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# PALEOSCENE #6. Biogeochemistry of Fossil Marine Invertebrates

Uwe Brand and Joan O. Morrison[1]
*Department of Geological Sciences*
*Brock University*
*St. Catharines, Ontario L2S 3A1*

Present address:

[1] *Ottawa-Carleton Centre for*
*Geoscience Studies*
*Department of Geology*
*University of Ottawa*
*Ottawa, Ontario K1N 6N5*

## Introduction

The biogeochemistry of marine invertebrate shells/skeletons is highly complex and problematic (summary and additional references in Milliman, 1974; Dodd and Stanton, 1981; Morrison and Brand, 1986a). Complex shell chemistries are usually a reflection of the varied nature of life, where the organism and its life are greatly influenced by the physiochemical conditions of the ambient sea water. For studies of Recent invertebrates, the sea water conditions can be monitored and recorded, and taken into consideration when evaluating the chemistry of Holocene organisms (*e.g.*, Lowenstam, 1963; Dodd, 1965, 1967; Brand *et al.*, 1986). Besides water conditions influencing the chemistry of invertebrate shells, the organism itself can complicate matters by exerting a biological control and metabolic effect over its trace element and stable isotope compositions (*e.g.*, Weber, 1968; Lowenstam, 1961; Brand and Veizer, 1980). Chemical trends due to biologic and metabolic processes are difficult to define, because they vary greatly between individuals of the same species as well as between species (*e.g.*, Weber and Raup, 1966a,b). Dodd and Stanton (1981, p. 117) referred to these processes as physiologic factors, which "... under genetic control presumably have a biochemical basis that could be explained in physical chemical terms if they were adequately known".

For fossils, the matter is further complicated by the effects of diagenesis and by the inorganic and organic evolution of the terrestrial biosphere. Diagenesis is the alteration of the pristine state which affects the mineralogy of shells and skeletons of terrestrial and marine fossil invertebrates. Not only is mineralogy affected by diagenesis, but skeletal/shell microstructures and biogeochemistry are also unequivocally altered during this process. In many instances, morphological features of fossils are preserved while the original shell-carbonate is replaced by either pyrite, silica, dolomite or other secondary diagenetic minerals. These wholesale mineralogical replacements generally obliterate depositional chemical characteristics of carbonate fossils. Biogenic carbonates, in this instance fossils, precipitated in marine waters usually experience some physical and chemical changes in the presence of meteoric and submarine waters and other diagenetic fluids during their burial over geologic time (*e.g.*, Brand and Veizer, 1980; Baker *et al.*, 1982).

In addition to diagenetic effects, fossils and their biogeochemistry are influenced by evolutionary events. Extinctions or new appearances sometimes cause a change in the mineralogy, and consequently in the chemistry of exo- or endo-skeletons of organisms. An example of mineralogical evolution is exhibited by the extinct rugose corals with their calcitic skeletons which gave way to the extant scleractinians with their aragonitic exoskeletons (*cf.* Wilkinson, 1979). Along with genetic evolutionary changes in organisms, chemical and physical changes of ancient sea water probably caused significant evolution and adaptation in the morphologies and biogeochemistries of shells and skeletons of marine invertebrates. It is difficult to assess these biogeochemical changes when, in most instances, we are compelled to derive interpretations based on analogies with extant invertebrates or in other cases to closely related groups for extinct marine invertebrates. In the context of geologic time and biogeochemistry this can be a most hazardous undertaking.

Interpretations are further biased by the researcher, who selects certain invertebrates over others, and has preferences for chemical methods and data evaluation. Selection of one species over another by researchers is usually dictated by the objectives of the research. The greatest (apparent) chemical variation results from the way in which the data are calculated by the researchers. Methods of reporting isotopic values follow strict rules and norms, whereas elemental compositions are calculated following the researchers' preferences. This is the weakest point in comparing data of one researcher to those of another. A uniform way of handling data is urgently required and reporting on a 100% carbonate (insoluble residue-free) basis is preferred over other methods. In this approach, geochemical variations due to silicification, pyritization, organic matter content and/or adhering foreign matter of the fossil analyzed are minimized, which allows for intersample correlation of the carbonate-bound tracers (*cf.* Brand and Veizer, 1980; Veizer, 1974). Because of this, biogeochemical data of some fossils where the "geochemical variation" is of uncertain origin and difficult to interpret will not be included in this review paper. Furthermore, some fossil groups will not be represented, which is simply a reflection of the individual group's importance as a sediment contributor (*cf.* Wilkinson, 1979), ease of unravelling past environments, or as a result of researcher's preference.

## Preservation

Preservation has a double meaning, one to the paleontologist and another to the biogeochemist. To the paleontologist, a plant or animal is considered preserved if some form of its original morphological structure is found intact in rock units. In contrast, the biogeochemist requires for his study not only preservation of structural features but also that of the organism's skeletal or shell material.

Only a small fraction of organisms are preserved as fossils, and this low preservation rate is to a large extent controlled by biologic and geologic factors such as organic, physical and chemical destruction by scavenging organisms, weathering, erosion and diagenesis. According to Raup and Stanley (1971, p. 3), "not all plants and animals have an equal chance of being preserved as fossils, and not all geologic environments are equally favourable for preservation". Described fossil species represent only about 9% of all living species described to date. This discrepancy in numbers is striking when we consider the fact that the fossils represent the vast expanse of geologic time, and consequently, fossil species should outnumber their living representatives. Several factors can explain this apparent paucity of fossils. One explanation is related to the evolution of life with its marked increase in diversity and abundance, or another to the greater thicknesses and better exposure of younger sedimentary rocks (Raup and Stanley, 1971). Estimates put the number of preservable species since life began on the earth, as high as 4 billion. Many different estimates have been put forth by paleontologists, but it is clear from the numbers that only a tiny fraction of preservable species have been discovered. An even smaller percentage of the preserved morphospecies are also preserved in their original skeletal and shell material.

The best preservation of fossils is assured when they are encapsulated in materials that effectively seal air, water and fluids out, and prevent penetration of biological scavengers and predators. Biological destruction of fossils is recognized as an important factor in limiting the fossil record. Ice, amber, tar and chert are very effective sealants and fossils found in them are often preserved in their pristine state (*e.g.*, the fossils of the Buckhorn asphalt pits of southern Oklahoma; Squires, 1973; Crick and Ottensman, 1983).

Many of the Carboniferous fossils from the Buckhorn asphalt are not only preserved in their original shell mineralogy and chemistry but also show excellent pigmentation. However, these environments do not represent the normal habitat for most organisms, especially marine invertebrates the preservation of which depends on rapidly deposited sediments to protect them from post-mortem biological, mechanical and geochemical destruction.

Mineralogy of carbonate fossils plays only a subordinate role in preserving original morphochemical characteristics. Instead, the lithology of the enclosing rock and lack of interaction with diagenetic fluids play major roles in preserving carbonate fossils. Coal and shale, because of their impervious nature, generally deflect water flow, thus partially shielding the enclosed fossils from the effects and contact with diagenetic fluids. Furthermore, these sediments can be deposited in biologically inhospitable environments, which reduces the activity of predators and scavengers. As long as the remains of marine invertebrates reside in the marine environment, the skeletal material is relatively certain to be preserved provided physical degradation and biological processes are minimal. In this setting the different carbonate minerals, such as aragonite, high-Mg calcite and low-Mg calcite are relatively stable with respect to the depositional waters. Physically degraded shell and skeletal material may not be useful for paleontological study, but these fragments may still hold important clues to the original mineralogy, microstructures and biogeochemistry of the organism(s). However, in the presence of diagenetic fluids such as meteoric and/or burial waters and brines, aragonite and high-Mg calcite are metastable and alter readily to diagenetic low-Mg calcite (*e.g.*, Pingitore, 1976, 1978; additional references in Brand and Veizer, 1980). Other mineralogies, such as low-Mg calcite and apatite are relatively resistant to alteration by diagenetic fluids (*e.g.*, Veizer, 1983a,b). Preservation of the pristine state of fossil carbonate material is enhanced by the organic tissue surrounding the individual crystallites and the periostracum covering the whole shell; thus their resistance to alteration by diagenetic fluids is increased (Hudson, 1967; Clark, 1980).

The biogeochemistry of the least-altered fossil material is an invaluable aid in deciphering the paleoenvironmental history of the enclosing rock unit. Therefore, it is critical that only the *best* preserved material be used, however, its selection and reliability depend in large part on the method(s) employed by the researcher.

## Diagenetic Evaluation

Evaluation of the degree of preservation is of utmost importance when dealing with fossils. The following discussion addresses the susceptibility to alteration of carbonate minerals and biogenic apatite only, whereas other mineralogies and their state of preservation are not addressed. This bias is a reflection of the state of our understanding and knowledge of the different mineralogies and of their interactions with diagenetic fluids.

***Apatite.*** Conodonts consist of a calcium phosphate which belongs to the apatite group, making them susceptible to dissolution by hydrochloric, sulphuric and nitric acids. Chemical analysis of these organisms shows that they are: $Ca_5Na_{0.14}(PO_4)_{3.01}(CO_3)_{0.16}F_{0.73}(H_2O)_{0.85}$, which is the carbonate apatite, francolite (Pietzner *et al.*, 1968; Ziegler and Lindström, 1981). According to some studies, apatite is relatively inert in the diagenetic environment (*e.g.*, Urey *et al.*, 1951; Tudge, 1960). Because of the apatite mineralogy, it is assumed that conodonts are preserved in their original biogeochemistry. However, it is probable that in the presence of acidic groundwaters, the mineralogy and chemistry of conodonts could be altered or even totally dissolved (*e.g.*, Lindström, 1964). Besides diagenesis, the elemental as well as isotopic chemistry of conodonts could be subject to biogenic fractionation and vital effects as recorded in molluscs (Sr), brachiopods (Na), corals and echinoderms ($\delta^{18}O$ and $\delta^{13}C$; references in Morrison and Brand, 1986a). Until full geochemical criteria are established which define the "least-altered' specimen(s) and the above mentioned effects are fully investigated, we recommend that caution be used in analyzing and interpreting biogeochemical data of conodonts.

***Aragonite.*** Diagenesis of aragonite is a myriad of complex geochemical processes, which can proceed in the presence or absence of diagenetic fluids (*e.g.*, Bathurst, 1975; Carlson, 1983). The dry process is referred to as polymorphic inversion, and is largely dependent on the temperature of the diagenetic environment. At near-surface temperatures (25°C), the inversion of aragonite to calcite is a slow process and may take tens of millions of years or more. Transformation rates vary according to the type of aragonite (organic, inorganic) involved in the inversion process (*e.g.*, Land, 1966).

Wet transformation of aragonite to calcite is much faster than the dry process. In this instance, water acts as a catalyst by reducing the activation energy of the transformation, thus speeding its completion (*e.g.*, Bathurst, 1975). Depending on the openness of the system, the diagenetic calcite replacing the

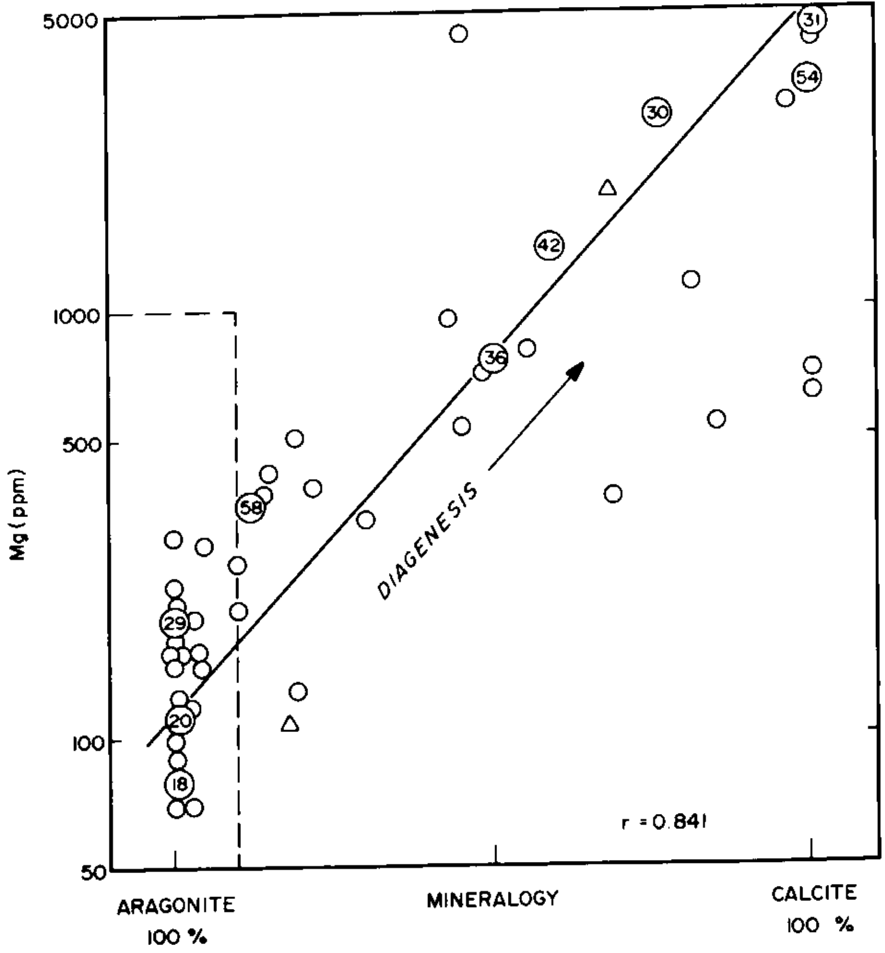

**Figure 1** *Variation in magnesium content and mineralogy of originally aragonitic molluscs with increasing diagenetic alteration (from Brand, 1985, in press). Magnesium composition increases as the original aragonite of the shell is replaced by diagenetic calcite. Open circles are cephalopods, triangles are bivalves, numbered symbols are represented by SEM pictures.*

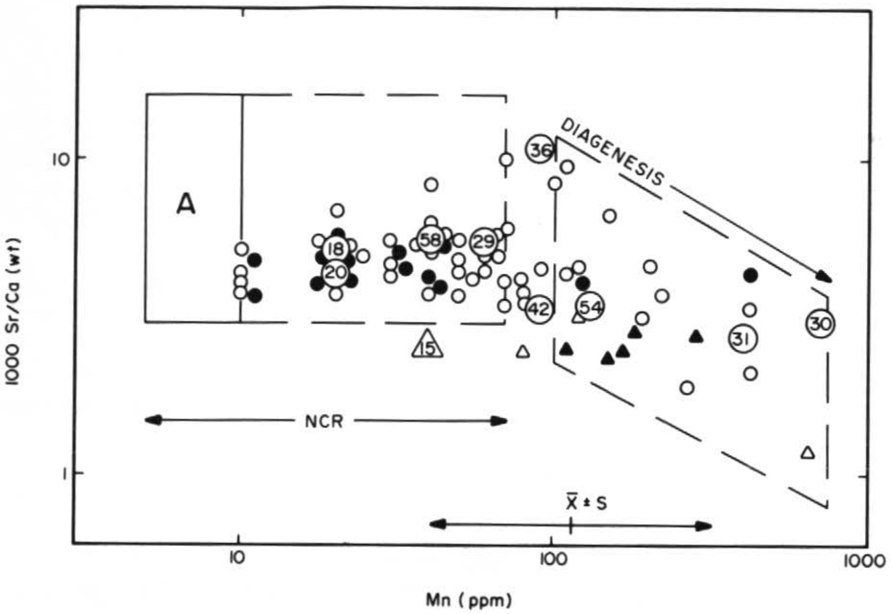

**Figure 2** *Chemical diagenesis of biogenic aragonite. 1000 Sr/Ca-Mn scatter diagram depicting the diagenetic pathway of originally aragonitic molluscs (data from Brand, 1985, in press). The x ± s is the mean and standard deviation of Paleozoic fossils and carbonates (in Brand and Veizer, 1980). The NCR depicts the natural chemical range of Mn in originally aragonitic molluscs. Symbols as in Figure 1.*

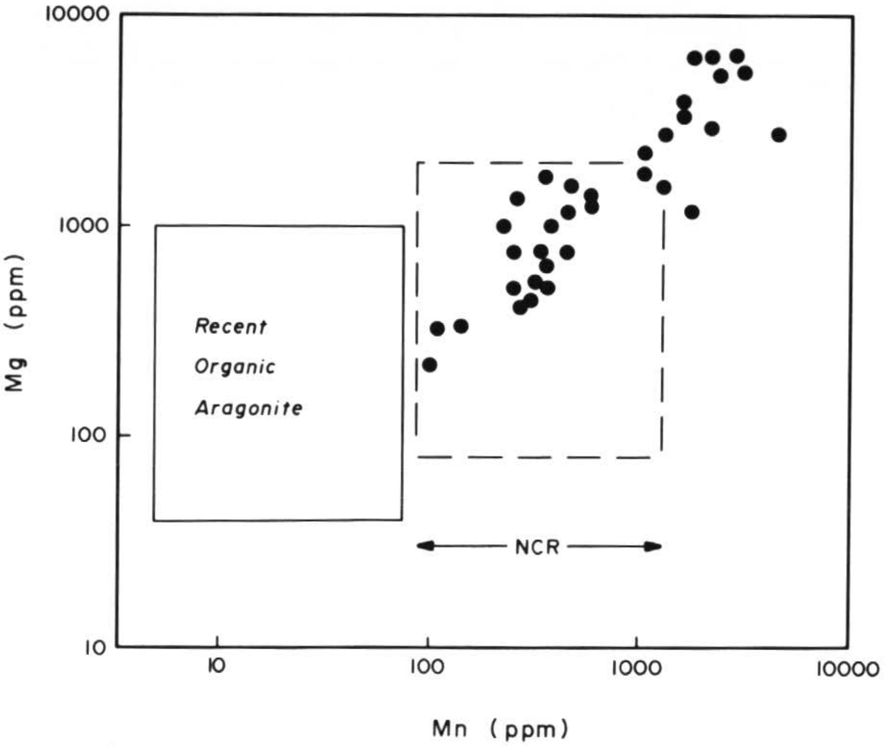

**Figure 3** *Environmental control of chemistry in fossil shells. Mg-Mn scatter diagram of molluscs (●) from the Breathitt Formation, eastern Kentucky, and field of Recent biogenic aragonite precipitated in normal seawater (data from Brand, 1983). The Mn range defined for Recent molluscs has to be expanded (NCR field) to include the well-preserved aragonitic molluscs of the Kendrick and Magoffin marine horizons.*

original material will retain, in degrees, some of the original geochemical information. This is also referred to as the size of the thin-film between the aragonite and the diagenetic calcite (*e.g.*, Pingitore, 1976, 1978). Aragonitic fossils altered in open systems are usually replaced by clear calcite spar, whereas those altered in less open diagenetic systems, the skeletal/shell aragonite are usually replaced by microspar, with more morphological and geochemical information passed on to the diagenetic product.

One way to determine the degree of preservation of fossils is by using an x-ray diffractometer, and with this method the postulated original mineralogy is based on an analogy with those of Recent counterparts. Mineralogical changes can be easily traced in mono-mineralic aragonitic fossils (Figure 1), whereas this is considerably more difficult for bi-mineralic fossils. The easiest way to detect diagenetic effects in the latter, is to separate the different mineralogical layers and to examine them separately.

Usually, one method is not considered sufficient to identify positively the state/degree of alteration of fossil material. Further tests, such as examining trace element concentrations, are required to evaluate the fossils properly. During diagenesis, the depositional biogeochemistry of marine invertebrates is altered as the calcium carbonate is dissolved and subsequently reprecipitated as diagenetic calcite. In this process, minor and trace elements are exchanged in 'predictable' ways, useful in deciphering the degree of alteration for a particular fossil. For example, Figure 2 shows that the Sr content decreases, whereas the Mn content increases in aragonite progressively altered to diagenetic low-Mg calcite. Magnitude of the elemental shift in biogenic aragonites during diagenesis is greatly influenced by the original biogeochemistry of the organism under investigation.

It should be kept in mind that ranges of elemental concentrations of Recent organisms may not necessarily apply to ancient counterparts. Chemical data of modern invertebrates are most abundant for organisms inhabiting normal marine environments. Therefore, this limitation should be kept in mind when analyzing and interpreting data of fossil material. In more restricted environments, fossils may incorporate more of some and less of other elements/isotopes into their skeletal carbonate. For example, Veizer (1977a) postulated that calcite precipitated in equilibrium with reducing sea water would contain more Fe and Mn than normal seawater calcite. This should also be the case for aragonite precipitated in comparable environments. Such considerations would expand the normally expected Natural Chemical Range (NCR)(Figure 3; Brand, 1983, 1984) for many trace elements, especially Mn and Fe. The samples within the NCR field are preserved as aragonite, but fall outside the field characterizing Recent organic aragonite (Figure 3). Not knowing this information, the high Mn values would have been interpreted as alteration of the original carbonate material. This demonstrates that diagenetic evaluations based on one method may lead to false interpretations of the fossil's diagenetic state. Thus a multi-method approach (x-ray diffraction, scanning electron microscopy, cathode luminescence, trace element and stable isotope geochemistry) is the only assured way to positively identify the best-preserved fossil material.

Figure 4 summarizes the trends and magnitudes recorded for the different elements and isotopes during the alteration of aragonite with diagenetic fluids (Brand, 1985, in press). Generally these trends are as predicted by theoretical considerations (Pingitore, 1976, 1978; Brand and Veizer, 1980, 1981), although the magnitudes can differ significantly between theorized and natural conditions (*cf.* Veizer, 1983b, Fig. 14). Some elements do not exhibit any change in concentration with increasing alteration (Figure 4: Ba, Zn, Cu, Ni, Pb), which is contrary to theoretical calculations. This demonstrates how complex the natural situation is and how feeble are the attempts to quantify it. At the same time it underscores the need for a multi-method approach for identification of diagenetic events.

***High-Mg Calcite.*** Alteration of high-Mg calcite follows a diagenetic pathway similar to that of aragonite. Their solubilities in sea water are similar at a temperature of 30°C (Weyl, 1967) and possibly in other fluids as well. With progressive alteration to diagenetic low-Mg calcite, the Mg and Sr concentrations decrease (Figure 5). Initially, the Mg content decreases while there is no significant shift in the Sr concentrations. Samples that plot in this area of the diagram have retained some of their morphological integrity (*e.g.*, the open space of the stroma in crinoids). In crinoids from other localities, both Mg and Sr concentrations decrease proportionally. This does not imply a sequential decrease with further alteration. Instead, a particular sample population and its position represents distinctive diagenetic processes and fluid chemistries.

Figure 6 shows the summary trends of the different elements and isotopes during the increasing alteration of high-Mg calcite (data from Brand, 1986a). The $\delta^{13}C$ composition can decrease or increase and the direction is in part dictated by the type of solution involved in the alteration process. In the presence of marine burial fluids, the carbon isotope values increase (*e.g.*, Baker *et al.*, 1982), whereas in the presence of meteoric water a decrease is commonly, but not exclusively, noted in the diagenetic product (Brand and Veizer, 1981). Except for Mg, the trends of the alteration of high-Mg calcite to diagenetic calcite are similar in direction to those noted for the aragonite-calcite transformation (Figure 4). Ultrastructure as well as mineralogy play an important role in the dissolution of biogenic carbonates (*e.g.*, Morse, 1983).

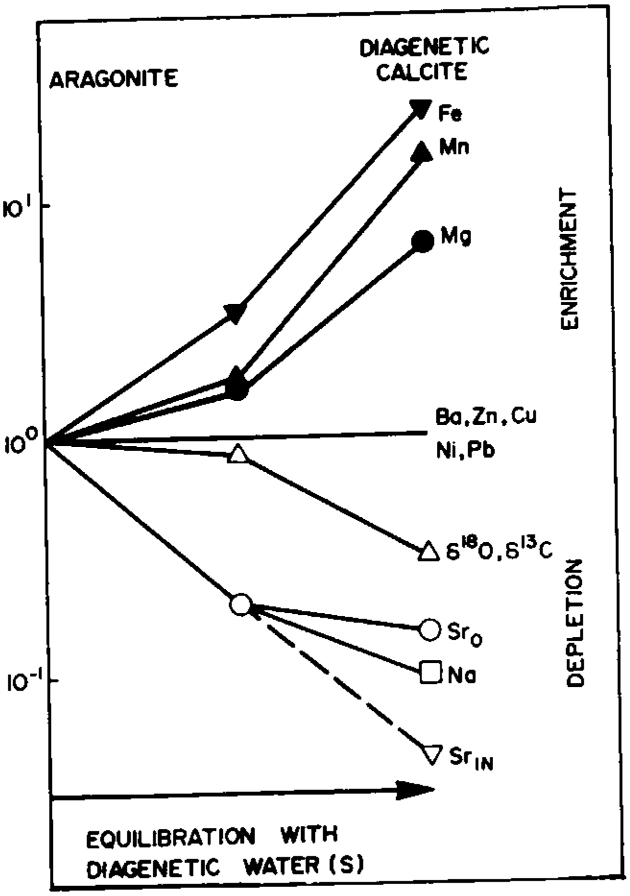

**Figure 4** *Diagenetic trends for trace elements and stable isotopes determined from direct measurements of aragonitic fossil samples showing direction, rate and magnitude of the alteration process (from Brand, 1985, in press). Starting point was determined using well-preserved fossils, and the trends were computed using progressively more altered samples. No changes in chemical composition were noted for Ba, Zn, Cu, Ni and Pb with chemical diagenesis. Note the divergence in the Sr contents of diagenetically altered biogenic ($Sr_O$) and inorganic ($Sr_{IN}$) aragonite*

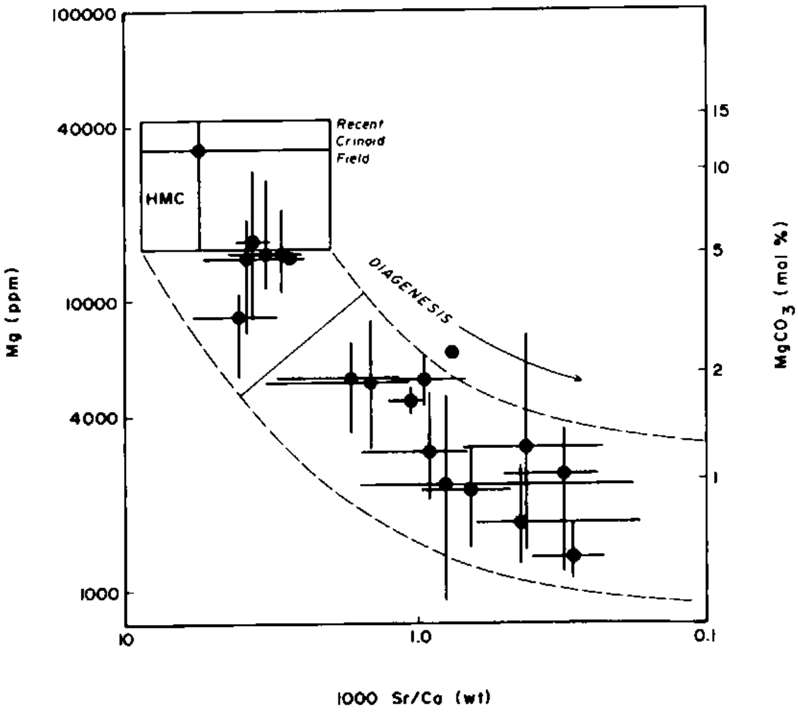

**Figure 5** *Chemical diagenesis of biogenic high-Mg calcite. Mg-Sr/Ca scatter diagram for originally high-Mg calcite crinoids from numerous Carboniferous localities of North America. HMC field represents unaltered Recent echinoderm samples (from Morrison and Brand, 1986a; Brand, 1986a); dots represent means and bars are the total observed chemical variation.*

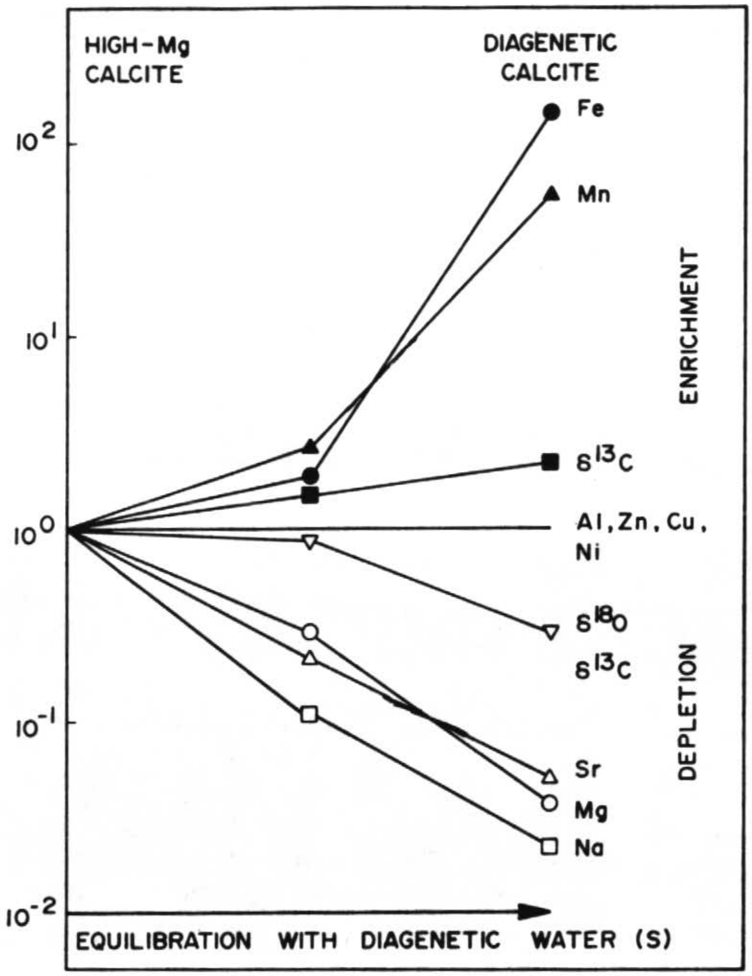

**Figure 6** *Diagenetic trends for trace elements and stable isotopes determined from direct measurement of high-Mg calcite fossil samples showing direction, rate and magnitude of the alteration process (from Brand, 1986b). Computation of trends is based on progressively altered crinoid samples* (cf. *Figure 4). The* $\delta^{13}C$ *composition increases in samples altered by diagenetic fluids of marine origin, whereas alteration in the presence of meteoric water brings about a negative shift in the original values.*

***Low-Mg Calcite.*** Low-Mg calcite is thermodynamically the most stable of the calcium carbonate species commonly found in extinct and extant marine invertebrates, thus no significant alteration is to be expected in the biogeochemical composition of fossils (*cf.* Veizer, 1983a, b). This does not preclude the alteration of low-Mg calcite fossils, because calcitic brachiopod shells can be replaced by pyrite or silica. Generally no significant differences in the Sr/Ca ratios are noted between Recent shallow-water and ancient brachiopods, especially if rigorous criteria are followed in the selection and subsequent evaluation processes (*e.g.*, Al-Aasm and Veizer, 1982; Popp *et al.*, 1986). Microstructurally, brachiopod shells are usually well preserved; signs of alteration, dissolution or cement filling are lacking (*cf.* Morrison and Brand, 1984). Thus, Morrison and Brand (1984) and Popp *et al.* (1986) stated that brachiopods and their biogeochemistries should be useful indicators of past ocean chemistries and temperatures.

### Fossil Mineralogy

In most instances, marine invertebrates and their extinct representatives secreted shells or skeletons of similar mineralogy (Figure 7). This degree of mineralogical certainty can be applied to the carbonate tests of coccoliths, foraminifera, bivalves, gastropods, brachiopods, crinoids, echinoids, and coralline green algae. Paleozoic corals precipitated skeletons consisting mostly of magnesian calcite, whereas the majority of their Recent counterparts secrete skeletons of high-Sr aragonite. Mineralogy of the ancestors of green algae and bryozoans is uncertain, whereas evidence is still lacking concerning the mineralogy for the carapaces of the extinct trilobites (Figure 7).

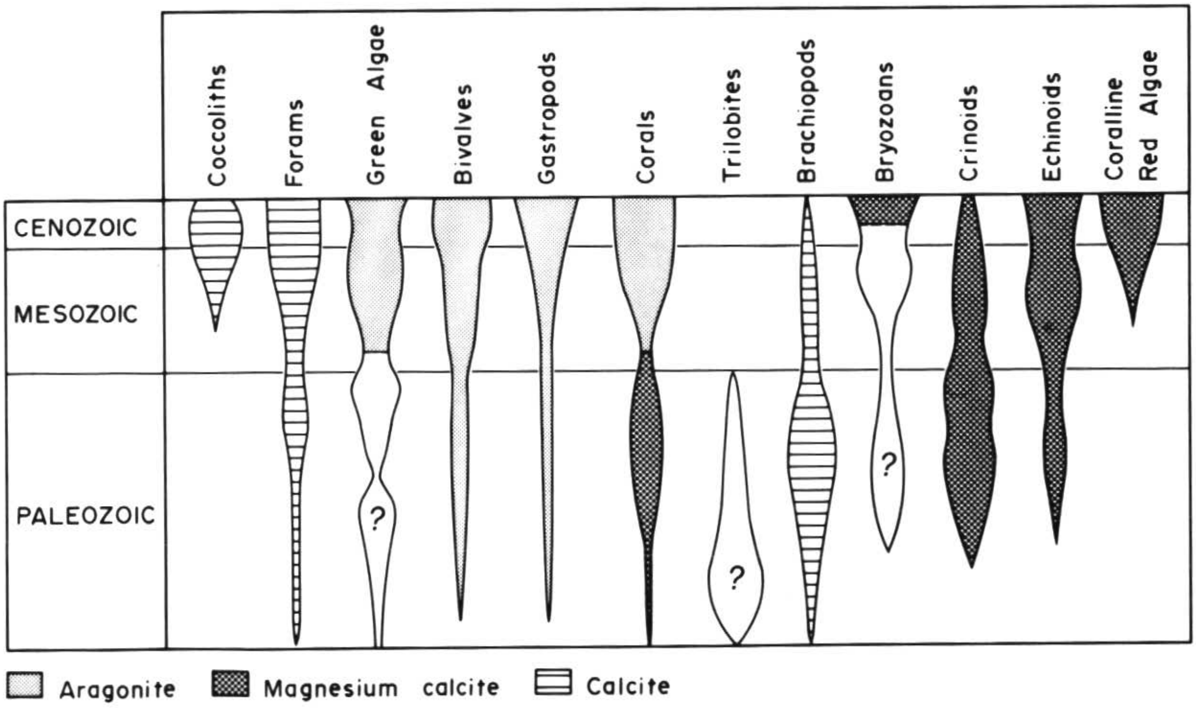

**Figure 7** *Relative abundance and mineralogy of the major fossil groups for the Paleozoic, Mesozoic and Cenozoic (from McAlester, 1968; Lipps, 1970). Uncertainty of mineralogy in various extinct fossil groups is indicated by a question mark.*

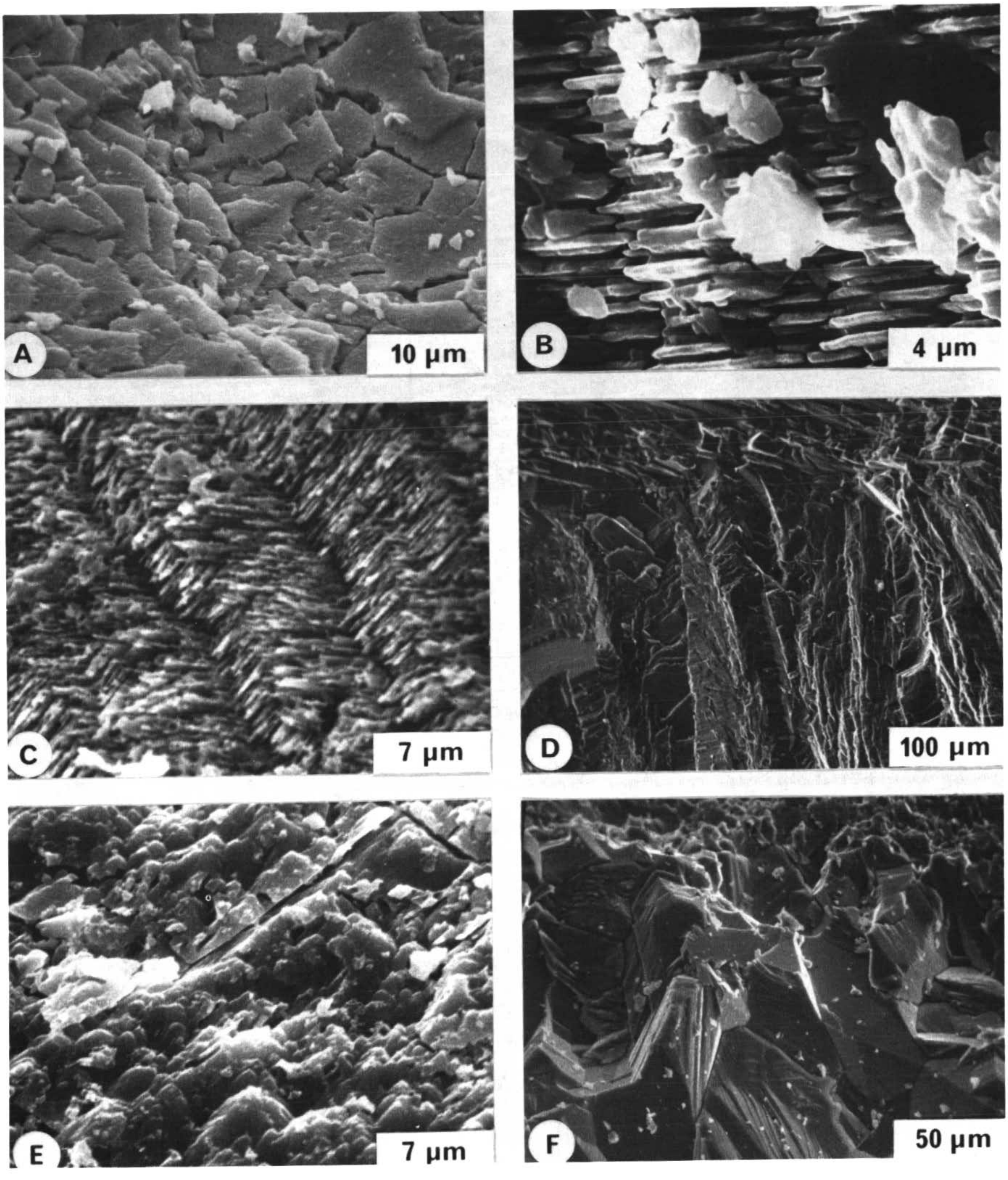

**Figure 8** *Scanning electron micrographs of shell structures in molluscs, brachiopods, crinoids and rugose corals.*

***A, B*** *top and side views of nacreous tablets in the shell of a well-preserved mollusc from the Carboniferous Kendrick Member, Breathitt Formation of eastern Kentucky* (cf. *Brand, 1981).*

***C*** *crossed-lamellae, originally aragonitic microstructures observed in molluscs.*

***D*** *two-layer fibrous calcite in brachiopods from the Boggy Formation of Oklahoma (Brand, 1982).*

***E*** *crinoid (Carboniferous) with stroma filled by diagenetic calcite cement* (e.g., *Brand and Veizer, 1980).*

***F*** *rugose corals (Devonian); the original microstructure is disrupted (replaced by coarse calcite mosaic; lower half of picture), but in some specimens from the Kendrick Member, original (?) trabecular structures have been observed by Sorauf (1977).*

### Fossil Microstructures

Internal shell or skeletal structures (= microstructures) can also provide important information on the state of preservation of carbonate fossils. Figure 8 shows some microstructures encountered in well-preserved molluscs and brachiopods (Figure 8 A-D), and the usually altered features found in crinoid and coral skeletal material (Figure 8 E-F). The first three plates show microstructures in fossil molluscs, which by comparison with structures observed in Recent representatives are interpreted to represent original biogenic aragonite. Figure 8D shows the typical two-layer fibrous calcite noted in brachiopods. This calcite structure closely resembles the features observed in extant brachiopods. In contrast, the depositional microstructures of crinoids (Figure 8E) and rugose corals are commonly obliterated by coarse calcite mosaic. Thus, microstructural analysis in conjunction with mineralogy can give the researcher a good indication of the state of preservation of fossil specimens. But, further biogeochemical testing of skeletal material is strongly advised so researchers may be more certain about the pristine state and preservation of fossil remains.

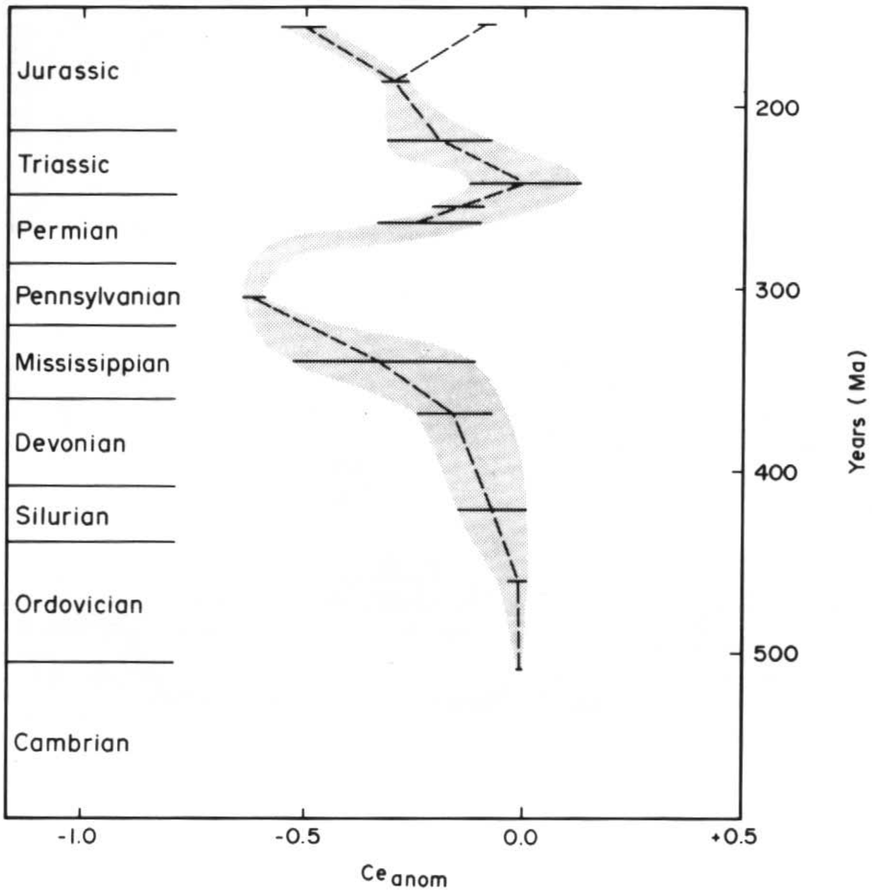

**Figure 9** *Trend of anomalous cesium in conodonts from Cambrian to Jurassic time (modified from Wright, 1985). Bars represent variation in Ce contents, which diverge during the Jurassic. See text and Wright (1985) for explanation of trends.*

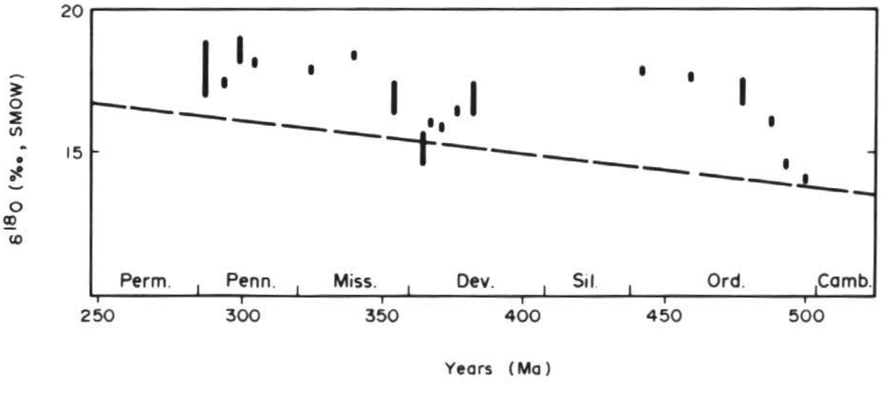

**Figure 10** *Oxygen isotopic composition of conodonts and its variation with respect to values determined for marine phosphates; dashed line (modified from Luz* et al., *1984b). Deviation of conodont $\delta^{18}O$ values from those of marine phosphates is probably related to fractionation at the organism level. Bars represent range of multiple analyses.*

### Fossil Biogeochemistry

The following sections provide discussion of the biogeochemistry of those fossil groups which were either significant sediment contributors, or played an important role in evolutionary history.

***Conodonts.*** Researchers working on the geochemistry of conodonts believe that the chemistry of the apatite has suffered no diagenetic alteration (*e.g.*, Tudge, 1960; Urey *et al.*, 1951), and thus their elemental and isotopic compositions should reflect paleoenvironmental conditions of the ambient water (*e.g.*, Wright *et al.*, 1987; Geitgey and Carr, 1987; Wright, 1985; Luz *et al.*, 1984b). At this stage, it has not been proven unequivocally that the remains of conodonts are free from diagenetic alteration. However, some interesting observations have been made concerning the relationship of colour and organic geochemistry of conodonts (*e.g.*, Epstein *et al.*, 1977). The change in conodont colour is related to the thermal history of the rock and reflects the maturation of organic matter within the conodont-apatite. Conodonts belong to an animal of uncertain affinity that roamed the seas from the Cambrian until Triassic time (*e.g.*, Epstein *et al.*, 1977; Wright, 1985).

The search for accurate paleoclimatic indicators has increased the search for noncarbonate samples that might fulfil this purpose. Wright and co-workers (Wright, 1985; Wright *et al.*, 1987) demonstrated that the REE content of conodonts, in particular cesium, varies systematically through geologic time (Figure 9). They postulated that these trends reflect variations in the original seawater composition, more specifically the redox potential of the water. Using modern fish debris analogues, Wright (1985) postulated that Lower Paleozoic and Triassic waters were generally reducing, whereas during the Upper Paleozoic the water was for the most part oxidizing (Figure 9). Furthermore, the Ce trend observed in conodonts correlates with the $\delta^{34}S$ age curves of marine evaporites through geologic time (Claypool *et al.*, 1980). Thus, the interpretations may be more far-reaching than simply the redox potential of ancient seas.

Another paleoclimatic application has been developed using the oxygen isotope composition of conodonts (*e.g.*, Luz *et al.*, 1984b). Because of the scarcity of preserved

Paleozoic carbonate fossils, the conodonts may fill the gap for paleotemperature determinations similar to the forams of the Meso-zoic-Cenozoic. Figure 10 shows an apparent trend in the $\delta^{18}O$ compositions of conodonts, with highs during the Pennsylvanian, Mississippian and Upper Ordovician, and with lows during the Devonian and Lower Ordovician (Luz *et al.*, 1984b). These trends agree with paleoclimatic curves based on analyses of marine phosphorites. Comparing water temperatures calculated with the $\delta^{18}O$ of conodonts (Figure 11) and brachiopods (Table 1) shows that there is a significant difference between the two data sets. Those values computed with the conodont data are usually higher by about 10-20°C. We believe that if conodonts are preserved in their depositional chemistry, then the observed difference in temperature values is probably related to some vital effect in conodonts. Luz *et al.* (1984a) found a vital effect in the isotopic composition of mammalian bone-phosphate, but whether this observation applies to the apatite of marine conodonts is uncertain; more specific research will have to resolve this question.

In general, the reader is cautioned when evaluating the chemistry of conodonts, because the questions of diagenetic alteration, biologic fractionation and metabolic effects have not as yet been satisfactorily resolved.

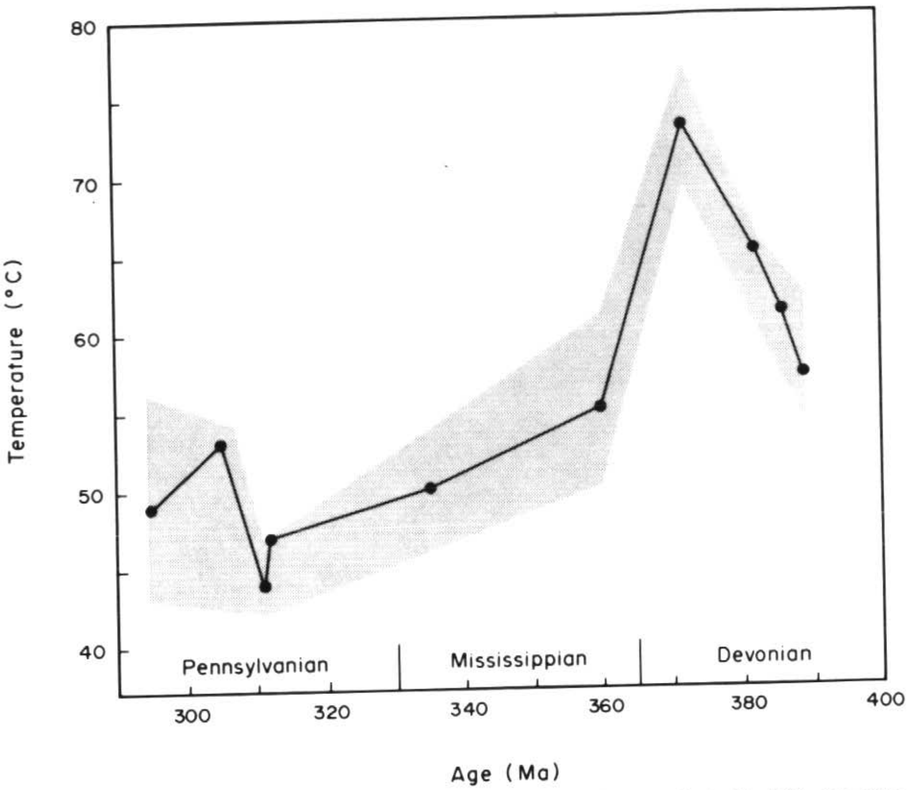

**Figure 11** *Temperature variation graph of Carboniferous and Devonian conodonts. The* $\delta^{18}O$ *data of the conodonts are from Luz* et al. *(1984b) and Karhu and Epstein (1986). The temperature equation (see page 104, equation 4 of this text) is from Karhu and Epstein (1986). Area around mean temperature values represent ranges of calculated* $\delta^{18}O$ *values, and these are significantly different from temperatures calculated with* $\delta^{18}O$ *data of brachiopods* (e.g., *Morrison and Brand, 1984; Veizer* et al., *1986; Popp* et al., *1986a).*

**Table 1** Paleotemperatures calculated with the $\delta^{18}O$ of well-preserved brachiopods (B) and molluscs (M). The first set of temperatures are determined without any corrections, whereas the second set was determined with a correction for the plausible secular variation of $\delta^{18}O$ in seawater. For reference of data see Figure 27.

| Age | Fossil | $\delta^{18}O$ (‰, PDB) | | | Temperature (°C) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $\bar{x}$ | Low | High | $\bar{x}$ | Low | High | Correction (‰) | $\bar{x}$ | Low | High |
| Pleistocene | M | -2.2 | -11.7 | +0.7 | 26.4 | 16.1 | 63.7 | | | | |
| Miocene | M | +0.3 | -1.4 | +2.5 | 17.4 | 10.5 | 23.5 | | | | |
| Oligocene | M | -1.5 | -3.2 | +1.5 | 23.8 | 13.3 | 30.0 | | | | |
| Paleocene | M | -0.3 | -1.9 | +0.5 | 19.6 | 16.7 | 25.3 | | | | |
| Cretaceous | M | -2.2 | -4.5 | -0.3 | 26.4 | 19.6 | 34.9 | | | | |
| Jurassic | M | -2.0 | -6.5 | +0.8 | 25.6 | 15.7 | 42.6 | | | | |
| Permian | B | -3.6 | -10.6 | -0.7 | 33.4 | 19.3 | 77.2 | -1.5 | 25.8 | 13.0 | 66.6 |
| Carboniferous | B | -5.2 | -8.6 | -2.3 | 42.2 | 26.8 | 63.3 | -1.5 | 33.9 | 19.8 | 53.6 |
| | | -4.6 | -7.3 | +0.5 | 35.3 | 16.7 | 45.7 | -1.5 | 29.7 | 11.6 | 39.9 |
| Devonian | B | -6.2 | -10.7 | -4.4 | 48.1 | 37.7 | 77.9 | -4.0 | 26.3 | 18.0 | 51.1 |
| Silurian | B | -6.5 | -7.8 | -4.4 | 49.9 | 37.7 | 58.0 | -4.0 | 27.8 | 18.0 | 34.5 |
| Ordovician | B | -4.9 | -5.5 | -4.5 | 40.5 | 38.3 | 44.0 | -4.0 | 20.2 | 18.5 | 23.0 |

***Foraminifera.*** Isotopic compositions of foraminifera are an indispensible tool in Mesozoic-Cenozoic paleoceanography, and the field has undergone rapid expansion since the pioneering days of Emiliani (1955). In the initial stages of foraminiferal geochemistry, paleotemperature reconstructions and depth assignments to the various planktonic species were the central theme of theses studies (Emiliani, 1955, 1966). Subsequently, more attention has been paid to possible biologic-temperature-ice interactions, and to extend the work and concepts to Tertiary and Mesozoic foraminifera. Much of this work has been summarized by Hecht (1976), Savin (1977), Shackleton (1977) and Duplessy (1978). Another theme was, and remains, the separation of the temperature signal from that induced by changes in the ice volume (Shackleton, 1977; Imbrie *et al.*, 1973; Shackleton and Opdyke, 1973), and refinement of the time scale for the Pleistocene (Broecker and van Donk, 1970). While more detailed studies of Pleistocene glacial and interglacial events proceeded, other researchers evaluated the original assumption that foraminifera as a group incorporate stable isotopes into their tests in equilibrium with ambient seawater (*e.g.*, Savin and Douglas, 1973; Buchardt and Hansen, 1977; Williams *et al.*, 1977; Berger *et al.*, 1978; Kahn, 1979; Woodruff *et al.*, 1980). These and other studies suggest that disequilibrium instead of equilibrium precipitation is the norm for both benthic and planktonic foraminifera (Erez and Luz, 1982; Wefer and Berger, 1980; Vergnaud-Grazzini, 1976; others listed above). The degree of isotopic disequilibrium can be complicated by niche, habitat, depth migration, and growth stages of foraminifera, and by seasonality and horizontal advection of the water mass they live in. These observations suggest that a renewed interest in foraminiferal geochemistry is under way with many contradictory results, and these may "... fan the flames of controversy" (Berger, 1981, p. 5).

Foraminifera are uni-cellular organisms that precipitate skeletons consisting of either low-Mg calcite, aragonite or high-Mg calcite, or tests agglutinated with detrital material (*e.g.*, Milliman, 1974). Generally, tests of benthic foraminifera consist of high-Mg calcite, whereas those of planktonic foraminifera consist of low-Mg calcite (Blackman and Todd, 1959; Emiliani, 1955). Under identical post-depositional conditions, tests of benthic foraminifera would be subject to greater diagenetic alteration than those of the planktonic group. Furthermore, studies have demonstrated that benthic foraminifera probably reflect more closely sediment pore-water chemistry than bottom waters of the sea, because of their tendency to establish microhabitats within the top centimetres of the sediment. Their $\delta^{18}O$ composition has been linked to water temperature and salinity, and this correlation varies from locality to locality, but not in conjunction with water temperature (Kerr, 1986). With repect to $\delta^{13}C$, the composition of benthic forams, according to Corliss (in Kerr, 1986, p. 427) "... may tell more about the biological productivity of overlying waters than about bottom water". These problems may be overcome by analyzing various groups of foraminifera from different habitats. Planktonic foraminifera, although precipitating tests of more stable low-Mg calcite, have special problems with their geochemistry which can vary from core to core and between size fractions (references and discussion in Kerr, 1986).

Despite these discussed geochemical difficulties with foraminifera, Figure 12 shows that the atom ratios of Sr/Ca and Na/Ca of several species of Upper Pleistocene foraminifera vary within and between sample size fractions. It is uncertain whether a biochemical or a physiological process is responsible for the observed variance. Bender *et al.* (1975) detemined this correlation between relative growth depth and Na/Ca, Mg/Ca and Sr/Ca (atom ratios) of various species (Figure 12). Similar observations were also made by other researchers (*e.g.*, Kilbourne and Sen Gupta, 1973; Savin and Douglas, 1973). It has been postulated that these variations are not due to temperature changes, but are related to the calcification rate, or other unknown factors.

Emiliani (1955, 1966, 1971) demonstrated the usefulness of foraminifera as a paleo-

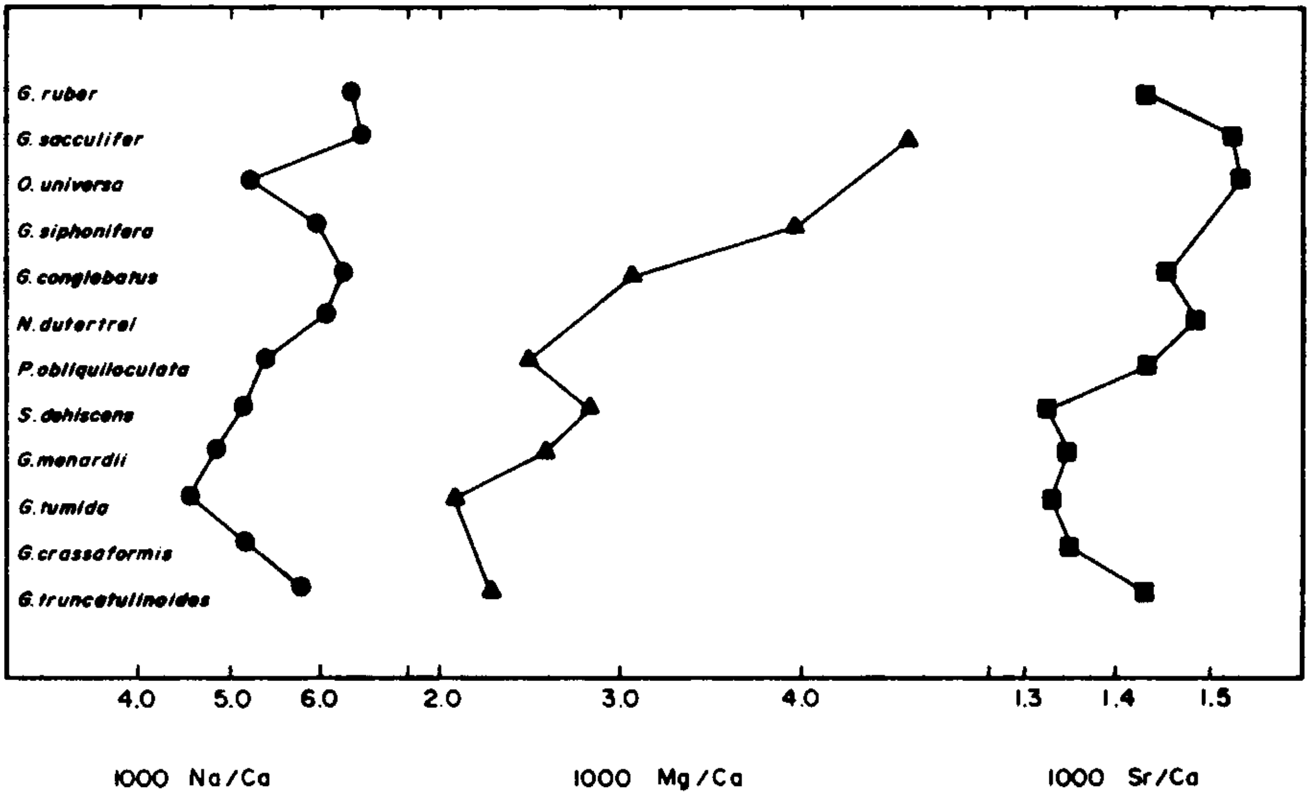

**Figure 12** *Variation in trace chemistry of different foraminifera species with growth depth. 1000 Sr/Ca and 1000 Mg/Ca ratios of foraminifera vary significantly with growth depth (modified from Bender* et al.*, 1975). No significant trends are defined by the 1000 Na/Ca ratios.*

oceanographic tool. He related their isotopic compositions to ambient water conditions, and constructed a $\delta^{18}O$ curve for the Pleistocene with isotope stages representing the different glacial stages (Figure 13). The pattern of the curve indicates rapid changes from glacial to interglacial conditions (Broecker and van Donk, 1970), and the sudden shift in the isotopic composition at Stage 22 has been correlated to the advent of continental glaciation. Emiliani (1955, 1966, 1978) related these $\delta^{18}O$ changes to variations in the water temperature during glacial and interglacial stages. High temperatures are reflected by negative $\delta^{18}O$ values and vice versa, while only a small portion in the isotopic variation was attributed to ice volume. As early as 1967, Shackleton (1967, p. 17) suggested that isotopic curves have to be re-read, "... taking 'cold' to mean 'extensive continental glaciation' and 'warm' to mean 'glaciers reduced to their present level'." This concept has been redefined in the context of non-linear ice-volume models (Mix and Ruddiman, 1984), and despite all of these different models, the time sequence (isotope stages) of the events remains relevant today.

Another important application of foraminifera and their stable isotope compositions is in resolving temperature problems of Cenozoic-Mesozoic seawater (*e.g.*, Saito and van Donk, 1974), provided the reader keeps in mind the alternatives proposed to the simple $\delta^{18}O$-temperature interpretations. Figure 14 represents the isotopic composition of both planktonic and of benthic foraminifera from mid (B) and low (A) latitudes. Water temperatures apparently increased from the Aptian to the Coniacian, and subsequently decreased steadily during the rest of the Mesozoic and Tertiary. Furthermore, Figure 14A shows that there were significant thermal differences between the shallow and deeper waters of the Central Pacific. This suggests that surface temperatures at low latitudes varied little, whereas high-latitude waters varied greatly as reflected in the isotopic compositions of the benthic foraminifera. The changes in water temperature during the Paleocene-Eocene and Miocene have been interpreted to reflect the onset of glaciation (*e.g.*, Savin *et al.*, 1975). It is difficult to argue with these trends, but the reader should be aware that an apparent metabolic effect has been found in the planktonic foraminifera *Globigerinoides sacculifer* by Erez and Luz (1982), and in other planktonic and benthic species (*e.g.*, Savin and Douglas, 1973; Kahn, 1979; Woodruff *et al.*, 1980).

**Molluscs.** Molluscs are one of the minor sediment contributors of Phanerozoic seas (Wilkinson, 1979; James, 1984). Three groups, the bivalves, cephalopods and gastropods, are the major representatives of the molluscs. Most of them precipitate shells consisting of aragonite (Fig. 7; Wilkinson, 1979); fewer, but still important, groups secrete shells of calcite

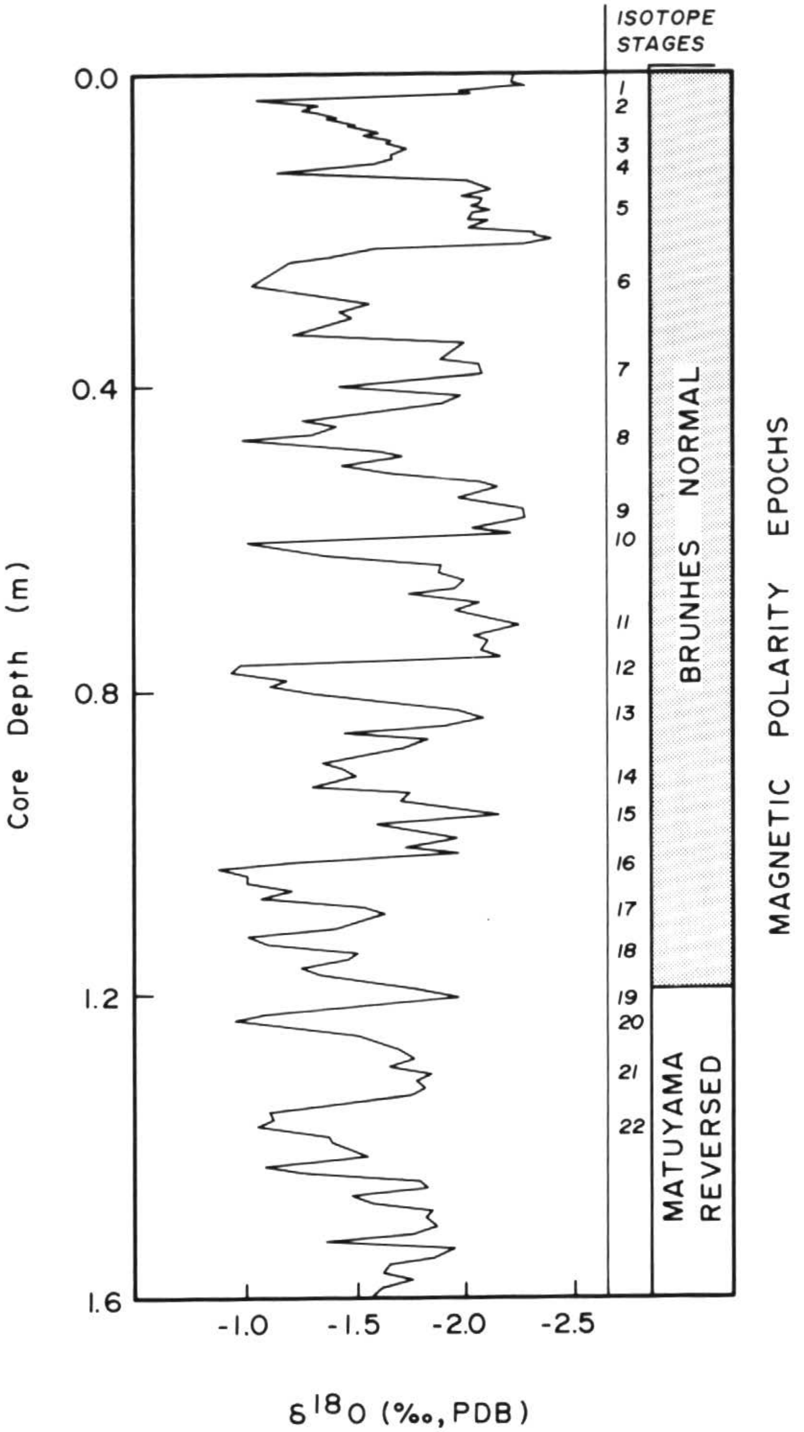

**Figure 13** *Oxygen isotopic variation in Pleistocene benthic foraminifera. Peaks in $\delta^{18}O$ composition (positive shifts) are related to the various Pleistocene glacial stades. Interglacials are identified by lighter values and troughs. Isotope stratigraphy is that of Emiliani (1966). A significant change in amplitude and frequency of isotopic trend occurs at the Matuyama-Brunhes boundary (approx. 700,000 B.P.).*

and mixed-mineralogy (*e.g.* Morrison and Brand, 1986b). Preservation of the metastable aragonite mineralogy is limited to specimens of Pennsylvanian age and younger, which of course greatly biases our data collection as well as paleontological and biogeochemical interpretations. Data presented in the following figures are mostly aragonitic molluscs, although in many instances the precise degree of preservation is uncertain due to lack of information.

Figure 15 shows the Sr/Ca ratios of aragonitic cephalopods, bivalves and gastropods from different time periods. The strontium levels in the ancient molluscs are similar, except for a few anomalous occurrences, to those recorded in Recent representatives. The anomalous trends for the Paleocene molluscs may be due, in part, to the minor diagenetic alteration noticed in the specimens (Buchardt, 1977). In contrast, the high strontium levels found in the Jurassic bivalves and the Carboniferous gastropods are probably related to unusual environmental conditions. For the gastropods, Brand (1986b) speculated that the high Sr levels are related to efforts by the organisms to maintain iso-osmotic equilibrium between body fluids and the ambient brackish seawater. Similar trends were also noted in the molluscs from the normal (western region, low Sr levels) and brackish marine (eastern region, high Sr levels) part of the Brush Creek (Morrison *et al.*, 1985). Overall, the Sr discrimination effect observed in Recent molluscs (*e.g.*, Bathurst, 1975) was already well established in their ancestors from the Carboniferous (Figure 15; Brand, 1987b).

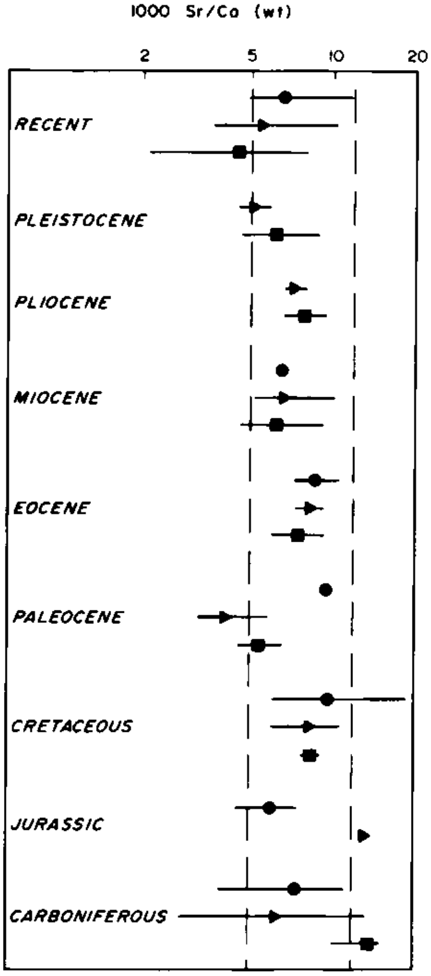

**Figure 15** *Strontium composition of aragonitic bivalves (▲), cephalopods (●), and gastropods (■) of different ages (data from Brand, 1981a, 1986b; Buchardt, 1977; Buchardt and Weiner, 1981, Crick and Ottensman, 1983; Hallam and Price, 1966; Kulp* et al., *1952; Lowenstam, 1963a,b; Marshall, 1981; Morrison* et al., *1985; Morrison and Brand, in press; Pilkey and Goodell, 1964, Ragland* et al., *1979; Scherer, 1977; Turekian and Armstrong, 1961; Weiner and Lowenstam, 1980). Symbols are the mean values and the bars are the ranges encountered in a particular group. Generally the 1000 Sr/Ca ratios of fossil molluscs are similar to those encountered in Recent counterparts (area defined by the dashed line, references in Morrison and Brand, 1986a). Environmental and/or diagenetic factors may account for the slight deviation of the values from the norm (e.g., Brand, 1983).*

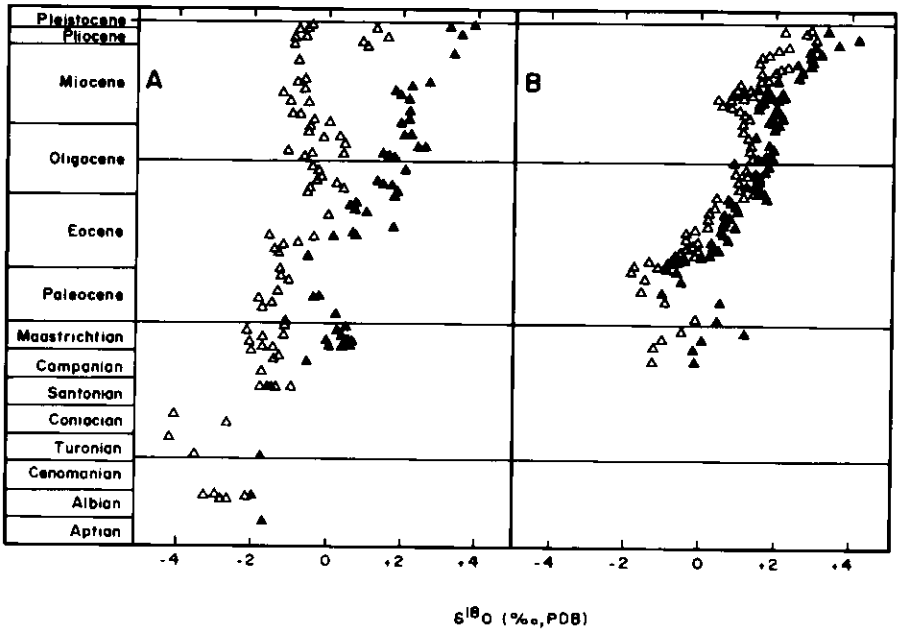

**Figure 14** *Oxygen isotopic variation measured in Cretaceous-Tertiary foraminifera. The $\delta^{18}O$ compositions are of foraminifera from the central Pacific (A) and from intermediate latitudes. Open triangles are planktonic, closed triangles are benthic foraminifera (from Savin, 1977; Savin* et al., *1975; Savin and Yeh, 1981; Shackleton and Kennett, 1975).*

In general, the magnesium levels determined in aragonitic fossil molluscs are similar to those observed in their Recent counterparts (Figure 16). Only, the Cretaceous molluscs contain unusually high concentrations of Mg, which may be related to diagenetic alteration of the shells or to environmental factors. Because of the invariance of the Sr data (Figure 15) with the Mg data, a diagenetic effect is discounted for the observed anomaly. Calcitic bivalves show a wide range of Mg concentrations, similar to the wide variation observed in their Recent counterparts (*e.g.*, Milliman, 1974; Morrison and Brand, 1986a).

Sodium levels in the aragonitic and calcitic molluscs, bivalves, gastropods and cephalopods are higher than those expected for their mineralogies precipitated in chemical equilibrium with ambient seawater (Figure 17). For low-Mg calcite, the normal Na concentration is about 230 ppm, which is easily exceeded by the contents measured in the ancient bivalves. A biological control is probably responsible for the anomalous ranges observed in the Pleistocene, Cretaceous and Carboniferous bivalves. Furthermore, according to White (1977) inorganic aragonite should contain about 2500 ppm Na, whereas the aragonitic fossils have Na levels that range from 1000 to 8000 ppm Na (Figure 17). Okumura and Kitano (1986) determined that the behaviour and state of $Na^+$ for biogenic mineralization may be different from that of inorganic processes, and set a Na range of 2000 to 6000 ppm for molluscan aragonite precipitated in equilibrium with ambient seawater. It is interesting to note that in two sets of Carboniferous cephalopods preserved as aragonite, the group from the normal marine environment (Buckhorn, Oklahoma; Brand, 1987b) contains more Na in their skeletal material than those molluscs from the brackish marine setting (Breathitt, Kentucky; Brand, 1987a). Sodium trapped in fluid inclusions is not believed to be responsible for the observed Na trends in the aragonitic molluscs (*cf.* Gaffey, 1984), because it accounts for only 5% of the observed variation in the data (Brand, 1987a). In calcite, the distribution process is more complicated because significant amounts of Na may be located interstitially in lattice defects (Busenberg and Plummer, 1985). Whether this observation also applies to biogenic calcite and aragonite is not certain, but in any case caution is advised when applying Na levels in molluscs to paleoenvironmental problems and paleontological and sedimentological evidence should be consulted wherever possible.

The $\delta^{18}O$ of aragonitic molluscs steadily decreases from the Pleistocene through to the Carboniferous (Figure 18). This change to lighter $\delta^{18}O$ values has been ascribed to either warming seawater temperatures (*e.g.*, Knauth and Epstein, 1976) or to the secular variation of seawater-$^{18}O$ with geologic time (*e.g.*, Perry and Tan, 1972; Brand and Veizer,

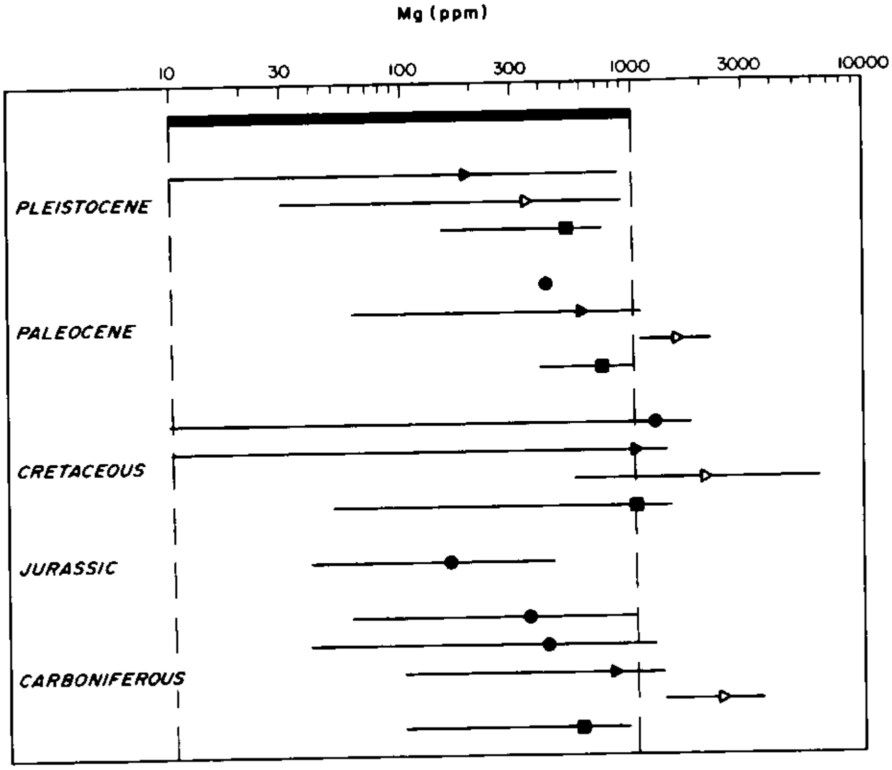

**Figure 16** *Magnesium means and ranges for molluscs of different ages. Solid bar represents composition encountered in Recent aragonitic molluscs. Solid symbols are aragonitic molluscs, whereas the open triangles are calcitic bivalves. Other explanations and references as in Figure 15.*

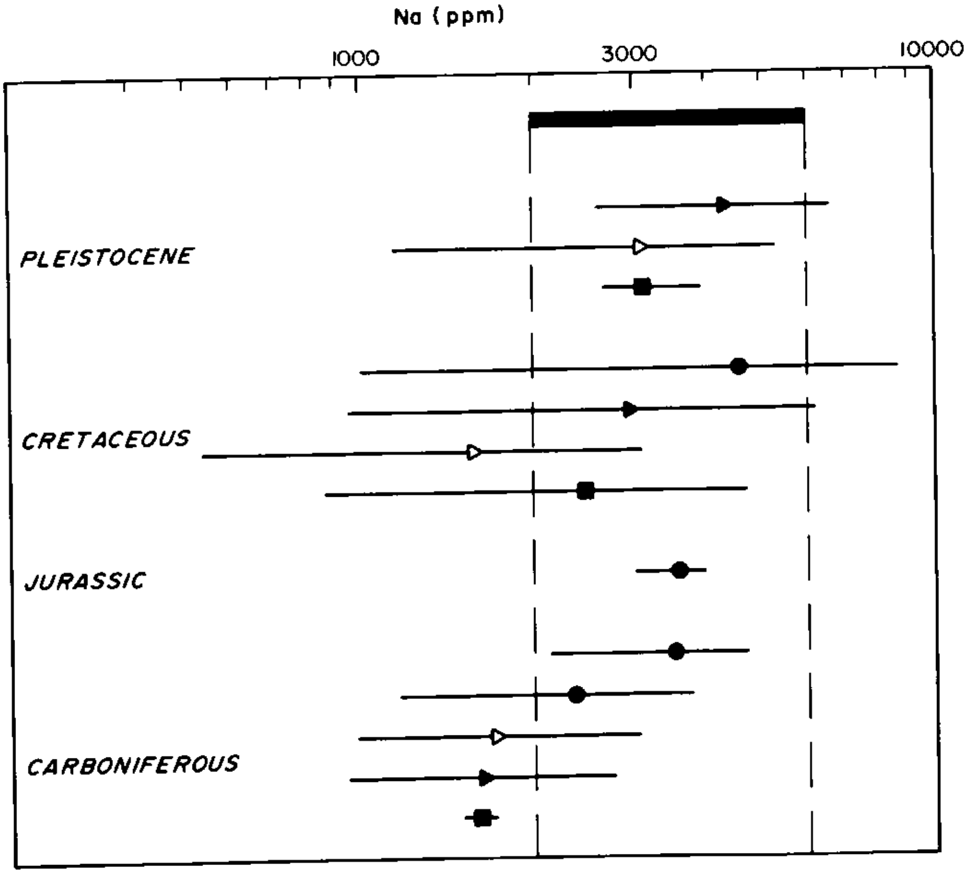

**Figure 17** *Sodium means and ranges for molluscs of different ages. The lower Na content observed in the Carboniferous molluscs is probably related to environment, because a large number of samples are from brackish marine environments (e.g., Brush Creek of Pennsylvania; Norton, 1975; Morrison et al., 1985). Symbols, explanations and references as in Figure 15.*

1981). Fractionation at the species level by some molluscs may account for some of the observed isotopic variation (*cf.* Kiyashko, 1982; Brand *et al.*, 1987). Unfortunately these problems have not been resolved at this time and a decision between the two alternatives and fractionation is still open to debate. Other factors have been identified, where the extremely light $\delta^{18}O$ values of the Pleistocene bivalves reflect flooding of inland marine seas (*e.g.*, Champlain Sea) by isotopically-light glacial meltwater (*cf.* Hillaire-Marcel, 1977, 1981; Wassenaar *et al.*, 1986). In a more detailed study, Buchardt (1978) evaluated the isotopic compositions of European molluscs ranging in age from Danian to Pleistocene (Figure 19). The oxygen isotope data show that the water temperatures for the shelf areas of the North Sea were higher during the Paleocene/Eocene with subsequent and rapid cooling during early Oligocene. Since the Oligocene, only minor deviations have been recorded in the $\delta^{18}O$-derived water temperatures; more detailed analysis for the Pleistocene, based on the $\delta^{18}O$ of foraminifera, is presented in Figure 13. Thus, for unaltered samples younger than Carboniferous, the $\delta^{18}O$ values and calculated paleotemperatures provide first-order approximations of thermal changes in ancient marine waters.

Figure 15 shows the Sr/Ca ranges and means for aragonitic molluscs as old as Carboniferous. Statistically no significant variation in the Sr/Ca content with geologic time is found. Similarily, no age trend is apparent for the $\delta^{13}C$ values of aragonitic molluscs (Figure 20), which, however, does not preclude a trend in the $\delta^{13}C$ composition of sea water with geologic time (*e.g.*, Veizer *et al.*, 1980; Holser, 1984). Detailed analyses and comparisons between inorganic carbonates and the data of unaltered molluscs and other fossil groups are required for better time resolution and interpretations of $\delta^{13}C$ secular curves. The $\delta^{13}C$ ranges of Carboniferous molluscs extend beyond the normal range of 0 to +5‰ defined by Recent molluscs. It is possible that paleoenvironmental factors (*i.e.* changes in salinity, upwelling currents, atmospheric $CO_2$, etc.) may be responsible for these variations.

***Rugose Corals.*** Some Paleozoic corals belong to the order of zoantharians called Tetracoralla (Rugosa). These corals exhibit solitary or colonial growth forms (Moore *et al.*, 1952). On most specimens of solitary rugose corals, the outer wall consists of thick calcite, although its original mineralogy is still in doubt. Some researchers (*e.g.*, Flügel, 1976; Oekentorp, 1972) believe that Rugosa originally precipitated aragonitic skeletons, whereas others believe that they precipitated calcite skeletons with varying amounts of Mg (*e.g.*, Richter, 1972; Sorauf, 1977; Sandberg, 1975; Lowenstam, 1961). These conclusions are based, in large part, on the different skeletal structures and various states of preservation

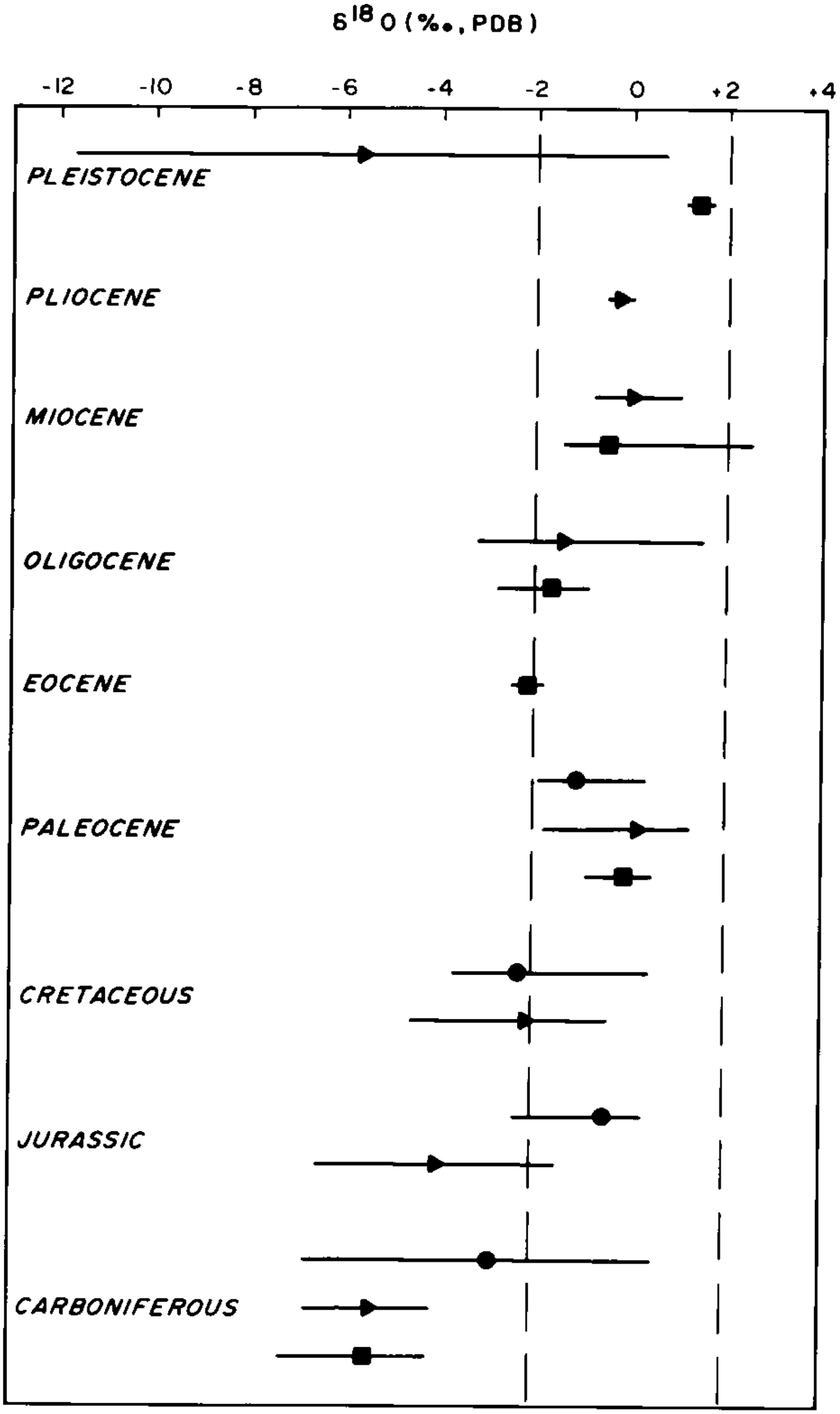

**Figure 18** *Oxygen isotope means and ranges for molluscs of different ages. Dashed field represents calcite/aragonite precipitated in isotopic equilibrium with ambient Recent sea water (references in Milliman, 1974 and Morrison and Brand, 1986a). Additional data were obtained from Brand (1981b, 1982), Hillaire-Marcel (1981), Keith and Weber (1964), Rothe* et al. *(1974), Stahl and Jordan (1969), Tan and Hudson (1974), Tan* et al. *(1970), and Wassenaar* et al. *(in press). Light $\delta^{18}O$ values of Pleistocene samples are related to mixing of marine waters with isotopically-light glacial melt-water. The lighter values for the Carboniferous molluscs has been related to (a) secular variation in the isotopic composition of sea water, or (b) higher water temperatures of ancient seas. For additional explanations and symbols see Figure 15.*

observed in the skeletal material (*e.g.*, Kato, 1963; Sandberg, 1975).

The Mg and Sr chemistries of Silurian rugose corals indicate that their original mineralogy must have been an intermediate-Mg calcite, because the diagenetic trend (Figure 21) differs from that exhibited by the chemical data for crinoids (Figure 5; Brand and Veizer, 1980, Figs. 5,7; Brand, 1981a, unpublished data). For samples subjected to similar hydrologic conditions during diagenesis, the different chemistries of Silurian rugose corals and crinoids support the assertion of different skeletal mineralogies for these two groups. Because of their diagenetically altered state, chemistry of rugose corals provides no information toward unravelling paleoenvironmental problems, but the data provide a basis to compare it with that of other fossils to determine original mineralogies and degrees of alteration (Figure 22). In most instances, rugose coral skeletal material is biogeochemically better preserved than that of crinoids at the trace element but not at the stable isotope level (Figure 23; Brand, 1981b).

***Crinoids.*** Fossil crinoids belong to the phylum Echinodermata and are one of the five major living groups. Their endoskeleton encompasses the organic stroma and the calcareous stereom, which consists of high-Mg calcite (see references in Milliman, 1974, Table 36). The organic tissue of the skeleton decomposes quickly after death of the organism. Because high-Mg calcite is thermodynamically metastable in the diagenetic environment, crinoidal calcite is seldom preserved in its original mineralogy or chemistry (*cf.* Figure 5; Brand, 1986a). Only in special instances is the mineralogy and chemistry of ancient crinoids preserved or slightly altered, as is the case for the crinoids from the Buckhorn asphalt of Oklahoma (Blake *et al.*, 1982) and from the Brush Creek of Pennsylvania (Morrison *et al.*, 1985). In both cases, the formations hosting the crinoids also carry well-preserved aragonitic molluscan faunas (references in mollusc section).

Strontium contents of ancient crinoids usually represent diagenetic values (Figure 22). This is also evident for the $\delta^{13}C$ and $\delta^{18}O$ values of crinoids (Figure 23). Weber (1968) and Weber and Raup (1968) demonstrated that the oxygen and carbon compositions of Recent Echinoderms are controlled by metabolic processes and are thus of little use in reconstructing environments or calculating water temperatures (*cf.* Brand and Veizer, 1981). Similar processes are also postulated to have affected ancient crinoids (Brand, 1981b, 1982). Although this diminishes their usefulness as paleoenvironmental indicators, the chemistries can still reveal important information about the waters involved in the diagenetic alteration process (Blake *et al.*, 1982).

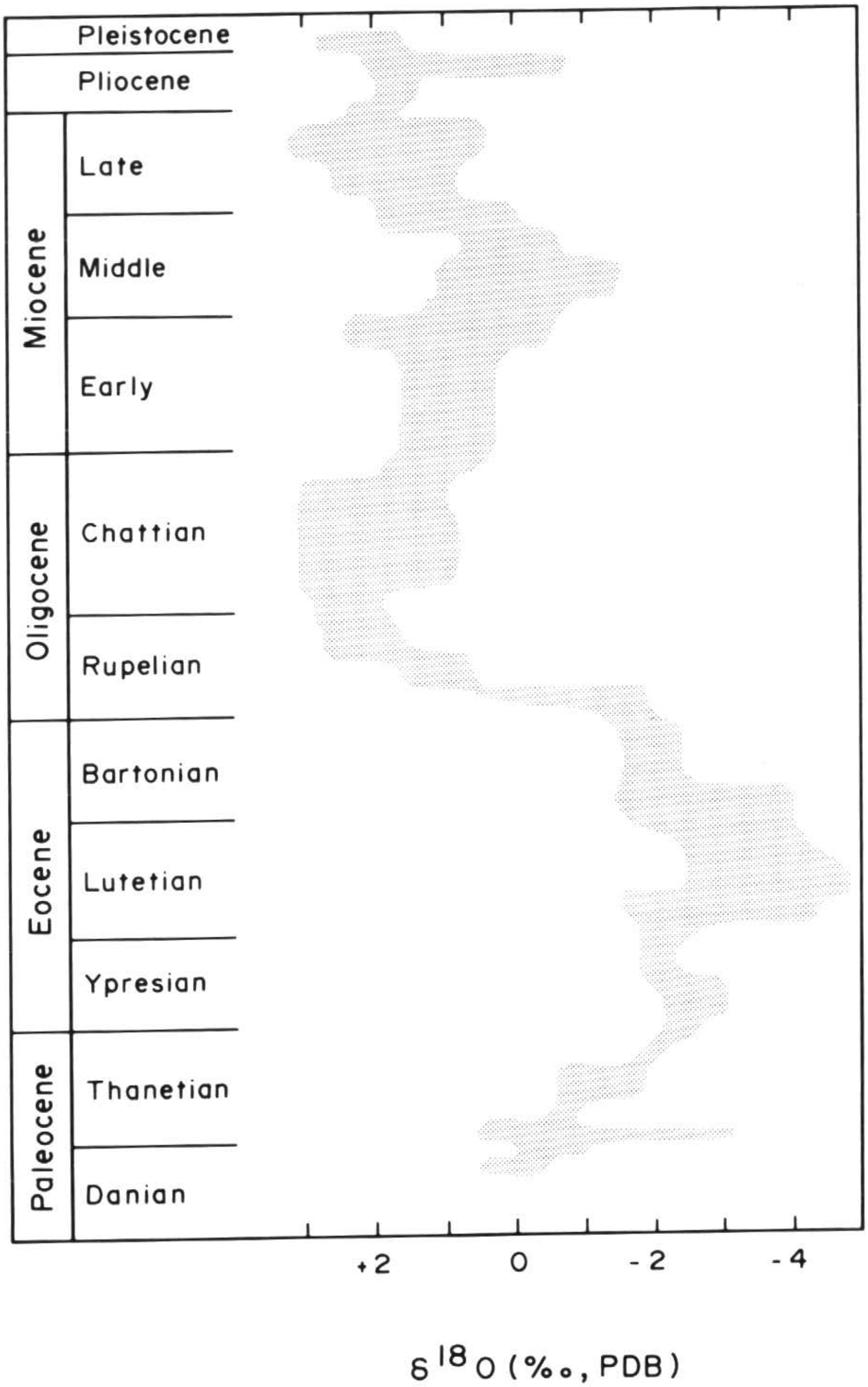

**Figure 19** *Variation in the $\delta^{18}O$ of Cenozoic molluscs from northwest Europe. Degree of uncertainty is defined by the length of the field. Trends suggest heating from Danian to Lutetian with subsequent cooling and minor temperature fluctuations of the ambient sea water. Data and diagram after Buchardt (1978).*

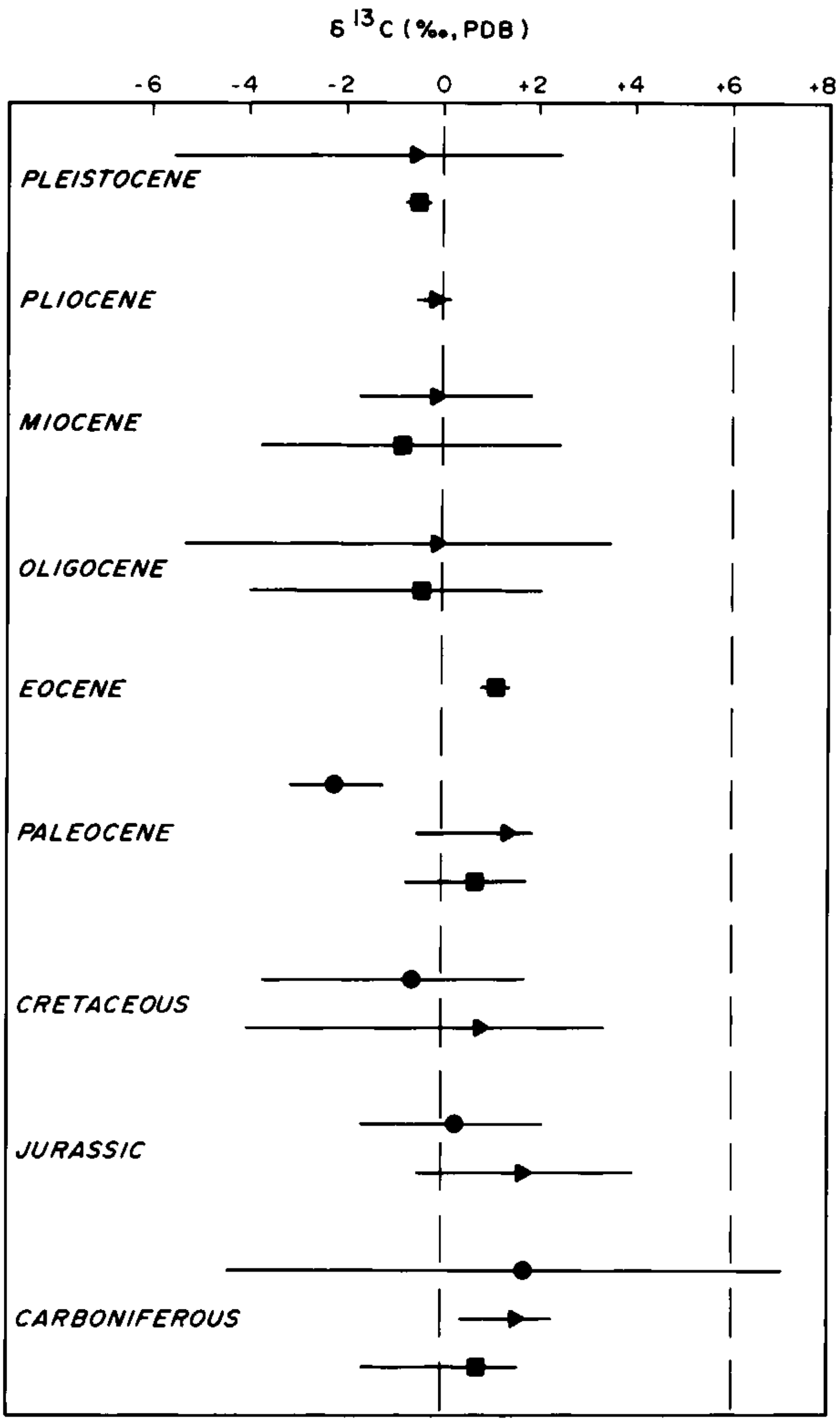

**Figure 20** *Carbon isotope means and ranges for molluscs of different ages. No variation with respect to environment or water temperatures has been detected in the $\delta^{13}C$ composition of molluscs. References, symbols and explanations as in Figures 15 and 18.*

***Brachiopods.*** These marine invertebrates probably developed during the Precambrian and the first hard-parts (shells) are found in Lower Cambrian rocks (Moore *et al.*, 1952). Of the two major groups recognized, the inarticulate brachiopods have phosphatic shells (McConnell, 1963), whereas the articulates secrete calcitic shells covered by a chitinous periostracum. Shells of articulate brachiopods are arranged in layers with calcite fibres oriented parallel, or at an angle, to the shell wall (Figure 8; Williams, 1966). Many brachiopod species died out at the close of the Paleozoic, but over 200 species are still extant.

Brachiopods secrete low-Mg calcite valves and their chemistry is precipitated in elemental and isotopic equilibrium with ambient sea water (*e.g.*, Lowenstam, 1961). However, the equilibrium incorporation into shell carbonate is in doubt for Na and carbon (Brand and Veizer, 1980; Veizer *et al.*, 1986). The relative stability of low-Mg calcite in the presence of diagenetic fluids makes calcitic brachiopods and their shell biogeochemistries useful indicators of depositional conditions for the hydrosphere (*e.g.*, Popp *et al.*, 1986a, b).

Figure 24 shows that the Sr levels of brachiopods are in agreement with their original low-Mg calcite mineralogy and that they compare favourably with those recorded in their Recent counterparts (Milliman, 1974; Morrison and Brand, 1986a). From the uniform trend, we can speculate that most brachiopod shells are mineralogically and geochemically well preserved. The biological fractionation of Na in brachiopods as determined by Brand and Veizer (1980) is clearly shown by the data in Figure 25. Sodium is enriched by 5-10 times in brachiopod calcite compared to low-Mg calcite precipitated in Na equilibrium with ambient sea water. The reason for this uptake of excess Na into shell calcite by brachiopods remains unresolved. In a recent study, Al-Aasm and Veizer (1982) showed that brachiopods shells can be altered by as much as 20%. This conclusion was based essentially on the high Mn chemistry of specimens from the Ordovician Ellis Bay Formation of Anticosti Island. Other studies have demonstrated that the Mn content in fossils is strongly influenced by facies; those from shales are always enriched in Mn relative to their counterparts from limestone lithologies (Veizer, 1977b; Morrison and Brand, 1984; Morrison *et al.*, 1985; Brand, 1987a, b). Thus we feel that the brachiopods from Anticosti Island are not altered, instead the higher than normal Mn levels observed in most fossil brachiopods is related to the oxygen level and amount of Mn present in the depositional environment (Figure 26). The basis for our statement is the excellent correlation of the Sr contents, lack of diagenetic features noted in SEM micrographs and the co-variance of Mn contents with the host lithology (Brand, 1987a, b).

Oxygen-18 compositions of brachiopods represent equilibrium conditions and, therefore, the values should represent ambient water conditions (composition and temperature; Lowenstam, 1961). A bimodal distribution is apparent from Figure 27, where Mesozoic brachiopods fall into the heavy $\delta^{18}O$ group, and the Paleozoic brachiopods fall into the light $\delta^{18}O$ group. This suggests that either variation in seawater temperature or secular variation in seawater-$^{18}O$ are responsible for the lighter oxygen values observed in the Paleozoic brachiopods (Figure 23; *e.g.*, Knauth and Epstein, 1976; Brand and Veizer, 1981). At present, the two possibilities are debated by various researchers. Several studies have applied the $\delta^{18}O$ composition to paleoenvironmental problems, and Lowenstam and Epstein (1954) showed that water temperature for the Cretaceous gradually increased from the Albian to the Coniacian/Santonian with subsequent and continual cooling toward the end of the Cretaceous Period (Figure 28). Veizer *et al.* (1986) and Popp *et al.* (1986a) showed similar $\delta^{18}O$ trends for Paleozoic brachiopods. Recent studies have demonstrated that modern brachiopods may exert a vital control over their $\delta^{13}C$ compositions (discussion and references in Veizer *et al.*, 1986). The data compiled from various sources (Figure 29) suggest that ancient brachiopods probably incorporated $\delta^{13}C$ into shell carbonate in isotopic eqilibrium with ambient sea water, and the observed trends have been linked to secular variation in seawater-$^{13}C$. In summary, because of their relatively stable mineralogy brachiopod shells should prove to be useful tools in paleoceanographic studies.

***Belemnites.*** Among the dibranchiates, the belemnoids were important during Mesozoic time. These molluscs secreted massive skeletons composed of four parts, of which the phragmocone is most important, both paleontologically and geochemically (Moore *et al.*, 1952). Belemnite phragmocones consist of low-Mg calcite which most researchers believe to be its original mineralogy, but diagenetic alteration seems to affect these skeletal components (*cf.* Veizer, 1974; Veizer and Fritz, 1976). If this observation is correct, the isotopic compositions of belemnites and the resulting interpretations are severely questioned (*e.g.*, Spaeth *et al.*, 1971). We recommend more rigorous studies into the diagenetic stability and preservation of belemnite phragmocones (Stevens, 1971).

In general, the few trace element and stable isotope data available for belemnites follow the trend exhibited by that of the low-Mg calcite brachiopods (Figures 24-29). A biological control for Na found in the brachiopods is also displayed by the belemnite values (Figure 25), although diagenetic alteration of the phragmocones cannot be ruled out in this case. Belemnite calcite similar to that of brachiopods is enriched in Mn for those from shales relative to skeletal material

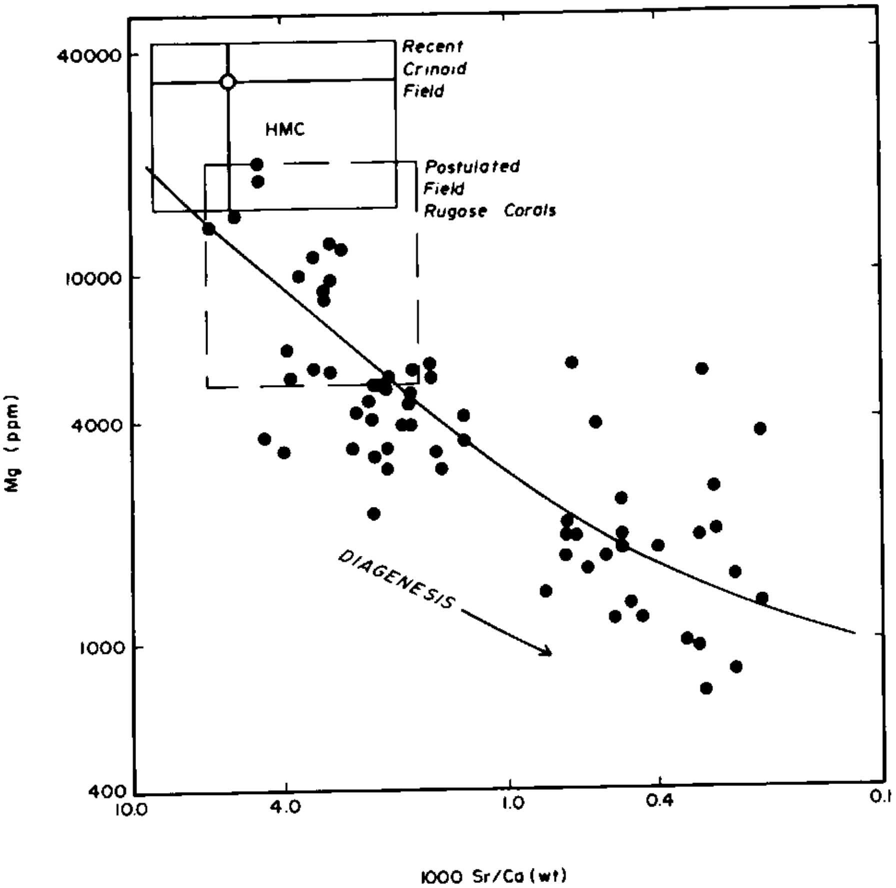

**Figure 21** *Diagenetic alteration trend of lower Phanerozoic rugose corals. Progressively altered samples contain less Mg and Sr. The field for Recent high-Mg calcite crinoids is included for reference. The least-altered coral sample(s) contains less Mg and Sr than the crinoid material. On this basis an original intermediate-Mg calcite mineralogy is postulated for the extinct rugose corals (cf. Brand and Veizer, 1980; Brand, 1981a; Milinkovich and Brand, 1984).*

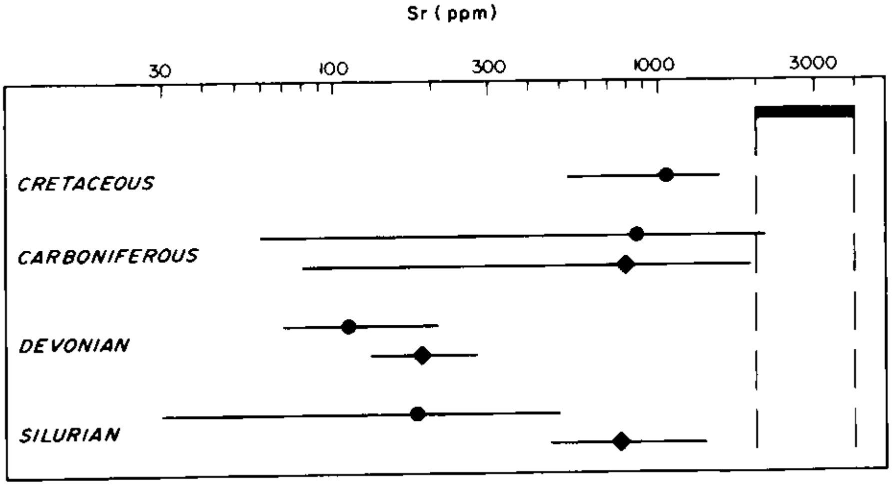

**Figure 22** *Strontium distribution diagram of crinoids (●) and rugose corals (◆) of different ages. Solid bar represents Sr range expected in intermediate- and high-Mg calcites (references in Morrison and Brand, 1986a). In general, the corals contain more Sr than crinoids collected from the same formation. This in part supports the assertion of the more stable mineralogy postulated for rugose corals compared to that of crinoids.*

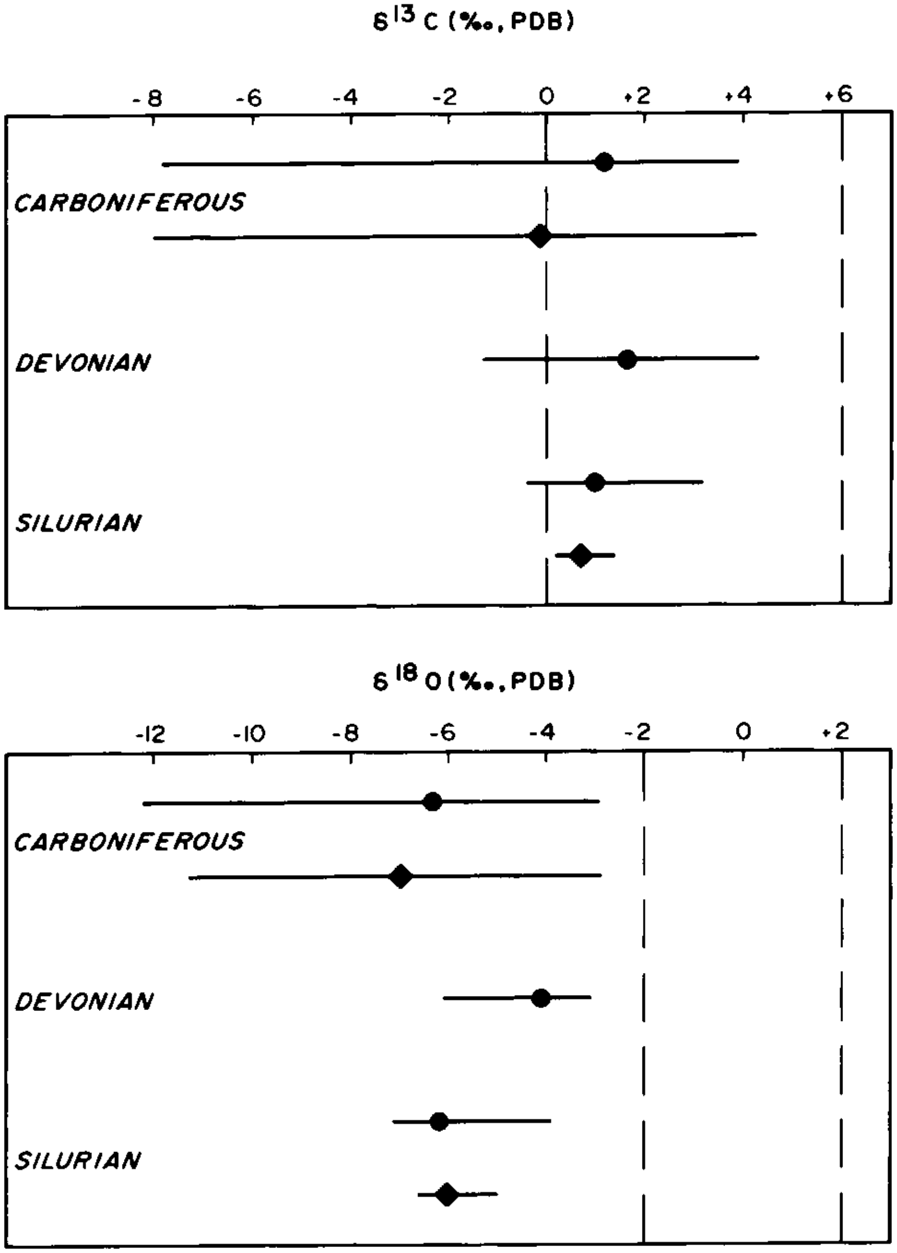

**Figure 23** *Carbon and oxygen isotopic distribution in Paleozoic crinoids and rugose corals of different ages. The dashed fields represent calcite precipitated in isotopic equilibrium with ambient sea water (data from Weber, 1968; Weber and Raup, 1968; additional references in Morrison and Brand, 1986a). The δ¹³C values of the better preserved specimens suggest that fossil crinoids and corals probably exerted a biological control over their isotopic compositions. In addition, the negative δ¹⁸O values suggest further that the original compositions of these specimens have been diagenetically altered (cf. Brand and Veizer, 1981; Brand, 1983).*

found in limestones. A strong facies control is also advocated by this co-variance. With respect to the stable isotopes, belemnites have $\delta^{13}C$ and $\delta^{18}O$ values that tend to be slightly heavier than those of brachiopods (Figures 27-29). Lowenstam and Epstein (1954) studied brachiopods and belemnites of Europe and their results are presented in Figure 28. Temperatures calculated with $\delta^{18}O$ values of the belemnites are consistently lower than those calculated with brachiopod data. Several possibilities can explain this phenomenon. One explanation suggests that the brachiopods are diagenetically altered, although this possibility is discounted for reasons discussed in the brachiopod section. Another possibility is that belemnites, as a group, controlled their isotopic compositions, but no concrete evidence is available to support this assertion. Another possibility is that the mobile belemnites spent part of their lives in cool and deep waters whereas the brachiopods seem to prefer shallower and warmer waters.

**Isotopic Applications**

The geochemistry of unaltered fossil material, if not originally controlled by biological and metabolic processes, should reflect the physiochemical conditions of the ambient sea water. Of the different geochemical techniques, oxygen isotope determinations are the best known and most widely applied in solving paleoenvironmental as well as diagenetic problems (*e.g.*, Brand and Veizer, 1980, 1981; Popp *et al.*, 1986a,b; Lowenstam, 1961; Epstein *et al.*, 1953; just to mention a few studies). In most instances, metabolic effects can be characterized for fossil groups based on studies of Recent representatives, and material showing such effects can then be avoided. Diagenetic alteration of fossils can usually be recognized by the methods explained earlier. Once all of these factors have been identified and isolated, the isotopic chemistry of fossils should reflect the physiochemical characteristics of the ambient depositional water. The first paleotemperature determinations were published by Urey *et al.* (1951).

The isotopic composition of a sample is always measured relative to a known ratio of a standard, and values are usually reported in δ (delta or del) values in per mil (‰)(Faure, 1977). This relationship is defined as:

$$^{18}O = 1000 \times \left[ \frac{(^{18}O/^{16}O)_{sample} - (^{18}O/^{16}O)_{standard}}{(^{18}O/^{16}O)_{standard}} \right] \quad (1)$$

Calcite values are usually reported relative to PDB (belemnite specimens of *Belemnitella americana* from the Peedee Formation of South Carolina), whereas waters are referred to the SMOW standard (Standard Mean Ocean Water). Secondary standards, which have been calibrated to the original standards, are used today in most laboratories.

***Temperature.*** Oxygen atoms are incorporated into carbonate in isotopic equilibrium with the oxygen atoms in the water in which the skeleton formed. Studies show further that the $^{18}O/^{16}O$ ratio of the carbonate is not only related to the oxygen ratio of the water but also to its temperature (Urey *et al.*, 1951; Epstein and Mayeda, 1953; Faure, 1977). Epstein *et al.* (1953) determined the relationship between $\delta^{18}O$ in molluscs and growth temperature by analyzing organisms grown in carefully monitored laboratory and natural experiments. Other applications and conditions of isotopic variation are fully discussed by Faure (1977), Dodd and Stanton (1981), and Anderson and Arthur (1983). The following equations are the results of studies by Urey and his co-workers as well as other researchers.

Ambient seawater temperature can be calculated using the $\delta^{18}O$ composition of unaltered fossils that precipitated aragonitic shells in isotopic equilibrium with the surrounding water and the following equation:

$$T°C = 19.0 - 3.52(\delta_A-\delta_W) + 0.03(\delta_A-\delta_W)^2 \quad (2)$$

where the $\delta_A$ is the $^{18}O/^{16}O$ of the fossil carbonate (PDB), and the $\delta_W$ is the $^{18}O/^{16}O$ of the water, which in most instances is assumed to be 0‰ (SMOW; Grossman and Ku, 1981). For originally calcitic and unaltered fossils the following equation is used:

$$T°C = 16.9 - 0.21(\delta_C-\delta_W) + 0.14(\delta_C-\delta_W)^2 \quad (3)$$

where $\delta_C$ and $\delta_W$ are the $^{18}O/^{16}O$ of the fossil (PDB) and water (SMOW), respectively (Epstein *et al.*, 1953). For biogenic phosphate (*e.g.*, conodonts), Karhu and Epstein (1986) presented the following equation:

$$\Delta^{18}O(PO_4-H_2O) = 2.17 \times 10^6/T^2 - 1.94 \quad (4)$$

where **T** is in degrees absolute (0°C = 273.15K), and the $^{18}O/^{16}O$ of the phosphate and water is in SMOW. Great uncertainty is introduced in calculating paleotemperatures using equations 2, 3 and 4, because the water composition cannot be measured directly for ancient seas. Salinity (evaporation, mixing with isotopically light fresh water) directly influences the $\delta^{18}O$ composition of sea water. A 5 ppt shift in salinity causes a corresponding change of 1‰ in $\delta^{18}O$ of sea water and consequently the carbonate of marine invertebrates (Epstein and Mayeda, 1953). In turn, this changes the calculated temperature by about 5°C. Thus fossils from hyposaline or glacial environments may give temperatures that can be anomalous by about 20°C (*e.g.*, Pleistocene fossils; Table 1). Without any correction factors, calculated water temperatures are anomalously high at about 77.7°C (Devonian brachiopods;

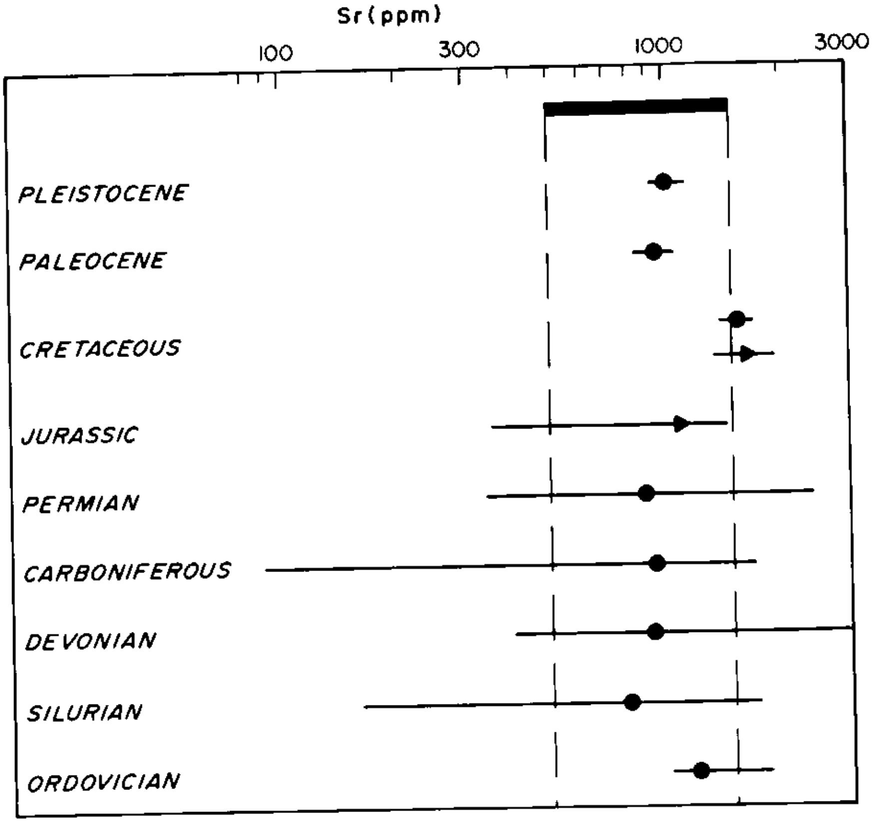

**Figure 24** *Strontium composition diagram of low-Mg calcite brachiopods (●) and belemnites (▲) from various ages and localities (Veizer, 1974; Morrison and Brand, in press; Al-Aasm and Veizer, 1982; Brand, 1982; Lowenstam, 1961; Popp, 1981; Veizer* et al., *1986; Popp* et al., *1986a). The solid field represents low-Mg calcite precipitated in chemical equilibrium with ambient seawater (references in Morrison and Brand, 1986a). Large variation in Sr content is related to possible environmental controls.*

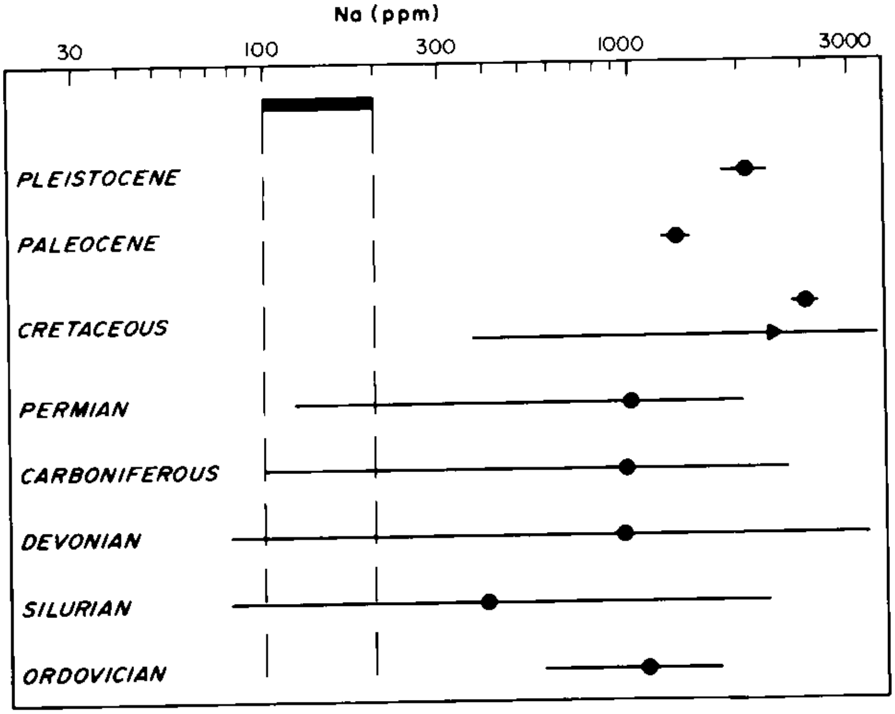

**Figure 25** *Sodium composition diagram of brachiopods and belemnites. Solid field represents inorganic low-Mg calcite precipitated in chemical equilibrium with ambient sea water (references in Morrison and Brand, 1986a). Large deviations from equilibrium contents are related to a biological control by the brachiopods at the species level (cf. Brand and Veizer, 1980; Morrison* et al., *1985; Morrison and Brand, 1986a). Other explanations and symbols as in Figure 24.*

Table 1). Even with a secular variation correction factor for seawater-$^{18}$O, the calculated water temperatures are still somewhat high. Glacial or salinity effects could account for these values (Brand, 1984; Wassenaar *et al.*, 1986). Thus, until the question of the $\delta_W$ value can be answered unequivocally, calculated paleotemperatures using the $\delta^{18}$O of fossils are subject to serious interpretational flaws.

**Salinity.** Mook (1971) proposed that the $\delta^{13}$C composition of molluscs can be used to gauge the salinity of the ambient sea water (Eisma *et al.*, 1976). Although definite trends have been identified, major deviations may occur because of the complex interaction of seawater TDC (total dissolved carbon) and DOC (dissolved organic carbon; *cf.* Anderson and Arthur, 1983). Using a different approach, a salinity-trace element correlation was found in some aragonitic molluscs and seawater salinity (Brand, 1984). Many studies have tried to find trace element and water salinity relationships in mollusc shell material with variable success (good discussion in Milliman, 1974; Dodd and Stanton, 1981). Many problems persist with this relationship and it is advisable always to consider sedimentological as well as paleontological information with biogeochemical data for water salinity interpretations.

### Final Comment

It is hoped that the reader has gained a fuller understanding of the complexity in the biogeochemistry of fossils and of the problems that remain to be solved with respect to original skeletal mineralogy, diagenesis and paleo-oceanography. Only the major references were used in this paper to limit its length, and the texts referred to in the paper should be considered starting points in the search for fossil biogeochemistry.

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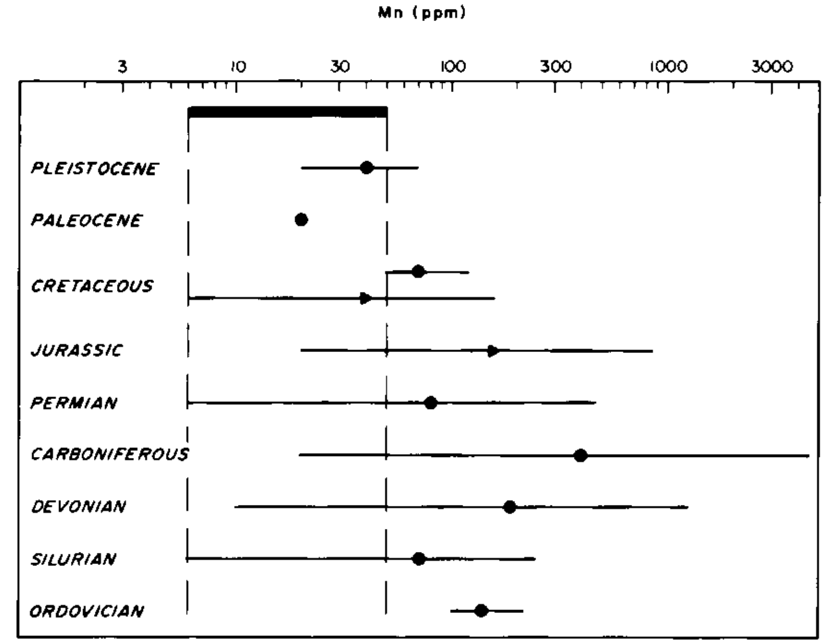

**Figure 26** *Manganese composition diagram of brachiopods and belemnites. Solid bar represents low-Mg calcite precipitated in marine waters of normal dissolved oxygen levels. The large range in values is related to lithology of the host formation, with high Mn levels observed for brachiopods from shale facies and lower concentrations for those from limestone lithologies* (cf. *Morrison and Brand, 1984; Morrison* et al., *1985). Other explanations and symbols as in Figure 24.*

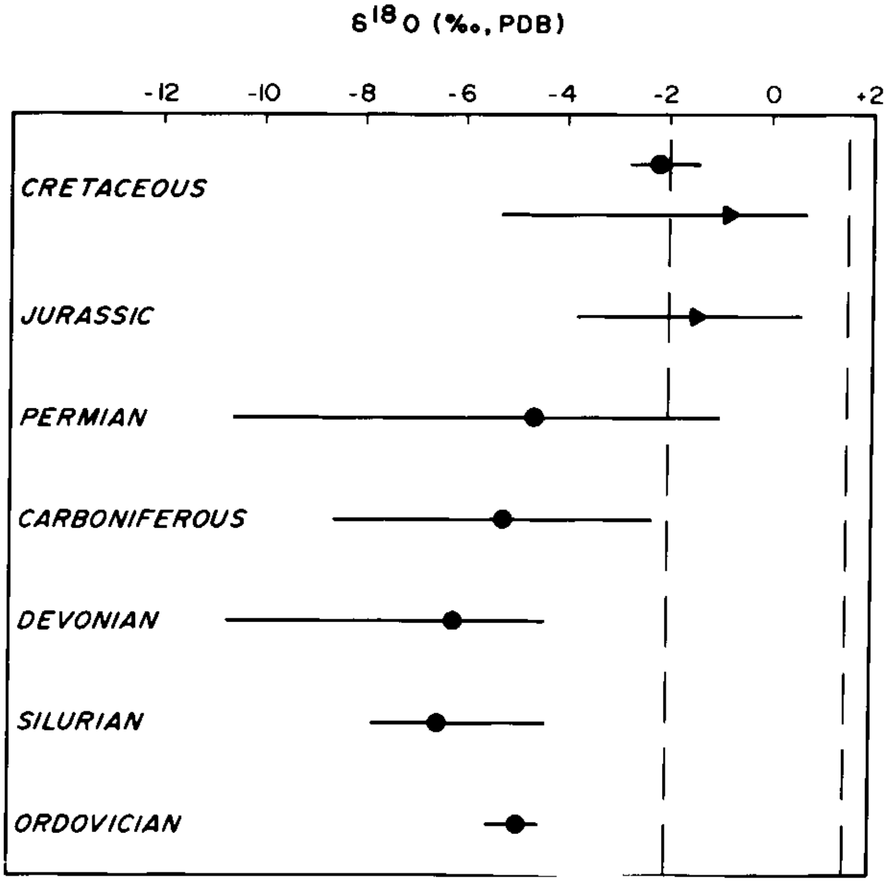

**Figure 27** *Oxygen isotopic variation in brachiopods and belemnites (Bowen, 1961; Bowen and Fritz, 1961; Fritz, 1965; Longinelli, 1969; Rao and Green, 1982; Spaeth* et al., *1971; Stevens and Clayton, 1971; Tan* et al., *1970; Urey* et al., *1951; Veizer and Fritz, 1976; other references and symbols as in Figure 24). The shift toward lighter values has been related to the secular variation of ocean chemistry or higher water temperatures (e.g., Veizer* et al., *1986; Knauth and Epstein, 1976).*

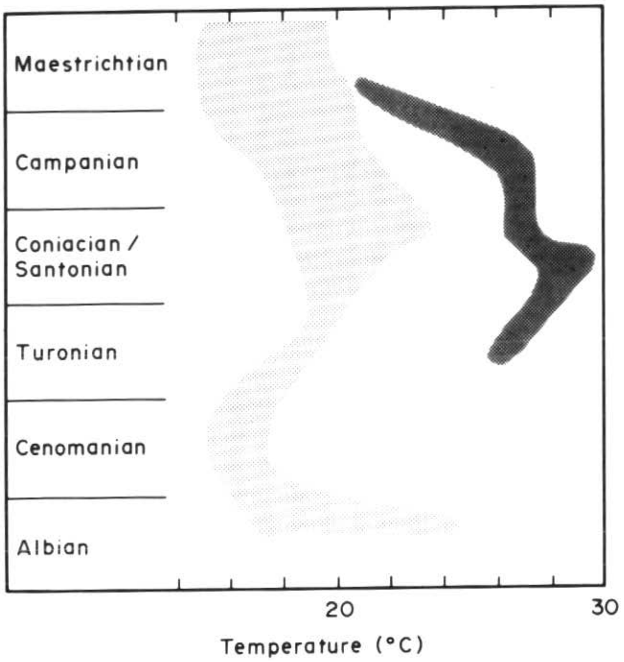

**Figure 28** *Paleotemperatures for the Cretaceous of western Europe using the $\delta^{18}O$ of brachiopods (dark pattern) and belemnites (light pattern)(after Lowenstam and Epstein, 1954). Values indicate a warming trend for the Albian-Santonian interval with subsequent cooling towards the close of the Cretaceous period. Lower temperatures calculated with the belemnite data suggest that these organisms probably inhabited the deeper and cooler waters, exerted a biological control over their isotopic compositions, or the brachiopod samples are diagenetically altered.*

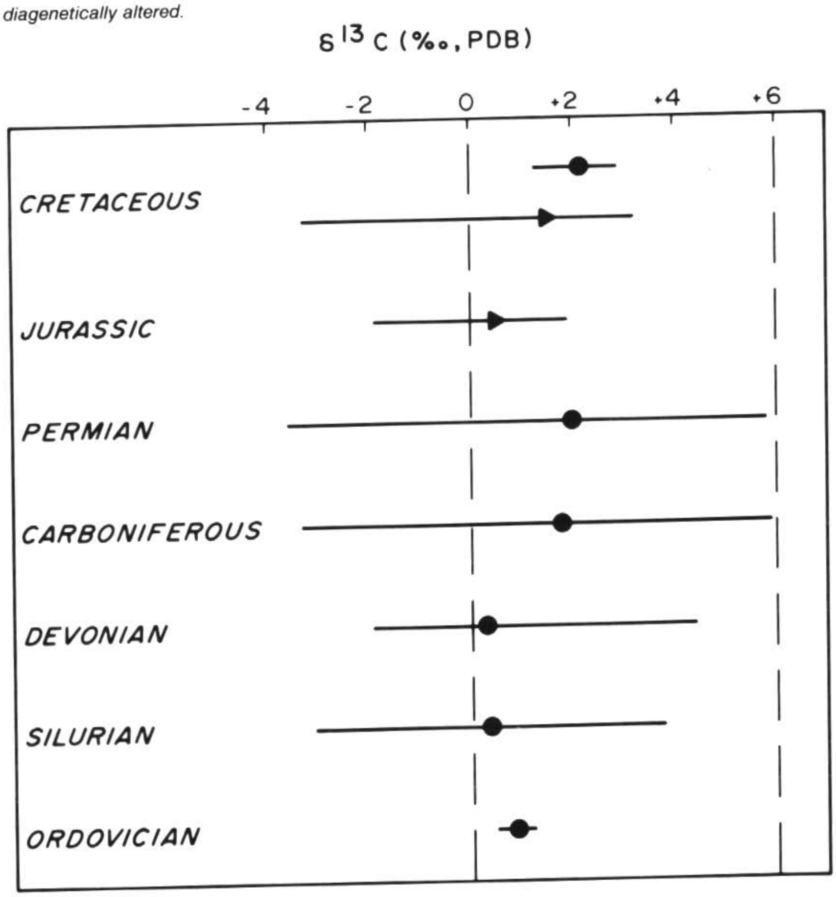

**Figure 29** *Carbon isotopic variation in brachiopods and belemnites. Means of populations are within the range encountered in Recent brachiopods, which suggests that these ancient counterparts probably incorporated $\delta^{13}C$ into shell carbonate in isotopic equilibrium with ambient seawater. References and symbols as in Figures 27, 28.*

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