Reports

Strontium Uptake in Shell Aragonite from the Freshwater Gastropod *Limnaea stagnalis*

Abstract. *Shell aragonite from 96 specimens of the freshwater gastropod* Limnaea stagnalis *grown in laboratory tanks at different temperatures in water with variable strontium/calcium ratios have been analyzed for its strontium content in order to evaluate the mechanisms of strontium uptake in molluskan aragonite. Within the limits defined by natural freshwater environments, the strontium/calcium ratio in the aragonite was found to be linearly related to the strontium/calcium ratio in the water. A distribution coefficient* $k^{A}_{Sr} = 0.237 \pm 0.029$, *unaffected by variations in temperature and growth rate, has been found. This finding substantiates the existence of a strontium-discriminating effect in aragonite precipitated by mollusks as compared to the case for nonbiogenic aragonite which contains about five times as much strontium when precipitated under the same conditions.*

Geochemical studies of fossil shell material have recently taken on increasing importance because of a growing interest in the paleoclimatological and paleoenvironmental information which can be obtained from such material. Any material used for such studies must have preserved its original chemical and isotopic composition since, for example, the composition of recrystallized shells will reflect the diagenetic but not the primary environment.

The Sr contents are used as one of the indicators for diagenetic changes in carbonates. However, without a thorough knowledge of the Sr distribution in modern shells it is not possible to interpret data from related fossil material. Studies of the Sr distribution in recent biogenic carbonates have been summarized by Bathurst (*1*) and Milliman (*2*). Calcium carbonate in its two polymorphs, calcite and aragonite, is by far the most important biogenic carbonate; Mg and Sr are, respectively, the most abundant minor elements in these minerals. The uptake of the Mg in calcite has been investigated thoroughly (*3*), but the incorporation of Sr in biogenic aragonites is less well understood.

Such is not the case for the inorganic uptake of Sr in aragonite, which was studied extensively by Kinsman and Holland (*4*). The partitioning of Sr between solution and crystal is usually expressed as a partitioning or distribution coefficient k^{A}_{Sr}, which is defined as the ratio of the Sr/Ca ratio of the solid phase to the Sr/Ca ratio in the water from which the crystal precipitated. In a more sophisticated way it can be defined as a function of the solubilities of strontianite ($SrCO_3$) and aragonite, the activities of Sr and Ca in solution, and the activity coefficients of the two ions in the crystal (*4*). This coefficient is dependent on temperature. However, the variations of k^{A}_{Sr} are negligible within the temperature range considered here and an inorganic distribution coefficient $k^{A}_{Sr} = 1.12$ has been determined (*4*).

This value corresponds to a Sr concentration in marine, inorganically precipitated aragonite close to 8000 parts per million (ppm), and is observed in many natural aragonites of inorganic as well as biogenic origin. However, aragonitic shell material may have Sr contents deviating from this "inorganic" value, reflecting the phylogenetic levels of the different groups of shell-forming animals (*1*, *5*). Most important in this respect are the mollusks, which consistently show much lower Sr contents. The Sr concentration in a diagenetically unaffected carbonate shell may thus be a function of one or more of the following factors: (i) shell mineralogy, (ii) phylogenetic Sr content, (iii) rate of growth, (iv) water temperature, (v) Sr and Ca concentrations in the surrounding water, and (vi) ion activity (salinity).

We describe here the results of a study on the partitioning of Sr between water and aragonite grown by the freshwater gastropod *Limnaea stagnalis* under controlled laboratory conditions, and its variation with temperature, growth rate, and chemical composition of the water. The ionic strength of the water was kept below 2×10^{-2} in all experiments. Studies with solutions of high ionic strength are still in progress and will be discussed elsewhere (*6*). Similar experiments were carried out by Odum (*7*), who discussed the uptake of Sr by freshwater snails and considered these data in the context of a worldwide Sr cycle (*7*, *8*). Additional data on freshwater mollusks were presented by Faure *et al.* (*9*), who discussed the Sr uptake by bivalves in the Great Lakes. However, both of these investigators considered extreme cases: Faure examined systems with extremely low Sr/Ca ratios in the waters, whereas Odum concentrated on unnaturally high Sr/Ca ratios. Our experiments cover the intermediate range including the Sr/Ca ratios of most natural freshwater systems.

The individual growth rates determined in our experiments and expressed as an increase in the total height of the shell per day are highly variable (coeffi-

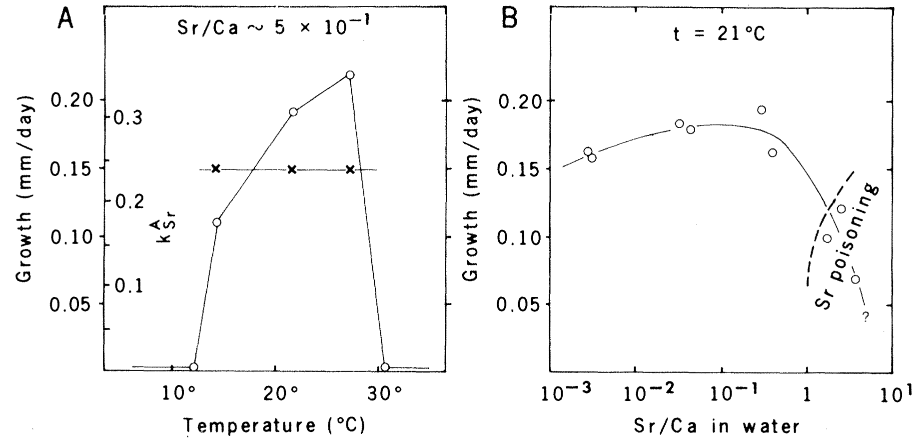

Fig. 1. (A) Growth rate (○) and distribution coefficient k^{A}_{Sr} (×) as a function of temperature. (B) Growth rate as a function of Sr/Ca ratios in tank water. Shells grown in water with a Sr/Ca ratio above 1.5 show distortion and reduced growth rate (Sr poisoning).

cient of variation up to 25 percent) within the population of a single tank. A typical tank population initially consisted of more than 15 specimens, and in most experiments more than 50 percent of the animals survived. Physical factors were kept constant during each experiment, and these variations in growth rate must be ascribed to unknown biological factors. Nevertheless, relationships between growth rate and temperature and growth rate and water chemistry can be identified on the basis of average growth rate values for each population. The temperature-defined growth interval for the investigated specimens falls between 13° and 28°C, beyond which no measurable growth takes place (Fig. 1A). Optimal growth occurred at 27°C.

Of the chemical parameters investigated, only the Sr/Ca ratios of the water have any well-defined influence on growth; Sr/Ca ratios above 1.5 result in distinct growth rate reductions (Fig. 1B) and distortions of the shells. These "Sr-poisoned" shells contained up to 27 percent (by weight) of elemental Sr (more than 50 percent $SrCO_3$), but x-ray diffractograms did not reveal any detectable amount of strontianite; only a shift of the aragonite peak toward the strontianite reflection was observed. High Sr/Ca ratios in the water obviously affect the physiology of the animals, and data on Sr uptake from these shells should be applied with caution. Neither absolute Ca and Sr concentrations in tank water nor ionic strength within the range of normal freshwater systems had any visible effect on the growth pattern.

The Sr/Ca ratios of the water are by far the most important parameter controlling the Sr uptake in *Limnaea stagnalis*. Neither variations in temperature nor variations in growth rate had any measurable influence on the Sr partitioning between water and shell aragonite (Fig. 1A). Figure 2 shows data from all tanks and indicates the existence of a linear relationship between Sr/Ca ratios in tank water and corresponding shells. If data from the "abnormal" Sr-poisoned tanks are excluded, the k values in six tanks vary between 0.10 and 0.29; statistical treatment of the results yields:

$$(\mathrm{Sr/Ca})_{\mathrm{ar}} = 0.23 \times (\mathrm{Sr/Ca}_{\mathrm{water}})^{0.99}$$

where the correlation coefficient r = 0.99. Expressed as an average value, one obtains $k_{\mathrm{Sr}}^{\mathrm{A}} = 0.237 \pm 0.029$. Data from three tanks with abnormal environments yield k values between 0.34 and 0.35, reflecting higher Sr concentration in these snails.

Data by Odum (*7*) and Faure *et al.* (*9*) are also compiled in Fig. 2. Despite the fact that the Sr content of the water varies from very low values (approximately 20 parts per billion) to more than 10 times that observed in nature (250 ppm), the Sr/Ca ratios in water and aragonite from the different gastropod species investigated are strongly correlated, yielding an overall distribution coefficient of $k_{\mathrm{Sr}}^{\mathrm{A}} \approx 0.25$. This result suggests that the Sr uptake by many freshwater mollusks is independent of taxonomy, absolute Sr and Ca concentrations in the water, and temperature.

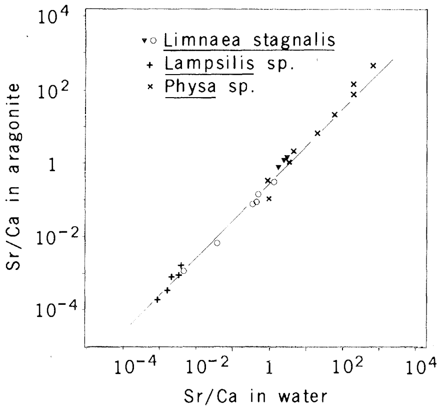

Fig. 2. Uptake of Sr (Sr/Ca ratio in aragonite) as a function of the Sr/Ca ratio in tank water: ○, shells grown at $\mathrm{Sr/Ca}_{\mathrm{water}}$ lower than 1.5; ▼, shells grown at $\mathrm{Sr/Ca}_{\mathrm{water}}$ above 1.5, showing Sr poisoning; ×, Sr data from *Physa* sp. grown in tanks by Odum (*7*); +, Sr data from *Lampsilis* sp. collected in the Great Lakes by Faure *et al.* (*9*). The ionic strength in our experiments was always less than 2×10^{-2}, and it was lower by about an order of magnitude in the Great Lakes where Faure *et al.* collected their material.

The $k_{\mathrm{Sr}}^{\mathrm{A}} = 0.237$ for *L. stagnalis* is somewhat lower than the value for *Physa* of 0.288 given by Odum (*7*) but is in good agreement with the *Lampsilis* data of Faure *et al.* (*9*). Odum's results, however, were based on tank experiments with Sr/Ca ratios in water as high as 200; these snails were probably affected by a Sr poisoning effect, leading to a greater Sr enrichment in the aragonite. No information on the total chemistry of Odum's solutions is available to us.

Compared to the inorganic $k_{\mathrm{Sr}}^{\mathrm{A}} = 1.12$ for aragonite precipitated at 25°C (*4*), the observed value of 0.237 is more than four times smaller. This result confirms the existence of a biochemical discrimination of Sr uptake during formation of shell aragonite in mollusks. No experimentally documented $k_{\mathrm{Sr}}^{\mathrm{A}}$ values are available for marine mollusks, but data given by Lowenstam (*5*) and Milliman (*2*) for free-living organisms yield similar values (*10*). The effect is probably related to the internal precipitation of shell carbonate in mollusks in contact with the pallial fluid in a microenvironment separated from the surrounding water by the mantle, a process involving transportation of ions across biological membranes. If the Sr uptake in ancient mollusks was controlled by the same factors, it would be possible to estimate the Sr/Ca ratio in fossil shell aragonite unaffected by diagenetic processes (assuming that the Sr/Ca ratio in ancient oceans was identical to the conditions at present).

Several investigators have related variations in the Sr concentration in mollusk aragonite with salinity and temperature variations (*11*). Our findings indicate that the important factor controlling the Sr uptake in natural environments is the Sr/Ca ratio of the water, and that temperature and absolute Sr concentration exert little or no influence. Therefore, unless variations in the Sr/Ca ratios in the water in ancient environments are known or inferred, paleoenvironmental conclusions based on Sr analyses of fossil shell aragonite should be considered with great caution.

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10. The Sr and Ca data from Palau in (*5*) yield $k_{\mathrm{Sr}}^{\mathrm{A}}$ values for gastropods and pelecypods of 0.25 and 0.27, respectively; standard deviations are 0.05 (N = 26) and 0.03 (N = 15). Average values from (*2*) for both gastropods and pelecypods from marine environments are close to 0.28, but are biased from a lack of information about water composition. For Polyplacophora, which do not discriminate against Sr as the other mollusks do, the Sr/Ca ratio of the water appears to be the most important factor determining the Sr/Ca ratio of the shell [H. A. Lowenstam, *Sea* **5**, 728 (1974) and figure 2].
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12. We acknowledge the assistance of J. Catterall and R. J. Drimmie in the growth experiments and in the analysis of the samples. Financial support was obtained through National Research Council grant A 7954 to P.F. and through Danish Natural Science Research Council grant 511-6571 to B.B.

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