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Biogeochemistry of Late Paleozoic North American brachiopods and secular variation of seawater composition

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Abstract. Sr/Ca ratios in modern brachiopod shells reflect variations in ambient seawater, whereas their Na contents show no relationship with water depth or habitat. Their Mn and Fe contents are controlled, in part, by leaching of these elements from oxide coatings or the low input/sedimentation rate of detrital material into depositional areas such as Quatsino Sound.

For most Carboniferous brachiopods from North America, the Mn and Fe contents are similar to those recorded by their Recent counterparts. The high Mn and Fe contents in the brachiopods from shales suggest several possibilities for these levels. One possibility is the leaching of Mn and Fe from oxide coatings/matrix which was not completely removed in the cleaning process, or the high levels in part reflect unusual depositional conditions (some degree of anoxia) for the local shaly environments.

The Sr/Ca ratio of brachiopods and, by inference, complementary seawater, did not vary significantly during the Carboniferous. The Sr/Ca minimum observed in brachiopods of Mississippian age coincides with a dip in the $^{87}Sr/^{86}Sr$ curve and correlates with the Hercynian orogeny. This is attributed to the cycling of seawater through mid-ocean ridge basalts, and postulated exchange reactions account for variation in the composition of seawater-Ca. The unidirectional trend of heavier $\delta^{13}C$ values from the Devonian to the Permian is intricately coupled with the evolution of the terrestrial biomass. In addition to expansion of terrestrial plants, burial of reduced carbon in the form of coal (organic matter) contributed to the observed shift. The start of the Permo-Pennsylvanian glaciation is marked by a negative excursion of the secular carbon trend, which is linked to weathering of reduced carbon and its return to the oceanic reservoir with its oxidized carbon. The oxygen isotope values reflect the unidirectional trend towards higher values of the carbon data with decreasing geologic age. Negative excursions of the trend may be related to extensive weathering of terrestrial and submarine rocks, whereas positive excursions may be related to hydrothermal alteration of submarine rocks and dehydration of oceanic crust during times of active sea-floor spreading. Oxygen-calculated water temperatures of unaltered brachiopod material are unrealistically high for all of the Devonian, and the Chesterian-Meramecian, Desmoinesian-Missourian, and Artinskian Epochs. During these times maximum water temperatures of 42° to 56 °C are well above the thermal threshold of protein denaturation. This process, which is lethal to most higher organisms, demands an adjustment in oxygen of −2.5‰ for samples older than Missourian, and of −1.25‰ for samples spanning the Missourian-Artinskian interval. With these adjustments and salinity considerations made prior to calculations, water temperatures become reasonable for the Late Paleozoic epeiric, tropical seas of North America.

Introduction

Modern articulate brachiopods secrete low-Mg calcite (LMC) shells with $MgCO_3$ concentrations of about 0.5 to 7 mol% (Lowenstam 1961; Morrison & Brand 1986). Shells consist of prismatic and fibrous layers of calcite crystallites covered by organic matter referred to as the periostracum (Johnson 1951; Williams 1971). This microstructural arrangement, except for the periostracum, is preserved in many fossil brachiopods. Geochemical compositions of brachiopod shells generally reflect complex depositional conditions during the calcification process which may or may not be related to fractionation/vital effects exerted by the organism. Lowenstam (1961) found a correlation between increasing ambient water temperature and the Sr and Mg contents in shells of modern brachiopods. But in a subsequent paper, he demonstrated that brachiopods physiologically control their Sr chemistry (Lowenstam 1963). Brand & Veizer (1980) argued that brachiopods also control their Mg and Na contents by disciminating against the uptake of Mg while Na is preferentially incorporated into their shell carbonate. These discrimination effects are well established in brachiopods as old as Ordovician (Brand & Morrison 1987). Lack of data allows no conclusion to be reached for Cambrian brachiopods. Apart from a few studies, isotopic data of modern brachiopod material are very limited (cf. Epstein et al. 1953; Lowenstam 1961; Wefer 1985) but suggest that these organisms incorporate oxygen into shell carbonate in equilibrium with ambient seawater and the $\delta^{18}O$ values reflect variations in seawater composition and/or temperature. A similar relationship was also assumed for the carbon composition. However, Wefer's (1985) observations, based on specimens from Bermuda imply that brachiopods possibly discriminate against the incorporation of ^{13}C by about 4–5‰.

In addition to these physiological characteristics, the LMC shells of brachiopods are considered by some researchers to be quite resistant to diagenetic alteration under most conditions (e.g., Brand & Veizer 1980, 1981; Popp et al. 1986a, b), whereas others challenge this resistance, suggesting that (LMC) brachiopod shells may be extensively altered during burial (e.g., Al-Aasm & Veizer 1982). The purpose of this study is to evaluate the diagenetic stability of brachiopod LMC and define criteria for recognizing unaltered material from different depositional environments. Only material which is unaltered is useful in evaluating the physicochemical properties of Mg, Na and ^{13}C in brachiopods. Finally, unaltered material identified in this study is used to examine secular trends of seawater Sr/Ca, carbon isotopes, oxygen isotopes and temperature for the Permian-Devonian interval of North America.

Localities

Recent

Recent brachiopods can be divided into groups inhabiting deep- and shallow waters. Shallow water brachiopods are from depths of less than 100 m, whereas deep water specimens are from depths greater than 500 m (Table 1).

Carboniferous

Pennsylvanian and Mississippian brachiopods of North America were collected from outcrops located within 20 degrees of their respective paleoequators (Fig. 1). Based on host rock lithology, the samples can be divided into limestone and shale populations (Table 2). For detailed descriptions of the lithology and fauna of formations the reader is referred to the authors listed after each locality.

Methods

Brachiopod material was manually separated from its enclosing rock matrix and then leached with 15% (v/v) HCl to remove any matrix remaining in the shell crevices and oxides coating the shell carbonate. After cleaning, a fragment of each sample was coated with gold-palladium in a sputter-coater. Fracture surfaces of fossil fragments were evaluated for structures of the shell layers using an ISI scanning electron microscope. Mineralogy of the fossil and rock samples was determined with a Picker X-ray diffractometer using Cu-K_α radiation, and an aragonite standard was used to calibrate the

Table 1. Locality and depth information of Recent brachiopods (Coppers pers. comm. 1982).

Species	Locality	Depth (m)
Gryphus vitreous	Sardinia, Italy	150–160
Laqueus vancouverensis	Port Alice, British Columbia	12
Liothyrella notorcadensis	Arthur Harbour, Antarctica	15
Magasella sanguinea	Steward Is., New Zealand	?
Magellania (*A.*) *macquariensis*	54°30′S, 158°59′E	112–124
Neothyris lenticularis	Antipodes Is., New Zealand	103
Terebratulina septentrionalis	Nantucket, Massachusetts	3
Tichosina floridensis	Gulf of Mexico, Florida	3
Chlidonophora incerta	SE of Puerto Rico	≈3940
Gyrothyris mawsoni antipodensis	Antipodes Is., New Zealand	≈ 510
Neorhynchia profunda	off Baja California	≈3750

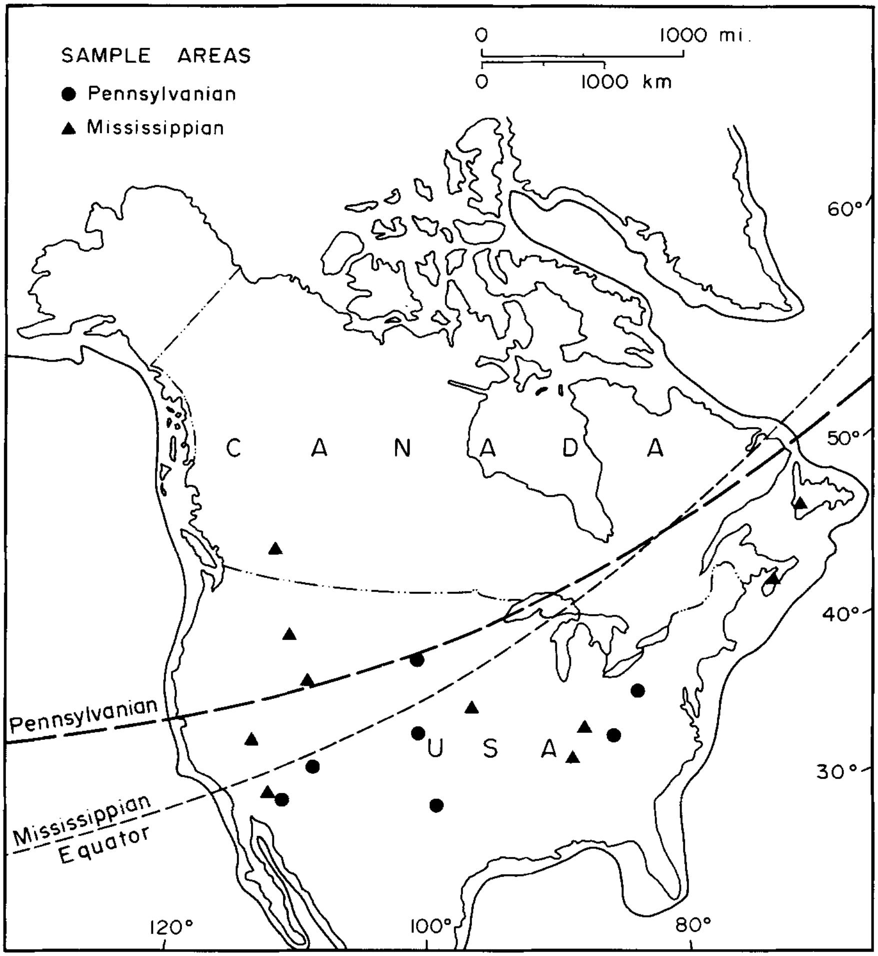

Fig. 1. Sampling areas of the Mississippian and Pennsylvanian brachiopods in Canada and the USA. Sample sites are all within 20 degrees of the respective paleoequators (from Dott & Batten 1971; Scotese et al. 1979).

diffractometer. For additional details of X-ray analysis, procedures and errors see Milliman (1974, pp. 22–29).

A total of 268 (23 modern and 245 fossil brachiopods) samples were analyzed. Approximately 0.5 g of each sample was digested in 18 mL of 5% (v/v) HCl for 5 h; this method limits leaching of elements from the non-carbonate portion still adhering to the samples (Brand & Veizer 1980). All samples were analyzed for Ca, Mg, Sr, Mn, Na, Al, Fe, Ba, Zn, Cu, Ni and Pb on a Varian 1475 atomic absorption spectrophotometer. Average accuracy compared with recommended values of N.B.S. (633, 634, 636) stan-

Table 2. Formation, age, locality, lithology (L = limestone, S = shale) and reference information of North American Carboniferous brachiopods

Formation	Age	Locality	Lithology	Reference
Shawnee	M. Virgillian	Kansas	S	von Bitter 1972
Kiewitz	L. Missourian	Nebraska	S	Mudge & Yochelson 1962
Brush Creek	E. Missourian	Pennsylvania	S	Norton 1975
Naco	L. Desmoinesian	Arizona	S	Brew & Beus 1976
Boggy	M. Desmoinesian	Oklahoma	L	Squires 1973
Oswaldo	Atokan	New Mexico	L	Spencer & Paige 1935
Magoffin	E. Atokan	Kentucky	S	Dennis & Lawrence 1979
Kendrick	L. Morrowan	Kentucky	S	Jillson 1919
McCully	L. Morrowan	Oklahoma	L	Sutherland & Henry 1977
Sausbee	E. Morrowan	Oklahoma	L	Sutherland & Henry 1977
Great Blue	Chesterian	Utah	L	Lindsay 1977
Bangor	E. Chesterian	Tennessee	L	Smith 1890
Monte Cristo	Meramecian	Nevada	L	Langenheim & Webster 1979
Lake Valley	Osagean	New Mexico	L	Meyers 1974
Banff	L. Osagean	Alberta	L	Bamber et al. 1981
Codroy/Windsor	L. Osagean	Nova Scotia	L	von Bitter & Plint-Geberl 1982
Codroy/Windsor	L. Osagean	Newfoundland	L	von Bitter & Plint-Geberl 1982
Edwardsville	L. Osagean	Indiana	S	Lane 1973
Burlington	M. Osagean	Missouri	L	Harris & Parker 1964
Shunda	E. Osagean	Alberta	L	Bamber et al. 1981
Pekisko	L. Kinderhookian	Alberta	L	Bamber et al. 1981
Lodgepole	E. Kinderhookian	Montana	L	Sando et al. 1969

dard rocks, and average precision based on duplicate analyses were: Ca (4.1, 3.3), Mg (3.9, 2.5), Sr (2.8, 2.6) Mn (3.2, 1.8), Na (8.8, 7.5), Al (12.3, 5.4), Fe (6.7, 5.3), Ba (15.1, 14.8), Zn (11.2, 6.1), Cu (8.9, 5.8), Ni (11.2, 4.9), and Pb (14.1, 12.7), relative percent, respectively. Average precision of the insoluble residue (I.R.) by gravimetric determination exceeded 5.0 relative percent. All discussion in the text is based on elemental concentrations recalculated on a 100% carbonate (insoluble residue-free) basis.

One-hundred and twenty-nine fossil and eighteen modern samples were also analyzed for carbon and oxygen isotopes on a V.G. Micromass 602D mass spectrometer. These samples were selected after careful evaluation of fabric and trace element data. Approximately 10 mg of powder of each sample was reacted with 100% phosphoric acid at 50 °C for $\frac{1}{2}$ h. The isotopic ratios are expressed in the conventional (δ) notation relative to PDB in ‰. The ^{17}O correction of Craig (1957) was applied to the data. Average accuracy and precision of data (duplicate analyses) as compared to recommended values for N.B.S. 20 (Solenhofen Limestone) standard rock (cf. Craig 1957) were: $\delta^{18}O$ (0.2, 0.1) and $\delta^{13}C$ (0.12, 0.1) ‰, respectively.

Tables of geochemical data are available for a nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario, Canada K1A OS2.

Recent brachiopods

Biogeochemistry of recent brachiopods shows several interesting features related to habitat (water depth) of the studied organisms. Data in Fig. 2 show that there are significant differences in the Sr/Ca ratios but not the Na contents, between shallow- and deep-water brachiopods. The deep-water brachiopod *Neorhynchia profunda* exhibits Na levels similar to that of the other deep-sea specimens, but its Sr/Ca ratios are lower than that of the group and do not fall on the general regression line. This deviation from the norm way may be related to unusual depositional conditions prevailing on the abyssal plain off Baja California. This assertion may be, in part, further supported by the trends observed in the Mn and Fe contents of the brachiopods (Fig. 3). The Fe contents of the shallow-water and deep-water brachipods are significantly different at the 95% confidence level (Fig. 3), whereas their Mn contents are similar. It is possible that the different Fe contents observed in the two brachiopod groups are related to the redox state of the ambient water or to input and sedimentation rate of detrital

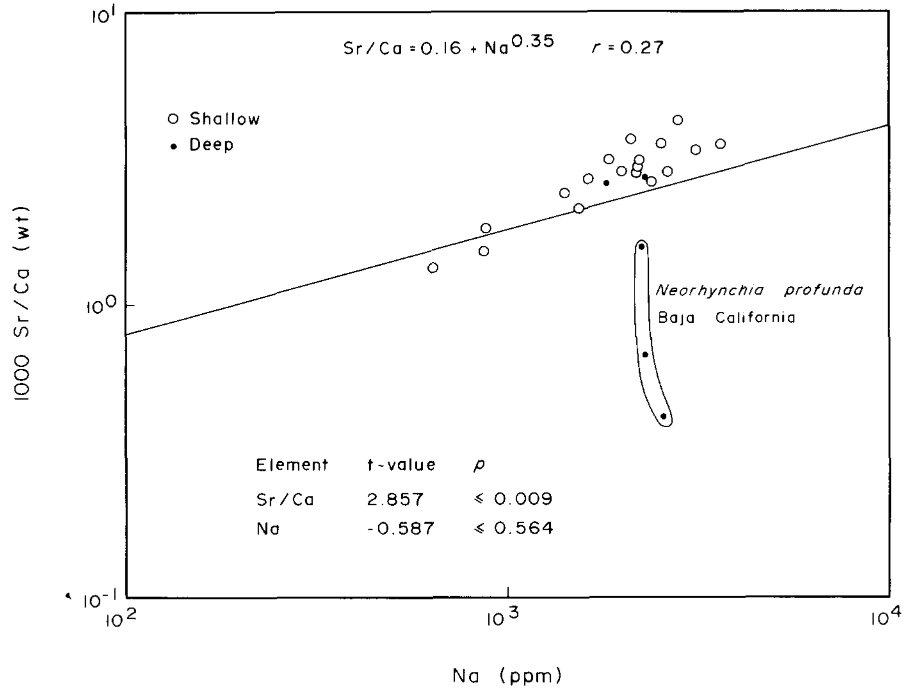

Fig. 2. Geochemical distribution diagram (Sr/Ca-Na) for Recent brachiopods. Two populations, based on water depth, are recognized and show a significant difference in the Sr/Ca ratios but not in Na contents.

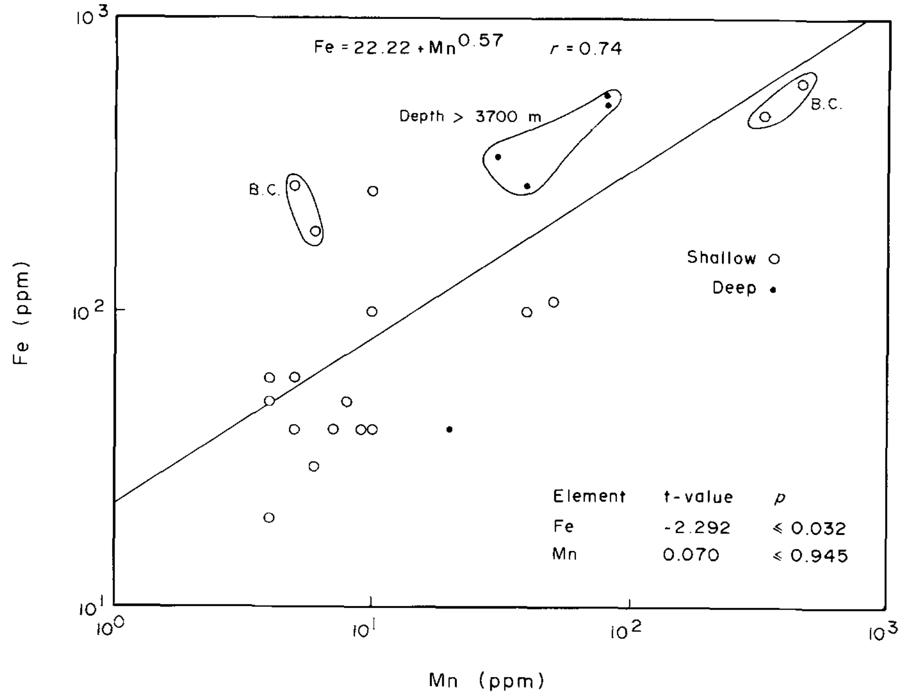

Fig. 3. Geochemical distribution diagram (Fe-Mn) for Recent brachiopods. Elemental contents are influenced by acid-soluble components from oxide coatings and possibly by physicochemical conditions of the ambient seawater (cf. Veizer 1977; Morrison et al. 1985; Brand 1987a). B.C. refers to specimens from Port Alice, British Columbia.

material into the depositional environment (Veizer 1977; Morrison et al. 1985; Brand 1987a). Oxide coating-derived Fe and Mn (Sherwood et al. 1987) are discounted because of the extensive cleaning of the specimens prior to chemical analysis. Diffusive conditions near the sediment-water interface are probably responsible for the elevated Fe and Mn levels observed in the brachiopods from water depths greater than 3700 m (Thomson et al. 1986), whereas the intermediate elemental levels are from a brachiopod collected at a depth of about 550 m (Fig. 3). The higher than normal levels probably relate to the breakdown of metastable Mn/Fe oxyhydroxides, diffusion of Mn and Fe towards oxic conditions and subsequent incorporation into calcite (Thomson et al. 1986). In contrast, the intermediate to high Fe and Mn levels in the shallow-water brachiopods from Port Alice, British Columbia are probably influenced by either influx of detrial material into the fjord or organic waste material from the pulp and paper mill, or both (Fig. 3). Generally, the brachiopods, of this study from normal, open, shallow marine environments contain less Fe ($\bar{x}$ = 71, 20–260 ppm) and Mn ($\bar{x}$ = 12,

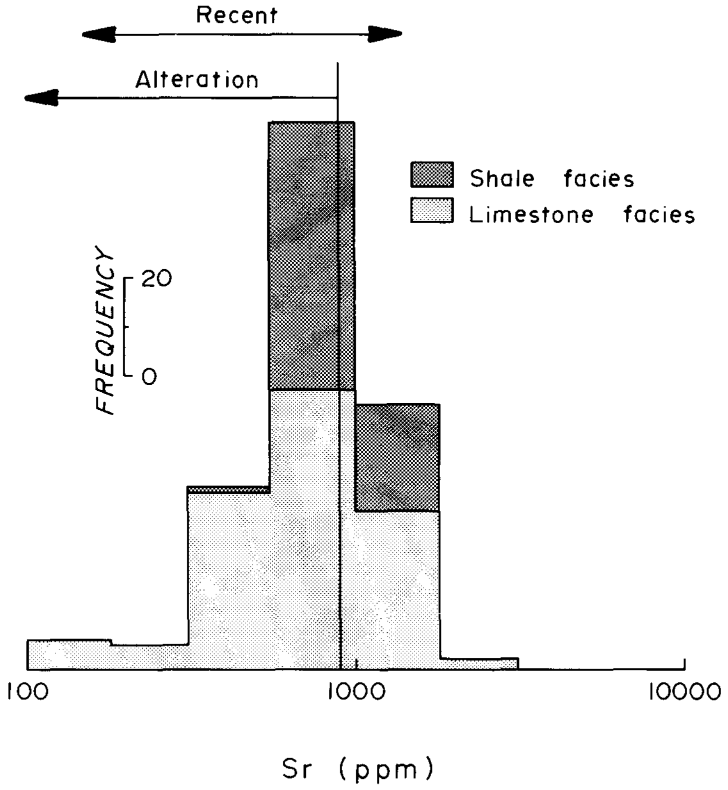

Fig. 4. Histogram of Sr distribution in Carboniferous brachiopods from shales and limestones. The "Recent" represents the range of Sr contents observed in unaltered Recent brachiopods (Morrison & Brand 1986; this study). The "Alteration" trend represents direction of Sr changes with post-depositional alteration of low-Mg calcite, and an upper limit for well-preserved brachiopod material (Veizer et al. 1986).

4–50 ppm) than their counterparts from fjords (e.g., Port Alice, Quatsino Sound; $\bar{x} = 385$, 190–610 ppm Fe; $\bar{x} = 200$, 5–460 ppm Mn), or deep waters ($\bar{x} = 417$, 270–550 ppm Fe; $\bar{x} = 58$, 30–80 ppm Mn). None of the studied specimens show any signs of diagenetic alteration.

Fossil brachiopods

Diagenetic evaluation

Reliable methods and criteria are needed to select least-altered fossil material of different ages, host material and diagenetic histories. Al-Aasm &

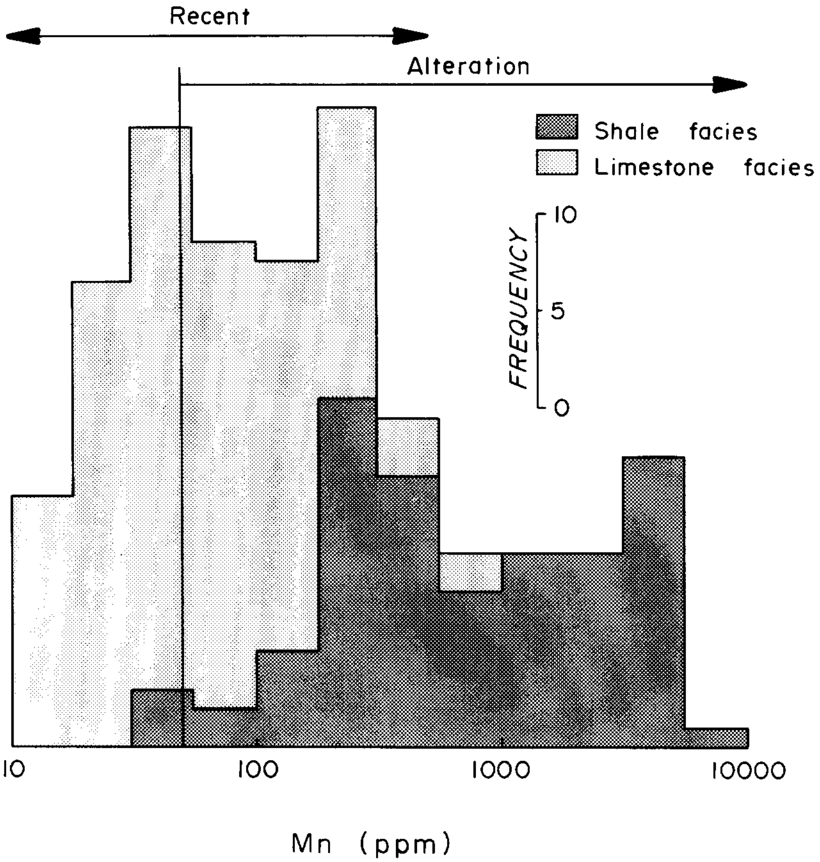

Fig. 5. Histogram of Mn distribution in Carboniferous brachiopods from limestones and shales. Explanations for Mn of "recent" and "Alteration" as in Fig. 4.

Veizer (1982), and Veizer et al. (1986) used trace element compositions to select the best-preserved brachiopod material. They assumed that samples with Sr contents less than 900 ppm and Mn of more than 70 ppm are altered, and as such, unsuitable for further analysis. If we use these exacting criteria, then a majority of the Recent brachiopod samples would have to be rejected because of apparent alteration effects (lower Sr and higher Mn contents; Figs. 4, 5). Also, if we followed this rationale, a large proportion of Carboniferous samples would be eliminated from further analysis because of their low Sr and high Mn contents. This would certainly apply to most brachiopods from shales and a great number from limestones (Figs. 4, 5), because their contents do not fall into the range of concentrations observed in inorganic calciate preciptitated in equilibrium with modern seawater. This assumes that 'all' brachiopods lived in normal, shallow marine environments, and

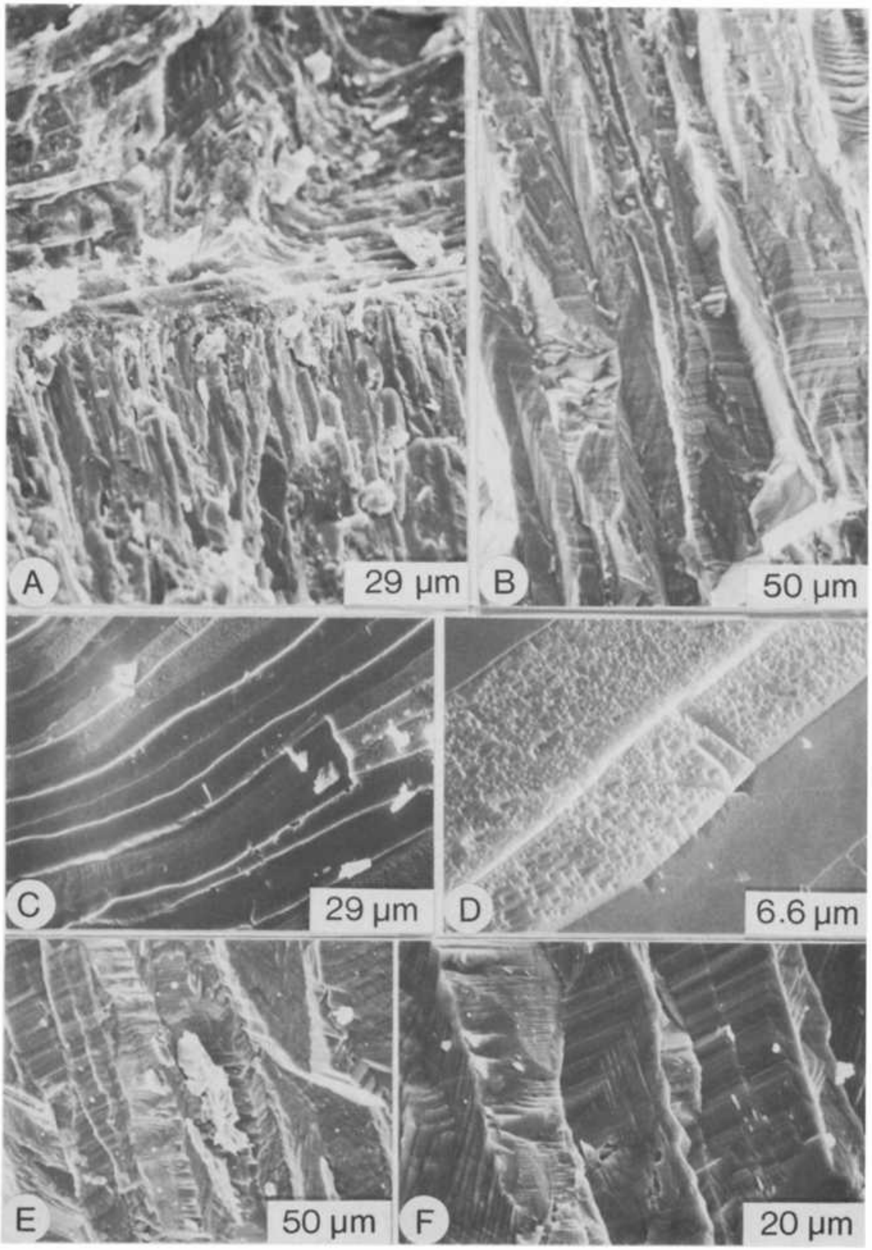

Fig. 6. Microstructures in Recent and Carboniferous brachiopods. (A) shows the two-layer structural arrangement in a brachiopod from the Boggy Formation (Pennsylvanian), (B) shows trabecular calcite fibres in *Neothyris lenticularis* (Antipodes Island, New Zealand), (C) is a top-view of calcite fibres in a *Neospirifer* sp. from the Shawnee Group (Pennsylvanian), (D) is a top-view of trabecular calcite fibres in *Composita* sp. from the Naco Formation (Pennsylvanian), (E) transverse view of trabecular fibres in a spiriferid brachiopod from the Banff Formation (Mississippian), (F) are trabecular fibres in a specimen of *Spirifer gorei* from the Sausbee Formation (Pennsylvanian).

ignores the possible effects of oxide coatings and detrital input/sedimentation rate on the Mn and Fe contents of inorganically as well as organically precipitated carbonates (Veizer 1977; Morrison et al. 1985; Brand 1987a). The assertion that Sr contents of less than 900 ppm and Mn of higher than 70 ppm imply alteration disagrees with data of Carboniferous brachiopods with high Mn and Fe contents from shales which also contain a well-preserved aragonitic molluscan fauna (e.g., Breathitt and Brush Creek Formations; Brand 1987a; Morrison et al. 1985). Furthermore, microstructures (Fig. 6a, c, d, e, f; these are representative of the majority of specimens) in these brachiopods are similar to those recorded in their modern counterparts (Fig. 6b). Not only are the textures/shell fabrics similar, but dissolution, diagenetic alteration and cementation features are lacking in a large majority of the brachiopod shells. These results suggest that diagenetic interpretations of fossils of many ages and formations treated as a group and irrespective of host lithology, leads to serious misinterpretation and the unnecessary deletion of valuable material.

Popp et al. (1986a) used fabric criteria in conjunction with cathode luminescence to determine the state of alteration of brachiopod calcite. They assumed that nonluminescence of carbonate brachiopods implied low Mn contents, whereas segments with high Mn contents luminesced brightly and therefore represented diagenetic cement or diagenetically altered primary carbonate (Popp et al. 1986a, b). However, Machel (1985) and Fairchild (1983) found that luminescence is not simply a consequence of either low or high Mn contents, but, it reflects a complex interaction of different elements present in various concentrations in the studied carbonate (Frank et al. 1982). If we accept, despite the caution by authors, the argument that luminescing brachiopod-calcite represents diagenetically altered material, samples from deep seas or areas of high detrial input or shales could easily be interpreted as altered (Figs. 3, 4, 5). Similarity of fabrics and the retention of the integrity of the individual crystallites in the layers suggest a high degree of preservation of pristine material in both Recent (shallow and deep) and fossil brachiopod shells (Fig. 6).

These findings have important implications in evaluating the state of diagenetic preservation of fossil material; especially that from shales (Brand 1987a; Morrison et al. 1985; Veizer 1977). The multi-faceted approach and criteria used to differentiate between altered and unaltered brachiopod shell material will be discussed extensively in the following sections.

Trace element evaluation

Factor analysis (Nie et al. 1975) of the North American Carboniferous brachiopods shows that three factors explain the observed geochemical

Table 3. Factor analysis (varimax rotated factor matrix; Nie et al. 1975) of the brachiopod trace-element data (N = 220). Diagnosis is based on applied and theoretical geochemical considerations (cf. Brand and Veizer 1980)

	Factor 1	Factor 2	Factor 3	Communality
log IR	0.62543	*	*	0.42158
log Ca	*	*	*	0.19768
log Mg	0.45712	*	*	0.23856
log Sr	*	0.70472	*	0.56255
log Mn	0.67379	*	*	0.63422
log Na	*	0.76904	*	0.62830
log Al	0.81404	*	*	0.70094
log Fe	0.86933	*	*	0.83303
log Zn	*	*	0.62991	0.39703
log Cu	*	*	0.64082	0.48512
Log Ni	*	*	*	0.08470

Factor	Eigenvalue	Percent of variation	Diagnosis
1	2.88983	55.9	Facies control/Laboratory leaching
2	1.49781	28.6	Environment/Diagenesis
3	0.80406	15.5	Essential nutrient control (?)

*, $\leqslant \pm$ 0.40000 (non-significant value), IR is insoluble residue, underline corresponds to variables identified with specific interpretation (Factor 1).

variation (Table 1; cf. Brand & Veizer 1980, 1981), and the loading of the elements on the factors is similar to that observed by Al-Aasm & Veizer (1982, Table 1) and Veizer et al. (1986, Tables 1, 2, 3). However, it is in the interpretations of these factors that we differ. Some of this may be related to differences in population size, cleaning procedures, digestion method, or other unknown factors.

Factor 1 of the data base has two interpretations (Table 3). The correlation between IR and Al represents laboratory acid-leaching of this element from matrix (limestone or shale) still adhering to the specimens. Although Mg, Fe, and Mn are also loaded on this factor, their overall correlation with IR is insignificant (Fe, mean = 0.45, range = 0.01–0.97; Mn, mean = 0.44, range = 0.04–0.88). Correlation for both Fe and Mn with IR is significant only for specimens from the McCully Formation (0.97; 0.88, respectively), unpaired significant coefficients are recorded for specimens retrieved from the Magoffin (*0.90*, Fe; 0.53, Mn), Kiewitz (0.49, Fe; *0.86*, Mn), and Bangor Formations (*0.76*, Fe; 0.14, Mn). Coefficients of all other data are less than 0.68, and show no correlation of Fe and Mn with IR. Therefore, following the assertion of Brand (1983, 1987a) and Morrison et al. (1985), the Mn and Fe contents of fossils, in part, were probably controlled by soluble oxide coatings (Sherwood et al. 1987), or sediment leached-diffused oxyhydroxide and calcite adsorbed metal fractions (Thomson et al. 1986), or redox conditions of the ambient depositional waters (Veizer 1977), or all of them.

Figure 7 shows the distribution of Fe and Mn contents in the brachiopods with respect to their host lithologies. All of the material with high Fe and Mn contents, which fall outside the limits of the field, would be tentatively regarded by researchers as altered. This demonstrates that the best-preserved fossils must be selected on the basis of other criteria in addition to chemical limits of Mn and Fe, and limited to individual formations/outcrops (Fig. 8). The application of mineralogical, microstructural and geochemical tests on fossils from individuals outcrops/formations easily identifies the material which is diagenetically altered (Popp et al. 1986a; Brand 1987a, b). Otherwise, there may be considerable overlap in the geochemistry of unaltered and altered fossil material, which may reflect variations in lithologies, paleoenvironmental settings or post-depositional histories (Fig. 7; cf. Veizer 1977; Brand 1987a).

According to the results of Recent brachiopods, only a few Carboniferous

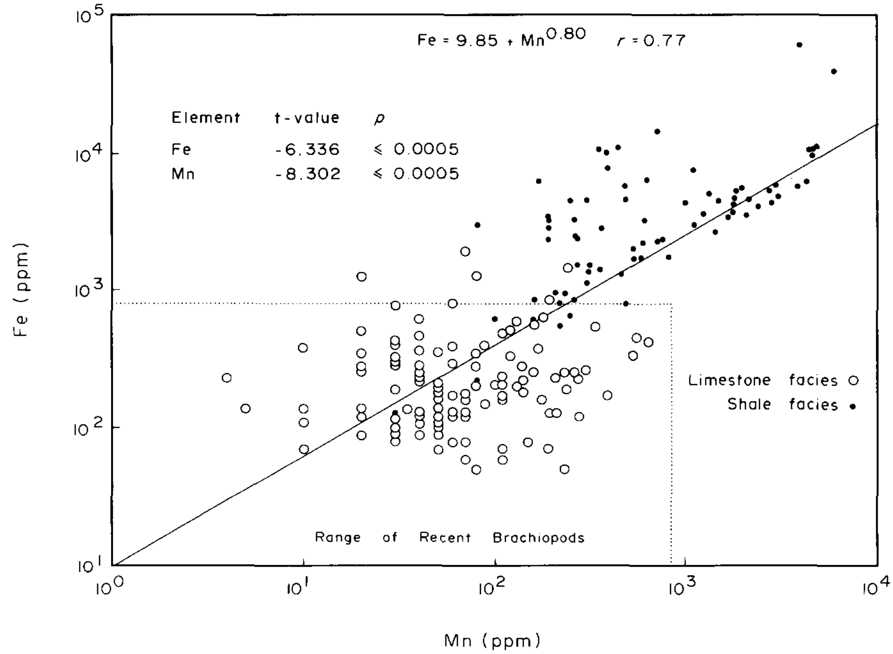

Fig. 7. Distribution diagram of Fe and Mn contents of Carboniferous brachiopods. The chemical range of Recent brachiopods is included (from Fig. 3). Some extensively altered specimens are not included in the diagram (e.g., Great Blue brachiopods).

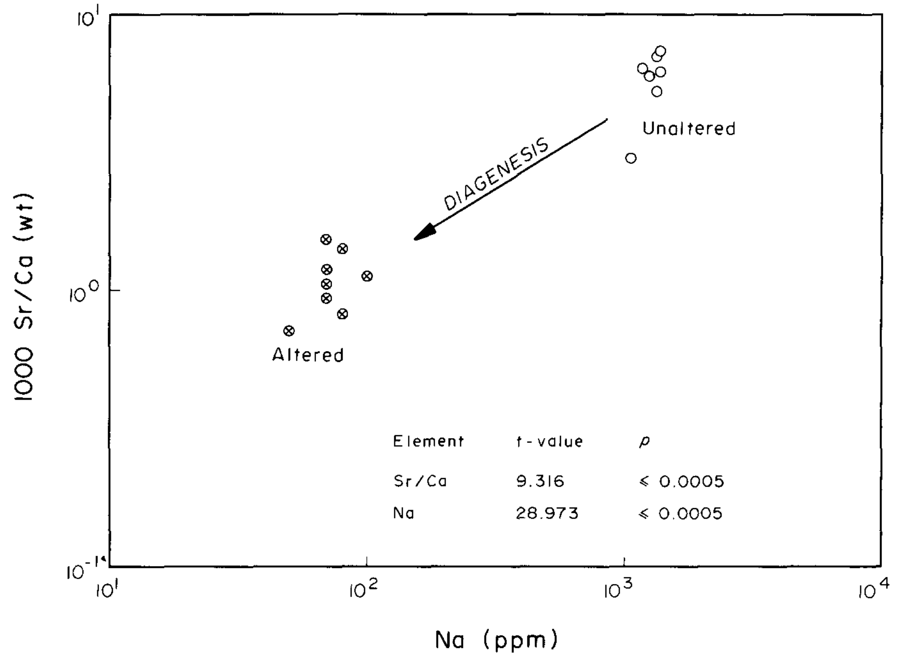

Fig. 8. Diagenetic trend of Sr/Ca and Na for the brachiopods from the Codroy Formation. Post-depositional alteration lowers the Sr/Ca ratios and Na contents of low-Mg calcite brachiopods. Mg is also lower in the altered specimens, whereas Mn and Fe show significantly higher contents than their unaltered counterparts (not shown; Geochemical Table).

specimens lived in waters that can be classified as open, normal marine (Fig. 7; Mn and Fe less than 100 ppm). Instead, the data of brachiopods from limestones fall into the field depicting lower redox or high-detrital input conditions, and most specimens from shales fall outside this area. Data are significantly different for both Fe and Mn contents of the brachiopods from the limestone and shale facies (Fig. 7), which supports the assertion of a strong environmental control over the concentrations of these elements in ancient marine invertebrates (Veizer 1977; Brand 1981, 1987a; Morrison et al. 1985; Sherwood et al. 1987). These results imply that Carboniferous epeiric seas of a restricted nature such as the eastern Brush Creek Basin (Norton 1975) were less oxic than modern shallow or deep oceans (Figs. 3, 7), and some ancient brachiopods thrived in these near dysaerobic waters and in environments with high detrital input.

Factor 2 is loaded exclusively by Sr and Na, and is interpreted to represent an environmental control (Table 3). Brand & Veizer (1980) postulated that brachiopods controlled the Na compositions in their shells, and an apparent physiological control for Sr was advocated by Lowenstam (1963). Group analysis reveals that Sr-Na contents correlate significantly only for specimens from five formations (Rundle, 0.93; Monte cristo, 0.96; Windsor/Codroy, 0.97; Buckhorn, 0.85; and Bangor, 0.93). The level of significance decreases when only unaltered specimens are considered in the calculations. For example, the high correlation of Sr and Na for the Windsor/Codroy specimens is lowered to 0.71 with removal of the altered brachiopod specimens (Fig. 8). In contrast to the unaltered brachiopods, altered specimens exhibit disrupted fabrics (calcite crystallites are replaced and cement filled) and unusually low (Sr, Na, Mg; Fig. 8) and high (Mn, Fe) elemental concentrations. The non-correlation between Sr and Na and the equilibrium values of Sr encountered in the (Brand & Veizer 1980), negates a biological control over Sr by the organisms. Instead, the significant difference in the Na contents of the brachiopods from shales and limestones (Fig. 9) suggests a primary environmental control over the incorporation of this element into shell carbonate. Environmental parameters such as temperature, salinity, or water chemistry may be responsible for the observed co-variance which is similar to that observed in modern brachiopods (Fig. 2). Therefore, factor 2 and the loading of Sr and Na is partly explained by

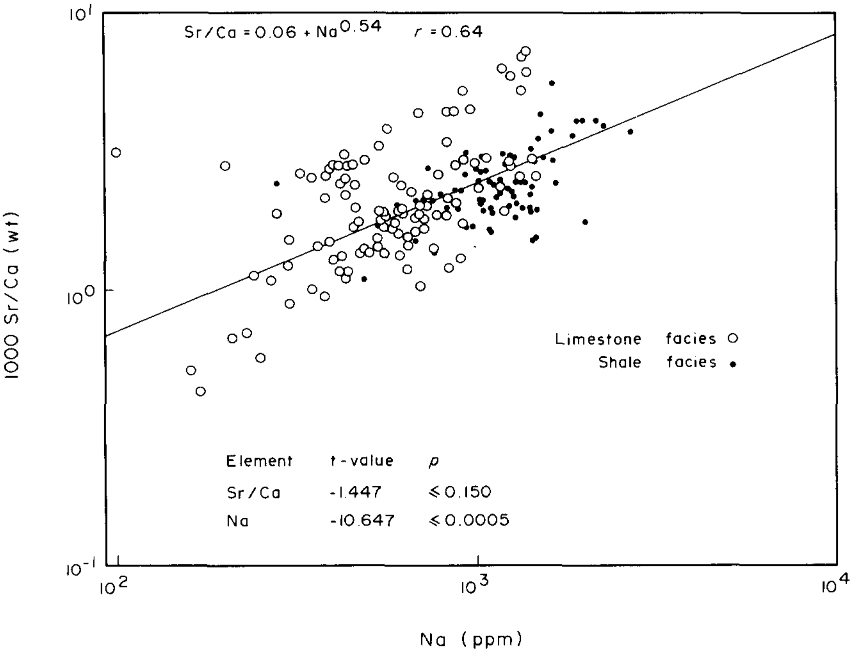

Fig. 9. Distribution diagram of Sr/Ca-Na contents of Carboniferous brachiopods. Extensively altered specimens are not included in this figure.

diagenetic alteration of the brachiopods (Fig. 8), and partly, by environmental controls (Fig. 9; Lowenstam 1961; Brand & Veizer 1980).

Factor 3 is loaded by Zn and Cu, and is the most difficult to interpret (Table 3). Tentatively, a nutrient control is postulated for the observed co-variance. Critical data from Recent brachiopods are lacking to define the possible controls of these two elements in their shell carbonate. The low communality and eigenvalue cast doubt on the significance of this factor and the elemental co-variance (Table 3).

Stable isotope evaluation

Only unaltered brachiopod material, based on undisturbed fabrics (e.g., Fig. 6) and concurrent high levels of Sr, Na and Mg (e.g., upper right of Fig. 8) and low levels of Mn and Fe (not shown), was used in the following evaluation of stable isotope trends. Figure 10 shows the distribution of oxygen and carbon of well-preserved brachiopods, which represent about 53% of the studied population. Most of the data fall outside the field which defines calcium carbonate precipitated by brachiopods in equilibrium with ambient modern seawater (Fig. 10; Lowenstam 1961; Wefer 1985; this study). In this case, data suggest a vital effect was asserted by Carboniferous brachiopods over their $\delta^{13}C$ and $\delta^{18}O$ similar to the carbon control postulated for modern brachiopods by Wefer (1985). Interestingly, most of the $\delta^{13}C$ values fall within the range suggesting incorporation and precipitation in equilibrium with ambient seawater (Fig. 10). Diagenesis cannot account for the light $\delta^{18}O$ values, because only the best-preserved brachiopod material, based on fabric and trace element data, was used to construct Fig. 10. Figure 11 shows the $\delta^{18}O$ distribution of brachiopods from the Codroy, Great Blue and Banff Formations. The Codroy samples identified as altered from trace element evaluations (lower left of Fig. 8) show an enrichment in ^{13}C and depletion in ^{18}O with progresive post-depositional alteration. This distribution of isotope values suggests a marine-derived origin for the diagenetic fluids (e.g., Baker et al. 1982; Elderfield et al. 1982). In contrast, some of the samples from the Great Blue and Banff Formations show enrichment of the light isotopes in progressively altered material, which suggests alteration of the calcium carbonate in the presence of meteoric waters (e.g., Land 1970; Brand & Veizer 1981).

Thus, the $\delta^{13}C$ and $\delta^{18}O$ values of the Carboniferous brachiopods represent isotopic composition and/or temperature of the depositional seawater (Lowenstam 1961). Computations suggest that the $\delta^{13}C$ of brachiopods from limestones and shales are significantly different at the 99.95% confidence level (Fig. 10), and the confidence level changes little if salinity

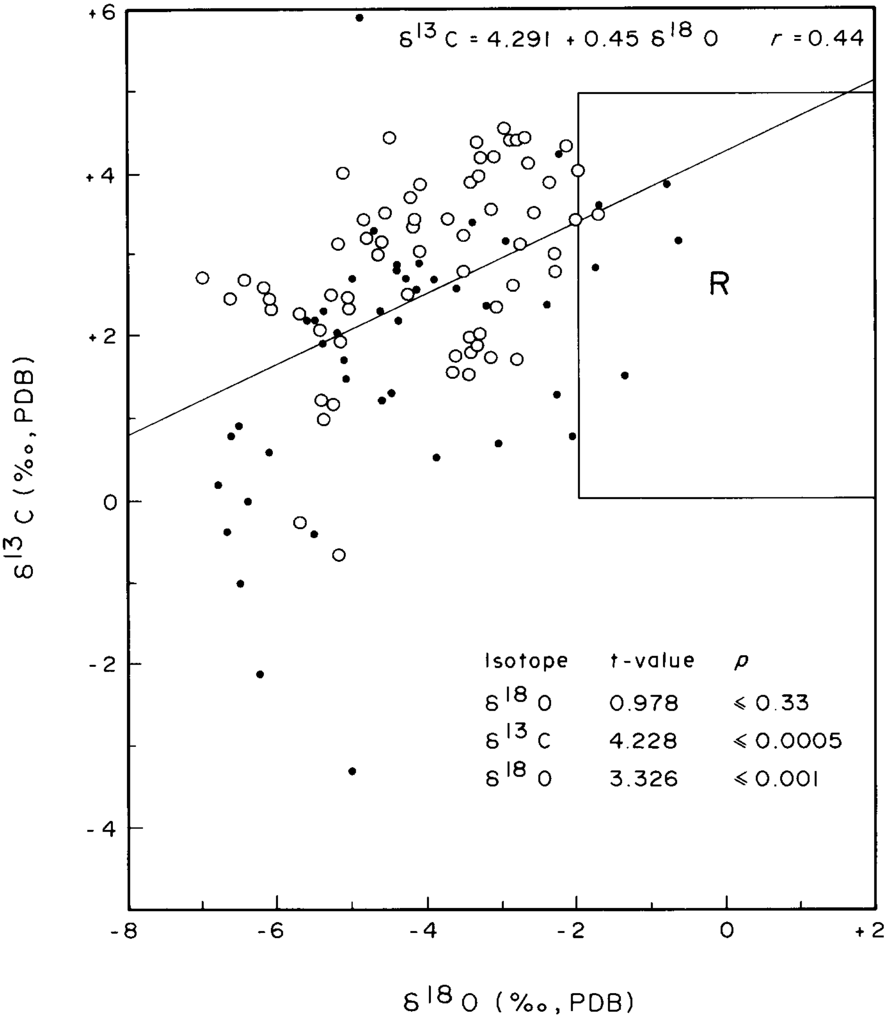

Fig. 10. Distribution diagram of isotopic compositions of Carboniferous brachiopods. In the initial data set, the $\delta^{18}O$ values were not adjusted for environmental factors ($p < 0.001$), but with salinity corrections applied to Breathitt and Brush Creek brachiopods (Brand 1987a; Morrison et al. 1985), significance of population data changes drastically ($p < 0.33$). No significant difference in the p value for $\delta^{13}C$ was observed with or without salinity corrections. The "R" represents modern calcite precipitated in equilibrium with ambient seawater (Lowenstam 1961; Milliman 1974; Wefer 1985; this study). The solid and open data points are brachiopods from shales and limestones, respectively.

and other environmental parameters are considered in subsequent computations. In contrast, the confidence level (99.9%) of dissimilar $\delta^{18}O$ values of the limestone and shale brachiopod-populations changes to a non-significant level (67%) when corrections for low salinity (Epstein & Mayeda 1954)

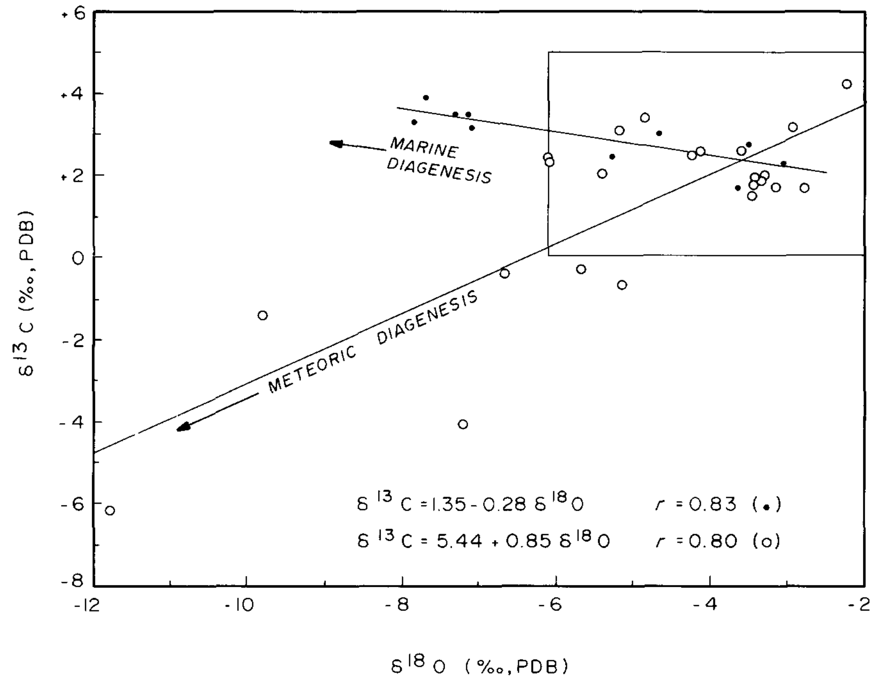

Fig. 11. Diagenetic trend of oxygen and carbon for the brachiopods from the Codroy (postulated marine water diagenesis; closed circles) and the Great Blue Formation (meteoric water diagenesis; open circles). Enclosed field represents calcium carbonate precipitated in isotopic equilibrium with ambient Carboniferous seawater (Brand 1982).

are made to the brachiopod data from the Brush Creek and Breathitt Formations (Morrison et al. 1985; Brand 1987a). Thus, depositional factors, such as salinity, are considered primary controls in the variation of $\delta^{18}O$ in brachiopods from different environments, whereas these had a secondary influence on $\delta^{13}C$ observed in ancient brachiopods.

Summary

Theoretical and applied elemental and isotopic re-distribution diagrams are available depicting the fluid-controlled-dissolution or open system exchange (Veizer 1983) and diffusion-controlled-dissolution or closed system exchange of organic and inorganic aragonite as well as high-Mg calcite with diagenetic water(s) (Brand & Morrison 1987). Figure 12 depicts the re-partitioning of trace elements and stable isotopes during the post-depositional alteration of brachiopod low-Mg calcite. Because of the overall preservation of depositional geochemical signatures in the diagenetic

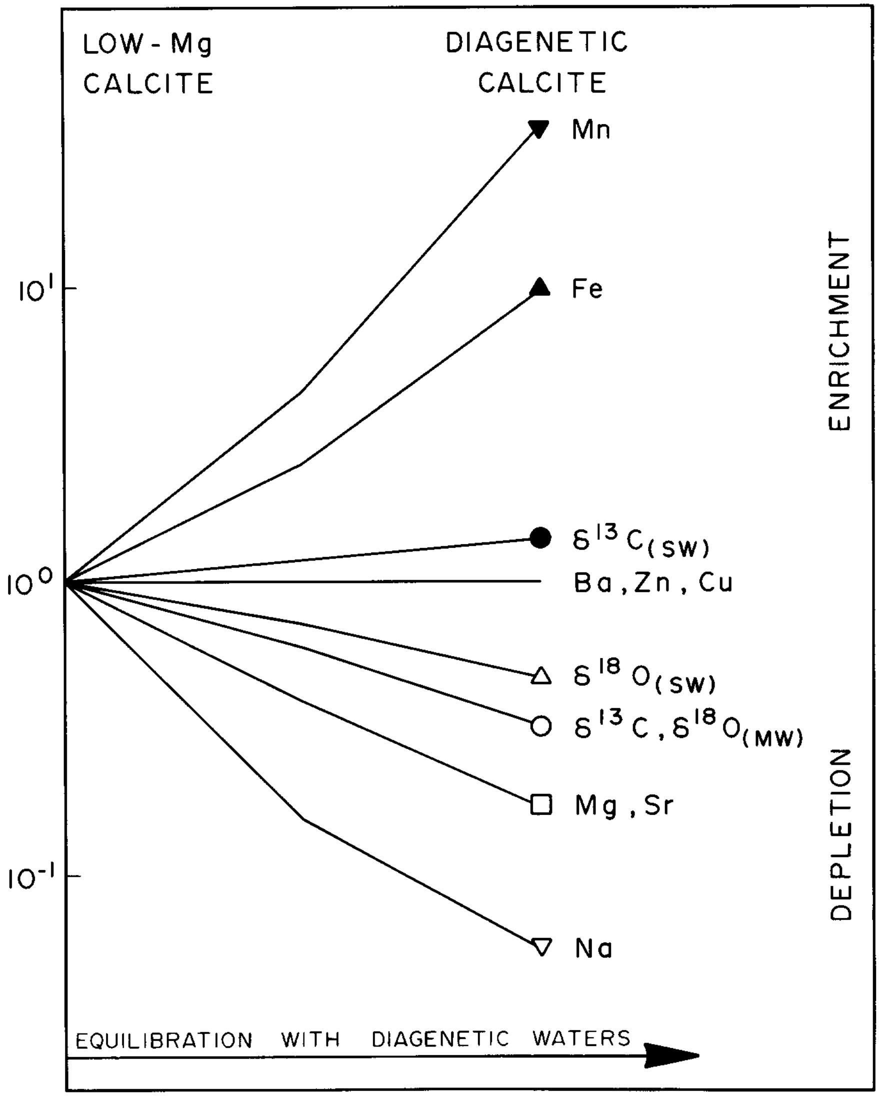

Fig. 12. Summary of directions and magnitudes of elemental and isotopic re-partitioning with progressive post-depositional alteration. These trends define diffusion-controlled-dissolution of low-Mg calcite in the presence of diagenetic fluids. SW is seawater, and MW is meteoric water.

product, this represents an example of closed system recrystallization of low-Mg calcite in diagenetic fluids of both marine (e.g., brachiopods from the Codroy Formation) and meteoric (e.g., specimens from the Great Blue Formation) derivation. Magnitudes and shifts of elemental compositions in the diagenetic low-Mg calcite are similar and independent of type of diagenetic fluid (Baker et al. 1982). In contrast, the magnitudes and shifts of the stable isotope re-distributions are strongly dependent on the water type (Figs. 11, 12). As expected, $\delta^{13}C$ values become heavier with alteration by marine-derived waters, whereas ^{18}O and ^{13}C decrease in carbonates altered in the presence of meteoric waters. $\delta^{18}O$ also decreases in low-Mg calcite altered by marine-derived waters, but the magnitude is different from material altered by meteoric waters (Figs. 11, 12). No significant trends were observed for Ba, Zn, and Cu with post-depositional alteration of low-Mg calcite (Fig. 12). Similar observations were also made for these and a few other elements during the progressive alteration by diffusion-controlled processes of aragonite and high-Mg calcite (Brand & Morrison 1987). Explanations of this invariance must be sought in the water chemistry of depositional and diagenetic waters as well as the partition coefficients of these elements.

It is advocated here that evaluations of preservation/alteration of fossil material be carried out on small populations characterized by specific species/genera, lithology and locality data (e.g., Figs. 6, 8, 11). Evaluations of large sample bases, which disregard lithologic and other pertinent fossil information, leads to gross misinterpretations of the state of preservation/alteration of fossil shell/skeletal carbonate (e.g., Figs. 4, 5, 7, 9). Precise elemental/isotopic limits can not be set to differentiate between altered and unaltered material as has been done by many authors, because rigid limits fail to account for chemical variation induced by the biological and/or depositional systems (Brand 1987a, b). Furthermore, *all* elemental and isotopic trends (e.g., Fig. 12) (not just of Mn) and all fabric information should be used to separate altered and from unaltered material. Nevertheless, with the available textural information and chemical data we can identify not only altered material, but we can also determine the degree and type of alteration and the waters/fluids involved in the diagenetic process.

Secular variation of seawater

The secular isotopic variation of seawater composition over geologic time for carbon, oxygen, sulphur, and strontium are documented with qualified success. Secular trends of carbonates (matrix) are fraught with a major problem, because this material is rarely preserved in its original mineralogy, and, therefore, its isotopic composition, at best, reflects different degrees of diagenetic alteration (Popp et al. 1986a). Fossils accord the best material and geochemical data, provided they are extensively tested for their state of preservation by detailed textural, elemental and isotopic work (Lowenstam 1961, 1963; Pingitore 1976, 1978; Veizer & Fritz 1976; Brand & Veizer 1980, 1981; Popp et al. 1986a; Veizer et al. 1986; Brand & Morrison 1987). Following this testing procedure is imperative, because even "thermodynamically" stable low-Mg calcite brachiopods can contain up to 20% diagenetic calcite in their shells (e.g., Al-Aasm & Veizer 1982). Similar degrees of alteration were also observed by Popp et al. (1986a, b) in shell-carbonate of Late Paleozoic brachiopods from North America, Europe and Asia.

Strontium/calcium

The concentration of Sr is quite uniform throughout the modern oceans, and this is also assumed for the ancient oceans and seas because the residence time of Sr in seawater is orders of magnitude greater than the mixing time (Holland 1978). The shell content of organisms, if it is not influenced by biological factors, should reflect the water composition of the ambient depositional environment. Furthermore, if the contents of organisms have not varied significantly as a result of evolutionary processes, then the Sr/Ca of shells can be used to define first-order variations of the Sr/Ca ratio of ancient seawater (e.g., Turekian 1955; Lowenstam 1961; Holland 1984; Brand & Morrison 1987).

Amounts of Sr in brachiopod low-Mg calcite have remained relatively constant for the Ordovician-Pleistocene interval (Brand & Morrison 1987; Fig. 24; Lowenstam 1961). The Sr content of seawater is not particularly sensitive to seawater cycling through hot or cold basalts at Mid-Ocean-Ridges (MOR), and the Sr (trend $r = 0.22$) of the Carboniferous brachiopods (Fig. 13) supports the postulated conservative behavior of Sr for mid-Phanerozoic seawater (Holland 1984). However, the Ca content of seawater increases with cycling of seawater through MOR basalts at elevated temperatures. Thus, it can significantly influence the Sr/Ca ratio of seawater and of organisms incorporating these elements in equilibrium with their ambient medium. It is interesting that the decrease in Sr/Ca ratio observed in mid-Mississippian brachiopods (Fig. 13) corresponds to the dip observed in the $^{87}Sr/^{86}Sr$ ratio of seawater (Burke et al. 1982), which coincides with the Hercynian orogeny. Changes in the $^{87}Sr/^{86}Sr$ ratio of seawater are related to the cycling of seawater through, and, reaction with basalts at MOR's (Staudigel et al. 1981; Burke et al. 1982; Holland 1984). The observed trend in the Sr/Ca ratio of Carboniferous is considered a primary feature, but more data and additional evidence from other geologic periods are required to test the apparent Sr/Ca-$^{87}Sr/^{86}Sr$ covariance.

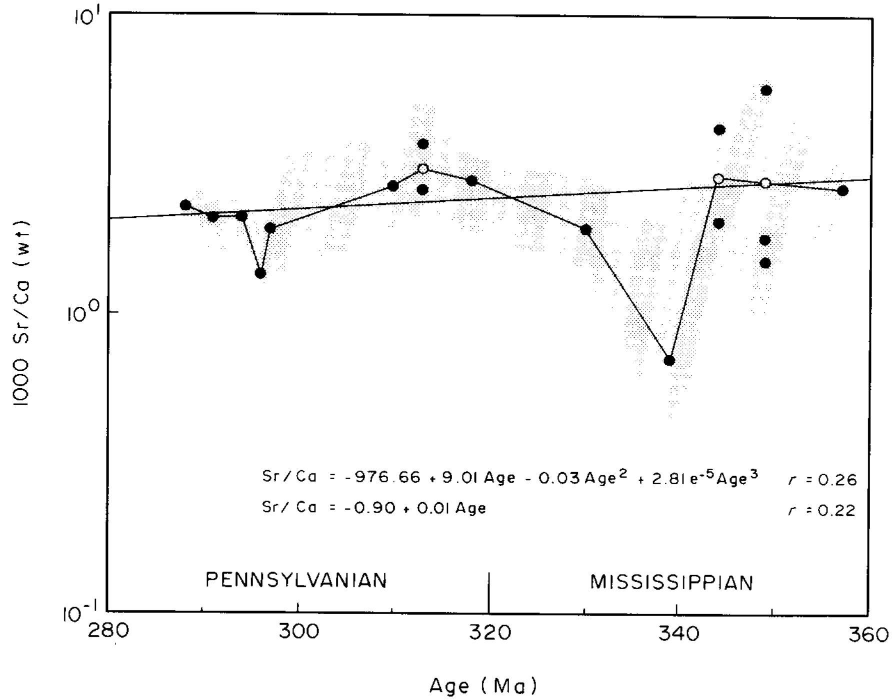

Fig. 13. Secular variation curve of seawater strontium with geologic age (North America). No significant trend is defined by the well-preserved brachiopod data. Solid dots are means and shaded area is the range of data; open symbols are means of several populations from the same time period. Deviations of Sr from mean curve are probably controlled at the generic/species level and/or by environmental conditions.

Carbon

Wefer (1985) suggested that carbon isotopic compositions in modern and ancient brachiopods are subject to a vital effect at the species and genus levels. The data base for modern brachiopods is so small that it does not provide unequivocal proof of a vital effect for carbon. A re-examination of the data contained in Veizer et al. (1986) shows that the δ^{13} C of *Atrypa* from the Bird Formation but of different ages (Eifelian-Emsian) are not significantly different (t-value = -0.353, $p = 0.727$). In contrast, the δ^{13}C of *Atrypa* are significnatly different for samples from different formations (Bird and Hay River Formations; t-value = -4.049, $p = 0.0005$). Similar observations are also made on other brachiopod species from various localities, formations and ages. Generally, the means of similar species but of different ages (Δ^{13}C = 0.49) show smaller deviations from the norm than do their standard deviations ($\Sigma^{13}C = 0.77$), and student t-test shows that paired-species data are significantly different at the 97.8% confidence level. These results suggest that biogenic fractionation of carbon by brachiopods is minor compared to the possible influence of lithology and environment of deposition on their shell composition.

Carbon isotopes shows a trend towards heavier values for Late Paleozoic carbonates, but the scatter within populations generally tends to exceed the variation between populations (e.g., Veizer et al. 1980; Lindh 1983; Holser 1984). Values of samples which deviate greatly from the mean possibly represent diagenetically altered material which passed through the screening process or material from unusual depositional environments.

Similar trends and variations are also depicted by the $\delta^{13}C$ data of Devonian-Permian brachiopods in Fig. 14. Mean $\delta^{13}C$ values vary from a low of $-0.1‰$ during the Emsian (~ 390 Ma) to a high of $+5.4‰$ during the Kungarian (~ 260 Ma), with correlation coefficients of 0.75 (linear) and 0.80 (3rd-order polynomial) for the secular trend. The unidirectional trend towards heavier values from the Devonian to the Permian is in contrast with the trend predicted by Garrels & Lerman (1981), but corresponds to shifts in $\delta^{34}S$ in evaporites for the Emsian-Frasnian interval and the postulated decoupling of the C-S system for the Mississippian-Permian (Claypool et al. 1980). According to Veizer et al. (1986, p. 1683) this observation is

> in accord with considerations based on residence times of oceanic sulfate and bicarbonate.

This shift towards more positive values from the Early Devonian to the Late Permian reflects greater burial of reduced carbon in sediments and/or increased uptake of organic carbon by the expanding terrestrial biomass (mean $\delta^{13}C = -26‰$) relative to that of the marine realm (mean $\delta^{13}C = -20‰$; Broecker 1982). Coals first appeared during the Devonian, proliferated during the Permo-Carboniferous, and are intricately tied to the evolution of terrestrial plants. The Early Devonian saw the diversification of the psilophytes, and during the Late Devonian formed large forests in coastal lowlands. During the Carboniferous, the psilophytes were superseded by the hardier pteridosperms, with the addition of large lycopsids and sphenopsids during the Pennsylvanian and advent and diversification of conifers, cycads, cycadeoids and ginkgos during the Permian. The positive trend of $\delta^{13}C$ reflects the adaptive radiation of terrestrial plants, and burial of organic carbon in sediments (Fig. 14; e.g., Holland 1978; Garrels & Lerman 1981, 1984; Schidlowski & Junge 1981; Berner & Raiswell 1983; Kump & Garrels 1986). The negative $\delta^{13}C$ excursions probably reflect the

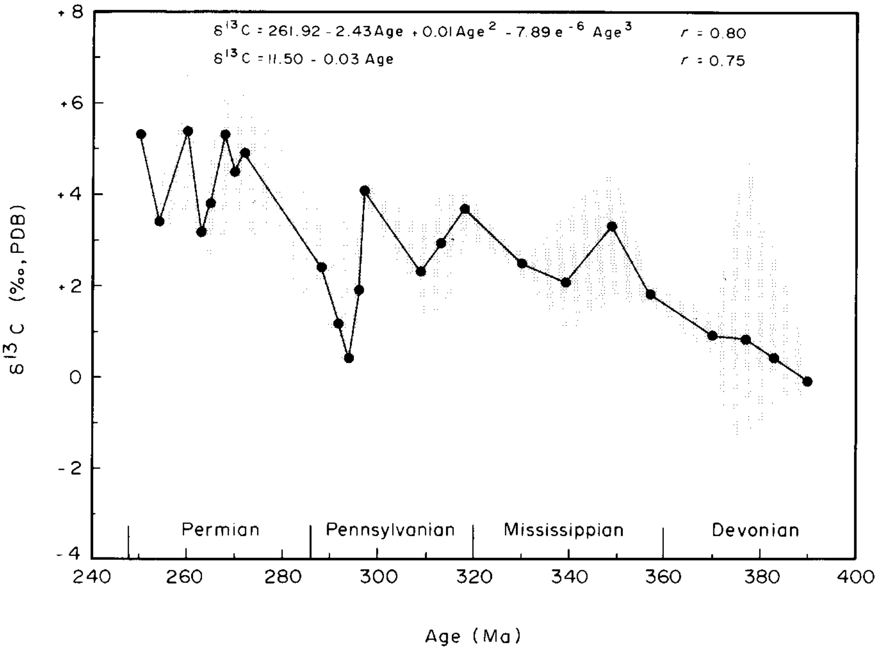

Fig. 14. Secular variation curve of seawater isotopic carbon with geologic age. Symbols and explanations are similar to those in Fig. 13. Devonian and Permian brachiopod data are from Veizer et al. (1986) and Popp et al. (1986).

return of large amounts of reduced carbon to the oceans, but this return of carbon to the ocean/atmosphere reservoir is more than balanced by the removal of carbon by fixation in the terrestrial biomass and its subsequent storage in sediments (Veizer et al. 1980; Lindh et al. 1981; Holland 1984). Keith (1982) offers a slightly different interpretation of the secular isotopic-carbon trend presented above. He postulates that trends and variations in carbonate-^{13}C not solely reflect the flux between the carbonate and organic carbon reservoirs, but also are signals of alternations between mixed and stagnant ocean conditions as well as changes in the carbon isotope ratios of the food web and biogenic carbonates. Carbon isotope values according to this model indicate stagnant oceanic conditions during the Early Paleozoic, Mid Devonian, Late Pennsylvanian and mid Permian (Fig. 14; Keith 1982; Berner 1984). Clarification of the proposed models and interpretations is needed, but are apparently hampered by the complexity of nature and the slow acquisition of reliable isotopic carbonate$_{\text{carbon-oxygen}}$ numbers for the Paleozoic.

Oxygen

The $\delta^{18}O$ trend for Devonian-Permian brachiopods from the paleotropics of North America is presented in Fig. 15. Boundaries between the Devonian-Mississippian and Mississippian-Pennsylvanian are marked by significant positive shifts in seawater ^{18}O of about 3‰, whereas the Pennsylvanian-Permian boundary is marked by a more subdued change in ^{18}O of about 1‰. The trend towards slightly heavier and variable $\delta^{18}O$ values in Permian brachiopods could be, in part, a reflection of global glaciation effects (ice volume signal) during the Permo-Pennsylvanian (Dott & Batten 1976; Frakes 1981). Some of the more extreme $\delta^{18}O$ pertubations noted during the Permian (Fig. 15) may represent localized effects such as seawater dilution by isotopically-light glacial meltwater (e.g., Wassenaar et al. 1988).

Positive shifts in $\delta^{18}O$ are related to increased high-temperature hydrothermal alteration and dehydration of oceanic crust at Mid-Ocean Ridges (Holland 1984, chapter 6.4). Conversely, the negative shifts in $\delta^{18}O$ are postulated to represent increased weathering of both continental and submarine rocks (Muehlenbachs & Clayton 1976; Holland 1984, p. 244). The positive correlation of the $\delta^{13}C$ and $\delta^{18}O$ data of the brachiopods spanning the Devonian-Permian interval, is defined by the following regression equation:

$$\delta^{13}C = 4.529 + 0.516\delta^{18}O, \; r = 0.681$$

and is best explained by the direct coupling of the carbon and oxygen cycles (Holland 1984). With the carbon cycle intricately linked to the sulphur cycle, according to Veizer et al. (1980, p. 582),

> oxygen produced by photosynthesis of carbon dioxide and burial of organic carbon is used up by oxidation of pyrite sulfur to sulfate.

The slightly lower correlation between the carbon and oxygen data probably reflects natural variations in redox reactions, weathering rates, and biological reduction at normal surface conditions. The above discussion demonstrates that O_2 used in weathering is balanced by the production of O_2 by the burial of organic carbon and reduced sulfur, and variations in the reservoirs are generally compensated by the feedback mechanisms (Holland 1978, 1984). These modelers assumed 'steady state' cycles and systems, in which there is no net transfer of materials and isotopes between the various reservoirs. This model was modified by Garrels & Lerman (1984) and Kump & Garrels (1986). They incorporated the atmosphere as a disparate O_2

reservoir subject to new sets of 'flux relations/pertubations' between the different sedimentary reservoirs active within the steady state model. According to Kump & Garrels (1984, p. 358) when

> (the) average, global, CH_2O depositional environment is either non-marine or euxinic, the C and S cycles may be more or less compensatory, and O_2 fluctuations may only be moderate. Under normal marine conditions, however, the C and S cycles store or release oxygen in concord, and O_2 fluctuations may be significant.

Normal marine conditions and consequently large atmospheric O_2 fluctuations were probably likely during most of the Devonian, Mississippian, and Early-Mid Pennsylvanian (Fig. 15; Keith 1982; Berner 1984; Kump and Garrels 1984).

Temperature

Two schools of thought have developed in the geological fraternity regarding the light $\delta^{18}O$ values-high temperatures derived from well-preserved

Fig. 15. Secular variation curve of seawater isotopic oxygen with geologic age. Symbols, explanations and sources of data as in Fig. 14. Data have not been adjusted for ice-volume signal, salinity variations, and freshwater run-off (cf. Brand 1987a, b; Wassenaar et al. (1988).

Early Paleozoic fossil material. One group supports the hypothesis that the water temperatures of the Early Paleozoic oceans were higher with a maximum of 65 °C recorded for seawater during the Cambrian (e.g., Knauth & Epstein 1976; Karhu & Epstein 1986), because significant shifts in the seawater-^{18}O composition are not in agreement with data of seawater cycling through Mid-Ocean ridge basalts. Hydrothermal alteration and weathering processes at low and high temperatures generally buffer any large-scale variation of seawater-^{18}O (e.g., Muehlenbachs & Clayton 1976; Gregory & Taylor 1981; Holland 1984).

The other group postulates that the seawater-^{18}O composition has varied with geologic time, because faunal and sedimentological evidence generally supports environmental conditions similar to those encountered in normal marine oceans (e.g., Perry & Tan 1972; Brand & Veizer 1981; Veizer et al. 1986). The most compelling evidence for variation in seawater-^{18}O composition comes from studies of proteins and enzymes. Proteins are fragile molecules and exposure to even moderate water temperatures of about 37 °C elicits their slow denaturation (Mahler & Cordes 1971), which places an upper-thermal tolerance limit of about 38 °C on aquatic vertebrates and invertebrates (e.g., Brock 1985). Evolutionary processes can not be invoked to explain higher thermal tolerance limits for proteins, because according to Schulz & Schirmer (1979, p. 178)

> the evolution of regulatory genes rather than the evolution of structural genes and the corresponding proteins is at the basis of organismal evolution.

Therefore thermal denaturation occurs in regulatory as well as structural genes and applies equally to proteins of animals regardless of their evolutionary position (Wilson et al. 1974).

Without adjustments in the $\delta^{18}O$ values, calculated water temperatures would reach unrealistic levels of 56 °C during the Eifelian, 47 °C during the Chesterian, and equally unrealistic conditions of 42 °C and 44 °C during the Desmoinesian and Artinskian, respectively. For most of the Devonian, uncorrected water temperatures (means of 36–46 °C, upper limit of 56 °C) would be well above the thermal limit of marine vertebrates and invertebrates ($\sim$ 38 °C, Brock 1985). Therefore, for realistic environmental and biological conditions, water temperature data before calculations are adjusted by $-2.5‰$ for samples older than Desmoinesian, and by $-1.25‰$ for Artinskian to Missourian brachiopods reflecting secular variation of seawater-^{18}O. With these adjustments, the calculated water temperatures of brachiopods spaning the Devonian-Permian interval are within the thermal tolerance limit of marine vertebrates and invertebrates. Oxygen isotope values of material younger than Kungurian need not be adjusted for seawater-^{18}O secular variations, but Late Pennsylvanian and Permian data were adjusted by + 1‰ for glacial effects and the sum of these corrections are presented in Fig. 16.

A large temperature excursion marks the Frasnian-Famennian interval, with an average drop in temperature of about 12 °C. Similar temperature excursions are also documented for the Chesterian-Morrowan and the Missourian-Virgillian intervals (Fig. 16). The first one is associated with

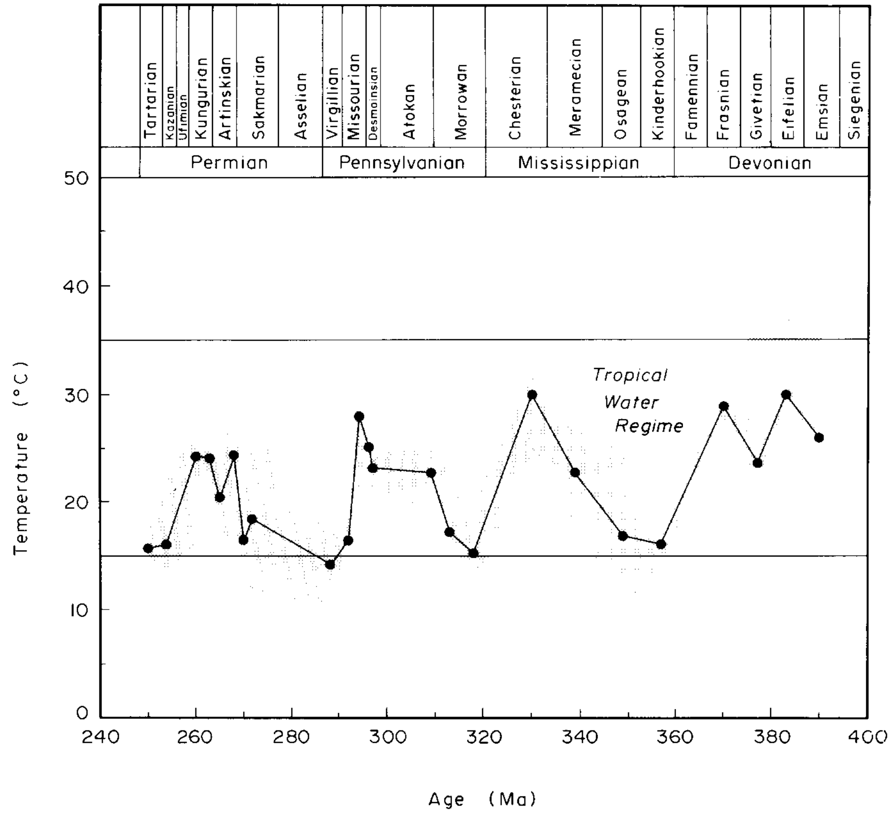

Fig. 16. Secular variation curve of seawater temperature for the Late Paleozoic. Data sources and symbols as in Fig. 14, and time scale is from Harland et al. (1982). Tropical water regime defines the upper and lower limits of temperature in modern tropical waters (Milliman 1974; Bathurst 1975). Temperature has been adjusted for secular variation of Early Paleozoic seawater (– 2.5‰), ice-volume signal during the late Pennsylvanian and Permian (1.0‰), and for salinity variations of the Brush Creek (Morrison et al. 1985) and Breathitt seas (Brand 1987a). A standard value of – 1.0‰ was used for water in the temperature equation following the rationale of Karhu & Epstein (1986).

transgression of the sea, whereas major regressions are evidenced during the other two temperature excursions (Dott & Batten 1971; Vail & Mitchum 1979). The drop in temperature for the Missourian-Virgillian interval coincides with the onset of large-scale glaciation during the Late Paleozoic (Stephanian-Kungurian; Frakes 1981). Therefore, causes other than transgressing-regressing seas must be responsible for these significant temperature variations, some of which such as CO_2 and greenhouse effect, impacts of extraterrestrial bodies, increased cosmic radiation, reversals in Earth's magnetic field, just to name a few mechanisms were discussed by Herman (1981). The effect of these temperature variations in biotic extinctions and diversifications was debated by Stanley (1984).

Conclusions

Evaluation of modern and Devonian-Permian brachiopods of North America suggest the following results pertaining to the diagenesis of low-Mg calcite and the secular variation of Late Paleozoic seawater.

- In Recent brachiopods, their Sr/Ca ratio is controlled by that of the seawater, whereas Na contents show no relationship with water depth or habitat. Manganese and iron contents are controlled by leaching of oxide coatings and possibly redox conditions as well as input with slow sedimentation rate of detrital material into depositional areas.
- Application of rigid guidelines to selecting diagenetically altered material generally dismisses many pristine carbonate samples. Selection procedures must be sensitive to the natural chemical range observed in samples reflecting variations in habitat, temperature, salinity and biologic factors. Afterwards, the sum-total of mineralogic, fabric, and luminescence information, and elemental and isotopic analyses in conjunction with variations in host lithology should define the least-altered specimen(s).
- Altered specimens can only be identified with confidence by individual and group analysis based on outcrop, formation/member, and lithological parameters. The best-preserved sample(s) can be successfully separated from material which altered in the presence of either meteoric- or marine-derived diagenetic fluids. Trends, direction and magnitude of elemental and isotopic shifts assist in the selection process of either open or closed system recrystallized fossil material.
- The Mn and Fe contents of most Carboniferous brachiopods are similar to the ranges encountered in their Recent counterparts. The elevated Mn

and Fe contents in some of the Carboniferous brachiopods from shales suggests leaching of them from oxide coatings/matrix and possibly diffusion of these elements into the overlying water column implying near dysaerobic conditions for these depositional settings.

- The Sr/Ca ratios of brachiopods and complementary seawater have not varied significantly for the Carboniferous. However, the minimum during the Mississippian coincides with a dip in the $^{87}Sr/^{86}Sr$ curve and correlates with the Hercynian orogeny, and might be related to the cycling of seawater through mid-ocean ridge basalts and exchange reactions varying the composition of Ca.
- The unidirectional trend of heavier ^{13}C values from the Devonian to the Permian might be intricately coupled with the evolution and expansion of terrestrial plants. In addition, burial of organic carbon contributed to the shift with formation of extensive coal deposits. The start of the Permo-Pennsylvanian glaciation is marked by a negative excursion in the secular carbon trend, which is linked to weathering of organic carbon and its return to the oceanic reservoir.
- The oxygen isotope data mirrors the unidirectional trend towards heavier values of the carbon data with decreasing geologic age. Negative excursions of the trend may be related to extensive weathering of terrestrial and submarine rocks, whereas positive excursions and general trend may be related to hydrothermal alteration of submarine rocks and dehydration of oceanic crust during times of active sea-floor spreading.
- Oxygen-calculated water temperatures of unaltered brachiopod material are unrealistically high for the Devonian, Chesterian-Meramecian, Desmoinesian-Missourian, and Artinskian. Their respective maximum water temperatures of 56°, 47°, 42° and 44 °C are well above the thermal threshold of protein denaturation. This process which is lethal to all organisms, demands an adjustment of $-2.5‰$ for samples older than Missourian, and of $-1.25‰$ for samples spanning the Missourian-Artinskian interval. With these adjustments in seawater-^{18}O and salinity, calculated water temperatures become reasonable for the Late Paleozoic epeiric, tropical seas of North America.

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References

Al-Aasm IS & Veizer J (1982) Chemical stabilization of low-Mg calcite: an example of brachiopods. Journal of Sedimentary Petrology 52: 1101–1109

Baker PA, Gieskes JM & Elderfield H (1982) diagenesis of carbonates in deep sea sediments-evidence from Sr/Ca ratios and interstial Sr data. Journal of Sedimentary Petrology 52: 71–82

Bamber EW, Macqueen RW & Ollerenshaw NC (1981) Mississippian stratigraphy and sedimentology, Canyon Creek (Moose Mountain), Alberta. Geological Association of Canada Field Guides 7: 177–194

Bathurst RGC (1975) Carbonate Rocks and their Diagenesis. Elsevier

Berner RA (1984) Sedimentary pyrite formation: an update. Geochimica Cosmochimica Acta 48: 605–615

Berner RA & Raiswell R (1983) Burial of organic carbon and pyrite sulfur in sediments over Phanerozoic time: a new theory. Geochimica Cosmochimica Acta 47: 855–862

Brand U (1981) Mineralogy and chemistry of the lower Pennsylvanian Kendrick fauna, eastern Kentucky – 1: trace elements. Chemical Geology 32: 1–16

Brand U (1982) The oxygen and carbon isotope composition of Carboniferous fossil components: sea water effects. Sedimentology 29: 139–147

Brand U (1983) Mineralogy and chemistry of the lower Pennsylvanian Kendrick fauna, eastern Kentucky, USA, Chemical Geology 40: 167–181

Brand U (1987b) Depositional analysis of the Breathitt Formation's marine horizons, Kentucky: trace elements and stable isotopes. Isotope Geoscience 65; 117–136

Brand U (1987b) Biogeochemistry of nautiloids and paleoenvironmental conditions of Buckhorn seawater (Pennsylvanian), southern Oklahoma. Palaeoecology, Palaeoclimatology, Palaeogeography 61: 255–264

Brand U & Morrison JO (1987) Paleoscence No 6. Biogeochemistry of fossil marine invertebrates. Geoscience Canada 14: 85–107

Brand U & Veizer J (1980) Chemical diagenesis of a multicomponent carbonate system – 1: trace elements. Journal of Sedimentary Petrology 50: 1219–1236

Brand U & Veizer J (1981) Chemical diagenesis of a multicomponent carbonate system – 2: stable isotopes. Journal of Sedimentary Petrology 51: 987–997

Brew DC & Beus SS (1976) A Middle Pennsylvanian fauna from the Naco Formation near Kohl Ranch, central Arizona. Journal of Paleontology 50: 888–906

Brock TD (1985) Life at high temperatures. Science 230: 132–138

Broecker WS (1982) Ocean chemistry during glacial time. Geochimica Cosmochimica Acta 46: 1689–1705

Burke WH, Denison RE, Heatherington EA, Koepnick RB, Nelson HF & Oto JB (1982) Variation of seawater $^{87}Sr/^{86}Sr$ throughout Phanerozoic time. Geology 10: 516–519

Claypool GE, Holser WT, Kaplan IR, Sakai H & Zak I (1980) The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. Chemical Geology 28: 199–260

Craig H (1957) Isotopic standards for carbon and oxygen and correction factors for mass spectrometric analysis of carbon dioxide. Geochimica Cosmochimica Acta 12: 133–149

Dennis AMN & Lawrence DR (1979) Macro-fauna and fossil preservation in the magoffin marine zone, Pennsylvanian Breathitt Formation of eastern Kentucky. Southeastern Geology 20: 181–190

Dott RH & Batten RL (1976) Evolution of the Earth. McGraw-Hill Book Company

Elderfield H, Gieskes JM, Baker PA, Oldfield RK, Hawkesworth CJ & Miller R (1982) 87Sr/86Sr and 180/160 ratios, interstitial water chemistry and diagenesis in deep-sea carbonate sediments of the Ontong Java Plateau. Geochimica Cosmochimica Acta 46: 2259–2267

Epstein S, Buchsbaum R, Lowenstam HA & Urey HC (1953) Revised carbonate-water isotopic temperature scale. Geological Society of America Bulletin 64: 1315–1325

Fairchild IJ (1983) Chemical controls of cathodoluminescence of natural dolomites and calcites: new data and review. Sedimentology 30: 579–583

Frakes LA (1981) Late Paleoclimatology. In: McElhinny MW & Valencio DA (Eds.) Paleoreconstruction of the Continents. Geodynamics Series 2: 39–44

Frank JR, Carpenter AB & Oglesby TW (1982) Cathodoluminescence and composition of calcite cement in the Taum Sauk Limestone (Upper Cambrian), southeast Missouri. Journal of Sedimentary Petrology 52: 631–638

Garrels RM & Lerman A (1981) Phanerozoic cycles of sedimentary sulfur and carbon. Proceedings of National Academy of Science 78: 4652–4656

Garrels RM & Lerman A (1984) Coupling of sedimentary sulfur and carbon cycles – an improved model. American Journal of Science 284: 989–1007

Gregory RT & Taylor HP (1981) An oxygen isotope profile in a section of Cretaceous ocean crust, Samoil ophiolite, Oman: evidence for 180 buffering of the oceans by deep ($\geqslant 5$ km) seawater hydrothermal circulation at midocean ridges. Journal of Geophysical Research 86: 2737–2755

Harland WB, Cox AV, Llewellyn PG, Picton CAG, Smith AG and Walters R (1982) A Geologic Time Scale. Cambridge University Press, Cambridge, 131 pp

Harris SE & Parker MC (1964) Stratigraphy of the Osage series in southeastern Iowa. Iowa Geological Survey Report of Investigations 1: 52

Herman Y (1981) Causes of massive biotic extinctions and explosive evolutionary diversification throughout Phanerozoic time. Geology 9: 101–108

Holland HD (1978) The chemistry of the atmosphere and oceans. Wiley-Interscience

Holland HD (1984) The chemical evolution of the atmosphere and oceans. Princeton Press

Holser WT (1984) Gradual and abrupt shifts in ocean chemistry during Phanerozoic time. In: Holland HD & Trendall AF (Eds.) Patterns of Change in Earth Evolution, pp 123–143, Springer-Verlag

Jillson WR (1919) The Kendrick shale – a new calcareous fossil horizon in the coal measures of eastern Kentucky. Mineral and Forestry Resources of Kentucky 1: 96–104

Johnson JH (1951) An introduction to the study of organic limestones. Quarterly Colorado School of Mines 46: 1–85

Karhu J & Epstein S (1986) The implications of the oxygen isotope records in coexisting cherts and phosphates. Geochimica Cosmochimica Acta 50: 1745–1756

Knauth PA & Epstein S (1976) Hydrogen and oxygen isotope ratios in nodular and bedded cherts. Geochimica Cosmochimica Acta 40: 1095–1108

Keith ML (1982) Violent volcanism, stagnant oceans and some inferences regarding petroleum, strata-bound ores and mass extinctions. Geochimica Cosmochimica Acta 46: 2621–2637

Kump LR & Garrels RM (1986) Modeling atmospheric O_2 in the global sedimentary redox cycle. American Journal of Science 286: 337–360

Land LS (1970) Phreatic versus vadose meteoric diagenesis of limestone: Evidence for a fossil water table. Sedimentology 14: 175–185

Lane NG (1973) Paleontology and paleoecology of the Crawfordsville fossil site (upper Osagian, Indiana). California University Publications Geological Sciences 99: 141

Langenheim RL & Webster GD (1979) Carboniferous stratigraphy in the Grand Canyon country, northern Arizona and southern Nevada. American Geological Institute Guidebook Series, Field trip 13: 53–72

Lindh TB (1983) Temporal variations in 13C, 34S and global sedimentation during the Phanerozoic. Unpubl. M.Sc. thesis, University of Miami. 98 pp

Lindh TB, Saltzman ES, Sloan JL, Mattes BW & Holser WT (1981) A revised 13C-age curve (abs). Geological Society of America, Abstracts with Programs 13: 498

Lindsay RF (1977) Petrology and petrography of the Great Blue Formation at Wellsville Mountain, Utah. Brigham Young University Geology Studies 24: 115–140

Lowenstam HA (1961) Mineralogy, O^{18}/O^{16} ratios, and strontium and magnesium contents of Recent and fossil brachiopods and their bearing on the history of the oceans. Journal of Geology 69: 241–260

Lowenstam HA (1963) Biological problems relating to the composition and diagenesis of sediments. In: Donnelly TW (Ed), The Earth Sciences (pp 137–195). University of Chicago Press

Machel, H-G (1985) Cathodoluminescence in calcite and dolomite and its chemical interpretation. Geoscience Canada 12: 139–147

Mahler HR & Cordes EH (1971) Biological chemistry. Harper & Row Publishers. 1009

Meyers WJ (1974) Carbonate cement stratigraphy of the Lake Valley Formation (Mississippian), Sacramento Mountains, New Mexico. Journal of Sedimentary Petrology 44: 837–861

Millman JD (1974) Marine Carbonate. Springer-Verlag

Morrison JO & Brand U (1986) Paleoscence No 5. Geochemistry of Recent marine invertebrates. Geoscience Canada 13: 237–254

Morrison JO, Brand U & Rollins HB (1985) Paleoenvironmental and chemical analysis of the Pennsylvanian Brush Creek fossil allochems, Pennsylvania, USA, 10th International Carboniferous Congress, Compte Rendu (Madrid) 2: 271–280

Mudge MR & Yochelson EL (1962) Stratigraphy and paleontology of the uppermost Pennsylvanian and lowermost Permian rocks in Kansas. U.S. Geological Survey Professional Paper 323: 213

Muehlenbachs K & Clayton RN (1976) Oxygen isotope composition of the oceanic crust and its bearing on seawater. Journal of Geophysical Research 81: 4365–4369

Nie HH, Hull CH, Jenkins JG, Steinbrenner K & Bent DH (1975) Statistical Package for the Social Sciences. McGraw-Hill

Norton CW (1975) Foraminiferal distribution and paleogeography of the Brush Creek Marine event (Missourian: Pennsylvanian) in the Appalachian Basin. Unpubl. Ph.D. thesis, University of Pittsburgh. 146 pp

Perry EC & Tan FC (1972) Significance of oxygen and carbon isotope variations in Early Precambrian cherts and carbonate rocks of southern Africa. Geological Society of America Bulletin 83: 647–664

Pingitore NE Jr (1976) Vadose and phreatic diagenesis: Processes, products and their recognition in corals. Journal of Sedimentary Petrology 46: 985–1006

Pingitore NE Jr (1978) The behavior of Zn^{2+} and Mn^{2+} during diagenesis: Theory and application. Journal of Sedimentary Petrology 48: 799–814

Popp BN, Anderson TF & Sandberg PA (1986a) Textural, elemental, and isotopic variations among constituents in Middle Devonian limestones, North America. Journal of Sedimentary Petrology 56: 715–727

Popp BN, Anderson TF & Sandberg PA (1986b) Brachiopods as indicators of original isotopic compositions in some Paleozoic limestones. Geological Society of America Bulletin 97: 1262–1269

Popp BN, Podosek FA, Brannon JC, Anderson TF & Pier J (1986) $^{87}Sr/^{86}Sr$ ratios in Permo-Carboniferous sea water from the analyses of well-preserved brachiopod shells. Geochimica Cosmochimica Acta 50: 1321–1328

Sando WJ, Mamet BL & Dutro JT Jr (1969) Carboniferous megafaunal and microfaunal zonation in the northern Cordillera of the United States US Geological Survey Paper 613: 29

Schidlowski M & Junge CE (1981) Coupling among the terrestrial sulfur, carbon and oxygen cycles: numerical modeling based on revised Phanerozoic carbon isotope record. Geochimica Cosmoschimica Acta 45: 589–594

Schulz GE & Schirmer RH (1979) Principles of Protein Structure. Springer-Verlag. 314 pp

Scotese CR, Bambach RK, Barton C, van der Voo R & Ziegler AM (1979) Paleozoic base maps. Journal of Geology 87: 217–277

Sherwood BA, Sager SL & Holland HD (1987) Phosphorus in foraminiferal sediments from North Atlantic Ridge cores and in pure limestones. Geochimica Cosmochimica Acta 51: 1861–1866

Smith EA (1890) Geological structure and description of the valley regions adjacent to the Cahaba coal field. Geological survey of Alabama 2: 133–180

Spencer AC & Paige S (1935) Geology of the Santa Rita mining area, New Mexico. US Geological Survey Bulletin 859: 78

Squires RL (1973) Burial environment, diagenesis, mineralogy, and Mg & Sr contents of skeletal carbonates in the Buckhorn asphalt of Middle Pennsylvanian age, Arbuckle Mountains, Oklahoma. Unpubl. Ph.D. thesis, California Institute of Technology. 184 pp

Stanley SM (1984) Temperature and biotic crises in the marine realm. Geology 12: 205–208

Staudigel H, Muehlenbachs K, Richardson SH & Hart SR (1981) Agents of low-temperature ocean crust alteration. Contributions to Mineralogy and Petrology 77: 150–157

Sutherland SK & Henry TW (1977) Carbonate platform facies and new stratigraphic nomenclature of the Morrowan Series (Lower and Middle Pennsylvanian), northeastern Oklahoma. Geological Society of America Bulletin 88: 425–440

Thomson J, Higgs NC, Jarvis I, Hydes DJ, Colley S & Wilson TRS (1986) The behaviour of manganese in Atlantic carbonate sediments. Geochimica Cosmochimica Acta 50: 1807–1818

Turekian KK (1955) Paleoecological significance of the strontium-calcium ratio in fossils and sediments. Geological Society of America Bulletin 66: 155–158

Vail, PR & Mitchum RM (1979) Global cycles of relative changes of sea level from seismic stratigraphy. American Association of Petroleum Geologists Memoir 29: 469–472

Veizer J (1977) Geochemistry of lithographic limestones and dark marls from the Jurassic of southern Germany. Neues Jahrbuch für Geologie und Paläontologie 153: 129–146

Veizer J (1983) Trace elements and isotopes in sedimentary carbonates. Reviews in Mineralogy 11: 265–300

Veizer J & Fritz P (1976) Possible control of post-depositional alteration in oxygen paleotemperature determinations. Earth and Planetary Science Letter 33: 255–260

Veizer J, Holser WT & Wilgus CK (1980) Correlation of $^{13}C/^{12}C$ and $^{34}S/^{32}S$ secular variations. Geochimica Cosmochimica Acta 44: 579–587

Veizer J, Fritz P & Jones B (1986) Geochemistry of brachiopods: oxygen and carbon isotopic records of Paleozoic oceans. Geochimica Cosmochimica Acta 50: 1679–1696

von Bitter PH (1972) Environmental control of conodont distribution in the Shawnee Group (Upper Pennsylvanian) of eastern Kansas. The University of Kansas Publications 59: 105

von Bitter PH & Plint-Geberl HA (1982) conodont biostratigraphy of the Codroy Group (Lower Carboniferous), southwestern Newfoundland, Canada. Canadian Journal of Earth Sciences 19: 193–221

Wassenaar LI, Brand U & Terasmae J (1988) Geochemical and paleoecological investigation using invertebrate macrofossils of the Late Quarternary Champlain Sea, Ontario and Quebéc. Geological Association of Canada, Special Paper 35

Wefer G (1985) Die Verteilung stabiler Isotope in Kalkschalen mariner Organismen. Geologisches Jahrbuch A82: 3–111

Williams A (1971) Scanning electron microscopy of the calcareous skeleton of fossil and living brachiopods. In: Heywood VH (Ed) Scanning Electron Microscopy: Systematics and Evolutionary Applications. Academic Press

Wilson AC, Sarich VM & Maxson LR (1974) The importance of gene rearrangement in evolution: Evidence from studies on rates of chromosomal, protein, and anatomical evolution. Proceedings National Academy of Science 71: 3028–3030