LETTER

Crystal structure control on trace element partition in molluscan shell formation

We wish to propose a new model which clarifies mechanism in the formation of shells of molluscs: Trace element partition between molluscan shell and its mineralizing fluid is primarily determined by crystal structure of calcium carbonate. The model suggests: (1) The last-step in shell formation is controlled by a physicochemical process. (2) Divalent trace elements (alkaline earths and transition elements) occupy regularly a lattice site in the crystal structure. (3) Monovalent trace elements (alkali metals) are non-selectively distributed in a shell as inclusions of carbonates and/or amorphous compounds.

In molluscs, the shell is formed from its mineralizing solution called extrapallial fluid (DE WAELE, 1930) which is secreted by outer mantle epithelium. The extrapallial fluid is clearly isolated by cell membranes from environmental water where molluscs are living. Therefore, one has to take into account processes involving at least three-steps for trace element partition between shell and environmental water. The first-step is a liquid-liquid partition between environmental water and molluscan blood. The second-step is a liquid-liquid partition between molluscan blood and the extrapallial fluid. The third-step is a liquid-solid partition between the extrapallial fluid and shell.

Mechanism of the first two processes is not understood in detail. These processes are considered to be controlled by a series of complex physiological activities in molluscs. The purpose of this paper is to present a simple mechanism which is applicable to the last-step process in the biomineralization.

We consider the phenomena of the crystal growth are controlled by a physicochemical process. It may be said that the molluscs prepare an environment (extrapallial fluid) from which the crystal can grow. Thus, trace element partition on the last-step process must be primarily controlled by a physicochemical mechanism.

Similar phenomena have been observed in igneous processes involving phenocrysts (crystals) and groundmass (quenched liquid) in magma: Element partition between a crystal and a silicate

melt is controlled by structure of the crystal (ONUMA *et al.*, 1968; HIGUCHI and NAGASAWA, 1969; JENSEN, 1973; MATSUI *et al.*, 1977). Partition coefficient-ionic radius diagrams (PC-IR diagrams) for the systems show that each cation position in the crystal structure gives rise to a parabolic peak on the diagram. An example is shown in Fig. 1 (MATSUI *et al.*, 1977, Fig. 4). This is a PC-IR diagram for the plagioclase-groundmass system of a basalt from Taka-sima, Kyushu, Japan.

Roughly speaking, the structure of plagio-

Fig. 1. Partition coefficient-ionic radius diagram for plagioclase-groundmass system (Takasima alkali-olivine basalt). Half-solid half-open circle: mono-valent cation, open circle: di-valent cation, open triangle: tri-valent cation (after MATSUI *et al.*, 1977).

Table 1. Trace element contents (ppm) in inner shell layer (aragonite) and its extrapallial fluid of a marine bivalve mollusc (*Pinctada fucata*)

Element	Ionic Radius* (Å)	Shell** (ppm)	Extrapallial fluid** (ppm)	Partition Coefficient
Li	0.76	0.20	0.20	1.00
Na	1.02	7720	9800	0.79
K	1.38	78	490	0.16
Mg	0.72	190	1200	0.16
Cu	0.73	0.4	0.19	2.11
Zn	0.74	7.7	12.5	0.62
Fe	0.78	5.5	0.71	7.75
Mn	0.83	7.0	0.18	38.9
Ca	1.00	379000	390	972
Sr	1.18	940	6.7	140

* SHANNON (1976).

** WADA and FUJINUKI (1974, 1976); Extrapallial fluid, av. of 4 analyses; Shell, av. of 2 analyses.

clase provides two kinds of cation sites. The larger site is suitable for large cations such as Na^+ , Ca^{2+} and Sr^{2+} , and the smaller site for cations with four-fold coordination, which are responsible for a three-dimensional aluminosilicate framework. In Fig. 1, the curves can be seen as composed of two parabolas, one with a peak located near the plot for Al^{3+} and another with a peak near the plot for Sr^{2+} . The two peaks for larger ions and for smaller ions can certainly be assigned to the larger site and the smaller site, respectively, in the plagioclase crystal (cf. MATSUI *et al.*, 1977). The difference in heights between the parallel curves corresponds to the difference in energy required for exchange of cations with different valency (ONUMA *et al.*, 1968; see also BANNO and MATSUI, 1973).

The crystal structure control model predicts a similarity in the PC-IR diagram for the shell-extrapallial fluid system. Parabolic curves should appear for elements with a peak located near the plot for Ca^{2+} . In the calcium carbonate structure, there is a site which accommodates a large cation, such as Ca^{2+} . The hypothesis also suggests a large difference in the relative heights between divalent curve and mono- and tri-valent curves because of the absence of major cations with mono- and tri-valency in the calcium carbonate. If the prediction is the case, the last-step in biomineralization can be regarded as purely, physicochemical process.

Figure 2 shows a PC-IR diagram for inner shell layer (aragonite) and extrapallial fluid system of a marine bivalve (*Pinctada fucata*) from the Tatokujima waters of Ago Bay, Mie Prefecture, Japan. The partition coefficient is

defined here as the ratio of concentration of an element in the shell to that in the extrapallial fluid. The data employed in Fig. 2 are cited from WADA and FUJINUKI (1974, 1976) for the partition coefficients and from SHANNON (1976) for ionic radii, respectively. Both are shown in Table 1.

In Fig. 2, divalent ions such as alkaline earths and transition elements make a parabolic curve with a peak near the plot for Ca^{2+} . The curve verifies that the mechanism of crystal structure

Fig. 2. Partition coefficient-ionic radius diagram for inner shell layer (aragonite) and its extrapallial fluid of a marine bivalve mollusc (*Pinctada fucata*). Symbols are the same as those in Fig. 1.

control is valid even in biomineralization. The curve also indicates that these divalent ions occupy regularly the lattice site in the crystal structure of the calcium carbonate. Deviation of the plot for Cu^{2+} from the curve may imply that the excess amount of the element exists in the organic matrix of shell as organic complex (es). Thus, the PC-IR diagram suggests a capability of determining the state of existence of the transition elements in shell.

On the other hand, monovalent ions such as alkali metal elements do not make a parabolic curve with a peak near $1.0\text{\AA}$, as shown in Fig. 2. This suggests that majority of alkali metal elements have no tendency to occupy the lattice site of the crystal structure. Isomorphic substitution of monovalent elements for divalent elements in CaCO_3 is hardly expected, because such substitution should require coupled substitution such as $\text{CaCO}_3 \rightleftharpoons \text{NaNO}_3$, which involves water-soluble component(s). Therefore,

it is not surprising that the crystal structure control is not effective in monovalent element substitution. It follows that the distribution of monovalent ions should be considered to be beyond the control of crystal structure, and more likely, should be treated separately, as inclusions such as carbonates and/or amorphous compounds.

ICHIKUNI (1978) has claimed the crystal structure control model for trace element partition between inorganic calcite-aqueous solution, based on a parabolic curve for divalent cations (Mg, Zn, Fe, Mn, Ca and Sr) in the PC-IR diagram. The similar parabolic curves from the inorganic mineralization and the biomineralization emphasize that the last-step process in the shell formation is primarily controlled by a physicochemical process.

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