phylogenetic factors are the dominant factors in controling the Sr distribution of skeletons within a single species, the influnce of physico-chemical factors may be observed as well.

a) Mineralogy

The fact that Sr is associated more with aragonite than with calcite was already observed by W. Noll (1934). A. P. Vinogradov (1953) confirmed that this pattern is valid, in general, for many of marine organisms. T. G. Thompson and T. J. Chow (1955) observed that the average Sr/Ca ratio of the molluscs is increasing with mineralogical composition of theit skeletons as follows: calcite, mixture of aragonite and calcite, aragonite.

b) Temperature

Temperature may influence Sr content of the skeletons in two ways:

1. The changes in temperature may cause the changes in the skeletal mineralogy, thus influencing the Sr content of the whole skeleton as well.

2. Temperature changes may cause changes of the Sr concentration within the aragonitic or calcitic layers of the skeletons.

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H. T. Odum (1951), O. B. Boggild (1930) and J. L. Kulp et al. (1952) concluded that temperature is not an important factor. H. A. Lowenstam (1954b, c, 1960) found that the temperature may affect the carbonate mineralogy of the species which precipitate calcite and aragonite in their carbonate skeletons. However this is not valid for the mollusca (H. A. Lowenstanm 1963). Also J. R. Dodd (1963a) reported that young individuals of *Mytilus californianus* do not show a temperature effect in their shell mineralogy, but larger skeletons showed positive temperature-aragonite correlation. In subsequent reviews (J. R. Dodd 1963a, b) he concluded that some skeleton layers were seasonal depended. J. R. Dodd (1963a, b) stressed a strong phylogenetic effect on the temperature mineralogy relationship for different species of the same genus.

T. G. Thompson and T. J. Chow (1955) reported that Sr/Ca atom ratios of some types of marine organisms were nearly constant, regardless of the water temperature. Later O. H. Pilkey and J. Hower (1960) found, that Sr/Ca ratio is temperature dependent at the specific level but not at the class level. They also reported that Sr/Ca ratio showed positive correlation with temperature in aragonitic molluscs and poor negative correlation in some calcitic molluscs. Also O. H. Pilkey and H. G. Goodel (1963) found positive correlation of Sr with temperature in aragonitic molluscs and negative in the calcitic one. J. R. Dodd (1963a) described positive correlation of Sr with temperature in the calcitic prismatic layer of *Mytilus* whereas, Sr in aragonitic nacreous layer varied inversely with temperature. T. T. Davies (1964) and A. Hallam and N. B. Price (1968) observed negative Sr correlation with temperature in *Cardium edule*. The last mentioned authors also observed higher Sr concentration in the inner layers than in the outer layers of the skeletons. The different Sr concentrations reflected the differences in the mineralogy of these layers.

c) Salinity

H. T. Odum (1951), J. L. Kulp et al. (1952) concluded that the primary factor controling Sr/Ca ratio of the shells is the Sr/Ca ratio of the water, from which the shells were deposited, and thus the salinity of the water media. This was also confirmed experimentaly by H. T. Odum (1951). H. T. Odum (1957) and F. Leutwein (1963) stated that Sr/Ca ratio increases with increas in salinity. Similarly T. G. Thompson and T. J. Chow (1955) demonstrated that Sr content of the marine arthropoda and mollusca is higher than the Sr content of fresh water organisms, but the dilution or concentration of sea water within the tolerance of marine organisms would not be an influential factor on the Sr/Ca atom ratio of the calcareous skeletons. H. A. Lowenstam (1954b, c) and J. R. Dodd (1963a) found that salinity effects the mineralogy of certain pelecypods. The aragonite-calcite ratio increase with decrease in salinity.

O. H. Pilkey and J. Hower (1960) concluded that salinity could influence the Sr content of skeletons but the relationships are far from being simple. They also described an exellent negative relationship of salinity to Sr in the calcitic molluscs. They demonstrated, that differences in salinity resulted in greater modification of molluscs shell composition as was cased by the temperature variations, but that salinity above 25 ‰ did not markedly affect the composition of the skeletons. Also O. H. Pilkey and H. G. Goodel (1962) quoted, that except one species, an inverse relationship between salinity and Sr content was to some degree preserved in all the molluscs studied. The negative correlation of Mg + Sr (to salinity) was found by J. Rucker and J. W. Valentine (1961) in *Crassostrea virginica*.

Fig. 1. Map of the localities. Explanations: 1 — Black Sea (Ropotamo). 2 — Black Sea (Kavacite). 3 — Black Sea (Istrija). 4 — Adriatic Sea (Kaštielska Bay). 5 — Adriatic Sea (Dračianska Bay). 6 — Adriatic Sea (Omiš). 7 — Adriatic Sea (Roseto d. Abruzzi). 8 — Mediteranean Sea (Argéles s. Mer). 9 — Florida Strait (Shelf of Guanabo). 10 — Gulf of Mexico (Calo paraiso). 11 — Caribbean Sea (Cayos de los Ballenatos).

From the description above it is clear the relationships between Sr content and physico-chemical factors are complicated and are mostly phylogeneticaly controlled. Thus the inevitable assumption of the progress in this field is to select temperature or salinity sensitive species for futher detailed studies as it was already done by J. R. Dodd (1961, 1963a, b, 1964, 1965) in the case of *Mytilus californianus* and *Mytilus edulis*. This paper aims to be a small contribution in this field.

Analytical Techniques

The Sr determinations were made using PGS-2 optical spectrograph. Details of the method are given elsewhere (J. Medveď 1967, R. Demovič 1968). The reproducibility of the method expressed as per cent standard deviation was $\pm$ 9 %. The separation of the inner layer of the shells was made using dentist drilling maschine.

Samples

The samples studied, originated from the collection of Doc. Dr. J. Seneš Dr. Sc. He also gave temperature and salinity data. The authors are obliged to him for valuable help and discussion of the problem.

Samples were collected in Black Sea, Mediteranean Sea, Adriatic Sea, Gulf of Mexico and Florida Strait areas (fig. 1.).

Mineralogical Composition of the Pelecypod Skeletons

Skeletal material of carbonate shells is composed mainly of aragonite and calcite or calcite with various concentrations of $MgCO_3$ as solid solution (K. Chave 1954).

The composition of pelecypode skeletons is as follows (J. Piveteau 1952):

Table 1. *Venus gallina* L.

Locality	No. of samples	Average year temperature in °C	Average salinity in ‰	Sr content of the whole skeletons in ppm	
				range	average
Adriatic Sea (Roseto d. Abruzzi)	3	18.5	35	1320—1666	1459
Mediteranean Sea (Argèles s. Mer)	3	19.5	35	2090—2410	2140
Black Sea (Kavacite)	6	16.5	17	832—2520	1687
$\sum$	12			832—2520	1741

1. Outer layer (periostracum) is formed by organic matter.

2. Middle layer is formed either from aragonite or calcite.

In the aragonitic middle layer the external part is of a fibrous or prismatic and the internal part of a nacreous and porcelaineous or crossed texture.

In calcitic middle layer the external part is of a prismatic and the internal part of a crossed or lamelar texture (calciostracum).

3. The inner layer (hypoostracum) is mainly of an aragonitic composition. Less abundant is calcite with glassy texture.

4. The internal filling of the skeletons is mainly of a calcitic (nacreous, crossbedded or prismatic texture), and less common, of a aragonitic composition (foliage or fibreous texture).

However the above introduced description is to some extent only a generalisation and the composition of the skeletons varries with genera and species.

Sr Distribution

Venus gallina L.

Sr was determined in 12 whole skeletons of this species. The Sr distribution is given in table 1 and fig. 2.

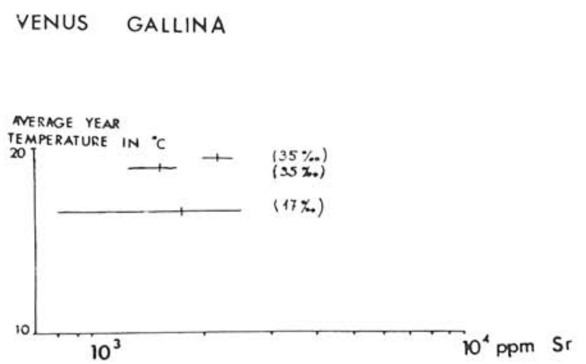

Fig. 2. Sr distribution in *Venus gallina*. Explanations: horizontal line — range; vertical line — average; number in brackets — average year salinity.

Table 2. *Chlamys glabra* L.

Locality	No. of samples	Average year temperature in °C	Average salinity in ‰	Sr content of the whole skeletons in ppm	
				range	average
Black Sea (Rapotamo)	2	16.5	17	1180—1260	1220
Adriatic Sea (Kaštielska Bay)	1	18.5	35	1030	1030
Σ	3			1030—1260	1147

Table 3. *Solen vaginata* L.

Locality	No. of samples	Average year temperature in °C	Average salinity in ‰	Sr content of the whole skeletons in ppm	
				range	average
Black Sea (Istria)	2	15.5	17	1410—2004	1725
Adriatic Sea (Dračianska Bay)	4	17.5	35	1635—3000	2770
Σ	6			1410—3000	2088

Table 4. *Donax trunculus* L.

Locality	No. of samples	Average year temperature in °C	Average salinity in ‰	Sr content of the whole skeletons in ppm	
				range	average
Black Sea (Kavacite)	4	16.5	17	1700—2240	2030
Adriatic Sea (Omiš)	6	18	14—17	1945—2410	2180
Mediteranean Sea (Argéles s. Mer)	4	19.5	35	1520—3000	2085
Σ	14			1520—3000	2105

The average Sr concentration in the regions of the same salinity, increases with the rise of temperature. In the case of Black sea samples (salinity 17 ‰) a big scatter of Sr concentrations was observed.

Chlamys glabra L.

Only three samples from two regions were studied. The Sr distribution is as follows (table 2, fig. 3).

Because of the small amount of samples, the results may be used only as a preliminary report concerning Sr concentration of this species.

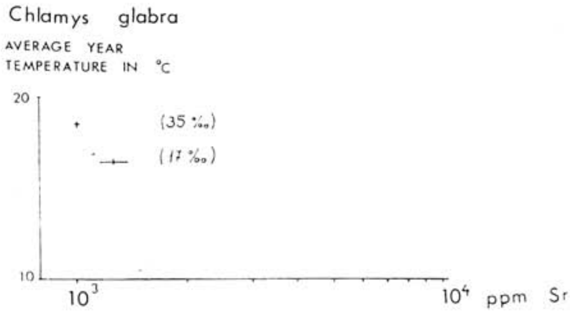

Fig. 3. Sr distribution in *Chlamys glabra*. Explanations: as fig. 2.

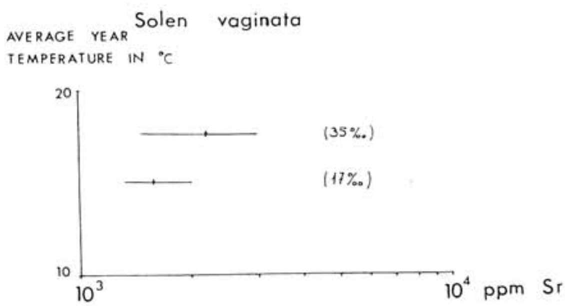

Fig. 4. Sr distribution in *Solen vaginata*. Explanations: as fig. 2.

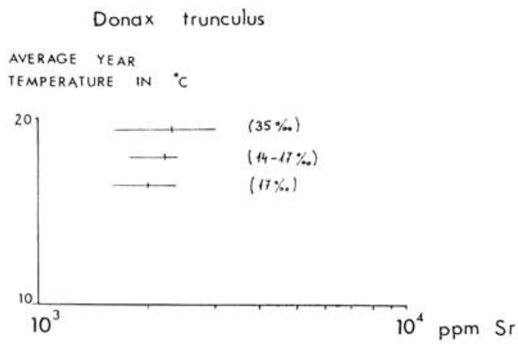

Fig. 5. Sr distribution in *Donax trunculus*. Explanations: as fig. 2.

Solen vaginata L.

Six samples of the whole skeletons were analysed. The Sr distribution is given in table 3, fig. 4.

The average Sr content increases with rise of temperature and salinity. Because it is impossible to distinguish between the influence of salinity and temperature, the reported results may serve only as a data af Sr concentration in the given species.

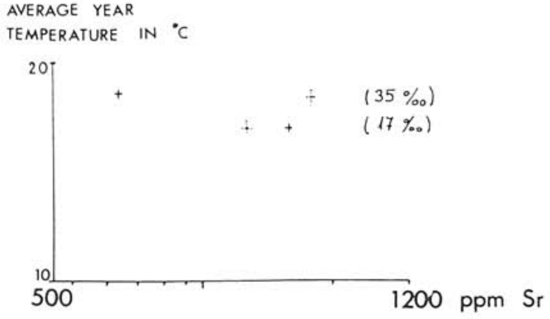

Fig. 6. Sr distribution in *Mytilus galloprovincialis*. Explanations: full crosses — whole shell analyses; dashed crosses — analyses of the internal layers; number in brackets — average year salinity.

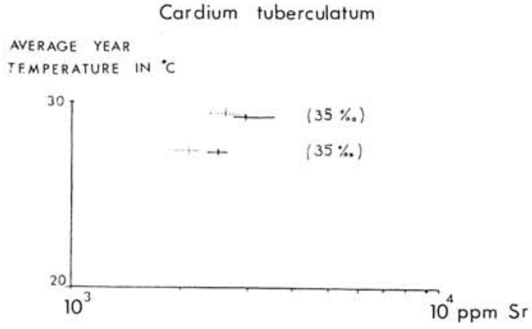

Fig. 7. Sr distribution in *Cardium tuberculatum*. Explanations: horizontal full line — range of the whole shell analyses; dashed horizontal line — range of the internal layer analyses; vertical crosses — averages; number in brackets — average year salinity.

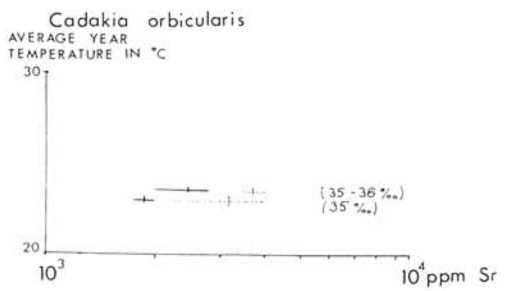

Fig. 8. Sr distribution in *Cadakia orbicularis*. Explanations: as fig. 7.

Table 5. *Mytilus galloprovincialis* L.

Locality	No. of samples	Average year temperature in °C	Average salinity in ‰	Sr content of the inner layers in ppm	Sr content of the whole skeletons in ppm
Black Sea (Kavacite)	1	16.5	17	1260	1440
Adriatic Sea (Kaštielska Bay)	1	18.5	35	1820	631
Σ	2			1540	1035

Table 6. *Cardium tuberculatum*

Locality	No. of samples	Average year temperature in °C	Average salinity in ‰	Sr content of the inner layers in ppm		Sr content of the whole skeletons in ppm	
				range	average	range	average
Jadran Sea (Dračianska Bay)	2	17.5	35	1910—2960	2036	2460—3550	2840
Mediteranean Sea (Argelés s. Mer.)	3	19.5	35	2630—3000	2860	3090	3090
Σ	5			1910—3090	2548	2410—3550	2904

Table 7. *Cadakia orbicularis* L.

Locality	No. of samples	Average year temperature in °C	Average salinity in ‰	Sr content of the inner layers in ppm		Sr content of the whole skeletons in ppm	
				range	average	range	average
Florida Strait Shelf of Guanabo)	2	23	35	2190—3990	3090	1780—2009	1890
Gulf of Mexico (Cayo Paraiso)	2	23.5	35	3550—3999	3775	2090—3009	2500
Σ	4			2190—3999	3432	1780—3090	2195

Donax trunculus L.

Fourteen whole skeleton Sr analyses of the species were carried out. The Sr distribution is given in table 4. fig. 5:

It seems reasonable to conclude that the average Sr content shows positive temperature correlation in spite of the lower salinity in the case of Black Sea samples.

Mytilus galloprovincialis L.

Only two samples were studied. Both. inner layer of the shell and bulk samples. were analysed. The Sr distribution is given in table 5. fig. 6.

Because of the small amount of samples. the results are only of informative value. The may be considered only as a data of Sr concentration in this species. However it is interesting to note the contradictory behaviour of Sr in the internal layer and the whole shell (fig. 6). The average Sr content of the inner layer is higher than of the bulk samples.

Cardium tuberculatum

Five samples have been analysed for Sr content of the inner layer as well as of the whole shells. The distribution is given in table 6. fig. 7.

The average Sr content shows positive correlation with temperature in the inner layer as well as in the bulk samples. The average Sr concentration of the inner layers is lower than that of the bulk samples.

Table 8. *Glycimeris* div. sp.

Species	Locality	No. of samples	Average year temperature in °C	Average salinity in ‰	Sr concentrations of the whole skeletons in ppm		Sr concentrations of the inner layers in ppm	
					range	average	range	average
Glycimeris undata I.	Florida Strait (Shelf of Guanabo)	4	21	35	3000—10000	5655	1260—4370	3292
Glycimeris undata II.	Caribbean Sea (Cayos de los Ballenattos)	3	23.5	35	3720—6310	4583	1590—3550	2380
Glycimeris violaceous	Mediteranean Sea (Argelés s. Mer)	2	19,5	35	6310—10000	8155	1660—2350	2005
Glycimeris pilosa	Adriatic Sea (Kaštielska Bay)	3	18,5	35	2520—5630	4313	1380—1410	1390
Glycimeris glycimeris	Mediteranean Sea (Argelés s. Mer)	2	19.5	35	3550—3720	3636	1590—2350	1970
Σ		14			2520—10000	5206	1260—4370	2316

Table 9.

	No. of samples	ppm of Sr	
		range	average
samples in which only whole skeleton analyses were carried out	35	832—3000	1895
samples in which analyses of inner layers and whole skeletons were carried out			
inner layers	25	1260—10000	4098
whole skeletons	25	631—4370	2312
total $\sum$ of the whole skeletons analyses	60	631—10000	2068

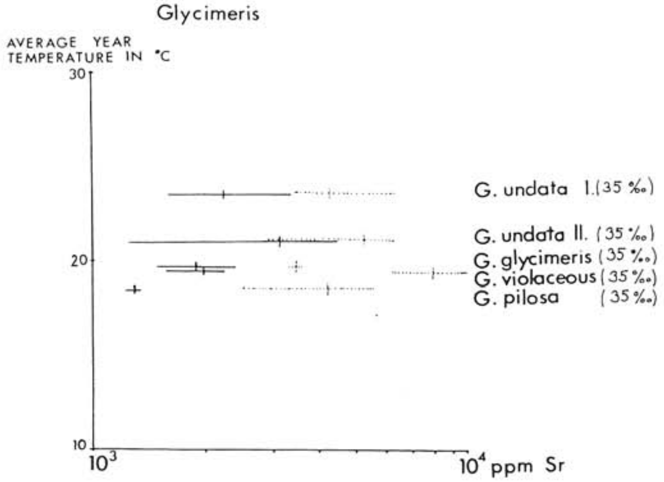

Fig. 9. Sr distribution in genera *Glycimeris*. Explanations: as fig. 7.

Cadakia orbicularis L.

Four samples were analysed. The Sr distribution is given in table 7, fig. 8.

The average Sr content positive correlation with temperature in the inner layers as well as in the bulk samples. The average Sr concentrations of the inner layer is higher than that of the bulk sample. However the amount of samples is too small to allove futher generalisations.

Glycimeris div. sp.

Fourteen samples of five species were analysed. The results are summarised in table 8, fig. 9.

No correlation can be supposed from this distribution pattern. The results indicate that Sr distribution is dependent on the phylogenetic factors even within the same genera (conform K. K. Turekian and R. L. Armstrong 1960 and others). It indicates, that the use of Sr as a paleotemperature or paleosalinity indicator, is limited to the interpretation of the Sr distribution only within the same species. The average Sr content of the inner layers, in all *Glycimeris* species studied, is significantly higher than the average Sr content of the whole shells.

With exception of *Cardium tuberculatum* the average Sr contents of the other seven

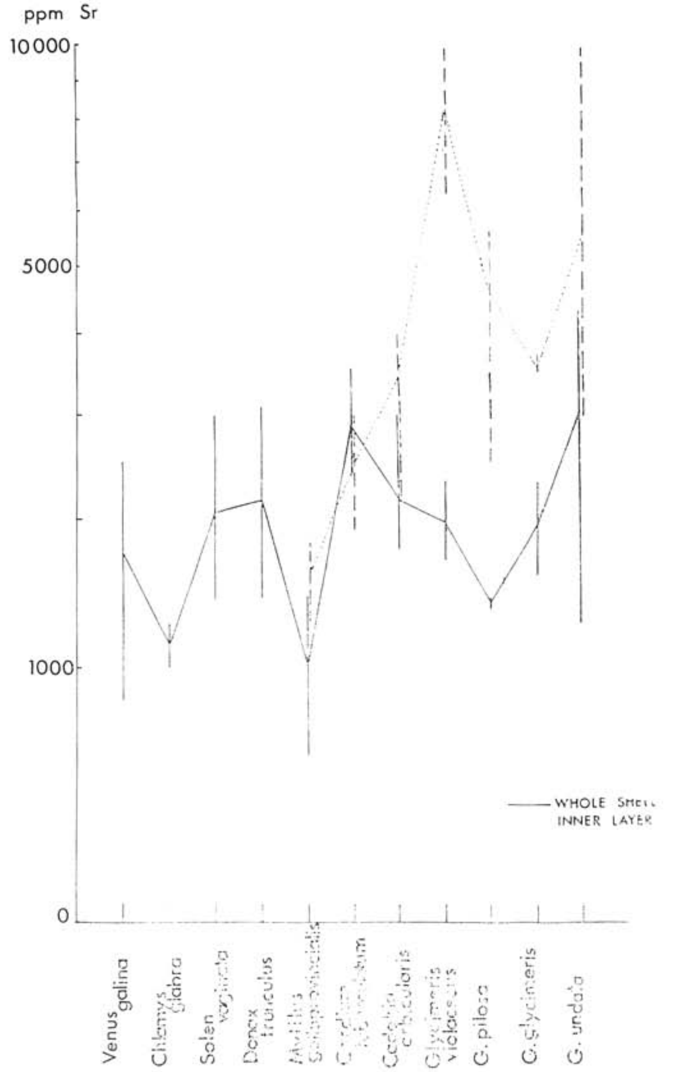

Fig. 10. Sr concentration of some pelecypod species. Explanations: vertical lines — ranges; „horizontal" lines — averages; full lines — whole shell analyses; dashed lines — analyses of inner layers.

species are higher than the average contents of the whole shells (table 9, fig. 10). The inner layer in most of the recent molluscs is formed of aragonite (J. P i v e t e a u 1952). The high Sr content is in agreement with this interpretation. However, using Feigel solution to test the mineralogy of skeletons, it was found that the majority of the skeletons are completely formed of calcite. However the DTA-VTA (J. K r i š t í n and X-ray diffraction analysis (E. Š a m a j o v á) of the shells with inner layer Sr concentrations of 10 000 ppm (*Glycimeris undosa* and *G. violaceous*) unequivocally indicated presence of aragonite within the shells. The leaves some doubt on the extent of the aragonite-calcite conversion in such recent shells. If this conversion is true, the higher Sr content of inner layers might indicate that same partition in Sr distribution could exist even after conversion of unstable aragonite to calcite. There is, however, little doubt about the existence of original aragonite in species with high Sr contents of the inner layers, since they are cleary exceeding the Sr concentration factor of calcite (cf. K i n s m a n 1969).

This conclusion about possible partition of Sr after conversion requires thus additional studies of the details of shell mineralogy as well as kinetics of this conversion.

Conclusions

1. New data of Sr concentrations in recent carbonate pelecypod shells are given. The highest average Sr content was established in the *Glycimeris undata* Florida Strait 21 °C and the lowest in the Mytilus galloprovincialis (Black Sea, 16.5 °C).

2. In agreement with previous results it was concluded that the phylogenetic factor is the most importent factor controlling Sr distribution in recent pelecypod shells.

3. The correlation of Sr concentrations with the temperature is complicated. Newetherless it seems reasonable to conclude that Sr increases with the temperature in *Donax trunculus, Cardium tuberculatum, Cadakia orbicularis* and probably in *Venus gallina* and *Solen vaginata* as well. *Donax trunculus* seems to be the most promissing from all described species for futher detailed studies although, the within mean differences are more significant than the between mean differences.

4. The average Sr concentrations of the inner layers of the skeletons are higher (with exeption of *Cardium tuberculatum*) than of the whole skeletons. It is assumed that it might be caused by the original aragonitic nature od these layers. It is not known to what extent the established ratio of Sr inner layers / Sr whole shell (~ 2) is due to a conversion of aragonite into calcite with subsequent loss of Sr or to a strong organic fractionation of Sr, which is typical of molluscs (cf. K i n s m a n 1969). The ratio of ~ 4 for the species with very high Sr content of inner layers (~ 8000 ppm) is lower then ~ 8, which should be expected from Sr distribution coefficients of calcite and aragonite. However, the average Sr content of the whole shells, which is 1939 ppm, also exceeds the predicted value for calcite by a factor of ~ 2. This strongly indicates a contribution of „aragonitic" Sr to the bulk shell analysis. At the present stage it is thus difficult to speculate about possible Sr fracionation factors of pelecypods, however it seems probable, that it varies from species to species, depending on organic processes, in the manner similar to that one described by K i n s m a n (1969) on the phyla level.

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Review by B. C a m b e l.