RICE UNIVERSITY

The Transfer of Strontium, Iron, and Magnesium from Sea Water to Skeletal Carbonate Material

by

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF ARTS

Thesis Director's signature:

John J. W. Rogers

Houston, Texas
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ABSTRACT

Analyses were performed for strontium, iron and magnesium in the skeletal material of three invertebrate species and in samples of sea water coexisting with the organisms. The results indicate that adsorption and crystal growth, skeletal mineralogy, and salinity may all, under certain circumstances, partially control the transfer of strontium and magnesium from sea water to skeletal material. Salinity effects were noted only in the skeletal material of specimens collected from waters of less than 6 (o/oo) salinity. Iron does not appear to be effectively controlled by phylogenetic association, skeletal mineralogy, or salinity.
INTRODUCTION AND PURPOSE OF STUDY

This investigation was initiated to delineate the major factors controlling the transfer of strontium, iron, and magnesium from sea water to skeletal carbonate material. Investigations by Chave (1954), Swan (1956), Turekian and Armstrong (1960), and Pilkey and Goodell (1963) have indicated that skeletal mineralogy, overall growth rate, phylogenetic level, and habitat (i.e., temperature and salinity) may all, to a greater or lesser degree, control the incorporation and distribution of minor elements in marine invertebrate skeletal material.

Particular consideration in this study is given to elucidating the role of adsorption and crystal growth kinetics in controlling the incorporation of minor elements into the skeletal material of three selected invertebrate species. If significant intraspecific and/or interspecific differences in the concentration, distribution, and variability of minor elements in invertebrate skeletons exist, and if these differences can be attributed to adsorption and/or crystal growth processes occurring during calcification, then the elucidation of these processes will lead to a more complete understanding of the calcification process and the role of the organism in the geochemical cycle.

In order to reduce the organic variables, this study has been conducted with particular emphasis on intraspecific variation of strontium, iron, and magnesium between
geographically distinct populations of three invertebrate species. The three species chosen for this study are *Balanus eburneus* Gould, a barnacle, *Littorina irrorata* Say, a gastropod, and *Crassostrea virginica* Gemlin, a pelecypod. All three species are intertidal organisms and are found over a rather extensive environmental range. A total of approximately 100 carbonate samples was analyzed for strontium, iron, and magnesium contents.

In order to evaluate correctly environmental versus physical and organic control of minor-element incorporation, it is necessary that the exact amount of a particular element available to an organism in its habitat be known. Approximately 40 sea-water samples were collected from the same localities as the organisms used in this study. The sea-water samples were analyzed for strontium, iron and magnesium contents and salinity. The correlation between elemental content and salinity is discussed.

The relationship between the individual elements, particularly minor elements, and the salinity of sea water is poorly defined. Inasmuch as salinity is a measure of the total amount of dissolved salt in solution, it may be expected that the major elements present in the sea water will exhibit a direct relationship to the bulk salinity. However, the minor elements represent an extremely small fraction of the total dissolved salts, and fluctuations in the concentration of minor elements are not detectable by salinity-measurement apparatus presently
in use. Also, a fluctuation in the major-element content of sea water and a corresponding fluctuation in salinity does not require a proportionate change in the minor-element concentrations of a particular sea water sample.

FIELD AND LABORATORY TECHNIQUES

Samples were taken in January, April, and August, 1963, along the Texas Gulf coast. Samples were also taken in March, April, and May, 1963, in the vicinity of Sapelo Island, Georgia. The collection localities and observed salinity ranges at each locality and for each species are presented in Tables 1 and 2.

All of the specimens chosen for this study were collected alive, the soft parts removed, and the shell material cleaned thoroughly with distilled water and a Clorox solution. After cleaning, the shells were ground manually to a fine powder in a ceramic mortar and pestle.

The powdered specimens were subjected to X-ray analysis, and all bimineralic specimens were rejected. Monomineralic specimens were selected to reduce the physical variables. The *C. virginica* and *B. eburneus* specimens used were 100% calcite and the *L. irrorata* specimens 100% aragonite. The X-ray analyses were performed on a Norelco X-ray diffractometer using Cu - Kα radiation.

The samples were subsequently put into solution using 0.6N nitric acid. For the majority of the analyses 0.5 grams of sample were dissolved in 50ml. of acid solution.
TABLE 1

Locality Data

<table>
<thead>
<tr>
<th>Number</th>
<th>Observed Salinity Range (o/oo)</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB</td>
<td>16.4-24.6</td>
<td>N. end of Copano Bay bridge, State Highway 35, approximately 10 mi. N. of Rockport, Texas.</td>
</tr>
<tr>
<td>WB</td>
<td>18.5-26.0</td>
<td>West Bay, Galveston, Texas.</td>
</tr>
<tr>
<td>JB</td>
<td>17.6-21.0</td>
<td>Jones Bay, Galveston, Texas.</td>
</tr>
<tr>
<td>P</td>
<td>21.0-25.2</td>
<td>Tres Palacios Bay, Palacios, Texas.</td>
</tr>
<tr>
<td>LB</td>
<td>19.0-25.0</td>
<td>S. end Lavaca Bay bridge, State Highway 35, Port Lavaca, Texas.</td>
</tr>
<tr>
<td>DI</td>
<td>6.6-24.8</td>
<td>W. side of Doboy Island, vicinity of Sapelo Island, Georgia.</td>
</tr>
<tr>
<td>ML</td>
<td>21.5-25.4</td>
<td>Marsh Landing, Duplin River, Sapelo Island, Georgia.</td>
</tr>
<tr>
<td>SP</td>
<td>21.1-23.1</td>
<td>Sawdust Pile, Duplin River, Sapelo Island, Georgia.</td>
</tr>
<tr>
<td>DB</td>
<td>1.0</td>
<td>Darien Bridge, U.S. Highway 17, Darien, Georgia.</td>
</tr>
<tr>
<td>Sample Size and Observed Salinity Ranges for Each Species</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------------------------------------------------</td>
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<td></td>
</tr>
<tr>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>TABLE 2</strong></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total no. of specimens</td>
<td>C. virginica</td>
<td>B. eburneus</td>
</tr>
<tr>
<td></td>
<td>46</td>
<td>26</td>
</tr>
<tr>
<td>No. populations sampled</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>Observed Salinity Range (o/oo)</td>
<td>7.0-26.0</td>
<td>1.0-26.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
For those samples containing greater than 1000 ppm strontium and magnesium, further dilution was required.

The chemical analyses were performed on a Perkin-Elmer model 214 atomic absorption spectrophotometer. A description of the instrumentation and techniques is presented in Appendix I.

Precision was determined by analyzing 10 of the carbonate samples in duplicate. The per cent deviation from the mean of each sample pair was averaged to obtain the precision. The precision for strontium in the skeletal material was ±3.0% of the amount present. The precision for iron was ±3.5% and for magnesium ±2.5% of the amount present.

All sea-water samples were collected concurrently with the organisms and stored in polyethylene bottles. The sea-water samples represent random intervals with reference to tidal fluctuations in most cases. A few systematic surveys over complete tidal cycles were performed at the Georgia localities. Salinity measurements were made at the time of collection with a hydrometer. A discussion of major and trace cation analysis of sea water by atomic absorption spectrometry will be presented elsewhere (Harriss and Billings, in preparation).

THE DISTRIBUTION OF STRONTIUM, IRON, AND MAGNESIUM IN COASTAL WATERS

The composition of sea water has been discussed by
several investigators including the excellent works of Lyman and Fleming (1940) and Krauskopf (1956); however, these investigators were dealing with sea-water samples not subjected to extensive tidal mixing and corresponding chemical variations. The present study deals with the skeletal chemistry of intertidal organisms, and it was important that knowledge of the chemical behavior of strontium, iron, and magnesium in shallow coastal waters be more clearly defined.

The relationships between strontium, iron, and magnesium contents and bulk salinity for both Texas and Georgia samples are presented in Figures 1-6 at the end of the text.

The following conclusions were drawn from this preliminary investigation of element-salinity relationships:

(1) Magnesium, as expected, exhibits a fairly consistent direct relationship to bulk salinity measurements over the salinity range investigated.

(2) The ionic ratios of strontium and iron to the major elements (i.e., Sr/Mg and Fe/Mg) are highly variable over the salinity range investigated. In particular, the Sr/Mg and Fe/Mg ratios are inconsistent with those expected on the basis of salinity measurements in the lower salinity ranges.

The failure of strontium and iron to exhibit a consistent relationship to bulk salinity cannot be attributed entirely to the effect of dilution by fresh water because, if this were the case, magnesium should show
similar effects. The present writer suggests that, particularly in the case of iron, which shows the greatest variability in the coastal waters studied, variations in the pH and Eh of the aqueous environment are a significant factor in determining the amount of dissolved iron present. Baas Becking et al. (1960) report a pH range of approximately 6.0 to 9.5 for sea water. A consideration of the solubility relationships of the more common precipitates of iron in the marine environment indicates that the concentration of iron in sea water is highly dependent on the pH.

Another factor which undoubtedly contributes to the observed minor element variability is the degree of organic productivity at a particular collection time and locality. For example, iron is known to be an important constituent in certain organic compounds, and if organic productivity is high at a particular location, then presumably the iron content of the water would be temporarily lower than adjacent areas of low productivity.

The variability of strontium in coastal waters, though less extreme than that of iron, exceeds that of the major elements. At present this writer has no explanation for the variability of strontium other than dilution, which as previously indicated, is probably only a partial affect at the most. It is possible that the formation of stable complex species with the chloride ion in sea water is a complicating factor. The instrumentation used in this study measures only elements which are in the ground state and form the atomic species in the flame. If strontium
is present as a stable chloride complex in sea water, the formation of the complex species is not directly related to the total chloride concentration over the salinity range investigated (see Figures 1 and 4).

The most important feature of these analytical results is that they demonstrate that large changes in salinity can occur without corresponding changes in the minor element concentrations in coastal sea water.

RESULTS

The analyses of skeletal carbonate are presented in Figures 7-9. The figures are a plot of the average concentration and standard deviation of each element in the skeletal material of each population. From five to ten specimens were analyzed from each population sampled.

The strontium and magnesium contents of the three species show a definite "phylogenetic effect". The interspecific differences are much greater than the intraspecific differences. Several other interesting points deserve mention. First, the largest difference in strontium content is between the two predominantly calcite-secreting organisms, C. virginica and B. eburneus. This suggests that skeletal mineralogy is not the predominant factor controlling minor-element incorporation. Second, the magnesium contents of the three species exhibit a significantly larger intraspecific variability than the strontium contents (see Table 5). Third, the B. eburneus specimens from the essentially fresh
TABLE 3

Distribution of Strontium, Iron, and Magnesium Within Individual Shells*

<table>
<thead>
<tr>
<th>Specimen</th>
<th>location on shell</th>
<th>organic content (gm/0.5gm CaCO₃)</th>
<th>ppm Sr</th>
<th>ppm Fe</th>
<th>ppm Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>C. virginica</td>
<td>Beak</td>
<td>0.003</td>
<td>1100</td>
<td>100</td>
<td>1760</td>
</tr>
<tr>
<td>C. virginica</td>
<td>Adductor Scar</td>
<td>0.004</td>
<td>1200</td>
<td>110</td>
<td>1720</td>
</tr>
<tr>
<td>C. virginica</td>
<td>Posterior Edge</td>
<td>0.007</td>
<td>1110</td>
<td>128</td>
<td>2260</td>
</tr>
</tbody>
</table>

*The values in this table represent the mean concentrations from the analysis of ten individual shells.
water locality (DB) exhibit a skeletal composition distinct from the other populations of *B. eburneus*. The low-salinity population exhibits a lower average strontium content and a higher average magnesium content than the three remaining populations of *B. eburneus* from the higher-salinity locations.

The iron contents of the three species, in contrast to the strontium and magnesium contents, do not exhibit distinct interspecific differences. However, the iron contents of the three species generally exhibit more intraspecific variation than either the strontium or magnesium contents for the majority of the specimens investigated. The *C. virginica* specimens collected from the Georgia coast exhibit higher average iron concentration than the *C. virginica* specimens from the Texas coast.

A brief investigation of the distribution of strontium, iron, and magnesium within individual shells of *C. virginica* revealed differences in the concentrations of all three elements between different areas of the individual shells (see Table 3). The average strontium content of the ten specimens analyzed was highest in the central region of the shell. The iron and magnesium contents of *C. virginica* were highest in the posterior region of the shell.

**DISCUSSION**

**Introduction**

Previous investigators have demonstrated the following
points concerning minor-element concentrations in invertebrate skeletal material.

(1) Chave (1954) has demonstrated that skeletal mineralogy can be an important factor in controlling the distribution of magnesium in calcareous skeletons. Chave suggests that biological complexity and water temperature are also controlling factors, but of secondary importance in comparison to mineralogy.

(2) In contrast to Chave, Turekian and Armstrong (1960) reported that taxonomic considerations, rather than water temperature and skeletal mineralogy, appeared to be the predominant factor controlling minor-element concentrations in some Recent molluscan shells.

(3) Pilkey and Goodell (1963) demonstrated that differences in salinity cause greater changes in shell composition than differences in temperature, but that salinities above 25 o/oo do not greatly affect shell composition.

In summary, it is possible to say that taxonomic considerations, skeletal mineralogy, water temperature and salinity are factors controlling the distribution of minor elements in skeletal material; however, the question of the relative importance of these factors in relation to each other and in relation to other factors is not well understood.
Several interesting relationships concerning the concentration and distribution of minor elements in calcareous skeletons cannot be satisfactorily explained on the basis of mineralogy, "phylogenetic association", water temperature and salinity alone. The following examples are representative.

(1) Calcite skeletons can contain significantly higher concentrations of strontium than aragonitic skeletons. This is contrary to what one would expect if skeletal mineralogy is the predominant factor controlling minor-element incorporation. In the case of organisms living in similar habitats, as for example coexisting populations of *B. eburneus* and *L. irrorata*, this effect might be attributed to "phylogenetic association". The question as to whether the apparent phylogenetic effect on minor-element concentrations is primarily a metabolic effect or a crystal growth effect is of extreme importance in evaluating the organic control of skeletal composition.

(2) The intraspecific variability of strontium and magnesium in skeletal material shows an inverse relationship to the variability of the same elements in the coastal water samples investigated. In the water, strontium is more variable than magnesium (see Figures 1-6).
and in the skeletal material, magnesium is more variable than strontium (see Table 5).

(3) The iron contents of the three species investigated in the present study are more variable than the strontium and magnesium contents and are apparently not effectively controlled by skeletal mineralogy, "phylogenetic association", or salinity.

In the remainder of this section, an attempt will be made to construct a qualitative self-consistent explanation of the incorporation and distribution of minor elements in invertebrate skeletal material. The first part of the following discussion will deal with the nucleation of mineral phases on organic membranes; the latter part will involve the development of a physical model to explain qualitatively the observed chemical relationships.

Comments on Calcification

Investigations by Bevelander and Benzer (1948), Gregoire (1957), Wilbur (1960), Travis (1960), and Hare (1963) have made a significant contribution towards the elucidation of the calcification mechanism in marine invertebrates.

In general, two distinct stages have been observed in connection with the formation of invertebrate skeletal material: (1) the development of a fibrous organic membrane, and (2) the nucleation and growth of mineral phases on the organic matrix (Bevelander and Benzer, 1948). This writer feels that the protein structure of the outer
pallial epithelium, by serving as a nucleation agent for the mineral phase, plays a predominant role in determining skeletal mineralogy, size and perfection of the individual crystallites, and consequently skeletal composition. Evidence specifically supporting this view has been presented by Hare (1963), who demonstrated distinct differences in the amino acid content of the various structural units of *Mytilus californianus*. The organic matrices from calcite layers of *M. californianus* demonstrate a consistently higher ratio of acidic to basic amino acids than the aragonitic shell units. Furthermore, uncalcified shell units have very few acidic residues, which Hare believes may account for the lack of mineralization.

An invertebrate skeleton is composed of an extremely large number of tiny crystallites bound together in a conchiolin matrix. During the construction of an invertebrate skeleton, the large number of individual crystallites which combine to produce a shell, present an enormous total surface area for ion transfer across the solid-liquid interface. Hence, the chemistry of invertebrate skeletal material may be, to a large degree, a problem of surface chemistry.

Electron micrographs of individual skeletal crystallites and groups of crystallites have been presented by Watabe et. al. (1958), Wilbur (1960), and Hay (1963). These studies have demonstrated that a large range in both size and form of individual crystallites occurs not only between various phylogenetic groups but also within a single skeleton.
However, the differences between phylogenetic groups appear to be of much greater extent than differences within a single skeleton. Using this information concerning nucleation and crystal size as a foundation, a physical model for minor-element incorporation will now be developed.

**Mechanism of Minor-Element Incorporation**

Following nucleation, consider each crystallite and the surrounding medium as a system composed of four distinct phases. The individual phases are: (1) the crystal interior, (2) the crystal surface, (3) a bound hydration layer, and (4) the bulk solution. The bound hydration layer, often termed the "Helmholtz double layer", results from the presence of unsatisfied chemical bonds at the crystal surface which set up a strong electric field in the vicinity of the crystal-solution interface (Weyl et al., 1953). For the case of calcium carbonate, the crystal surface is probably composed predominantly of partially bonded oxygen atoms, the layer of atoms beneath the crystal surface being composed of the less polarizable calcium and carbon atoms. The surface structure of calcium carbonate thus may be assumed to resemble that of an oxide of calcium and is negatively charged.

Crystal growth requires that specific ions diffuse through the surrounding media to the crystal surface where they may be incorporated into the lattice, thus increasing the size of the crystal. A problem with which this writer is particularly concerned is the mobility of various chemical species, relative to the calcium ion, during the
transfer of chemical elements from sea water to the crystal interior.

The ability of an organism to concentrate and reject certain chemical elements relative to their concentration in sea water is a result of the electropotential gradient set up by partially bonded atoms in the surface layers of the growing crystallites. There appear to be four possible types of ion-interactions between growing skeletal crystals and sea water:

(1) Ions which diffuse into the hydration shell of the growing crystallite but do not concentrate there, the concentration of the particular ion in the hydration shell being directly proportional to its concentration in sea water. Ions in this group, which includes mostly ions of low ionic potential (ionic potential \(=\text{charge}/\text{radius}\)), are not very effective in reducing the residual surface charge on the growing crystallite and, hence, are not concentrated in the hydration layer. The ions of this group which are incorporated into the growing crystallite, such as potassium and sodium, would tend to reflect more closely the chemistry of the coexisting sea water than any of the other chemical constituents of sea water. Evidence to support this view has been presented by Rucker and Valentine (1961), who
found a statistically significant correlation between the sodium contents and mean annual salinity in 71 specimens of *C. virginica* from 11 stations along the Atlantic coast of the United States.

(2) The second group of ions to be considered are those which enter the hydration shell and participate to a large degree in the neutralization of surface charge. In this case the concentration of an ion in the hydrated layer need not be related to its concentration in the sea water. Those ions which are most successful in reducing the surface charge would tend to become concentrated in the hydration shell, while others would be present in proportions equal to or less than their concentrations in sea water. This group probably includes all of those ions present which have ionic potentials greater than 1.0. This excludes mainly the monovalent ions whose small charge-to-radius ratio results in little adsorption of these ions on the crystallite surface.

(3) The third type of ion-interaction includes those ions which enter the hydration shell and subsequently are incorporated into the crystal surface. The ability of an ion to become incorporated into the crystal surface depends
chiefly on its ability to satisfy the requirements of the calcium or carbonate site in the surface layer of the crystal lattice. Ions in this group will generally be found concentrated in the skeletal material relative to the seawater. Strontium, magnesium, manganese, ferrous and ferric iron, and cadmium are examples of this group of ions.

The final group of ions to be considered are those which are incorporated into the crystal interior during crystal growth, presumably diadochically with calcium. The requirements for this case are similar to those of case (3). The ions must adequately fulfill the electrovalency and size requirements of the sites which they occupy in the crystal lattice. However, certain ions may satisfy surface requirements and not the requirements of the inner lattice, and these ions are, hence, surface-limited. An example of a probable surface-limited ion occurs in the case of magnesium in the aragonite structure. Leaching experiments presently being performed by this writer have demonstrated that magnesium is removed very rapidly from the aragonitic material in comparison to strontium and iron. In the case of calcite, the magnesium appears
to be only slightly more mobile than strontium and iron during alteration. Magnesium would be classified as a group (4) ion with respect to calcite and a group (3) ion with respect to the aragonite lattice.

If adsorption and crystal-growth kinetics control the incorporation of foreign elements into calcium carbonate skeletal material, it is evident why previous investigators did not observe good statistical correlation between the minor-element content (excepting sodium) of molluscan skeletal material and the environmental parameters, temperature and salinity. In terms of the adsorption-crystal growth model, proposed herein as a controlling factor on minor-element incorporation, the observed salinity effect may be explained as follows. The hydration layer of a growing crystallite can contain a definite concentration of ions. If the concentration of ions in the sea water is below that concentration required to saturate the hydration layer, then the concentration of ions in the hydration layer will vary in response to changes in the chemical composition of the coexisting sea water. However, once the concentration of ions in the sea water reaches the point where the hydration layer is saturated, then further increases in salinity have little effect on the concentration of ions in the hydration layer and correspondingly in the crystallite.

Several complicating factors must be considered in relation to the concentration and composition of ions
present in the hydration layer at any salinity. First, in coastal waters similar to those investigated in the present study, in which the ratio of minor elements to major elements increases with decreasing salinity, the concentration of minor elements relative to calcium in the skeletal material increases in low-salinity forms relative to higher-salinity forms. Second, the total minor-element concentration in a shell depends not only on the minor-to-major element ratios in the coexisting sea water but also on the growth rate of the individual crystallites. The faster-growing crystallites presumably contain a higher impurity content than the crystallites which grow slowly. The ability of various organic and inorganic substances to concentrate rare metals from sea water by adsorption has been demonstrated by Krauskopf (1956).

The data obtained in this investigation, as well as the other existing data on the minor-element content of calcium carbonate skeletal material, appear to satisfy the requirements of the proposed adsorption-crystal growth model. The concentrations of strontium, iron, and magnesium in the skeletal material of the three species investigated, relative to sea water, are presented in Table 4. It is obvious that strontium and iron are, in all cases, concentrated in the skeletal material relative to the sea water. Magnesium, in contrast to strontium and iron, is only slightly concentrated in the calcitic skeletal material
<table>
<thead>
<tr>
<th>Specimen</th>
<th>Sr</th>
<th>Fe</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crassostrea virginica</td>
<td>250</td>
<td>203</td>
<td>1.3</td>
</tr>
<tr>
<td>Balanus eburneus</td>
<td>798</td>
<td>151</td>
<td>2.8</td>
</tr>
<tr>
<td>Litorina irratoria</td>
<td>449</td>
<td>264</td>
<td>0.19</td>
</tr>
</tbody>
</table>

*The values presented in Table 4 are calculated in the following manner:
Average ppm element in skeletal material
Average ppm element in coexisting water

Value
of C. virginica and B. eburneus and is rejected by the aragonitic skeletal material of L. irrorata. The high ionic potential of magnesium makes it an effective ion for reducing residual surface charge; however, its small ionic radius prevents it from successfully occupying the calcium site in the aragonite lattice. Although magnesium is not highly concentrated relative to sea water in any of the three species investigated in the present study, the magnesium concentrations in the calcite shells are higher than those in the aragonitic shells. The higher concentrations of magnesium in calcite skeletal material are attributable, at least in part, to mineralogical effects, as demonstrated by Chave (1954). The calcium ion in calcite is in six-fold coordination with oxygen, while in aragonite calcium is in nine-fold coordination with oxygen. The magnesium ion, with its small ionic radius, is more favorable for the smaller coordinated site in the calcite lattice.

The effect of extremely low-salinity environments on the chemical composition of skeletal material has been demonstrated by Pilkey and Goodell (1963). In the present investigation, salinity effects were observed only in the case of one B. eburneus population collected from essentially fresh water (see Figures 7-9). If the concentration of calcium in the bulk-solution phase is insufficient to neutralize the total residual surface charge, the concentrations of other cations present in the hydrated
layer relative to calcium will increase, and consequently the concentration of foreign elements relative to calcium in the lattice will increase. The sea-water samples investigated indicated that large decreases in the major-element content of sea water are not always accompanied by proportionate decreases in minor-element content. Hence, it is to be expected that in many low-salinity environments the organisms present will exhibit higher concentrations of certain foreign elements than their counterparts in higher-salinity environments.

The apparent phylogenetic effect on the concentration of minor elements in the skeletal material (see Figures 7-9) is very likely, in part at least, a reflection of differences in the total surface area and the average growth rates of the individual crystallites. Species such as B. eburneus which have a very dense outer pallial epithelium and consequently many potential nuclei have a shell composed of an extremely large number of very small crystallites. Organisms such as C. virginica which have a less dense outer organic membrane build a shell composed of a smaller number of relatively large crystallites. The skeletal material composed of a large number of small crystallites exhibits a higher minor-element content. It is also interesting to note that, in the investigation of the distribution of minor elements within individual shells (see Table 3), areas of highest organic content and smaller individual crystallites are characterized by higher iron and magnesium concentrations.
Organic material was carefully analyzed. In no case were strontium, iron, or magnesium detected in significant amounts; hence, the distribution of minor elements within an individual shell appears to be attributable in a qualitative sense to the adsorption and crystal growth processes described above. However, the exact chemical composition of the solutions from which the crystallites form is not known. Most certainly, the sea water has been modified to some extent by the metabolic processes of the organism. High-magnesium calcite secreted by certain organisms is a good example of organic control on the incorporation of certain chemical constituents into skeletal material. Such high-magnesium calcites presumably cannot be formed by inorganic processes alone.

The average variability of strontium, iron and magnesium in the skeletal material of the nine different populations sampled has been calculated in the following manner:

\[
\% \text{ chemical variation} = \frac{\text{standard deviation (ppm)}}{\text{avg. concentration (ppm)}} \times 100
\]

where

\[
\text{standard deviation} = \sqrt{\frac{\sum (x_i - \overline{x})^2}{N-1}}
\]

The results of these calculations are given in Table 5. The variability of the elements in the skeletal material
TABLE 5

Chemical Variation in the Skeletal Material of *Crassostrea virginica*

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Chemical Variation in the Skeletal Material of *Littorina irrorata*

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Chemical Variation in the Skeletal Material of *Balanus eburneus*

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increases in the following order:

\[ \text{Fe} > \text{Mg} > \text{Sr}. \]

Although iron shows the greatest variation in both sea water and skeletal material, the variability relationship between strontium and magnesium in sea water and skeletal material is reversed. This evidence adds support to the hypothesis that, except at extremely low salinities, skeletal composition does not reflect the environment. The high variability of iron is probably attributable to the sensitivity of the various chemical species of iron to changes in the pH and Eh conditions of the local environment. The failure of iron to demonstrate a "phylogenetic effect" probably indicates that the iron present in the hydration layer is predominantly ferric iron and therefore exhibits very limited diadochy with calcium. The ferric iron would not satisfy the electrovalency or size requirements of the calcium site in the calcium carbonate lattice and would be present mainly as a surface-limited species with respect to marine carbonates.

In summary, the present investigation has demonstrated that the incorporation of minor elements into skeletal material is a complex process, the incorporation of the individual elements being controlled by adsorption and crystal growth, skeletal mineralogy, salinity, and an unevaluated metabolic effect.
CONCLUSIONS

The following conclusions are made on the basis of the results obtained in the present study.

(1) The incorporation and distribution of iron in calcium carbonate skeletal material, in contrast to strontium and magnesium, does not appear to be effectively controlled by phylogenetic association, skeletal mineralogy, or salinity.

(2) Salinity effects on the skeletal composition of the three species investigated were found only in extremely low-salinity environments. *B. eburneus* specimens living in waters of less than 6 (o/oo) salinity exhibit a higher trace-to-major-element ratio than specimens of the same species collected from higher-salinity environments.

(3) The intraspecific variability of the elemental constituents investigated exhibits the following sequence: Fe > Mg > Sr. This relationship appears to hold for both calcite and aragonite skeletons; iron and magnesium exhibit similar degrees of variation in aragonitic skeletal material. Strontium showed much less intraspecific variability than iron and magnesium in all of the specimens investigated in the present study.
Adsorption and crystal growth are possibly major factors controlling the minor-element distribution in invertebrate skeletal material. Skeletal mineralogy, metabolic processes, and salinity are secondary factors controlling minor-element distributions, and the relative importance of these secondary factors differs according to the organism and element under consideration.
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</tr>
<tr>
<td></td>
<td>JB - 8</td>
<td>2600</td>
<td>395</td>
<td>405</td>
</tr>
<tr>
<td></td>
<td>JB - 9</td>
<td>2070</td>
<td>260</td>
<td>215</td>
</tr>
<tr>
<td></td>
<td>JB - 10</td>
<td>2190</td>
<td>288</td>
<td>215</td>
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</table>
Fig. 1 - Salinity versus strontium content for Texas coastal waters.
Fig. 2 - Salinity versus iron content for Texas coastal waters.
Fig. 3 - Salinity versus magnesium content for Texas coastal waters.
Fig. 4 - Salinity versus Strontium content for Georgia coastal waters.
Fig. 5 - Salinity versus iron content for Georgia coastal waters.
Fig. 6 - Salinity versus magnesium content for Georgia coastal waters.
Fig. 7 - Strontium concentrations in populations of C. virginica, L. irrorata, and B. eburneus.
Fig. 8 - Iron concentrations in populations of _C. virginica_, _L. irrorata_, and _B. eburneus_.

Species and Location

ppm Fe
REFERENCES


APPENDIX I

TECHNIQUES FOR THE ANALYSIS OF CALCIUM CARBONATE SKELETAL MATERIAL BY ATOMIC ABSORPTION SPECTROMETRY

Introduction

Atomic absorption spectrometry was first proposed by Walsh (1955) and has since been applied to the analysis of major and minor elements in biological materials (Willis, 1962), soils (David, 1960), metals (Elwell and Gidley, 1962), sea water (Fabricand et al., 1962), and geological materials (Billings, 1962). In this study, techniques have been developed for the analysis of calcium carbonate skeletal material by atomic absorption spectrometry.

A detailed discussion of the theory of atomic absorption has been presented by Walsh (1955). Basically, the instrumentation used in atomic absorption spectrometry operates on the following principle. Energy of a specific wavelength is passed through a flame in which a sample is vaporized, and the intensity of the energy of this wavelength remaining after passage through the flame is compared with the intensity of the energy emitted by the source. The decrease in energy resulting from absorption in the flame provides a direct measure of the amount of element being analyzed in the vaporized solution and in the original sample. To be detected, an element should be in the ground state and form the atomic species in the flame. The major problem associated with atomic absorption spectrometry is the formation of complex species which do not break down in
the flame.

**Instrumentation**

The instrument used in this study was a Perkin-Elmer model 214 atomic absorption spectrophotometer. The basic analytical instrumentation required consists of a light source, flame burner, monochromator, and a detector and associated readout system. Hollow-cathode and Osram lamps provide spectral emission lines corresponding to the absorption lines of the various chemical elements. A dual-beam optical system permits exceptional stability by compensating for variations in the intensity of the source. The fuel used in this unit is a mixture of acetylene and compressed air.

**Sample preparation and analysis**

Four primary steps were taken in the development of the techniques described in this paper. First, standards were prepared by diluting stock reagent-grade salts with spectral-grade distilled water to required concentrations. Several artificial rock standards were prepared by mixing different amounts of calcium, magnesium, strontium, and iron together. The artificial rock standards were used to check possible chemical interferences between the various ions in solution.

Second, standard salt solutions and artificial rock standards were tested using various fuel mixtures to determine the optimum working conditions for each element.
Samples of dissolved skeletal material were also run at various fuel mixtures. The results of several of the flame tests are shown in Figure 10. Variations in the fuel mixture had the greatest effect on the analysis of strontium and magnesium. The analysis of iron was only slightly effected by variations in the fuel mixture.

Third, known amounts of strontium, iron, and magnesium were added to various types and concentrations of acids in order to determine type and concentration of acid in which chemical interferences would be at a minimum. The results of the acid tests for strontium, iron, and magnesium are shown in Figures 11 and 12. In all cases hydrochloric acid had a more pronounced effect on the ions in solution than nitric acid. Strontium, iron, and magnesium form more stable complexes with the chloride ion than with the nitrate ion. In the case of strontium it appears that the maximum absorption obtainable from a 5 ppm solution was not quite reached in the 0.6N nitric acid; however, at acid concentrations weaker than 0.6N the dissolution of the carbonate material was an extremely slow process.

Finally, various samples used by the writer were checked by analysts at the Shell Development Company, Houston, Texas, using an emission spectrograph, and the results agree in all cases to less than ±15% (see Table 5).

On the basis of the above tests the optimum conditions for the analysis of each element were selected and are listed in Table 6. An 0.6N nitric acid solution was used for the dissolution of all specimens investigated.
### TABLE 5

A Comparison Strontium Analysis Performed by Atomic Absorption Spectrophotometry and Emission Spectrography

<table>
<thead>
<tr>
<th>Specimen type and No.</th>
<th>Method of Analysis</th>
<th>ppm Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-SLP-3</td>
<td>emission spectrograph</td>
<td>2000</td>
</tr>
<tr>
<td>L-SLP-3</td>
<td>atomic absorption</td>
<td>1783</td>
</tr>
<tr>
<td>L-SLP-8</td>
<td>emission spectrograph</td>
<td>1800</td>
</tr>
<tr>
<td>L-SLP-8</td>
<td>atomic absorption</td>
<td>1851</td>
</tr>
<tr>
<td>B-ML-72</td>
<td>emission spectrograph</td>
<td>2000</td>
</tr>
<tr>
<td>B-ML-72</td>
<td>atomic absorption</td>
<td>2471</td>
</tr>
</tbody>
</table>
### TABLE 6

Optimum Instrumental Operating Parameters

<table>
<thead>
<tr>
<th>Element</th>
<th>Lamp Setting</th>
<th>High Voltage</th>
<th>Fuel Flow (psi)</th>
<th>Air Flow (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strontium</td>
<td>15ma</td>
<td>300</td>
<td>4.10</td>
<td>6.3</td>
</tr>
<tr>
<td>Iron</td>
<td>14ma</td>
<td>500</td>
<td>4.10</td>
<td>6.3</td>
</tr>
<tr>
<td>Magnesium</td>
<td>12ma</td>
<td>500</td>
<td>4.80</td>
<td>6.3</td>
</tr>
</tbody>
</table>
Fig. 10 - Variation in percent absorption with changing fuel mixture.
Fig. 11 - Variation in percent absorption with changing acid concentration.
Fig. 12 - Variation in percent absorption with changing acid concentration.