

## PALEOSCENE #5. Geochemistry of Recent Marine Invertebrates

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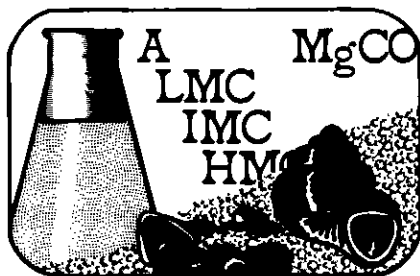
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# Articles



## PALEOSCENE #5. Geochemistry of Recent Marine Invertebrates

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### Introduction

Interpretations of geochemical data for Recent marine organisms are based on an understanding of the complex biological and chemical interactions between the environment and the organism. The researcher should be familiar with all aspects of the marine world, seawater chemistry being the prime consideration. Ocean water contains cations and anions of many major, minor and trace elements in specific concentrations. In fact, the elements sodium, calcium, magnesium, strontium, potassium, chlorine, bromine, carbon (mainly as carbonate or bicarbonate) and sulphur (primarily as sulphate) account for 99.9% of the total dissolved solids (TDS) in the ocean (Milliman, 1974; Bathurst, 1975). As a result of the predominance of these chemical elements in seawater, they are incorporated, to varying degrees, in the shells and skeletons of the invertebrates living in the marine environment. Variation in the ratios of these elements in seawater depends upon the environment and degree of biological and/or

chemical activity (Milliman, 1974; Bathurst, 1975). This activity is reflected in the variable shell chemistry of the organism inhabiting different areas. The uptake of elements into the shell-carbonate of marine invertebrates is dependent upon the mineralogy of the skeleton, salinity, temperature, oxygen level and concentrations of the elements in the surrounding seawater, as well as upon the metabolic activity of the organism. The Mg/Ca mol ratio of seawater is 5:1 and therefore should favour the inorganic precipitation of high-Mg calcite with about 1.6-7.5% Mg (cf. Berner, 1975; Mackenzie *et al.*, 1983), but this is not the case. Instead, aragonite precipitates more readily than high-Mg calcite. It is postulated that the Mg ion inhibits the precipitation of calcite, and this condition is known as the "Mg poisoning effect" (Bathurst, 1975; Morse, 1983).

The object of this paper is to relate chemical concentrations found in shells of various Recent marine invertebrates to seawater chemistry. In particular, to identify biological controls such as growth rate, nutrient uptake, and fluid pumping; isotopic fractionation and how it is affected by biological activity; and external physiochemical conditions and how they exert control over shell mineralogy and chemistry of all or part of the shell/skeleton of various marine invertebrates.

### Theoretical Considerations of Chemical Distribution

Before chemical data can be interpreted, an understanding of geochemical theory is required. Most carbonate shells are precipitated in chemical equilibrium with the surrounding seawater, and maintain thermodynamic stability in this depositional environment (Bathurst, 1975).

Calcium carbonate ( $\text{CaCO}_3$ ) formed in Recent environments can be composed of orthorhombic aragonite (A) or rhombohedral calcite (Graf, 1960). Calcite is subdivided into low-Mg calcite (LMC) with 0-5 mol%  $\text{MgCO}_3$ , intermediate-Mg calcite (IMC) with 5-8 mol%  $\text{MgCO}_3$ , and high-Mg calcite (HMC) with 8-28 mol%  $\text{MgCO}_3$  present in the  $\text{CaCO}_3$  lattice (Chave, 1954; Milliman, 1974). Thus, mineralogy and crystal structure determine, to a large extent, the concentration of a trace element in the calcium carbonate lattice (e.g. Brand and Veizer, 1980; Veizer, 1983a, b).

Minor and trace elements are incorporated into carbonate minerals in the following ways (McIntire, 1963; Zemann, 1969; see also Figure 1):

1. by direct substitution for Ca in the  $\text{CaCO}_3$  lattice (diadochic);
2. by emplacement interstitially between the lattice planes;
3. by occupation of vacant lattice positions due to structural defects;
4. by adsorption due to remnant ionic charges; and,
5. by presence in non-carbonate components, such as fluid inclusions and silicate impurities.

Factor 1 is fairly well understood and used as the general basis for geochemical studies, whereas factors 2 to 5 are random and, if they do exert an influence over the trace element distribution, are very difficult to interpret (Veizer, 1983a, b). If there is variation, it is usually due to factor 5 which involves the elemental leaching from the non-carbonate portion and therefore, if these factors are dominant, they render the geochemical data useless.

### Partition Coefficients

Partitioning of elements in carbonates follows the conditions outlined below:

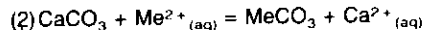
1. the amount of the precipitated solid phase must be minor in comparison to the volume of water for a state of equilibrium to exist;
2. where the volume of water is not much greater than the amount of the precipitated solid phase, the water changes its composition as precipitation progresses, and is reflected in trace-element concentration gradients in the solid phase. In this instance, the Doerner-Hoskins heterogeneous distribution law applies (Gordon *et al.*, 1959, chapter 9),

$$(1) \log (f^{\text{Me}}/i^{\text{Me}}) = D \log (f^{\text{Ca}}/i^{\text{Ca}})$$

where *i* and *f* indicate initial and final concentrations, respectively, of trace element (Me) and Ca in solution, and *D* is the distribution coefficient;

3. temperature and kinetic factors cause a variation of *D* even during precipitation of a single solid phase; and
4. the rate of precipitation is a controlling factor of *D*; with an increasing rate of precipitation, the element is enriched in the solid phase (Lorenz, 1981).

The incorporation of minor and trace elements (Me) into calcite ( $\text{CaCO}_3$ ) can be expressed by the following reaction (McIntire, 1963):



and the distribution coefficient  $D$  is related to the equilibrium constant  $K$  by several equations (Veizer, 1983b, p. 267-268). These show that the distribution coefficient is dependent on temperature, pressure and the chemical compositions of the liquid and solid phases. This complex relationship is generally represented by the following simplified equation:

$$(3) \quad (m\text{Me}/m\text{Ca})_s = D (m\text{Me}/m\text{Ca})_l$$

where  $m$  indicates molar concentrations,  $\text{Me}$  is the minor/trace element, and  $s$  and  $l$  represent the solid ( $\text{CaCO}_3$ ) and liquid phase, respectively. This relationship is only valid when the system is homogeneous and in equilibrium (Gordon *et al.*, 1959, chapter 9). In other words, the system must be at constant temperature and pressure, and there can be no concentration gradients in  $\text{Me}$  for the liquid and solid during precipitation.

Veizer (1983a, b) summarized the present theoretical status of partition coefficients involving the various minor and trace elements incorporated into  $\text{CaCO}_3$  during the precipitation of calcite and aragonite. Relative to major elements, such as Ca and/or Mg, the distribution of the minor and trace elements is governed by the following conditions of the distribution coefficient:

1. When  $D = 1$ , the precipitated carbonate contains similar amounts of Me relative to the carrier in both liquid and solid.
2. When  $D > 1$ , there is an enrichment of the Me concentration in the precipitated solid phase relative to its proportion in the liquid phase.
3. When  $D < 1$ , there is a proportional depletion of the minor and trace elements in the solid phase relative to their proportions in the liquid phase. The partition coefficients for most elements of aragonite and calcite are well known within orders of magnitude (e.g., Veizer, 1983a, p. 3-6, 3-8). In general, cations that are larger than Ca (e.g. Sr, Na, Ba, U) are preferentially incorporated into the open orthorhombic structure of aragonite. Cations that are smaller than Ca (e.g. Mg, Fe, Mn, Zn, Cu, Cd) are preferentially incorporated into the tighter rhombohedral structure of calcite. The precise calculation of  $D$  is only necessary to determine the exact water chemistry, but geochemistry is concerned with the direction (or trends) of chemical changes and the relative magnitude of chemical displacements (Veizer, 1983a, b). The magnitude and sign of  $D$  are sufficient to provide an indication of the seawater composition and the effect of diagenesis.

### Biological Fractionation

In addition to the complexities outlined above, the biogeochemistry of invertebrates can be further complicated by the organisms themselves exerting a biological control. This process of biological fractionation can lead to an enrichment or depletion of a specific trace element in the shell/skeletal carbonate. This fractionation effect is best exemplified by the Mg and Sr compositions of the major invertebrates.

As described earlier, the inorganic precipitation of high-Mg calcite in seawater is theoretically favoured, but biogenic discrimination against Mg allows for the precipitation of low-Mg calcite in the marine environment (Veizer, 1983a, b). On the other hand, molluscs that precipitate aragonite shells discriminate against the incorporation of Sr (e.g. Lowenstam, 1961, 1964). If a specific element is deficient in the environment, organisms tend to compensate by incorporating another element of similar ionic size that is present in the environment in order to maintain chemical equilibrium. Biological fractionation is an intricate process, but one that must be considered when interpreting geochemical data derived from marine invertebrate shell chemistry.

### Stable Isotope Fractionation

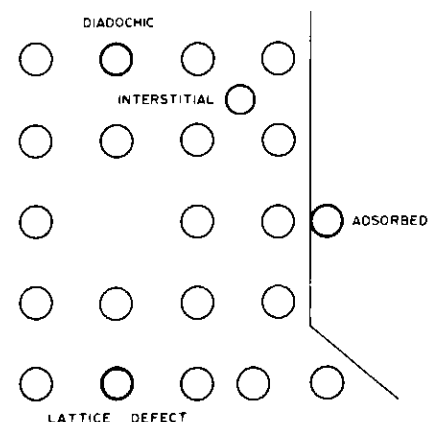
The stable isotopic composition of marine organisms is reported as a function of  $^{13}\text{C}$  and  $^{18}\text{O}$ , denoted by the " $\delta$ " notation and reported in permil (‰). The reported " $\delta$ " value depends upon the isotopic ratio of the standard used, and can be either positive (when the isotopic ratio is greater than the corresponding standard ratio), or negative (when the isotopic ratio is less than the corresponding standard ratio). Deviation from equilibrium values is mostly a reflection of changes in temperature and salinity of ambient seawater for many calcareous marine organisms. When reporting or interpreting the isotopic composition of biogenic carbonates, consideration must be given to fractionation factors which may govern their precipitation.

Lowenstam (1961) reported that some marine organisms secrete carbonate in oxygen and carbon isotopic equilibrium with the surrounding seawater, whereas others exert a vital control over their isotopic compositions producing anomalous values and trends (e.g. Weber, 1968). Organisms that display a vital effect incorporate and use both seawater-derived and metabolic-derived  $\text{CO}_2$  in their body fluids. This being responsible for the calcification process, the shell material they precipitate is consequently not in isotopic equilibrium with the surrounding seawater. As a result, when interpreting isotopic data, corrections must be made for this fractionation and considered in the subsequent conclusions.

### Sampling Procedures

Shells of marine invertebrates provide information about the organism, its biological life processes, organism-environment interaction(s) and physiochemical conditions of the ambient seawater. Detailed information about these processes, parameters and conditions is obtained through analysis of the shell mineralogy, which can be either calcite or aragonite or mixtures of these two minerals, and through analysis of trace elements (e.g. Mg, Sr, Na, Fe, Mn) and both stable (carbon, oxygen, sulphur) and radioactive (carbon-14, strontium) isotopes.

Two sampling techniques are used by researchers analyzing the shell mineralogy and chemistry of marine invertebrates. In one technique, whole or parts of shells are used in the analysis, whereas in the other technique, shells are sampled in increments which are apparently related to ontogeny. Both methods are flawed and this should be considered before analyzing marine shells. The whole shell method provides only mean chemical values that are not necessarily related solely to environmental conditions, and much information about salinity, temperature, storms, pollution and tidal cycles is not clearly represented (*cf.* Jones, 1985).



**Figure 1** Types of point and line defects in a simple crystal structure. The solid symbols are foreign cations (e.g.  $\text{Sr}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ) substituting for  $\text{Ca}^{2+}$  cations in the calcium carbonate structure. In diadochic replacement, foreign cations substitute directly for calcium cations on a 1:1 basis and in the proper lattice positions. During crystal growth, foreign cations can become trapped in-between the regular cations of the crystal structure; this is referred to as interstitial substitution. Cation vacancies in crystal structures create charge imbalances, and this electrical imbalance is compensated by the charge of adsorbed cations attracted to mineral/crystal surfaces. All of these described structural imperfections are considered point defects. Line defects involve the displacement of a row of cations during crystal growth caused by internal or external forces such as pressure or stress acting on the mineral. In this way foreign cations occupy lattice positions which otherwise would not have been available for elemental substitution.

Instead, some authors claim that by sectioning a shell along its optimum growth axis, a complete ontogenetic record can be obtained for bivalves (e.g. Jones, 1985; Rosenberg and Jones, 1975). However, this type of sampling is nearly impossible for complex coiled molluscs (cf. Jones, 1985). Lately, the significance and accuracy of the chemical trends have been challenged, because in populations dealing with more than one specimen, reproducibility of "seasonal" trends is at best, tenuous (e.g. Jones, 1985; Hughes and Clausen, 1980). Therefore, it is recommended that both sample size and population as well as geochemical methods are considered in context with the objectives of each specific study. If care is exercised, then shell chemistry should provide useful information related to physiochemical cycles of seawater, tidal patterns, paleoecology, archaeology, paleogeophysics, pollution studies and secular variation of seawater chemistry (cf. Jones, 1985).

Organic matter covers the whole shell as well as individual crystallites of the mineral layers. This can vary anywhere from 0 to 100% (e.g. Rosenberg, 1980), but in most instances, it is less (not considering the periostracum) than 3% by weight. In fossils, it is reduced to about 10% of the original percentage (Hudson, 1967). Thus, trace metals derived from the organic matter, such as Sr, Mg, Mn and Fe, probably play, in most instances, an insignificant role in influencing the generally observed chemical values and trends of shell carbonate (Brand *et al.*, 1986).

Specific procedures, besides those discussed above, must be followed to allow for the proper interpretation of chemical data of biogenic carbonates:

1. The organism must be properly identified;
2. Cleaning of the samples to avoid chemical contamination is essential;
3. Proper use of analytical procedures must be maintained to ensure reliability and accuracy of data;
4. The mineralogy of the organism should be determined; and,
5. The degree of preservation of the original mineralogy should be deduced utilizing scanning electron microscopy, petrographic and trace chemistry techniques.

When all of these criteria have been followed, proper interpretation of data is possible. Evaluation of mineralogy, stable isotope and trace element chemistry of Recent marine invertebrates are presented in the following text.

#### Articulate and Crustose Coralline Algae

Coralline algae (Order Cryptonemiales, Family Corallinaceae) have a rigid skeletal structure formed by the precipitation of carbonate both within and between the cell walls (Johnson, 1961). Calcification in some

members of the Order Nemalionales (Family Chaetangiaceae) is not as complete as in the algae of the Order Cryptonemiales, therefore these organisms are not considered significant carbonate sediment contributors in shallow marine environments (Adey and MacIntyre, 1973).

Coralline algae are subdivided into three subfamilies; Lithophylloideae, Mastophorideae and Melobesioideae (Adey and Johansen, 1972). However, for ease of geochemical comparison and data compilation, the older subdivision of Corallineae and Melobesioideae will be used in the review.

Melobesioideae are crustose and massive, prominent calcium carbonate sediment contributors, and inhabit areas from high energy to quiet waters. Specific crustose genera, *Porolithon*, *Neogoniolithon* and *Lithoporella* preferentially grow in the tropics, whereas *Lithothamnium* is found in tropical to polar seas. Its diversity increases in higher latitudes relative to the other species of coralline algae (Johnson, 1961; Adey and MacIntyre, 1973). *Lithophyllum* is also a genus found dominantly in tropical waters, but its range extends into more temperate waters. Articulate Corallineae are generally limited to sheltered environments, with the four common genera being *Amphiroa*, *Cheilosporum*, *Corallina* and *Jania*. *Amphiroa* is found mostly in tropical waters, whereas *Jania* and *Corallina* are distributed widely (Johnson, 1961).

Specimens of the genus *Galaxaura* (Order Nemalionales) precipitate skeletons that consist of aragonite, whereas crustose and articulate coralline algae have high-Mg calcite skeletal structures. Representatives of the Nemalionales have Mg concentrations as high as 7800 ppm; Corallineae have Mg contents ranging from 2.94 to 7.0% and Melobesia contain between 1.74 and 7.2% Mg in their carbonate skeleton (Figure 2). Their  $\text{MgCO}_3$  range of 6.0-25 mol% is well within the limits set for high-Mg calcite (cf. Chave, 1954; Milliman, 1974). However, the variable and large range in Mg content is probably related to factors such as nutrient level, salinity and/or temperature of the water, growth rate of the skeletal material, or some other factor at the biological level. Kolesar (1978) found a systematic variation of the Mg content in the coralline alga *Calliarthron*. He determined that during the summer months, growth of this alga is slow enough to allow for the demand of Mg during calcification to be matched by its seawater supply (Figure 3). In contrast, during rapid growth (winter months), the rate of diffusion of Mg into the cellular carbonate cannot keep pace with its demand (Figure 3). In this case, the Mg content of the coralline alga *Calliarthron* is a function of growth rate which in turn may be a function of water temperature (Kolesar, 1978).

The high Sr (0.95%) content of Nemalionales is indicative of the aragonite mineralogy of its skeletal material, and it further demonstrates that these algae incorporate Sr into carbonate in equilibrium with their ambient seawater (e.g. Kinsman, 1969; Milliman, 1974; Veizer, 1983a, b; Figure 4). Similar conclusions can be reached for the Sr levels in the articulate and crustose algae, although variations in the absolute contents are possibly related to growth rate, water temperature or other factors (Figure 4; cf. Kolesar, 1978).

Sodium contents of red, articulate and crustose algae are variable and high, relative to expected values (Figure 5). We believe that these unusually high sodium levels are related to Na derived from fluid/solid inclusions in the skeletal carbonate. However, work is needed to resolve this anomaly. The observed Fe and Mn levels in articulate and crustose algae are somewhat higher than those predicted from theoretical considerations of biogenically precipitated carbonates (Figures 6, 7; Brand and Veizer, 1980). It is possible that growth rate as observed by Kolesar (1978) in the alga *Calliarthron*, or some other, as yet unknown, factors may account for these higher Fe and Mn levels.

Coralline algae found in areas of reef growth are more important as encrusters and cementers than sediment contributors (Milliman, 1974). Warmer water temperatures in these regions may possibly influence the growth rate and thus calcification rates which can result in variations of the minor and trace element concentrations of the biogenic carbonate (Kolesar, 1978; Lorens, 1981).

Figure 8 shows the distribution of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  in the skeletal carbonate of articulate and crustose algae. Calcium carbonate precipitated in isotopic equilibrium with ambient seawater contains between -2.0 and +2.0‰  $\delta^{18}\text{O}$  and between 0.0 and +6.0‰  $\delta^{13}\text{C}$  (Keith and Weber, 1965). Thus the more negative values observed in the algae suggests that they incorporate metabolic and seawater-derived  $\text{CO}_2$  at the site of calcification (Figure 8; Keith and Weber, 1965; Craig, 1953; Wefer and Berger, 1981). This vital effect makes the isotopic composition of both articulate and crustose algae unreliable indicators of seawater isotopic compositions and temperature.

#### Green Algae

Calcifying green algae are represented by two families: Dasycladaceae with calcification occurring around a cylindrical central stem, and Codiaceae with a tubular thallus of intertwining and branching filaments (Johnson, 1961). Most of the prominent calcified green algae belong to the family Codiaceae, including *Penicillus*, *Rhipocephalus*, *Halimeda* and *Udotea*. Most green algae grow in tropical climates, in quiet, shallow

waters at depths no greater than 15 to 20 m (Milliman, 1974, p. 67). Some chlorophyta, such as *Halimeda* grow in diverse environments, from turbulent reefs to deep lagoons, as well as in tropical to temperate waters (Milliman, 1974). Most calcareous green algae are important carbonate sediment contributors.

The Mg concentrations observed in green algae are generally in accord with their aragonite mineralogy (Figure 2). This is also substantiated by their Sr contents which are in agreement for aragonite precipitated in chemical equilibrium with ambient seawater (Figure 4). Sodium levels (1800-2600 ppm) in *Halimeda* are in accord with their mineralogy, whereas the levels in *Cymopolia* are unusually high and possibly are related to fluid inclusions in the skeletal aragonite (Figure 5). The Fe concentrations are high and no explanation for this anomaly can be offered at this time (Figure 6). In contrast, the Mn values fall close to the range for inorganic carbonates precipitated in chemical equilibrium with ambient seawater.

The oxygen and carbon values of green algae are within the range postulated for carbonate precipitating in isotopic equilibrium with surrounding seawater (Figure 8; Keith and Weber, 1965). Lowenstam and Epstein (1957) found that the heads of *Penicillus* and *Rhipocephalus* are enriched in  $^{13}\text{C}$  and  $^{18}\text{O}$  relative to levels in their stems. It has been postulated that this is related to fractionation during photosynthesis (Craig, 1953), but generally the isotopic compositions of green algae reflect the composition of the seawater.

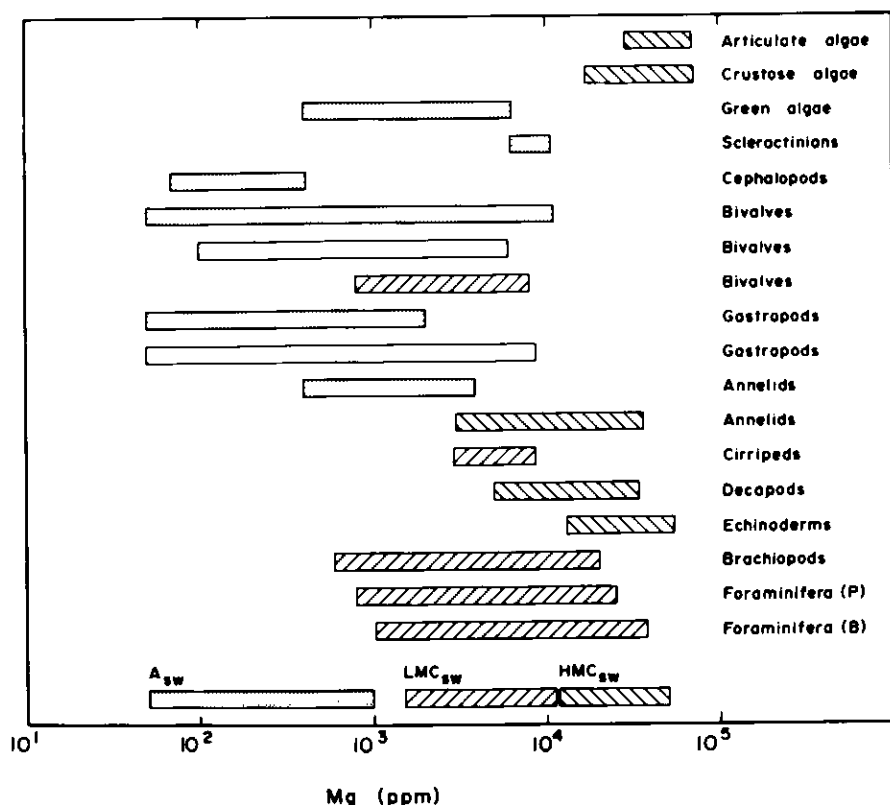
#### Coelenterata

Coelenterata consist of two major skeletal groups; the hydrocorals and scleractinians with stony skeletons, and the octocorals with soft skeletons. Hermatypic coelenterates are reef-builders, being most prominent in shallow waters (less than 20 m) with water temperatures between 25° and 30°C, and salinities between 34 and 37‰ (Milliman, 1974). MacIntyre and Pilkey (1969) and Kinsman (1964) found hermatypic corals in waters with temperatures of 11° to 40°C,

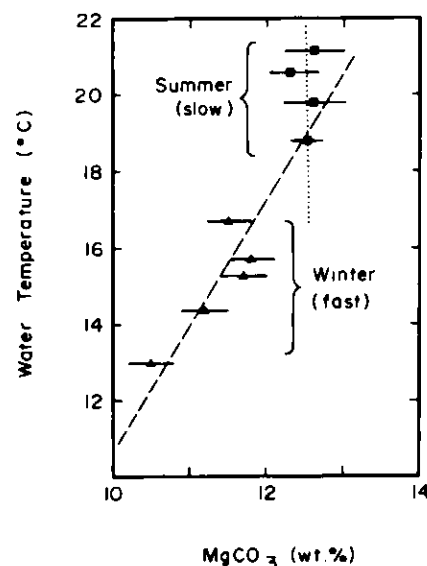
whereas Squires (1962) and Kinsman (1964) report hermatypic corals in water salinities ranging from brackish to greater than 60‰. In general, calcification rates for hermatypic corals are much higher than for those of the ahermatypic group (Milliman, 1974). Ahermatypic corals are found in waters of about 100 m and in temperatures not greater than 20°C (Milliman, 1974). All coelenterates are major carbonate producers.

**Hydrozoa.** In the class Hydrozoa, members of the Order Stylasterina live over a great range of depth and latitude, whereas members of the Order Milleporina prefer shallow, tropical water. In water temperatures warmer than 3°C, Stylasterina are aragonitic, whereas in colder waters, the skeletal mineralogy can be either completely or partially calcite (Lowenstam, 1964).

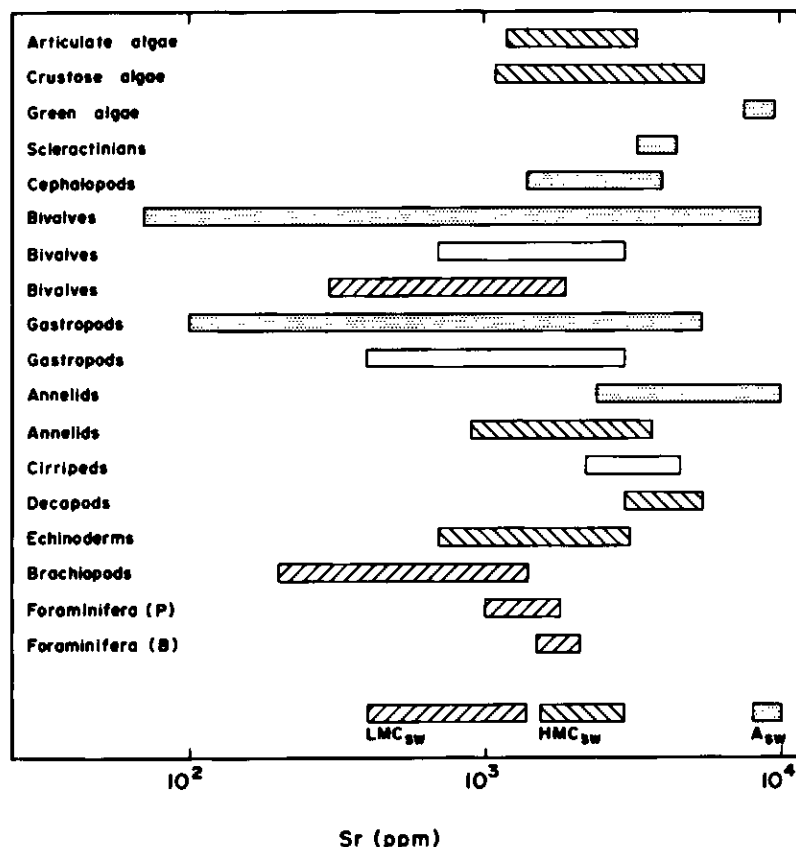
Magnesium contents of Hydrozoans are unusually low, relative to the Mg levels encountered in inorganic aragonite (Figure 2). In contrast, their Sr concentrations are within the range postulated for aragonite precipitated in chemical equilibrium with the ambient seawater (Figure 4).



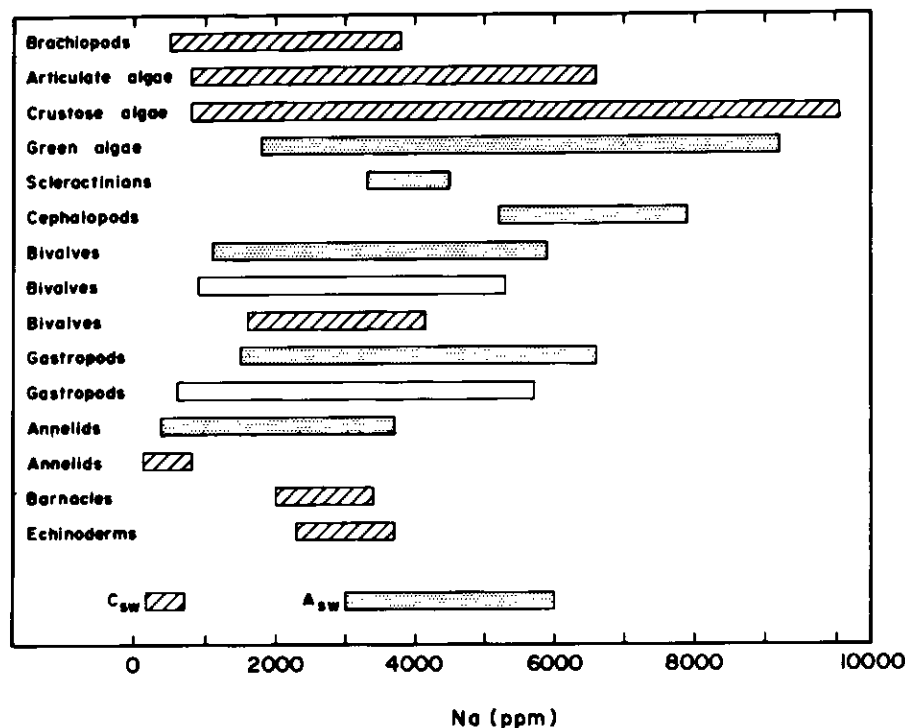
**Figure 2** Magnesium ranges in various marine invertebrates of aragonite (A, □), high-Mg calcite (HMC, ▨), low-Mg calcite (LMC, ▩) and mixed mineralogy (A-LMC, ▤).  $A_{sw}$ ,  $HMC_{sw}$  and  $LMC_{sw}$  represent grand ranges of Mg in biogenic carbonates precipitated in chemical equilibrium with ambient normal seawater. Values for biogenic carbonates that lie outside these theoretical ranges represent variations in the seawater chemistry, biological fractionation, kinetic effects, or other unknown factors which may be acting upon the organism's carbonate chemistry. Different factors may produce similar trends and concentration gradients in different organisms, thus a thorough evaluation of invertebrates' chemistries is warranted for obtaining reliable results and interpretations. Chemistry of invertebrates of mixed mineralogy are values for layers of aragonite/calcite of shells analyzed as one sample. Foraminifera are subdivided into planktonic (P) and benthic (B) groups.



**Figure 3** Variation in magnesium content of calcite segments with water temperature of the coralline alga *Calliarthron tuberculosum* (modified from Kolesar, 1978). Growth conditions, such as water temperature, salinity and/or nutrient level can affect the Mg content of algal segments. During the summer, growth rate is slow and Mg is incorporated into skeletal carbonate in proportions relative to those of the surrounding seawater. In contrast, with faster growth during the winter, the chemical composition of the algal segments is in disequilibrium with the Mg content of the ambient seawater.

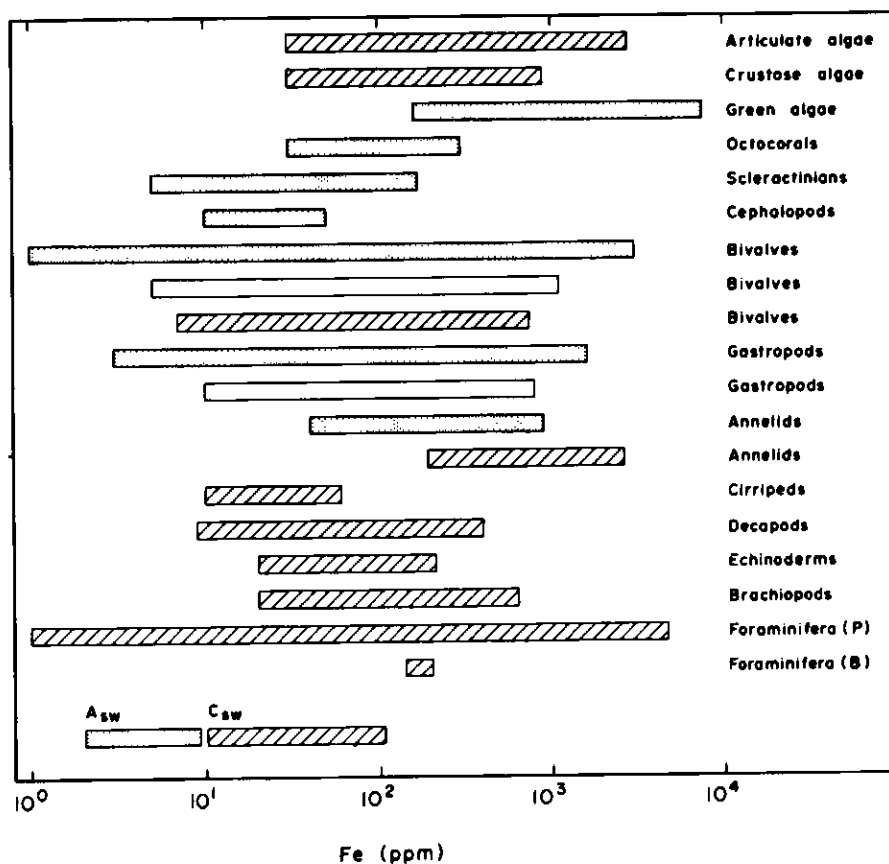


**Figure 4** Variation in strontium content for selected carbonate-secreting marine invertebrates. Chemical ranges of marine invertebrates which are similar to those of organic and inorganic carbonates (LMC<sub>sw</sub>, HMC<sub>sw</sub> and A<sub>sw</sub>) represent precipitation of calcium carbonate in equilibrium with ambient seawater. Values recorded in invertebrates outside these limits are influenced by either biologic, kinetic or other factors which affect the organism's carbonate chemistry. Molluscs as a group are the best example of biological fractionation of Sr in biogenic carbonate with values usually one-fifth of those found in carbonates precipitated in equilibrium with seawater. In contrast, green algae provide an example of aragonite needles precipitated in Sr equilibrium with ambient seawater. Symbols and data sources as in Figure 2.

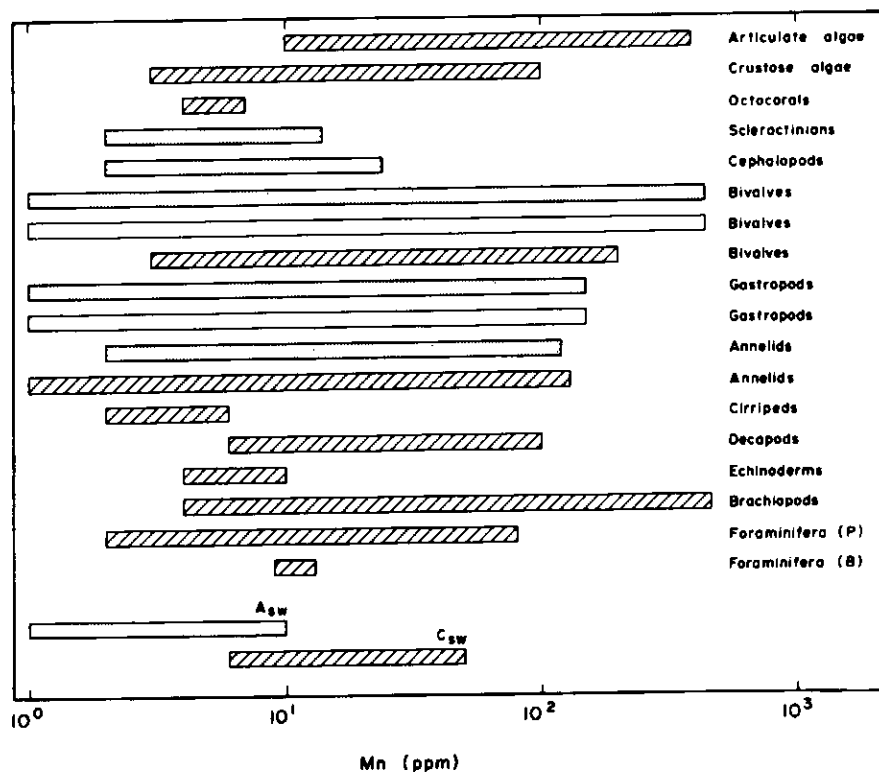


**Figure 5** Variation in sodium content for selected carbonate-secreting marine invertebrates. HMC and LMC invertebrates are represented by C<sub>sw</sub> (calcite, ▨), because sodium contents of these are not MgCO<sub>3</sub> content specific. In addition to biological fractionation, kinetic effects and other factors, fluid inclusions in skeletal carbonate may contribute significant amounts of sodium in the form of NaCl to the observed chemical ranges (cf. Fritz and Katz, 1972; Veizer et al., 1977). Sodium contents of marine invertebrates have to be interpreted with great care. Other symbols and explanations as in Figure 2.

**Figure 6** Variation in iron content for selected carbonate-secreting marine invertebrates. Fe contents of organic and inorganic carbonates are strongly dependent on the Eh and chemistry of the ambient water in addition to the other factors outlined in Figures 3 to 5. Thus, elevated concentrations in the carbonate chemistry may be reflecting slightly reducing water conditions that prevailed during the growth of the carbonate shell/skeleton. Explanations, symbols and data source as in Figure 5.



**Figure 7** Variation in manganese content for selected carbonate-secreting marine invertebrates. This element behaves similarly to Fe, being strongly dependent on the Eh and chemistry of the ambient water. Trends in the Mn chemistry observed in the carbonate of invertebrates are usually mirrored by the Fe concentrations in the same shell or skeleton. Explanations, symbols and data source as in Figure 5.



**Octocorallia.** *Heliopora*, one of the more common Octocorals, has an aragonitic skeleton, and it is a prominent reef-builder in Indo-Pacific coral reefs (Milliman, 1974). The remainder of the Octocorals precipitate skeletons consisting of high-Mg calcite, such as the Gorgonians that are found in low energy, back-reef areas of Caribbean reefs. Because *Heliopora* is the only aragonitic octocoral, its chemistry reflects this mineralogy. The Sr concentration is about 0.72% whereas the Mg concentration is about 0.28%, which is higher than in the aragonitic hydrocorals (Figures 2, 4). In contrast, the remaining octocorals have HMC skeletons, and display Sr values of 0.17 to 0.74%, with concentrations of Mg ranging from 2.7 to 5.0%

(Figures 2, 4). The deep-water octocoral *Corallium*, displays lesser concentrations of Mg and Sr than those of the shallow-water HMC octocorals (Chave, 1954).

**Zoantharia (Scleractinia).** All scleractinians precipitate skeletons of aragonite. The growth rate of each species appears to be dependent upon the temperature of the water. Scleractinians, such as *Acropora* grow 1.5 to 2 times faster in the summer months in Florida than in the winter (Shinn, 1966). In contrast, *Acropora* growing in more tropical areas, where they are not subject to seasonal fluctuations, grow even faster (Shinn, 1966). The aragonite mineralogy of scleractinians is reflected in the chemistry. The Sr concentrations are relatively high, ranging from 0.68%

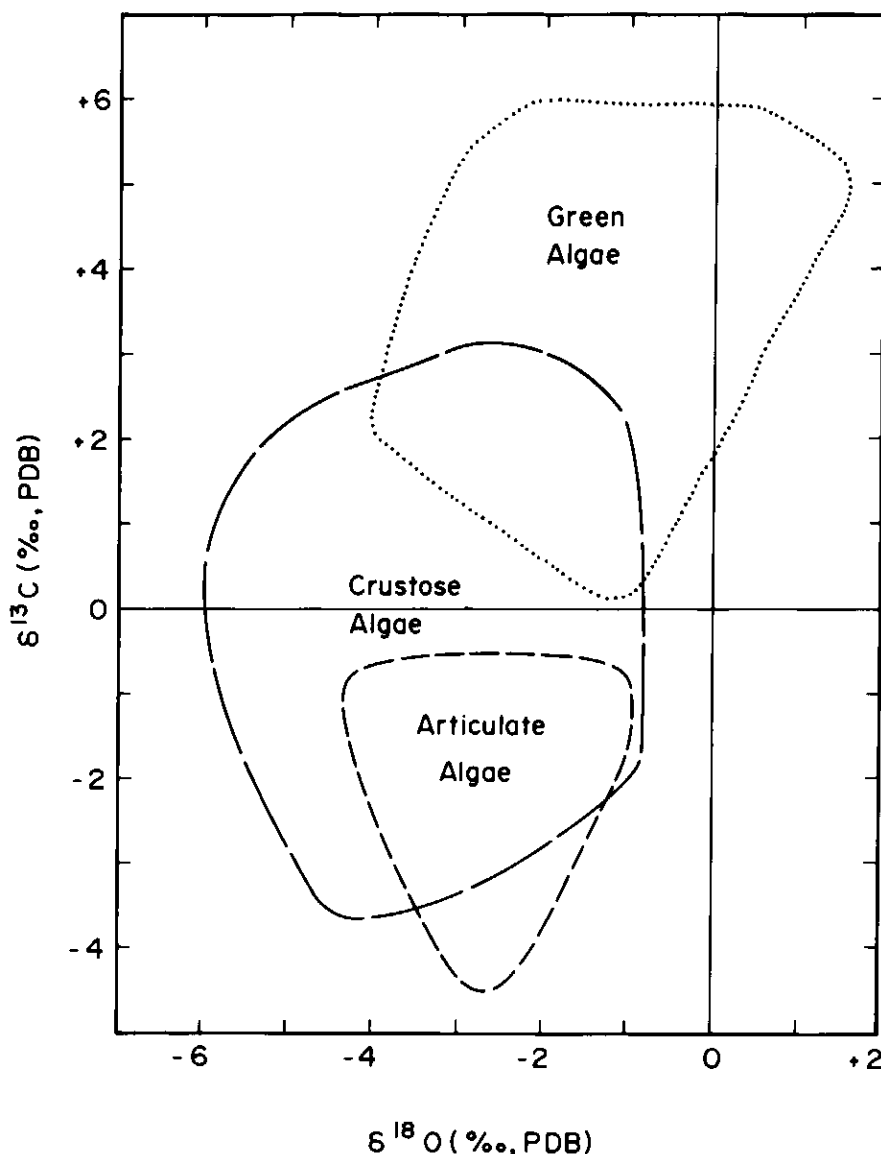
for *Montastrea* (a massive coral that has a slower growth rate than other scleractinians), to 0.96% for *Desmophyllum*, a coral of rapid growth rate (Lewis, 1968). The consistently low Mg values are found in the other scleractinians with aragonitic mineralogy, ranging from 0.01% to 0.28%. The other trace elements such as Fe, Mn and Cu also appear to be lower than those in the calcitic corals, but are in agreement with their aragonite mineralogy (Figures 6, 7).

**Stable Isotopes of Coelenterata.** Stable isotope values of coelenterates reveal that hermatypic corals are depleted in both  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  except for *Heliopora* that displays a  $\delta^{13}\text{C}$  value of +3.76‰ (PDB), and as a group exert a vital effect over their isotopic compositions (Figure 9). It is felt that this  $\delta^{13}\text{C}$  value is due to the symbiotic relationship with algae (Zooxanthellae) resulting in metabolic uptake of respiratory  $^{12}\text{C}$  by the algae during photosynthesis (Weber and Woodhead, 1970). Data also suggests that ahermatypic corals possess lower  $^{13}\text{C}$  than hermatypic types (Weber and Woodhead, 1970).

#### Cephalopoda

Except for the nautiloids, most Recent cephalopods have either very thin shells or none at all. The cephalopods *Sepia* and *Nautilus* are aragonitic while *Argonauta* is calcitic (Boggild, 1930). *Argonauta* displays a low Mg concentration of 1.22% for calcitic mineralogy, but a high Sr value of 0.39%, a fact that Chave (1954) explains as being due to shell precipitation by the arms and not the mantle. *Nautilus* has Sr concentrations ranging from 0.14 to 0.32%, and Mg values of 0.007 to 0.42%. The Mg values are within the limits for aragonite precipitated in chemical equilibrium with ambient seawater. In contrast, the Sr contents of both *Nautilus* and *Sepia* are lower than those expected under equilibrium precipitation by a factor of about 3-4. This type of control over elemental compositions is referred to as biological fractionation, and chemical contents are either higher or lower than those expected under inorganic equilibrium conditions (e.g. Brand and Veizer, 1980). Furthermore, Crick and Ottensmeyer (1983) demonstrated that there is an apparent species control by *Nautilus* of the Sr and Mg contents (Figure 10). The correlation for the trend is good with  $r = -0.974$  ( $\text{Sr}/\text{Ca} = -0.309$ ,  $\text{Mg}/\text{Ca} = +0.799$ ). Although a control at the species level is advocated for this trend, it is possible that some other factor (e.g. temperature, growth rate) may influence the observed chemical compositions.

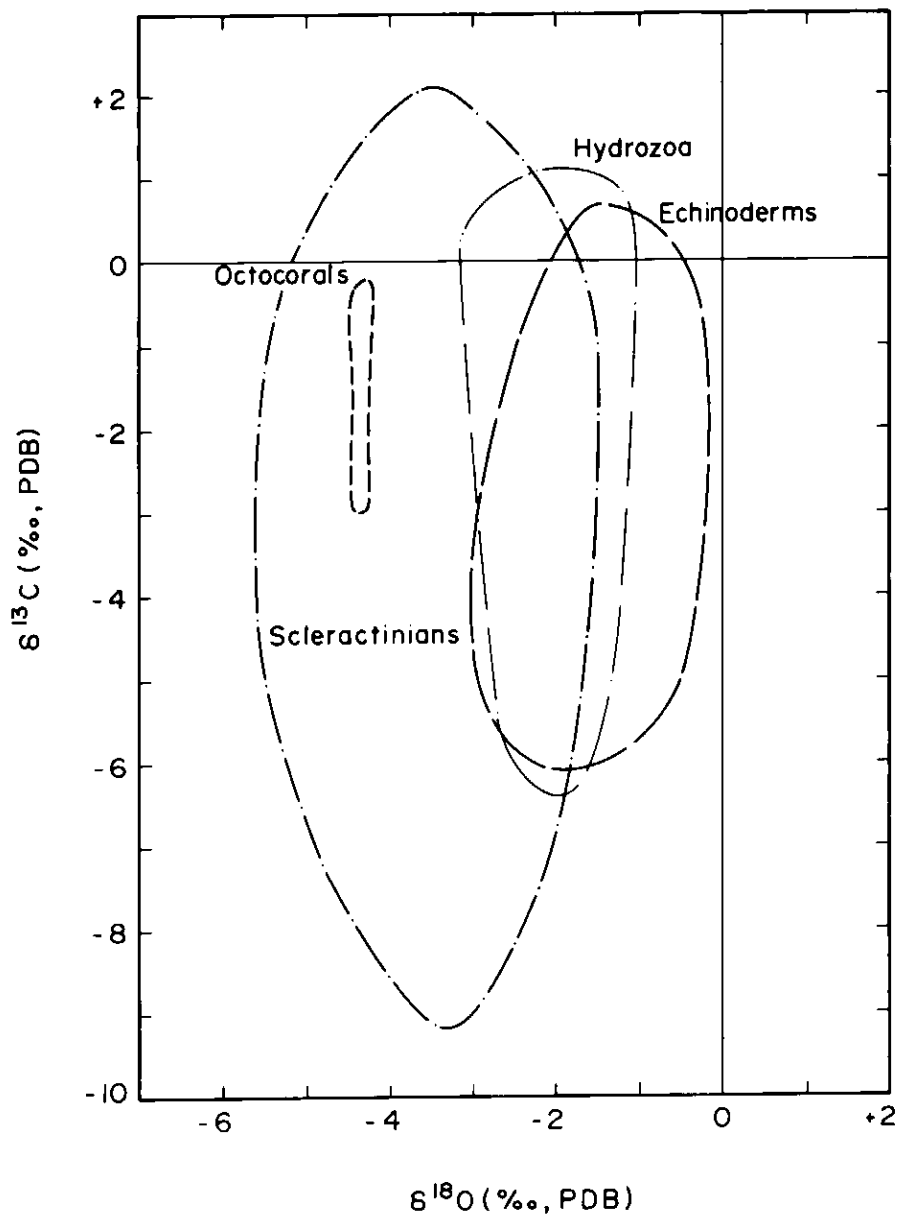
The oxygen and carbon isotopic compositions represent equilibrium values (Brand, 1983a) for *Nautilus* which live in water depths of up to 500 m (Figure 11; Ward and Martin, 1980). These  $^{18}\text{O}/^{16}\text{O}$  and  $^{13}\text{C}/^{12}\text{C}$  ratios are more positive than for those of their ancient counterparts, and Eichler and Ristedt (1966), suggested that modern *Nautilus* has migrated into deeper and cooler waters.



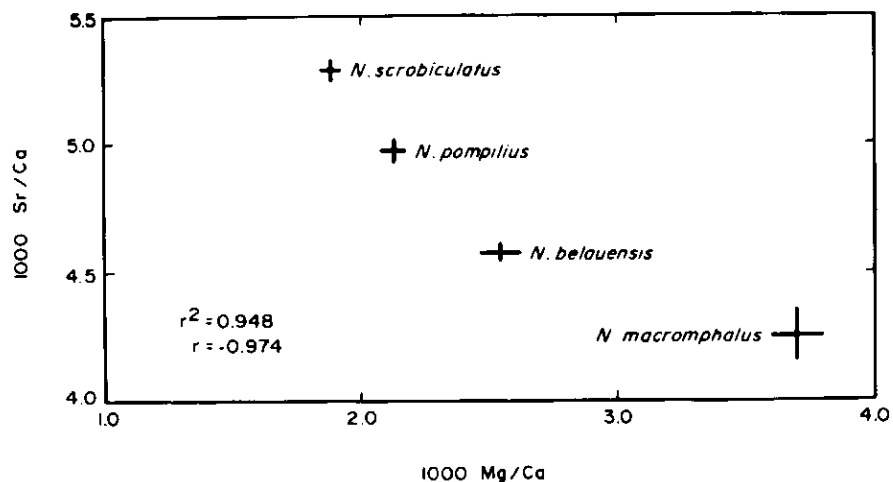
**Figure 8** Oxygen and carbon isotope compositions in green algae (A), crustose algae (HMC) and articulate algae (HMC). Carbonates precipitated in isotopic equilibrium under most ambient seawater conditions (normal salinity and temperature) have values ranging from 0 to +6.0‰  $\delta^{13}\text{C}$  and from -2.0 to +2.0‰  $\delta^{18}\text{O}$  (Keith and Weber, 1965). Most values observed in articulate and crustose algae are outside this equilibrium range, and a vital effect is responsible for these noted deviations. In contrast, aragonite of green algae is generally precipitated in isotopic equilibrium with the ambient seawater, reflecting its isotopic composition and temperature. A is aragonite, HMC is high-Mg calcite.



**Figure 9** Oxygen and carbon isotope compositions in hydrozoan (A), octocoral (HMC) and scleractinian (A) corals and echinoderms (HMC). Isotopic compositions of corals and echinoderms are subject to a vital effect and consequently their values do not reflect those of the ambient seawater. Metabolic  $\text{CO}_2$  incorporated during calcification of skeletal/shell carbonate is the major contributing factor or vital effect (e.g. Weber, 1968; Weber and Woodhead, 1970; other references in text). A is aragonite, HMC is high-Mg calcite.



**Figure 10** Sr/Ca versus Mg/Ca correlation for four species of Nautilus from the south Pacific (modified from Crick and Ottensm, 1983). They related the differences in Sr/Ca and Mg/Ca to differences at the species level of Nautilus. However, the strong correlation suggests that some other factor(s) such as water temperature, salinity, or water depth may have an influence on the observed chemistries in the different species.



## Bivalvia

Bivalves are found in many different marine environments. Their rate of growth is highly dependent upon environmental conditions and substrate (Swan, 1952). Bivalves living in high-energy environments tend to have thicker shells than those living in quiet waters. Also, bivalves living in cold water have thin, chalky shells, whereas those from warmer climates have a thicker shell with more consistent growth lines. In molluscs, the growth lines are thought to represent either yearly, monthly, biweekly or daily growth increments (cf. Rhoads and Lutz, 1980).

Most bivalves secrete monomineralic aragonitic shells, but some such as *Anomia*, *Pecten* and *Mytilus* secrete shells that contain a mixture of both aragonite and calcite. The oysters, *Ostrea* and *Crassostrea* possess monomineralic calcite shells (Milliman, 1974). Those bivalves with mixed mineralogy usually have outer layers of calcite and inner layers of aragonite (Milliman, 1974). Mean Mg concentrations of aragonitic bivalves are low and range from 0.005 to 0.13%, whereas Sr concentrations range from 0.007 to 0.3% (Figures 2, 4). Calcitic bivalves (or layers) contain Mg ranging from 0.15 to 0.43%, and Sr values ranging from 0.09 to 0.22% (Figures 2, 4). These bivalves also have, on average, higher Mn and Fe concentrations than aragonitic bivalves. Most molluscs precipitate their shells in isotopic equilibrium with the ambient water. Epstein and Lowenstam (1953) reported that in normal seawater, the  $\delta^{18}\text{O}/^{16}\text{O}$  ratio will reflect the temperature of the water, with  $\delta^{13}\text{C}$  averaging about 0.0‰ (PDB). In bivalves, the normal range for  $\delta^{18}\text{O}$  is from -4.0 to +3.0‰ and the normal range for  $\delta^{13}\text{C}$  is from -2.0 to +2.0‰ (Figure 11). However, the stable isotopes in bivalves can vary according to the salinity range of the seawater, as well as the result of possible seasonal calcification (Mook, 1971; Eisma et al., 1976; Brand, 1984; Jones, 1985).

Exhaustive studies have been done on the shell chemistry of *Mytilus* by a number of researchers (e.g. Dodd, 1965, 1966; Lorens and Bender, 1977). Lorens and Bender (1977) grew *Mytilus* in natural and synthetic seawater and demonstrated that this bivalve has the capacity to regulate the magnesium ion activity of the solution from which it grows its shell calcite (Figure 12). At low Mg/Ca solution ratios, equal or less than that of seawater, there is less fractionation against Mg and shell calcite is generally in equilibrium with that of the ambient seawater (natural and synthetic; Figure 12). In solutions of Mg/Ca ratios greater than seawater, the regulatory capability apparently breaks down and the body fluids are flooded with Mg. This results in a dramatic increase of the Mg/Ca ratio in shell carbonate of *Mytilus* (Figure 12). The authors noted no difference in the growth rate of *Mytilus* growing in solutions of different Mg/Ca ratios (Lorens and Bender, 1977). Excess Mg in solutions (> 13.5 Mg/Ca)

stopped the growth of the mussels completely. Whether these observations of ion control and growth stoppage apply to other bivalves is uncertain.

Dodd (1965) evaluated the Sr chemistry of the calcitic and aragonitic layers of *Mytilus* from Newport Bay. Chemical analysis of the last-formed portion of the shell layers shows that there is a negative correlation for Sr in the aragonite layer and a positive correlation for it in the calcite layer of the mussels with ambient water temperature (Figure 13). Furthermore, Dodd (1966) demonstrated that the Sr content of the calcite layer of *Mytilus* shells vary with ontogeny (growth history). Figure 14 clearly shows that the Sr content of the shell calcite varies "seasonally" with distance from the posterior end. It is difficult to assign any specific parameter (temperature, salinity, growth rate) to this observed pattern. In summary, the above observations demonstrate that with careful analysis, shell chemistry of bivalves can reveal a wealth of information about the life history of *Mytilus* and perhaps other bivalves.

## Gastropoda

Data show that all marine gastropods that have been analyzed precipitate shell of aragonite except for *Patella*, *Haliotis*, *Fissurella*, *Nerita*, *Littorina*, *Thais*, *Neptunea*, *Purpura* and *Tegula* that are reported to have a mixed mineralogy (Lowenstam, 1954; Waskowiak, 1962). The average life span of marine gastropods (3 to 5 years with a 10-year maximum) appears to be much shorter than for other marine molluscs, resulting in a higher population rate turnover (Cox, 1960). Gastropods are dissimilar to other molluscs in that they have a faster calcification rate, but are analogous to bivalves in that in colder, deeper waters their shells are generally thin-walled (Milliman, 1974).

Gastropods can be found in all types of marine environments. Some species precipitate shells all year round, whereas others calcify seasonally, explaining the variable  $\delta^{18}\text{O}$  data of some species (Epstein and Lowenstam, 1953; Keith et al., 1964; Figure 11). Gastropod species with aragonite mineralogy display mean Sr concentrations ranging from 0.11 to 0.30%, with corresponding Mg values ranging from 0.02 to 0.12% (Figures 2, 4). A comparison of Sr and Mg concentrations between aragonitic gastropods and bivalves displays lower Sr and higher Mg values for the gastropods (Figures 2, 4).

## Annelida

The mineralogy of polychaete annelids is variable. For example, *Onuphis* and *Hyalinacia* secrete calcium phosphate tubes with traces of calcite, whereas others such as *Pomatoceras*, *Filograna*, *Eudistylia* and *Dodecaceria* precipitate aragonite tubes (Mitterer, 1971). *Hydroides* and some *Spirobranchus* species precipitate tubes of

mixed mineralogy, while other *Spirobranchus* species precipitate tubes of aragonite or high-Mg calcite. *Spirorbis* and *Mercierella* possess tubes of high-Mg calcite. The rates of tube precipitation are as variable as the mineralogy, but this process is dependent upon temperature and climate (Milliman, 1974).

The geochemistry of annelid tubes clearly reflects the different mineralogies. Tubes consisting of high-Mg calcite display Mg values ranging from 1.35 to 2.98% (Figure 2). Chave (1954) reports that the  $\text{MgCO}_3$  concentration for these annelids is directly related to water temperature. However, Bornhold and Milliman (1973) reported that the mineralogy of annelid tubes is not always dependent upon temperature. The mean Sr concentrations of these specimens, except for *Hydroides*, range from 0.1 to 0.4% and are generally found to be around 0.2% (Figure 4). Annelid tubes of mixed mineralogy have concentrations of Mg and Sr that are indicative of the amount of aragonite in them. Those possessing between 0 and 60% aragonite have fairly consistent Mg concentration of 2 to 3%, and Sr values of 0.2 to 0.5%. Those organisms with higher than 60% aragonite in the tubes have concentrations of Mg and Sr in relation to the percentage of aragonite present. For example, samples of 100% aragonite possess a Sr content of 0.7 to 1.0%, and Mg values of 0.1 to 0.3%. The  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  appear to be depleted in aragonitic samples which could be a reflection of variable precipitation rates, water temperatures or possibly biological fractionation. More research is needed on the isotopic compositions of the calcium carbonate deposits of annelids.

## Arthropoda

The majority of arthropods have chitinous exoskeletons, except for members of the superclass Crustacea, which calcify their shells (Milliman 1974, p. 120). Of the crustaceans, three classes are prominent calcifiers: Cirripedia, Ostracoda and Decapoda (Milliman, 1974). Arthropods can be found in most climates, and the rate and thickness of shell production appears to depend upon depth, food supply and water temperature (Scott, 1961).

Lateral plates of the cirripedes *Balanus*, *Tetraclita* and *Catophragmus* are low-Mg calcite, whereas the basal plates of the latter two genera are aragonite and data are insufficient for the barnacle. In contrast, the two calcifying decapods *Cancer* and *Carcinus* secrete high-Mg calcite exoskeletons. Individual barnacles are not long-lived (Smith and Haderlie, 1969), and as a consequence of this high turnover rate, they are important carbonate sediment contributors.

Geochemical values vary with the different mineralogies, with low-Mg calcite having Mg concentrations of 0.3 to 1.01% and Sr values of 0.22 to 0.48%. The Mg level is lower by a

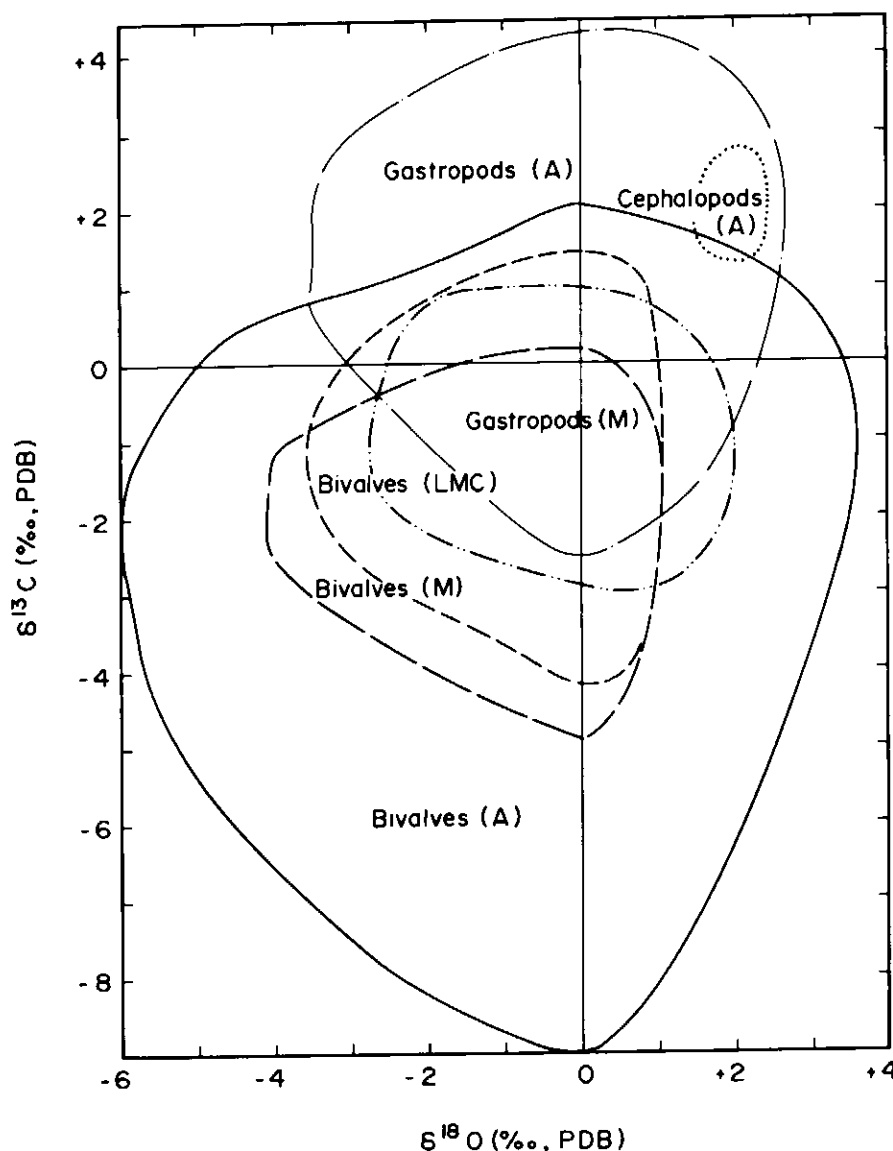
factor of 3 and the Sr level is higher by a factor of 1.5 in the lateral plates of *Balanus* than in those of the other two cirripedes. It is possible that this variation in Mg and Sr concentrations in the three balanoids is related to environmental parameters such as salinity and/or temperature (*cf.* Pilkey and Harriss, 1966). Basal plates/discs of the balanoids *Tetraclita* and *Catophragmus* are aragonite and as expected, the Mg concentrations are much lower (0.07-0.12%) than in the calcitic lateral plates. The Mg and Sr concentrations of the decapods *Cancer* and *Carcinus* are in

agreement with their high-Mg calcite mineralogy. These conclusions are also reached for the Na, Fe and Mn levels observed in all the calcifying arthropods.

The oxygen isotopic composition of the balanoid *Balanus* appears to be enriched in the low-Mg calcite lateral plates. However, Brand *et al.* (1986) determined that *Balanus* incorporates both oxygen and carbon into calcite in isotopic equilibrium with ambient seawater. The positive  $\delta^{18}\text{O}$  values simply reflect the low water temperatures at the collection site.

### Echinodermata

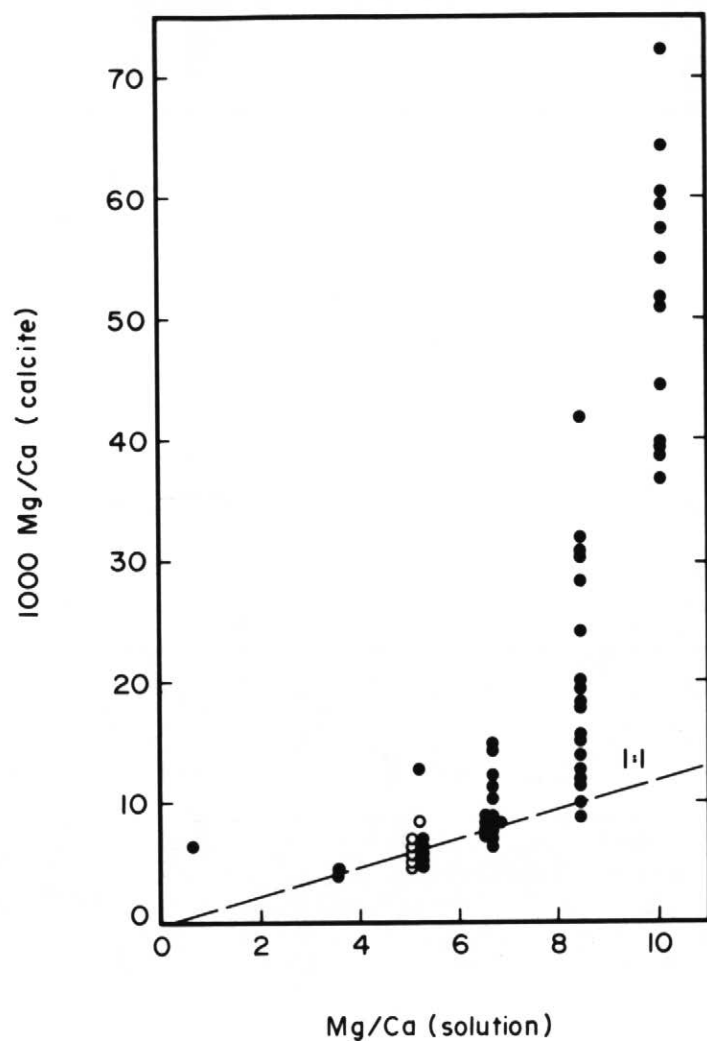
Echinoidea, Crinoidea, Asteroidea, Ophiuroidea and Holothuria make up the five major living groups of echinoderms. They all contain an endoskeleton made up of a calcareous strom and organic stroma that provides the nutrition necessary for growth (Raup, 1958). Unlike other marine invertebrates, the rate of skeletal precipitation for echinoderms is more rapid in cold water, producing more dense and thicker skeletons, and they are found in most marine environments (Raup, 1958; Swan, 1966).



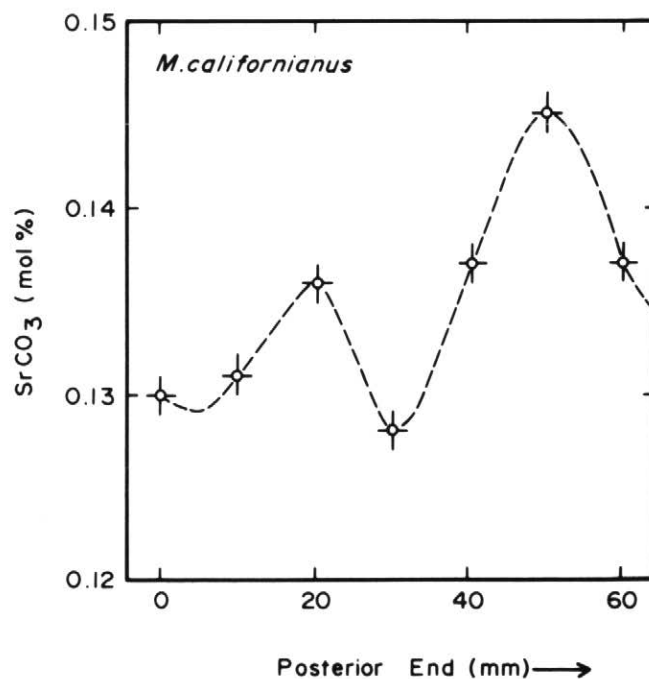
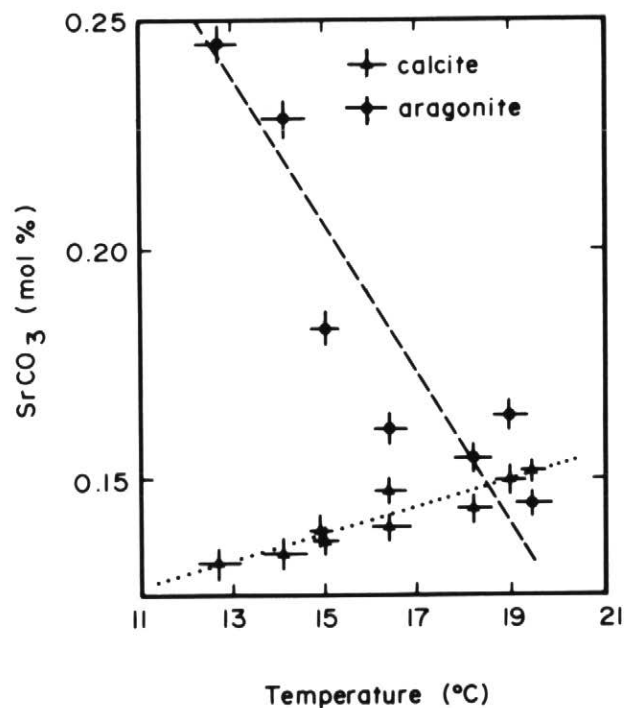
**Figure 11** Oxygen and carbon isotope compositions of cephalopods, bivalves, and gastropods. Isotopic compositions of most molluscs fall within the postulated range representing calcium carbonate precipitated in isotopic equilibrium with ambient seawater. Some of the observed anomalous values (e.g. aragonitic bivalves) may be reflecting unusual water temperatures/salinities (e.g. Eisma *et al.*, 1976), which can lower or raise the particular isotopic compositions. **A** is aragonite, **LMC** is low-Mg calcite and **M** is mixed mineralogy (**A-LMC**) mollusc shells.

**Figure 13 (facing page, lower left)** Variation of strontium content with temperature in the calcite (●) and aragonite (▲) layers of *Mytilus* (modified from Dodd, 1965). Strontium content decreases in the aragonite layer of *Mytilus* during shell growth with increasing water temperature, whereas in the outer calcite layer the Sr content shows only a slight increase under identical growth conditions

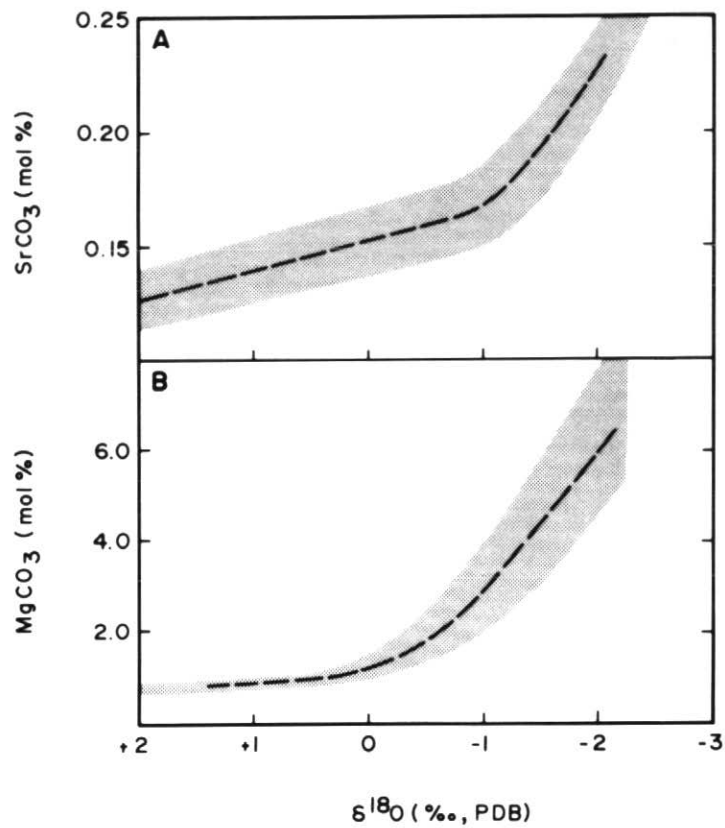
**Figure 14 (facing page, lower right)** Variation of strontium content in the calcite layer with distance from the posterior shell margin of *Mytilus californianus* (modified from Dodd, 1966). The cyclic trend in the Sr content is related to changes in seawater chemistry based on growth cycles (e.g. hours, days, months), tidal cycles or some other factors postulated by Dodd (1966) and Jones (1985). Exact interpretations as to their nature are not possible at this time.



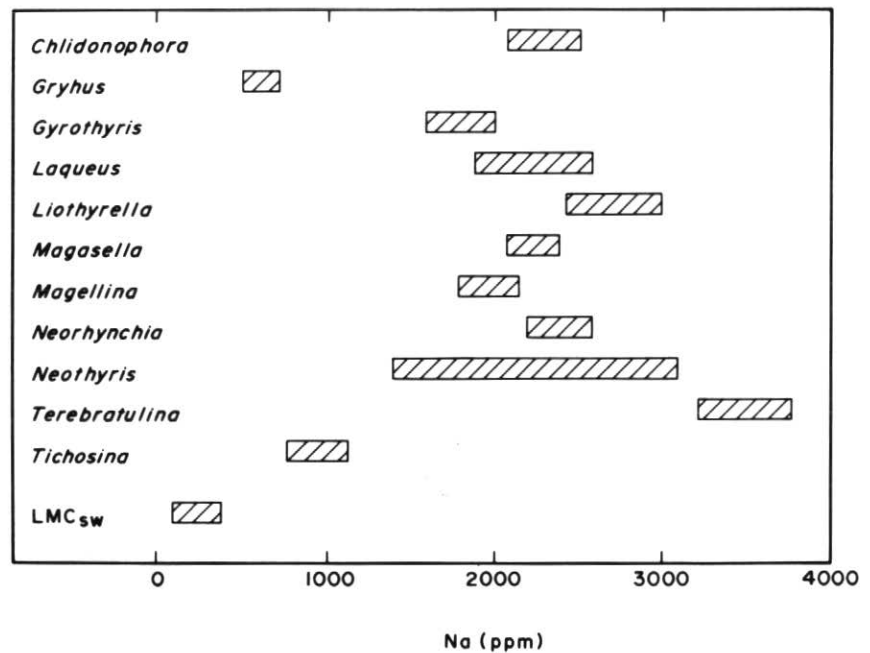
**Figure 12** Mg/Ca atom ratio in solution and in calcite of *Mytilus* grown in natural (●) and synthetic (○) seawater, respectively (modified from Lorens and Bender, 1977). At Mg/Ca levels of less than 5.17 (normal seawater ratio; Henderson, 1982) in natural or synthetic seawater, the ratio of the shell carbonate is in agreement with that of the ambient fluid (1:1 relationship). At levels greater than the normal seawater value, the Mg content in the shells drastically increases relative to that of ambient seawater. Levels of Mg/Ca greater than 11 caused the studied *Mytilus* bivalves to die. Seawater chemistry, or more precisely the chemical ratio of elements, has pronounced effects on the shell chemistry of bivalves as well as other marine and non-marine invertebrates.



**Figure 15** Variation of strontium (A) and magnesium (B) content with the water-corrected  $\delta^{18}\text{O}$  in the shell carbonate of Recent brachiopods (modified from Lowenstam, 1961). Oxygen values are intimately linked to ambient seawater temperatures and Lowenstam (1961) showed further that the Sr and Mg contents of Recent and ancient brachiopods shells are also possible water temperature indicators. Shaded area around the trend line indicates uncertainty in the measured values.



**Figure 16** Variation of sodium content in some Recent brachiopods (Morrison and Brand, 1984). None of the studied Recent brachiopods have Na contents comparable to levels expected in low-Mg calcite precipitated in chemical equilibrium with ambient seawater. The significant variation in the sodium levels of the shells suggests a biological control at the generic level.



Echinoderms have calcitic skeletons, the majority of them having a high-Mg calcite mineralogy, but with *Strongylocentrus* and *Dendraster* possessing an intermediate-Mg calcite mineralogy as well.

The chemistry of the high-Mg calcite skeletons display Mg values ranging from 2 to 4% and Sr concentrations from 0.1 to 0.3% (Figures 2, 4). Those of IMC mineralogy have Mg concentrations of 1 to 2% and Sr values of about 0.2%. Chave (1954) found that the magnesium content appears to be temperature dependent, whereas Pilkey and Hower (1960) reported a biologic control as well. As the water temperature increases, the Na concentration in the echinoid *Dendraster* increases while there is a concurrent decrease in the Mn and Sr contents. Systematic variations in the biogeochemical distribution of major, minor and trace elements between the various hard and soft parts of echinoderms have been recorded (Milliman, 1974, p. 133). This trend, though not parallel to trace element chemistry, is also seen in the stable isotopes.

There appears to be an enrichment of  $^{13}\text{C}$  in the spines of echinoids, but on the whole, echinoderms appear to be depleted in  $^{18}\text{O}$  and  $^{13}\text{C}$  (Figure 9). Weber and co-workers extensively studied the isotopic compositions of echinoderms (e.g. Weber and Raup, 1966, 1968; Weber, 1968). They concluded that echinoderms utilize both metabolic and seawater-derived  $\text{CO}_2$  during the calcification process. Consequently, their isotopic compositions show the vital effect and do not reflect the physiochemical conditions of the ambient seawater (cf. corals, Figure 9).

### Brachiopoda

All articulate brachiopods that have been analyzed secrete shells of low-Mg calcite covered by a chitinous periostracum, except for the species *Crania* which Clark and Wheeler (1922) reported to have high Mg values. The shells generally consist of thin outer lamellar and thick inner prismatic layers which are precipitated by the mantle (Johnson, 1951). Recent brachiopods live in water depths of less than 300 m, and can be found in temperate to tropical climates (Jackson *et al.*, 1971). The low-Mg calcite mineralogy is reflected in the shell chemistry with Mg concentrations ranging from 0.06 to 1.42%, and Sr values from 0.02 to 0.14% (Figures 2, 4).

Lowenstam (1961), in an extensive study, showed correlation between water temperature,  $^{18}\text{O}/^{16}\text{O}$  ratios,  $\text{SrCO}_3$  and  $\text{MgCO}_3$  contents in shells of Recent and fossil brachiopods. He found a consistent relationship between water temperature, calculated with the  $\delta^{18}\text{O}$  values of the shells, and the Sr (Figure 15A) and Mg (Figure 15B) contents. Similar trends were detected in brachiopods of Pliocene, Cretaceous, Permian and Mississippian age.

Overall, the Fe and Mn values of brachiopods are slightly higher than those expected for low-Mg calcite precipitated in equilibrium with normal seawater (Figures 6, 7). Perhaps the higher levels are related to unusual water and/or substrate conditions; more work is needed to clarify this sediment/facies dependence of Fe and Mn in brachiopods (cf. Morrison and Brand, 1984). Brand and Veizer (1980) demonstrated that ancient brachiopods biologically control their shell Na contents. Figure 16 clearly shows that the biological fractionation of Na observed in ancient brachiopods also applies to their extant counterparts. Overall, Na values are higher than those expected for low-Mg calcite precipitated in equilibrium. In addition, there appears to be considerable variation in the Na content at the generic level (Figure 16).

Lowenstam (1961) further demonstrated that modern brachiopods secrete shells in oxygen isotopic equilibrium with the surrounding seawater. Their  $\delta^{18}\text{O}$  values are simply a reflection of variable water temperatures (Figure 17). Recently, Wefer (1983; in Veizer, 1983b) demonstrated that some brachiopods exert a vital control over their shell carbon isotopic compositions. However, whether this observation applies to all brachiopods (extant and extinct) still remains to be clarified.

### Foraminifera

Information important to the summary of geochemistry of Foraminifera is found in Wood (1949), Phleger (1960), Loeblich and Tappan (1964), Berger (1971) and Boersma (1978). Based on wall structure, two major groups of calcareous foraminifera may be defined: porcellaneous and hyaline. Most porcellaneous foraminifera have imperforate tests while hyaline foraminifera have perforate tests. The majority of calcareous foraminifera are calcitic and can usually be designated as benthic or planktonic. Most of the calcareous benthic species prefer shallow water (shelf) environments and with mean densities of  $10^3\text{--}2 \times 10^6$  specimens  $\text{m}^{-2}$  are important sediment contributors. Among these benthics, the so-called larger ones like *Amphistegina* (or the Tertiary *Nummulites* in the Nummulites limestones used to build the pyramids in Egypt), inhabit backreefs, fore-reefs and carbonate platforms. Blackmon and Todd (1959) report that the five known imperforate porcellaneous species consist of high-Mg calcite, while the imperforate hyalines can be aragonite, magnesian calcite, calcite, or a mixed mineralogy. The shallow water benthic perforates, such as *Calcarina*, possess a high-Mg calcite mineralogy. Mixed assemblages of Recent and relict, as well as deep and shallow water benthic foraminifera are often found in the sediments at the edges of continental shelves. Benthic foraminifera gradually

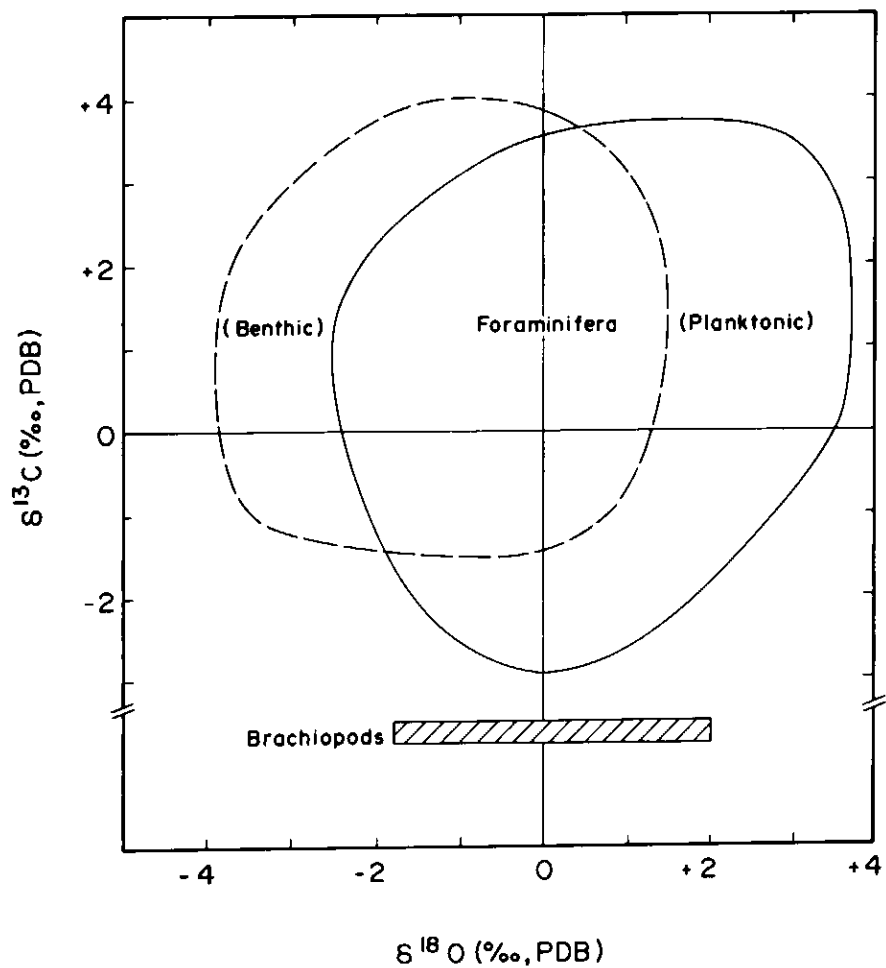
decrease in number from outer shelf and upper slope sediments giving way to a preponderance of planktonic foraminifera.

Planktonic foraminifera such as *Globigerinoides* and *Globorotalia* have dissimilar Mg contents, even though they are from the same sample and probably calcified at similar water temperatures (Figure 18). Savin and Douglas (1973) postulated that this difference in Mg content is related to biologic controls and by a secondary influence to environmental factors. These two foraminifera precipitate tests in water depths between 120 m and 700 m, whereas other planktonic species prefer to calcify in surface layers of the ocean above the thermocline. Productivity of planktonic foraminifera is highest in ocean-current convergence zones, like in the North Pacific and lowest in the mid-ocean, low productivity areas like the Sargasso Sea. Also, there is a decrease in productivity with increased distance from shore.

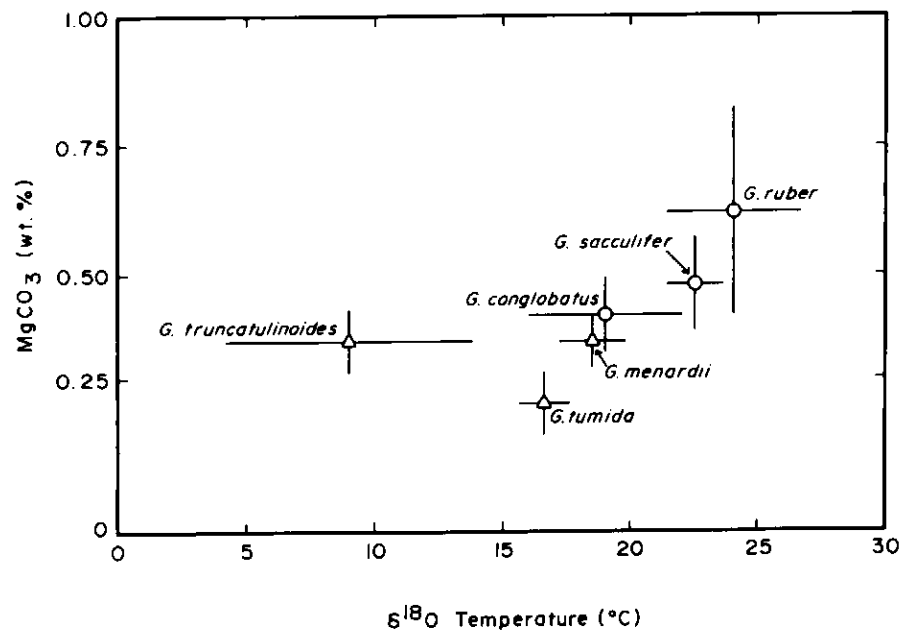
Initial studies reporting on the chemical concentrations of foraminifera from deep-sea oozes gave erroneous results due to contamination of samples by authigenic minerals and terrigenous clays (Emiliani, 1955a, b). Chave (1954) reported that the Mg content of foraminifera was slightly inconsistent with expected values for high-Mg calcite and was presumably controlled by biologic factors and temperature (1% Mg increase with every  $8^\circ\text{C}$  increase in water temperature). The Mg content appears to range from 1.2 to 3.7% for species of benthic foraminifera, and from 0.1 to 0.2% for the calcitic planktonic foraminifera (Figure 2). The Sr concentrations for the high-Mg calcite benthic foraminifera range from 0.1 to 0.2%, and 0.1 to 0.2% for calcitic planktonic species (Figure 4). Emiliani (1955a) felt that the concentrations of Mg, Mn, Fe, Si, Al and Ti in planktonic foraminifera were due to terrigenous contamination, with only the Sr values representing the shell bound proportions. Studies by Wangersky and Joensuu (1964), Lipps and Ribbe (1967), Carpenter (1969) and Duplessy *et al.* (1970) provide excellent reports of the biogeochemistry of shallow and deep-water benthic foraminifera as well as planktonic species.

Urey *et al.* (1951) and Epstein *et al.* (1953) reported that, like Recent brachiopods, foraminifera secrete their tests in isotopic equilibrium with the surrounding seawater (Figure 17). The assertion of equilibrium precipitation has been challenged by a number of studies (e.g. Van Donk, 1970; Shackleton *et al.*, 1973; Shackleton, 1974; Vinot-Bertouille and Duplessy, 1973; Williams *et al.*, 1977). Williams *et al.* (1977) examined a large population of planktonic foraminifera collected off Bermuda. Figure 19 shows clearly that the various planktonic species do not precipitate calcite tests in oxygen isotopic equilibrium with ambient seawater (large deviation from

**Figure 17** Oxygen and carbon isotope compositions in brachiopods and foraminifera (planktonic and benthic forms). Foraminifera and brachiopods, according to this data, apparently secrete calcium carbonate in isotopic equilibrium with ambient seawater (range given in Figure 8). These observations are in contrast with the conclusions based on the studies of several authors (data depicted in Figures 19 and 20).



**Figure 18** Variation of magnesium content with water temperature (calculated with oxygen isotopic values) of Globigerinoides (○) and Globorotalia (Δ) species (modified from Savin and Douglas, 1973). Globigerinoides contain more Mg than Globorotalia tests at similar temperature levels. At temperatures of less than 18°C, there is no significant change in the Mg content of Globorotalia, whereas at temperatures greater than 18°C, the Mg content in Globigerinoides tests steadily increases with increasing temperature. Magnesium content in these foraminifera is apparently influenced by the water temperature as well as the organism.



the line defining equilibrium conditions). It is difficult, at this time, to assign a vital effect to these trends. Instead, Williams *et al.* (1977) concluded that seasonal changes in water depth habitat account for the anomalous isotopic values observed in these planktonic foraminifera. Similar observations concerning isotopic disequilibrium in tests of benthic foraminifera have been made in several studies (e.g. Vinot-Bertouille and Duplessy, 1973; Woodruff *et al.*, 1980; Wefer and Berger, 1980). Figure 20 shows that the oxygen and carbon values of all benthic species that have been analyzed, except for *Alveolinella quoyi*, fall outside the range considered for calcite precipitation in equilibrium from ambient seawater. For accurate paleotemperature work, it is necessary to resolve the problem of a possible vital effect controlling the isotopic composition of both planktonic and benthic foraminifera. Until this question has been

resolved the paleotemperatures based on  $\delta^{18}\text{O}$  data of fossil foraminifera are in doubt.

#### Environmental Consideration

The chemistry of marine organisms is quite complex, being influenced by temperature, biological fractionation, the partition coefficient, growth rate, water chemistry, diagenesis and the original mineralogy of the precipitated skeleton (Brand, 1981a, b, 1983a, b). Environmental conditions influence the distribution of all living organisms. Any drastic change in these conditions will ultimately affect the organisms which in turn can be a deciding factor of survival, evolution or possibly extinction. It is our current knowledge of the living conditions and life modes of Recent marine organisms that may allow us to assume a uniformitarian point of view for studies of their fossil counterparts.

In aquatic environments, salinity, tempera-

ture and oxygen levels play a vital role in establishing general life modes and tolerance levels. The texture of the sediment, which is related to grain size, controls the establishment of benthic communities. For example, in argillaceous sediments, higher amounts of available organic matter favour detritus feeders (Gall, 1983).

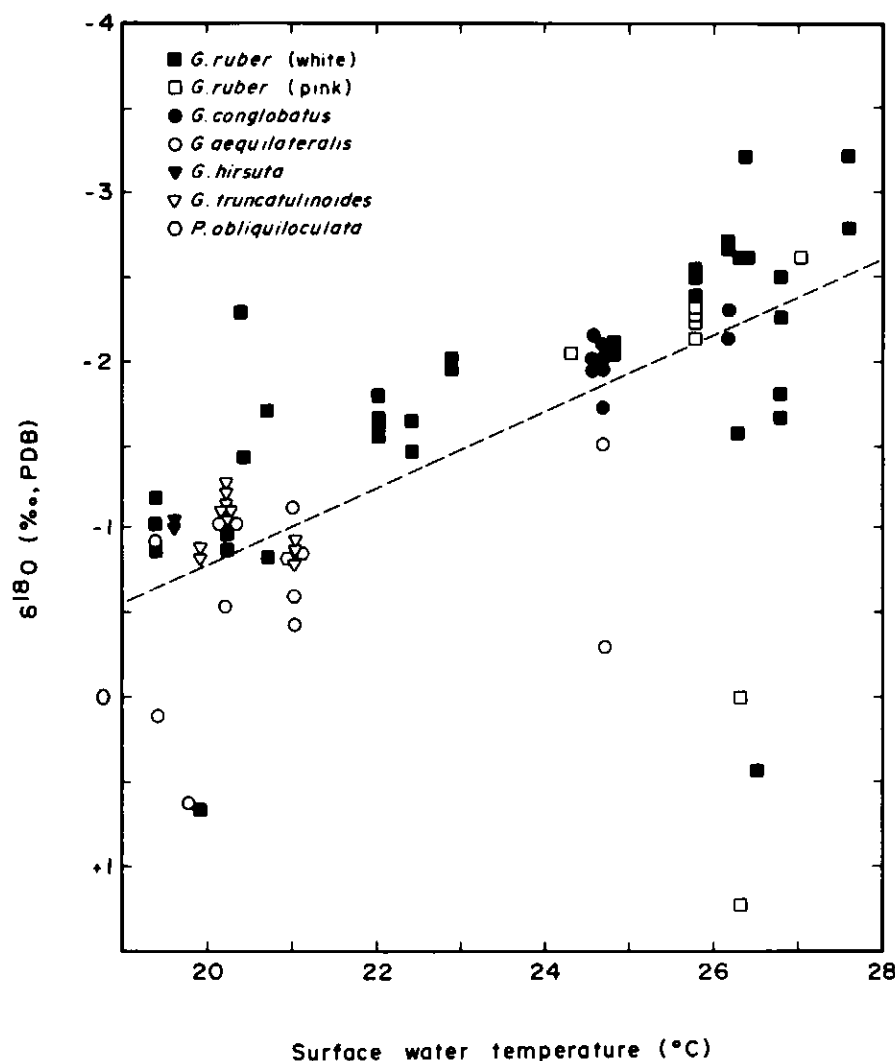
Salinity is one of the major controlling factors of the aquatic environment, since many organisms precipitate their skeletons in chemical equilibrium with the surrounding water (Lowenstam, 1961). Gall (1983) reports that organisms described as stenohaline, do not tolerate large salinity variations, whereas euryhaline organisms are tolerant of markedly different salinity levels. Salinity tolerance ranges for Recent marine organisms are discussed by Heckel (1972). Consequently, salinity tolerance levels can affect the trace and stable isotope chemistry of the organism being studied.

This same aspect holds true for oxygen levels in the marine environment. Many organisms have an extensive oxygen range. For example, molluscs, as a group, appear to have a greater tolerance of low oxygen levels, though their greatest abundance occurs in waters with normal dissolved oxygen concentration (Rhoads and Morse, 1971). As a result, organisms from near aerobic conditions seem to contain higher Mn, Fe and sometimes Mg values, as well as lighter stable isotope values. More studies evaluating organism/ water/ sediment interactions are required to resolve the many questions related to the biogeochemistry of marine invertebrates.

#### Summary

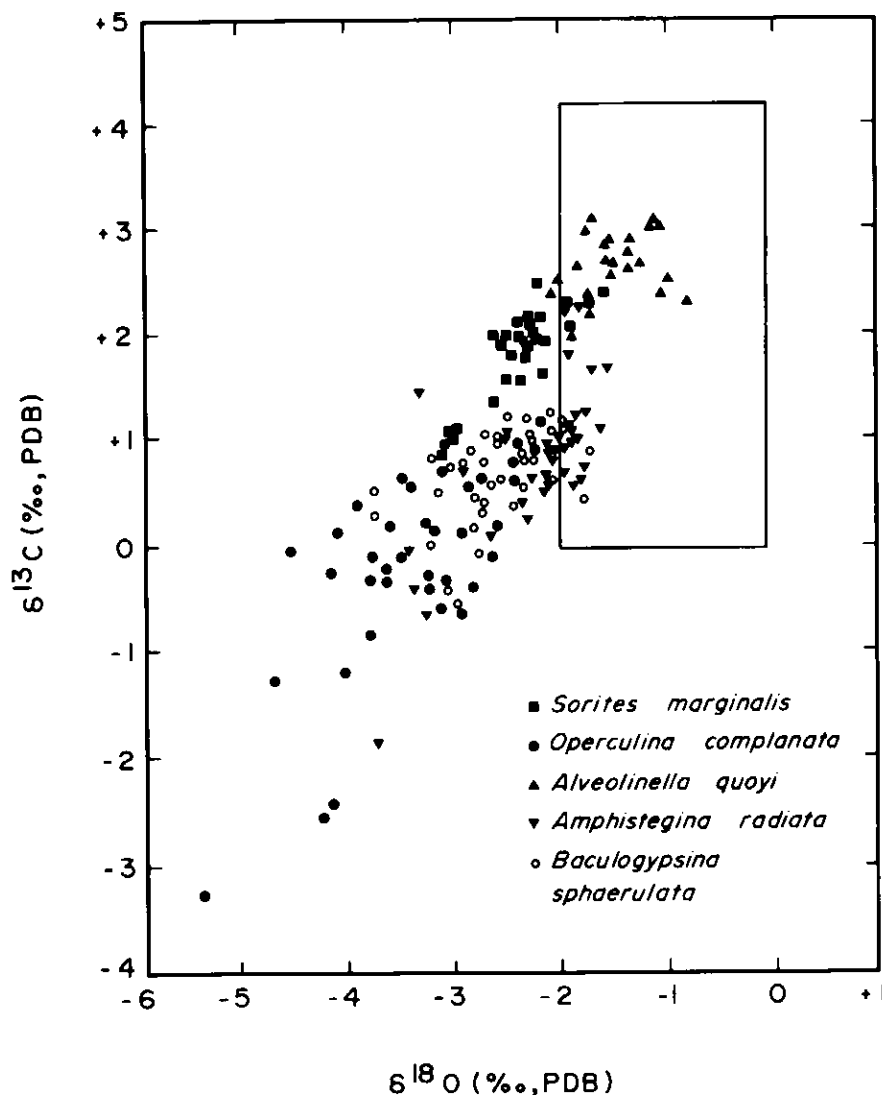
The major, minor and trace element and stable isotope geochemistry of Recent marine organisms is an important key in establishing criteria for comparisons with ancient environments. However, as discussed above, there are great complexities with regard to geochemical interpretations, although these difficulties are by no means insurmountable. Care must be taken in collection and preparation of samples for analysis. Most importantly, one must look at the full range of the biological and environmental factors when assessing and reporting conclusions. The combination of sedimentological, paleontological, and stratigraphical factors should be considered together with geochemical interpretations.

Each aspect appears to have an influence on the other, and this is revealed in the biogeochemistry of the organisms. It is only by developing a working knowledge in these many areas of geology that one is able to accurately determine useful results. By no means does this paper include all reported chemistry of Recent marine organisms. But the values that are shown indicate the chemical trends that should be realized for specific groups, and provide a good working basis for evaluation.



**Figure 19** Oxygen isotope composition of planktonic foraminifera collected at various water temperatures (modified from Williams *et al.*, 1977). Dashed line represents co-equilibrium trend and values for corresponding water temperatures and isotopic compositions of foraminiferal tests. Most measured isotopic values deviate from the equilibrium line suggesting that a vital effect controls the oxygen isotopic compositions of many planktonic foraminifera.





**Figure 20** Oxygen and carbon isotope compositions of various benthic foraminifera (modified from Vinot-Bertouille and Duplessy, 1973). The rectangular field defines the lower limits ( $-2.0\text{‰ } \delta^{18}\text{O}$ ;  $0\text{‰ } \delta^{13}\text{C}$ ) for calcium carbonate precipitated in isotopic equilibrium with ambient seawater under most near-surface conditions. Except for *Alveolinella quoyi*, all other benthic foraminifera have isotopic compositions outside the normal range. A vital effect is strongly indicated by the anomalous trends and values of these studied benthic foraminiferal tests.

Complete set of tabular data may be purchased from:

The Depository of Unpublished Data, CISTI  
National Research Council Canada  
Ottawa, Canada K1A 0S2

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