Geochemistry of brachiopods: Oxygen and carbon isotopic records of Paleozoic oceans*

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Abstract—Combined trace element and isotope studies of 319 brachiopods, covering the Ordovician to Permian time span, show that $\delta^{13}C$ and $\delta^{18}O$ in well preserved specimens varied during the Paleozoic. The overall $\delta^{13}C$ secular trend is in accord with the previously published observations, but its details are obscured by vital isotopic fractionation effects at generic level. Nonetheless, the results suggest that the negative correlation between marine $\delta^{13}C_{carbonate}$ and $\delta^{34}S_{sulfate}$ deteriorates at time scales of $\leq 10^6$ years, due to the long residence time, and thus slow response, of SO_4^{2-} in the ocean. For oxygen isotopes, all Devonian and older specimens have $\delta^{18}O$ of $\leq -4‰$, while the well preserved Permian samples have near-present day $\delta^{18}O$ of about $-1‰$ (PDB). This isotopic dichotomy is probably not due to post-depositional phenomena, salinity, or biogenic fractionation effects. This leaves open the perennial arguments for a change in $^{18}O/^{16}O$ of sea water *versus* warmer ancient oceans. The present data are difficult to explain solely by the temperature alternative. The coincidence of the proposed shift in $\delta^{18}O$ with the large Late Paleozoic changes in marine $^{87}Sr/^{86}Sr$, $^{13}C/^{12}C$, $^{34}S/^{32}S$, and "sea level stands" argues for a tectonic cause and for a change in $^{18}O/^{16}O$ of sea water, although such explanation is difficult to reconcile with global balance considerations and with isotopic patterns observed in alteration products of ancient basalts and ophiolites. Whatever the precise cause, or combination of causes, the implications for tectonism and/or paleoclimatology are of first order significance.

INTRODUCTION

THE TREND OF decreasing $\delta^{18}O$ values of marine chemical sediments with increasing age has been well documented. This trend has been observed for carbonates (BAERTSCHI, 1957; CLAYTON and DEGENS, 1959; DEGENS and EPSTEIN, 1962; KEITH and WEBER, 1964; WEBER, 1965a,b; DONTSOVA *et al.*, 1972; BAUSCH and HOEFS, 1972; PERRY and TAN, 1972; SCHIDLOWSKI *et al.*, 1975, 1983; VEIZER and HOEFS, 1976), cherts (DEGENS and EPSTEIN, 1962; PERRY, 1967; PERRY and TAN, 1972; KNAUTH and EPSTEIN, 1976; KNAUTH and LOWE, 1978), phosphorites (LONGINELLI and NUTI, 1968; SHEMESH *et al.*, 1983; LUZ *et al.*, 1984), and glauconites (FRIEDRICHSEN, 1984; KEPPENS and O'NEIL, 1985). The perennial question of the cause(s) of this isotopic shift is, however, still vigorously debated. Suggested causes include: (1) post-depositional equilibration with ^{18}O depleted meteoric waters, the degree of equilibration increasing with increasing geologic age (DEGENS and EPSTEIN, 1962; KILLINGLEY, 1983; and many of the above quoted authors), (2) higher temperatures of the earlier oceans, with the Archean and early Proterozoic water temperatures being in the range of $\geq 60°C$ (KNAUTH and EPSTEIN, 1976; KOLODNY and EPSTEIN, 1976; KNAUTH and LOWE, 1978; SHEMESH *et al.*, 1983; LUZ *et al.*, 1984), and (3) change in the oxygen isotopic composition of sea water over geologic time (WEBER, 1965a,b;

PERRY, 1967; DONTSOVA, 1970; DONTSOVA *et al.*, 1972; FRITZ, 1971; PERRY and TAN, 1972; PERRY *et al.*, 1978). The trend towards lower $\delta^{18}O$ values of chemical sediments, particularly carbonates, with increasing age is minor during the Cenozoic and Mesozoic, but is significant during the Paleozoic and the Precambrian (*cf.* VEIZER and HOEFS, 1976). For the Phanerozoic, there are indications of a major step in the $\delta^{18}O$ age curve during the Late Paleozoic times. If post-depositional alteration were the only cause of the observed secular trend, this could be of some importance for understanding the diagenetic evolution of (bio)chemical sediments, but would not require any modifications in our present understanding of the hydrologic cycle. Development of appropriate criteria (*e.g.* LOWENSTAM, 1961; VEIZER and FRITZ, 1976; VEIZER, 1983a) can aid in selection of the "least altered" samples and in utilization of such samples for classical paleothermometry (EPSTEIN *et al.*, 1951, 1953). Yet, it is curious that practically all published analyses of samples older than 300 million years (see the above references)—including texturally, mineralogically and chemically well preserved fossils from tight enclosing rocks—yield high isotopic "paleotemperatures", suggesting that the isotopic data may reflect a primary rather than a secondary feature. If this is correct, the implications are of considerable geological impact, regardless whether the ultimate cause was high temperature, low $^{18}O/^{16}O$ ratios of seawater, or a combination of the two. If the early oceans were warmer, it would be necessary to identify the cause and to reconcile this with the existing sedimentological and paleoecological records. Alternatively, a change in the

oxygen isotopic composition of seawater would demand modification of our understanding of global balances for rock-water interactions.

In contrast to the oxygen isotope record, secular oscillations in $\delta^{13}C$ of marine bicarbonate have been convincingly demonstrated on a variety of time scales (COMPSTON, 1960; WEBER, 1967; KROOPNICK et al., 1977; SHACKLETON, 1977, 1985; BERGER, 1977; FISCHER and ARTHUR, 1977; SCHOLLE and ARTHUR, 1980; VEIZER et al., 1980; LETOLLE and RENARD, 1980; ARTHUR, 1982; MAGARITZ et al., 1983; RENARD, 1985). In addition, on time scales of 10^7 years, the $\delta^{13}C_{carbonate}$ correlates negatively with $\delta^{34}S_{sulfate}$ (VEIZER et al., 1980) and these two variables also correlate with $^{87}Sr/^{86}Sr_{carbonate}$ and the Phanerozoic "sea level stands" (VEIZER et al., 1982, Table 1; HOLSER, 1984; VEIZER, 1985). To the best of our knowledge, no existing model linking the tectonic factors ($^{87}Sr/^{86}Sr$, "sea level") to the evolution of the biosphere-atmosphere-hydrosphere-sediment system ($\delta^{13}C$, $\delta^{34}S$) explains simultaneously all the observed *signs* of correlations (*cf.* VEIZER, 1985). A workable, geologically realistic, unified theory implied by the above relationships will have to await future developments. Nevertheless, the inverse S-C isotopic relationship is almost certainly a reflection of oxygen transfer, and thus of redox balance, between O and C exogenic cycles (GARRELS and PERRY, 1974; GARRELS and LERMAN, 1981; BERNER et al., 1983). The differences in residence times of marine sulfate and bicarbonate (7.9×10^6 vs 8×10^4 years; HOLLAND, 1978, Table 5-1), however, mean that the degree of coupling of the S and C cycles in the open oceans should be diminished on time scales of $\leqslant 10^6$ years. If so, there should be no correlation between $\delta^{13}C_{carbonate}$ and $\delta^{34}S_{sulfate}$ on a comparable time scale. GARRELS and LERMAN (1981), utilizing the better defined and much more pronounced $\delta^{34}S_{sulfate}$ record, predicted variations in $\delta^{13}C_{carbonate}$ for the Phanerozoic. Their model predicts rapid, large (3‰) oscillations in $^{13}C/^{12}C$ during the Devonian. Therefore, the Devonian record provides the opportunity to test the reality of the predicted $\delta^{13}C$ variations, and of C-S coupling, on time scales of 10^6 years.

It is the aim of this contribution to (1) evaluate whether the observed Paleozoic $\delta^{18}O$ secular trend is a primary or a post-depositional feature of the rock record; (2) if primary, explore the consequences for the terrestrial exogenic system; and (3) test whether the geologic redox coupling of C and S exogenic cycles is fully operative on time scales of $\leqslant 10^6$ years.

APPROACH AND SAMPLES

In order to decipher the isotopic record of ancient oceans it is essential to study mineral phases precipitated from seawater with known isotopic fractionations. In addition, these phases should be relatively stable during their post-depositional history. Among carbonate minerals, low-Mg calcite satisfies these conditions and low-Mg calcitic foraminifera and belemnites have

been routinely utilized for Cenozoic and Mesozoic paleoceanographic studies. For the Paleozoic, brachiopods, because of their abundance, widespread stratigraphic distribution, and low-Mg calcitic mineralogy of their shell may have been a suitable phylum. Virtually all Recent and fossil brachiopods have a multi-(usually two) layered valve composed entirely of low-Mg calcite (JOHNSON, 1951; LOWENSTAM, 1961; WILLIAMS, 1968, 1971; BATHURST, 1975). The only possible exception may have been the family Trimerellidae, where the shell could have been originally aragonitic (JAANUSSON, 1966). According to LOWENSTAM (1961), extant articulate brachiopods secrete their shells reasonably close to oxygen isotopic equilibrium with ambient water, but more definite data are required to exclude the possibility of minor biogenic fractionation. For carbon, recent work of WEFER (1983) demonstrated that living articulate brachiopods fractionate carbon isotopes at the generic level. This observation complicates the possibility of resolving the $\delta^{13}C$ secular variations on 10^6 years time scale, since the knowledge of the degrees of such fractionation for specific genera must be known. Alternatively, a single genus must be utilized for studies of this type.

Despite the relative post-depositional stability of low-Mg calcite, the preservation of the primary isotopic signal should not be *à priori* assumed. Variable degrees of recrystallization and filling of primary and secondary void spaces by diagenetic calcites may have occurred. Utilizing optical (microscopic, staining, SEM) and trace element techniques, AL-AASM and VEIZER (1982) showed that the presently discussed Ordovician brachiopods from Anticosti Island (see Appendix 1) contained $\leqslant 20\%$ diagenetic calcite in their shells. In the present study, we shall employ a similar stable isotope, trace element, and textural approach to evaluate the degree of secondary alteration. The theory and applications of the technique, originally developed for brachiopods as well as belemnites (LOWENSTAM, 1961; VEIZER, 1974; VEIZER and FRITZ, 1976), are summarized in detail in VEIZER (1983a,b). In short, alteration (due to a multitude of mutually reinforcing factors) usually leads to a decrease in Na and Sr and an increase in Mn and Fe contents of the progressively more altered calcites. These trends are frequently accompanied by depletions in ^{18}O and ^{13}C.

SAMPLES AND ANALYTICAL TECHNIQUES

A total of 319 Paleozoic fossils have been separated manually for this study. All were scanned optically, analyzed for $\delta^{18}O$ and $\delta^{13}C$, and 276 samples were analyzed also for trace (Sr, Na, Mn, Fe, Mg) and major (Ca, Insoluble Residue = I.R.) composition. Sample descriptions, locations and analytical data are summarized in Appendix I. Analytical techniques for chemical data and their precisions and accuracies have been described in VEIZER et al. (1978) and BRAND and VEIZER (1980). Isotopic analysis of carbon dioxide, produced by reaction of the sample with 100% H_3PO_4 at 50°C, were carried out on a semi-automatic MM 903 mass-spectrometer with tripple collector system. Analytical reproducibility for individual runs is better than $\pm 0.05‰$ for both $\delta^{18}O$ and $\delta^{13}C$.

The overall reproducibility with respect to the laboratory working standard, expressed in PDB, is $\sim 0.15‰$.

The samples studied range in age from Ordovician to Permian, but the bulk of fossils are of Devonian age, because this time interval was considered critical for the aims of the present study. The present sample population encompasses the families Athyrididae, Atrypidae, Brachythyrididae, Buxtoniidae, Chonetidae, Cyrtospiriferidae, Deltyrididae, Dictyoclostidae, Echinoconchidae, Enteletidae, Fardeniidae, Gigantoproductidae, Linoproductidae, Lissatrypidae, Meekellidae, Meristellidae, Nucleospiridae, Pentameridae, Pholidostrophiidae, Plaesiomyidae, Productellidae, Reticulariidae, Spiriferidae, and Trigonirhynchiidae and contains 38 genera. With the exception of 5 samples from Utah, Alaska, Oklahoma and Kansas, all studied specimens originated from various localities in Canada (Appendix 1). The general geology of Canada is summarized in DOUGLAS (1970).

OXYGEN AND CARBON ISOTOPIC RECORD

The histograms of $\delta^{18}O$ and $\delta^{13}C$ stratigraphic variations in Paleozoic brachiopods are given in Fig. 1. For oxygen, the data show a considerable spread of values, but the most ^{18}O-rich Ordovician, Silurian and Devonian samples are $\sim -4‰$ PDB. The $\delta^{18}O$ for younger samples increases to near-modern values of

FIG. 1. Variations with age of $\delta^{13}C$ and $\delta^{18}O$ in Paleozoic brachiopods.

about $-1‰$ during the Permian, in accord with the previously indicated Late Paleozoic oxygen isotopic shift (cf. VEIZER and HOEFS, 1976). Carbon isotopes show a similar trend towards heavier values, particularly during the Carboniferous and Permian. This is in agreement with the general features of the previously published $\delta^{13}C_{carbonate}$ secular trend (VEIZER et al., 1980; LINDH, 1983; HOLSER, 1984). Nevertheless, the spreads of $\delta^{18}O$ and $\delta^{13}C$ within populations (age groups) are similar to, or in excess of, variations between populations. It is therefore essential to evaluate the role of primary and secondary factors on within population variations of $^{18}O/^{16}O$ and $^{13}C/^{12}C$.

Post-depositional alteration of brachiopod shells

Consideration of the chemical composition of Paleozoic brachiopods shows that their modal values are shifted in the direction expected from post-depositional alteration, although a substantial number of shells still retain primary chemistry (Fig. 2). Factor analysis of the total population (Table 1) identifies four factors controlling the chemical and isotopic composition of brachiopod shells. Factor 1 represents simultaneous loss of Na and Sr from the shells as a result of post-depositional recrystallization. This is principally a consequence of Na and Sr partition coefficients between calcite and ambient water being less than 1 (cf. VEIZER, 1983a). Factor 2 represents mostly precipitation of a later diagenetic Fe, Mn-enriched calcite cement into primary and secondary void spaces. This may also slightly increase the Mg concentrations. These two factors are not a unique feature of the present sample set, but have been ubiquitously recovered and documented in many previous carbonate studies (e.g. BRAND and VEIZER, 1980, 1981; AL-AASM and VEIZER, 1986). Factor 3 is a sole control of carbon isotopic composition. The overall lack of correlation between trace elements and $\delta^{13}C$ is probably due to the fact that post-depositional carbon isotopic variations are of lesser magnitude than the primary scatter caused by the previously discussed biogenic fractionations (vital effect) and by secular variations in carbon isotopic composition of marine bicarbonate. The fourth factor, reflecting the complementary antithetic relationship between carbonate and noncarbonate contents of the shells, is of little interest for the present discussion. Oxygen isotopic composition shows only a very weak affinity to factors 1 and 3, indicating that secular variations in isotopic composition of seawater (or in temperature) and post-depositional recrystallization may all be involved, but the relationships are complex. If the isotopic composition (or the average temperature of seawater) were changing systematically during the Paleozoic, the constituent brachiopod age groups would have been characterized by different starting isotopic compositions. Each age group should be therefore evaluated independently. In particular, the Permian and Devonian populations are of critical importance, because the former may represent the begin-
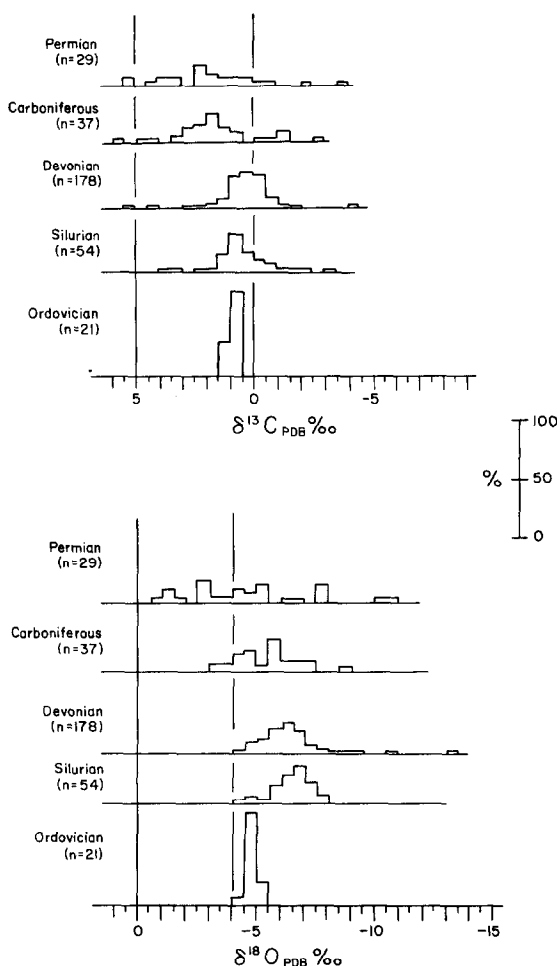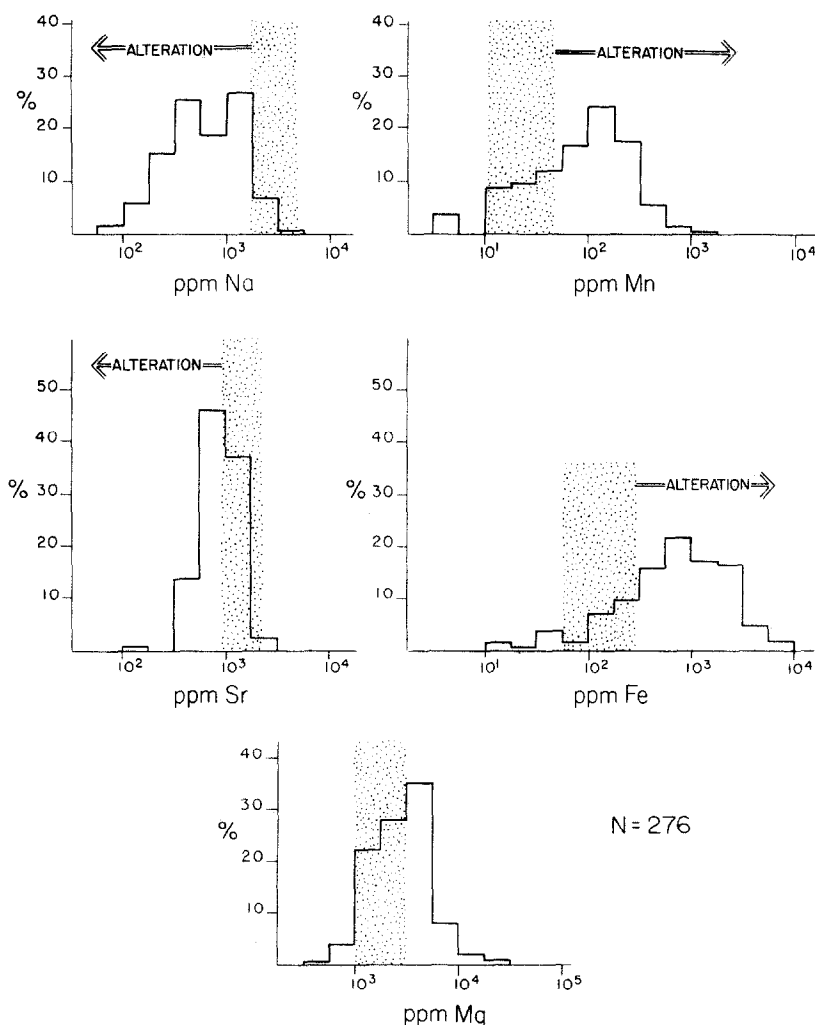
FIG. 2. Histograms of chemical composition of Paleozoic brachiopods. Heavily stippled area represents typical concentrations observed in Recent brachiopods (LOWENSTAM, 1961; POPP et al., 1986b; LEPZELTER et al., 1983; MORRISON and BRAND, 1984). Theoretically expected concentrations for inorganic calcite in equilibrium with present day sea water (cf. the summary in VEIZER, (1983a), as well as ISHIKAWA and ICHIKUNI (1984) and BUSENBERG and PLUMMER (1985) for sodium) fall within the stippled range.

ning of the near-modern conditions, while the latter would mark the termination of the Early-Middle Paleozoic steady-state (cf. Fig. 1).

Factor analyses of Permian brachiopods (Table 2) reveals three dominant factors controlling the chemical and isotopic composition of the shells. Disregarding factor 5 (leaching of Na and Fe from the Insoluble Residue during laboratory digestion of samples), ^{18}O depletion appears to have been controlled by post-depositional recrystallization of the shell calcite. This also causes the loss of Sr and Na (Factor 1). ^{13}C depletion, on the other hand, is related to a subsequent episode of void filling by Mn-rich calcite cement (Factor 2), although the simultaneous decrease in Na and Sr indicates that factors 2 and 1 are not entirely independent. The scattergram of Na (or Sr) versus $\delta^{18}O$ (Fig. 3) clearly shows the depletion of these variables with increasing degree of diagenetic alteration. At Na values typical for Quaternary marine low-Mg calcites, the $\delta^{18}O$

is as heavy as $-1\permil$ PDB. Although the primary $\delta^{18}O$ scatter, due to temperature variations, could be estimated as about $-2.5 \pm 1.5\permil$, the bulk of the trend is clearly due to post-depositional alteration. In a similar manner, the scattergram of $\delta^{13}C$ versus Na (or Mn, Sr) indicates $+4 \pm 1.5\permil$ PDB as the likely primary values (Fig. 4).

In the Devonian population, the trends are less pronounced but nevertheless discernible (Table 3). In this case, in contrast to the Permian, the depletion in ^{18}O is controlled by precipitation of Mn, Fe-rich calcite cement into primary and secondary void spaces (Factor 2). The small gradient in $\delta^{18}O$ (or $\delta^{13}C$), as opposed to the large Mn spread, is a consequence of chemical attributes of the void filling cement. This cement differed from the low-Mg calcite of the shells by more than two orders of magnitude in Mn content, but only by ~3–5‰ in $\delta^{18}O$. Consequently, a small to moderate cementation results in a discernible increase in Mn con-

TABLE 1
VARIMAX ROTATED FACTOR ANALYSIS OF ALL PALEOZOIC BRACHIOPODS

	FACTOR 1	FACTOR 2	FACTOR 3	FACTOR 4
$\delta^{13}C$	0.017	-0.075	0.725	0.089
$\delta^{18}O$	0.352	-0.140	0.351	0.133
log Ca	0.141	0.069	0.061	-0.581
log Mg	0.026	0.252	-0.208	0.025
log Na	0.916	0.006	-0.006	0.016
log Mn	-0.109	0.634	-0.327	-0.095
log Fe	-0.043	0.956	0.130	-0.009
log Sr	0.648	-0.036	0.032	-0.151
Log IR	0.077	0.045	0.269	0.573
Eigenvalue	1.712	1.291	0.951	0.512
Percent of variation explained	38.3	28.9	21.3	11.5
Interpretation	Post-depositional recrystallization and mineralogical stabilization	Void filling by ferroan calcite cement	?	Total carbonate

tent, but only in marginal alteration of the whole shell $\delta^{18}O$. ^{13}C depletion is a consequence of post-depositional recrystallization (Factor 1), the latter also causing the loss of Mg. The scattergram of $\delta^{18}O$ versus Mn (Fig. 5) shows that the heaviest $\delta^{18}O$, at Mn values for Quaternary marine low-Mg calcites, is about $-4‰$ PDB and a conservative estimate for the total primary range is perhaps $-5.5 \pm 1.5‰$. This is $\sim 3‰$ lighter than the estimate for the Permian, regardless whether the total range or the heaviest values are considered. Similarly, the primary range in $\delta^{13}C$ values appears to have been $-0.5 \pm 1.0‰$ PDB (Fig. 6), that is $\sim 4.5‰$ lighter than the Permian.

Similar evaluations for Silurian and Ordovician populations, although less well constrained due to smaller population sizes, indicate $\delta^{18}O$ of $\sim -6.5 \pm 1.5$ and $-5.0 \pm 0.5‰$, respectively. For carbon, the likely primary values are 0.0 ± 1.5 and $+1.0 \pm 0.5‰$. Carboniferous samples show a considerable spread and, at this stage, the likely primary values cannot be narrowed to better than $\sim -4.5 \pm 1.5‰$ for $\delta^{18}O$ and perhaps $+2.0 \pm 2.0‰$ for $\delta^{13}C$. This may be partially a reflection of a considerable secular drift during this time interval (see Fig. 1).

SECULAR VARIATIONS

The above evaluation shows, that the primary difference in $\delta^{18}O$ between the Permian and younger and the Devonian and older brachiopods is at least $3‰$. Complementary results on additional $\geqslant 700$ Paleozoic brachiopods, studied by a comparable trace element and isotope approach (LOWENSTAM, 1961; BRAND and VEIZER, 1981; BRAND, 1981, 1982, 1983; POPP et al., 1986a,b,c; ADLIS et al., 1985), are in full agreement with the outlined secular trend. This observation is supported also by the fact that several mineral phases, with variable stabilities and thus alteration potentials, show overall $\delta^{18}O$ secular trends of comparable magnitudes (cf. WEBER, 1965a,b; VEIZER and HOEFS, 1976; SHEMESH et al., 1983). Our sampling density does not permit the precise timing of the advocated shift, but it may have been confined to the Devonian-Mississippian

transition (POPP et al., 1986c). In the subsequent text, we shall explore the consequences of the above isotopic shift, but will not dwell on the finer scale age structure for $\delta^{18}O$.

Secular variations in $\delta^{13}C$ appear to indicate a continuous enrichment in ^{13}C from Silurian to Permian, in accord with the previously published Phanerozoic curves (VEIZER et al., 1980; LINDH, 1983; HOLSER, 1984). This overall trend is also visible in the Devonian period (Fig. 7), with the selected age groups each representing ~ 7 million years duration. However, the scatter of data is considerable and at least $1‰$ of the total variation can be attributed to differences in biogenic fractionation at the generic level and another $1‰$ represents within genera scatter (Fig. 8). Consequently, brachiopods can be utilized for studies of $\delta^{13}C$ secular variations only at a level of a single genus or even species. Sampling at this level over an extended time interval is, however, difficult. Nevertheless, the reality of the indicated unidirectional Devonian age trend (Fig. 7) is confirmed by the corresponding Eifelian to Frasnian shift in the average $\delta^{13}C$ for the genus Atrypa. No overlapping genera were sampled over the Emsian-Eifelian time span. These difficulties discourage studies of $\delta^{13}C$ secular variations on $\leqslant 10^6$ years time scales. The above qualifications notwithstanding, the unidirectional trend in Fig. 7 is clearly at variance with variations in $\delta^{13}C_{carbonate}$ as predicted by GARRELS and LERMAN (1981). According to their model, the $\delta^{13}C$ of sea water should have been heavy ($\geqslant +1‰$) for the Middle Devonian and light for both the Early and Late Devonian ($\leqslant -1‰$). The Frasnian (Late Devonian) discrepancy between the theory and measurements suggests deterioration of the indirect C-S redox coupling for time scales of $\leqslant 10^6$ years (cf. also HOLSER, 1984); an observation in accord with considerations based on residence times of oceanic sulfate and bicarbonate (see Introduction).

TABLE 2
VARIMAX ROTATED FACTOR ANALYSIS OF PERMIAN BRACHIOPODS

	FACTOR 1	FACTOR 2	FACTOR 5
$\delta^{13}C$	-0.062	0.828	0.337
$\delta^{18}O$	0.826	-0.025	0.347
log Ca	0.427	0.058	-0.220
log Mg	0.028	-0.552	0.449
log Na	0.532	0.347	0.669
log Mn	-0.148	-0.644	-0.009
log Fe	0.020	-0.047	0.804
log Sr	0.520	0.601	0.377
Log IR	0.036	0.252	0.788
Eigenvalue	0.960	1.490	3.303
Percent of variation explained	16.7	25.9	57.4
Interpretation	Post-depositional recrystallization and mineralogical stabilization	Void filling by sparry calcite cement	Leaching from Insoluble Residue during laboratory digestion of samples

Note that, for convenience, factors are numbered as in Table 1. They are not listed in the order of their relative importance.
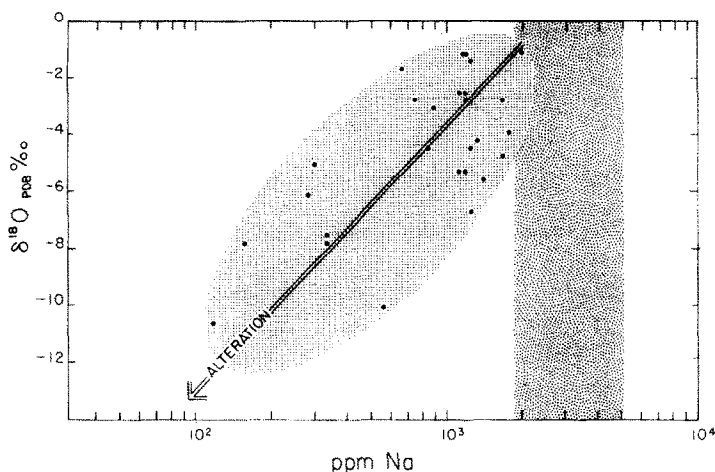
FIG. 3. Scattergram of $\delta^{18}O$ and Na concentrations in Permian brachiopods. See Fig. 2 for explanations.

CAUSES OF O^{18}/O^{16} SECULAR VARIATIONS

Accepting the primary nature of the observed $\delta^{18}O$ signal, it is essential to search for causal relationships.

Biogenic fractionation

It may be suggested that the changing Late Paleozoic $\delta^{18}O$ signal reflects an evolution in biogenic fractionation of oxygen isotopes by brachiopods. This, however, is unlikely because the trend is also observed in the well preserved skeletal material of other phyla, such as rugose corals, crinoids and some mollucs (BRAND and VEIZER, 1981; BRAND, 1981, 1982, 1983; LEU-TLOFF and MEYERS, 1984), in inorganic marine cements (LOHMAN, 1983; JAMES and CHOQUETTE, 1983), and in bulk rocks (VEIZER and HOEFS, 1976). This argues for a cause of more fundamental significance, such as changing salinity, temperature, or oxygen isotopic composition of sea water.

Salinity

Living and fossil brachiopods are exclusively marine organisms living in normal salinity waters (RUDWICK, 1970; TASCH, 1980). This and their usual association with tabulate corals and crinoids as a Paleozoic offshore community (SEPKOSKI and MILLER, 1985) preclude growth in water of other than normal salinity.

Temperature

Living brachiopods are known from all climatic zones, with inarticulates living predominantly in subtropical-tropical and articulates in temperate regions (RUDWICK, 1970, p. 159). Their present-day habitats therefore span the whole $\leqslant 30°C$ temperature range of oceanic water masses. The optimal habitats for Paleozoic brachiopods may have been comparable, but all presently studied specimens grew at low-paleolatitudes, as indicated by paleomagnetic (HABICHT, 1979) and
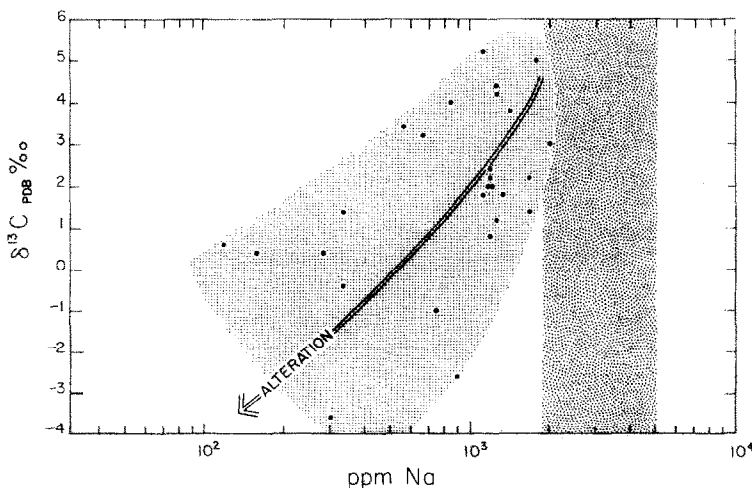

FIG. 4. Scattergram of $\delta^{13}C$ and Na concentrations in Permian brachiopods. See Fig. 2 for explanations.

TABLE 3
VARIMAX ROTATED FACTOR ANALYSIS OF DEVONIAN BRACHIOPODS

	FACTOR 1	FACTOR 2	FACTOR 4
$\delta^{13}C$	-0.473	-0.031	0.014
$\delta^{18}O$	0.081	-0.445	0.067
log Ca	-0.058	0.108	-0.436
log Mg	0.553	0.454	-0.020
log Na	0.744	-0.336	0.071
log Mn	-0.040	0.946	0.014
log Fe	-0.082	0.762	-0.208
log Sr	0.745	-0.195	0.141
Log IR	0.001	-0.020	0.859
Eigenvalue	1.519	2.287	0.790
Percent of variation explained	32.3	48.6	19.2
Interpretation	Post-depositional recrystallization and mineralogical stabilization	Void filling by ferroan sparry calcite cement	Total carbonate

Note: see Table 2.

sedimentological (FRAKES, 1979; ZIEGLER et al., 1977) criteria. The present day tropical-temperate temperature barrier is at winter temperatures of ~15-18°C (HALL, 1964; DODD and STANTON, 1981, p. 448) and this may or may not have been also the low-temperature limit for the studied Paleozoic communities. In any case, it is not the low, but the high-temperature limit, which is posing problems in subsequent interpretations. Assuming 0‰ SMOW as the oxygen isotopic composition of the surficial low-latitude Paleozoic sea water, the calculated temperature of the ambient Permian ocean water would be ~26 ± 5°C. In contrast, the ambient ocean temperature for Devonian and older seas would have to be at least ~35 ± 4°C, and possibly more for some marginal Devonian (Fig. 5) and Silurian samples. If "non-glacial" $\delta^{18}O_{water}$ of −1‰ SMOW (e.g. BERGER, 1979) were accepted, the above temperatures would decrease by ~4.5°C. For the present discussion, the glacial effect is considered of subordinate impor-

tance because both, the "cold" post- and the "warm" pre-Carboniferous oceans coexisted, at one time or another, with glacial as well as non-glacial climates. Yet, the ≥3‰ $\delta^{18}O$ difference between Early-Middle and Late Paleozoic brachiopods is a persistent feature. The validity of the above statement is, however, conditional on the assumption that Phanerozoic glaciations were of comparable magnitude to the Cenozoic one. The presently known large scale glaciations have been described from the Early Proterozoic, Late Proterozoic, Late Ordovician-Early Silurian, Late Devonian (Famennian)-Late Permian, and Cenozoic (SCHWARZ-BACH, 1963; FRAKES, 1979; BUDYKO, 1977; CROWELL, 1982; CAPUTO and CROWELL, 1985; HAMBREY and HARLAND, 1985), with the terminal Proterozoic one possibly reaching even low latitudes (MCWILLIAMS and MCELHINNY, 1980). Each of these glacial episodes lasted ≥10-20 million years (FAIRBRIDGE, 1982) and during the Paleozoic Era glaciations appear to have been the norm and not the exceptions (CAPUTO and CROWELL, 1985). The usual defense against coexistence of the supposedly "hot" (≥60°C) Proterozoic oceans with glacial climates is an invoked large diachronism of glacial and non-glacial sediments (e.g. KNAUTH and LOWE, 1978). A similar resort to diachronism is not a viable proposition for the Phanerozoic, where the synchroneity of glacial climates with the "warm" Paleozoic oceans is undeniable. In our view, 35 ± 4°C (and more for the Proterozoic) warm low-latitude oceans and simultaneous, possibly even low-latitude (e.g. the terminal Proterozoic), widespread glaciations are difficult to reconcile. Note that even during the ice free times of the Cretaceous, the equatorial surface ocean temperatures did not exceed, and likely were less than, 32°C (FRAKES, 1979, chapter 6; SAVIN and YEH, 1981), although the temperate climates stretched into high latitudes. Furthermore, the brachiopod community with coexisting rugose corals, crinoids, and other phyla was relatively stable during the Phanerozoic (RUD-
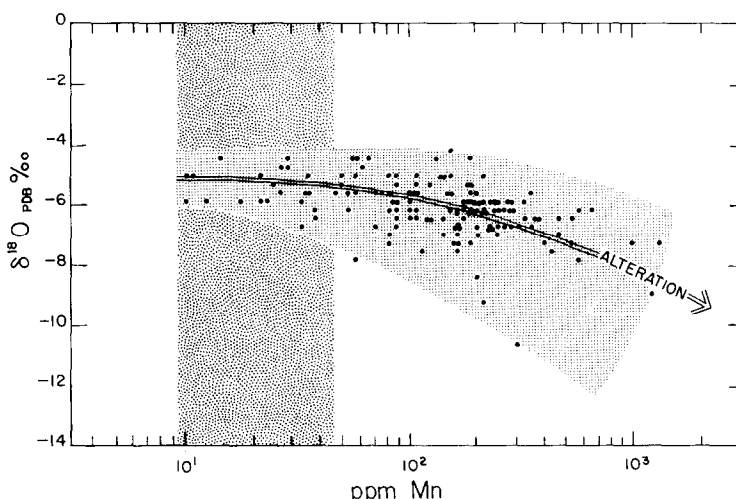
FIG. 5. Scattergram of $\delta^{18}O$ and Mn concentrations in Devonian brachiopods. See Fig. 2 for explanations.
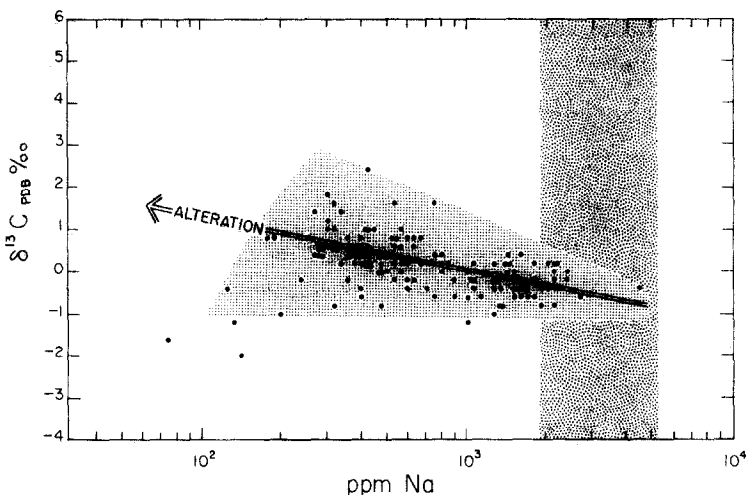
FIG. 6. Scattergram of $\delta^{13}C$ and Na concentrations in Devonian brachiopods. See Fig. 2 for explanations.

WICK, 1970; SEPKOSKI and MILLER, 1985) and the proposition that the same pre-Carboniferous community should have lived in habitats $\sim 10°C$ warmer than its later counterpart is paleoecologically unpalatable. This is quite apart from the question of whether living marine communities containing, among others, molluscs could have thrived, as opposed to barely survive, in permanent 35 ± 4°C habitats (cf. READ, 1963). For example, collagen, a body protein present in several metazoan phyla, collapses in thriving reproductive populations at upper limits of these temperatures (RIGBY, 1968; RIGBY and HAFEY, 1972). Furthermore, BROCK (1985) concluded that 38°C is the upper limit of tolerance for aquatic vertebrates. As a final point, some meteorologists argue that $\sim 31°C$ is an upper

limit on the temperature of the surface ocean water for atmospheric radiation balances not vastly departing from the present-day conditions (NEWELL and DOPPLICK, 1979).

We would like to emphasize that none of the above arguments is unequivocal (see, for example, VALENTINE, 1985), but their combined weight suggests that the temperature effect alone was not the principal cause of the observed Late Paleozoic $\delta^{18}O$ shift of $\sim 3‰$. Additional support comes from the extention of the isotopic record into the Proterozoic and the Archean. As stated above, the presently known record would demand $\geqslant 60°C$ warm oceans in temporal and/or spatial proximity with the well established Early Proterozoic glaciations (e.g. FRAKES, 1979, p. 38). Further-
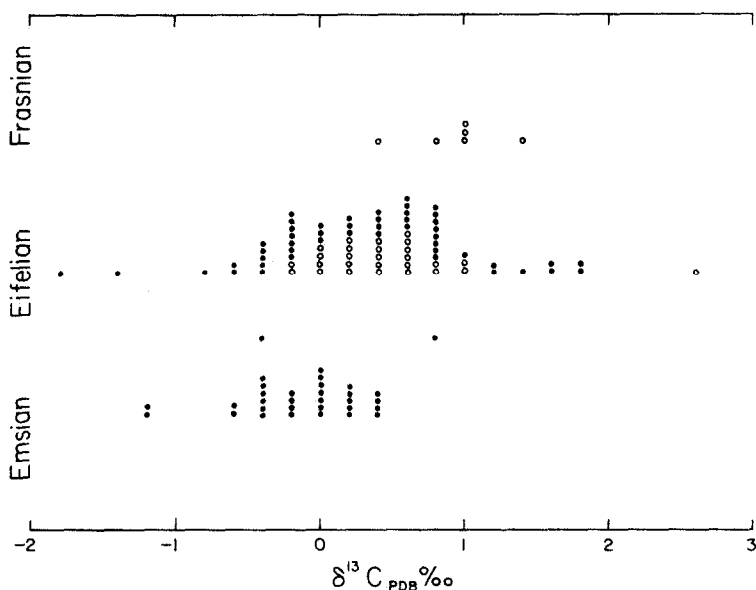
FIG. 7. Histogram of $\delta^{13}C$ variations in Emsian (Early Devonian), Eifelian (Middle Devonian) and Frasnian (Late Devonian) brachiopods. Empty circles—genus Atrypa, full dots—other genera.
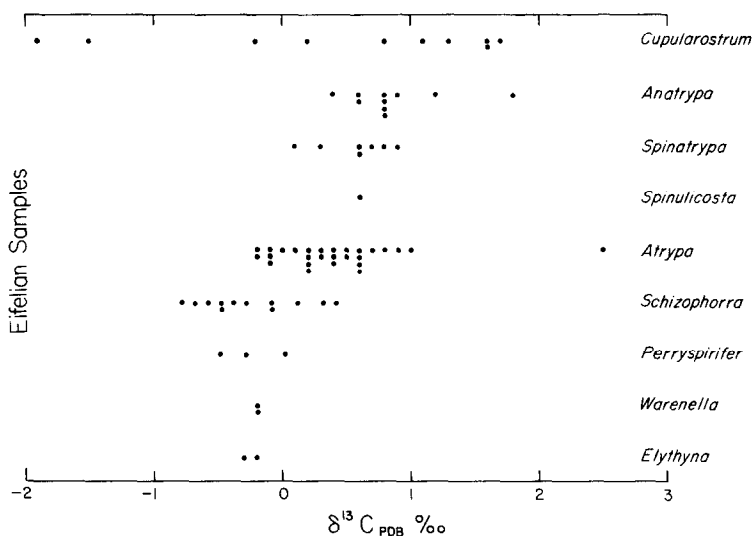
FIG. 8. $\delta^{13}C$ distribution in various Eifelian (Middle Devonian) brachiopod genera.

more, HOLLAND (1978, p. 205) pointed out that equilibrium temperature for sea water saturated with respect to halite, anhydrite, and gypsum is 18°C, and gypsum precipitates from seawater only at temperatures ≤58°C. The gypsum-halite association is therefore indicative of temperatures ≤25°C (HOLLAND, 1984, p. 427). Evaporites with this mineralogical assemblage, although not necessarily coprecipitated, have been ubiquitous throughout the Phanerozoic (e.g. BRAITCH, 1962) and they have been documented as far back as 1.6 Ga ago (MUIR, 1979). Furthermore, the discovery of gypsum casts in sequences as old as 3.5 Ga precludes at least the existence of the postulated 60–70°C Archean oceans (WALKER et al., 1983).

Isotopic composition of sea water

The above elimination process leaves the evolution in oxygen isotopic composition of sea water as the only presently known alternative. The buffering of $^{18}O/^{16}O$ in sea water by interactions with silicates at high- and low-temperatures (crossover ~300 ± 50°C) has been discussed previously by CHASE and PERRY (1972), MUEHLENBACHS and CLAYTON (1976), PERRY et al. (1978), LAWRENCE and GIESKES (1981) and GREGORY and TAYLOR (1981). Overall, a net enhancement of high-temperature interactions will tend to enrich sea water in ^{18}O and vice versa. The observed Late Paleozoic $\delta^{18}O$ increase of ~3‰ would therefore demand a substantial enhancement in the rate of high temperature oxygen isotopic exchange (plutonism, deep ocean ridge circulation, etc.) relative to low-temperature processes (e.g. shallow ridge circulation, submarine weathering). This is an attractive proposition, because the Late Paleozoic interval is also a time of very pronounced variations (Fig. 9) in marine $^{87}Sr/^{86}Sr$ (PETERMAN et al., 1970; VEIZER and COMPSTON, 1974; BURKE et al., 1982; POPP et al., 1986b), $\delta^{13}C$ (VEIZER et al., 1980; LINDH, 1983; HOLSER, 1984), $\delta^{34}S$ (CLAY-

POOL et al., 1980; HOLSER, 1984), and in "sea level" stands (VAIL and MITCHUM, 1979). These oscillations, at 10^7 years frequency, have likely been controlled by global tectonism (VEIZER, 1985) and global tectonism may have modulated also the rate of high/low-temperature exchange of oxygen between silicate crust and sea water. At this stage, we do not have the necessary stratigraphic sampling resolution to decide whether the inferred $\delta^{18}O$ shift coincides with a specific Late Paleozoic inflection in the complementary isotopic curves. Similarly, we are not in a position to establish or disclaim the existence of possible second order, less than ±1‰, variations within the overall Paleozoic $\delta^{18}O$ secular trend.

Despite our preference for this solution, three sets of arguments mitigate against its unquestionable acceptance. Firstly, KNAUTH et al. (1985) and KNAUTH and BEEUNAS (1986) analyzed fluid inclusions from Phanerozoic salts, believed to represent unmodified trapped sea water, and reported near-present day $\delta^{18}O$ (but not δD) values as far back as the Silurian. Secondly, the patterns of $\delta^{18}O$ distributions in secondary minerals of greenschist facies metabasalts on the modern ocean floor (MUEHLENBACHS and CLAYTON, 1972; STAKES and O'NEIL, 1982), in Cretaceous ophiolitic sections (GREGORY and TAYLOR, 1981), and in the Archean greenstones (BEATY and TAYLOR, 1982; SMITH et al., 1984) are similar. This is consistent with their interpretation as products of alteration by sea water with $\delta^{18}O$ of about 0‰ (SMOW). Thirdly, MUEHLENBACHS and CLAYTON (1976) and GREGORY and TAYLOR (1981) proposed that sea water $\delta^{18}O$ is buffered at 0‰ (SMOW) by the competing and complementary interactions with silicates of oceanic crust at low and high-temperatures. Accepting these balances, it is impossible to generate the inferred 3‰ shift in $\delta^{18}O$ of the Paleozoic sea water. The difficulty is compounded by preliminary indications (POPP et al., 1986c) that the oxygen isotopic shift may have been restricted to the
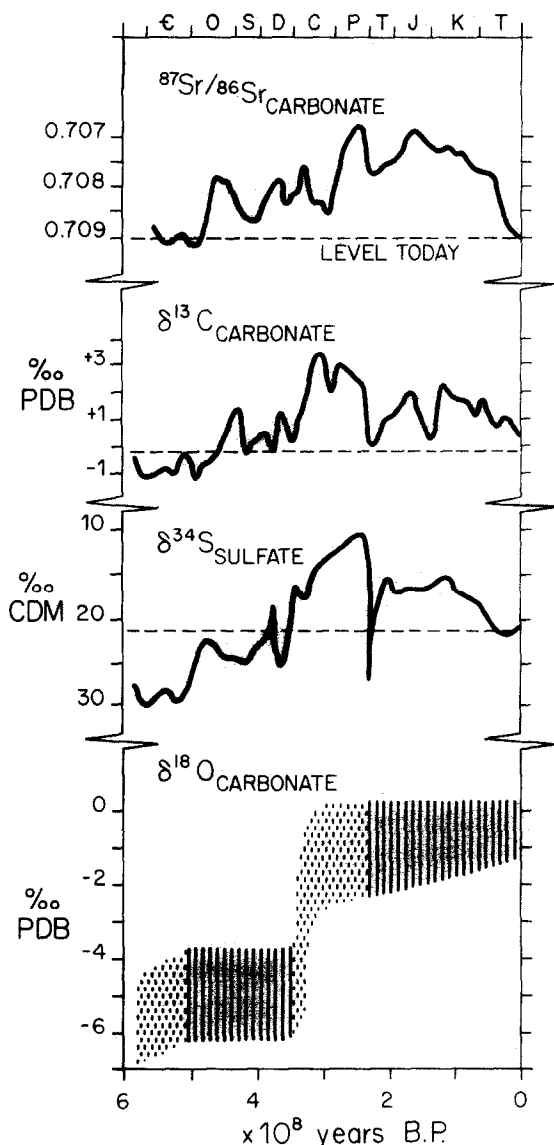
FIG. 9. Secular isotopic age curves for sea water as derived from (a) sulfur isotopes in evaporite sulfate, (b) carbon isotopes in carbonates, (c) strontium isotopes in carbonates and fossil apatites, and (d) the tentative oxygen isotopes in carbonates, principally brachiopods. For sources of these curves see the text and HOLSER (1984).

Devonian-Mississippian transition and thus could have been rapid.

As was the case with temperatures, none of the above arguments is unequivocal. The fluid inclusion studies need confirmation and explanation of the disparity between oxygen and hydrogen isotopic compositions. The plausible alteration argument entails a plethora of assumptions, such as the degree of sea water participation in alteration processes, the degree of silicate/water equilibration or water/rock ratio, the starting isotopic composition of parental material, metamorphic and crystallization temperatures, etc. This is particularly the case for the pre-Cretaceous studies. Finally, the tightness of the balance argument is conditional on

our present knowledge of the silicate/water exchange reservoir sizes and fluxes. These are open to discussion (PERRY et al., 1978), particularly around subduction zones and in orogenic belts. At this stage, we do not discount therefore the possibility that a change in the oxygen isotopic composition of sea water could have been induced by tectonic phenomena. A resolution or quantification of this question will not only improve our understanding of the hydrologic cycle, but may also provide a tool for understanding the tectonic evolution of the Earth and, after appropriate corrections, perhaps also the temperature history of its surface.

CONCLUSIONS

Combined trace element and isotopic study of Paleozoic brachiopod shells leads to the following conclusions:

1) Paleozoic brachiopods fractionated carbon isotopes at the generic level;

2) In accord with previous studies, Paleozoic brachiopods reflect a general enrichment in ^{13}C in the course of the Paleozoic, with major enrichment in the Permian;

3) The previously described negative correlation of marine $\delta^{34}S_{sulfate}$ and $\delta^{13}C_{carbonate}$ (VEIZER et al., 1980) is valid only at time resolutions of 10^7 years;

4) The $\delta^{18}O$ record of brachiopod shells shows $\sim 3\%_0$ depletion in ^{18}O during the Late Paleozoic, with Devonian and older samples having $\delta^{18}O$ of $\leqslant -4\%_0$ PDB;

5) The proposed oxygen isotopic shift may be a consequence of changing $^{18}O/^{16}O$ of the coeval sea water, of warmer (35 ± 4°C) Early and Mid-Paleozoic oceans, or both. Our preference is for the first alternative, but both solutions pose problems for complementary geological observations.

6) The acceptance of the Paleozoic brachiopod data as representative of secular variations for $\delta^{18}O$ leads to consequences of first order significance, regardless of the actual cause(s) of the oxygen isotopic shift. If the data indeed reflect a changing $^{18}O/^{16}O$ composition of sea water, they may indicate the existence of a global tectonic event(s) which caused a net increase of high-temperature oxygen exchange between sea water and silicate crust. If they reflect paleotemperatures, the co-existence of persistent Paleozoic glaciations with 35 ± 4°C low-latitude oceans requires reconsideration of the existing paleoclimatic models. If neither proposition proves satisfactory, alternative solutions must be explored, such as, for example, the possible consequences of the expansion of vascular plants and animals on land in the Devonian.

Al-Aasm; and discussions with Yehoshua Kolodny, L. S. Land, K. M. Towe, S. M. Savin, and J. R. O'Neil.

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APPENDIX 1: Sample descriptions by geologic age and locality. Mg to Sr on I.R. free basis.

SAMPLE NO.	SPECIES	PDB C 13	PDB O 18	PPM MG	PPM NA	PPM MN	PPM FE	PPM SR	% I.R.
PERMIAN									
Assistance Formation, Marie Bay, Melville Island, NWT									
410	Dictyoclostus sp.	1.9	-4.2	1709	1368	480	1292	929	3.80
411	Dictyoclostus sp.	2.0	-5.3	1705	1180	440	1406	836	2.96
Assistance Formation, Sabine Peninsula, Melville Island, NWT									
421	Liostella sp.	5.0	-3.8	2089	1804	54	1150	910	15.21
Takhandit Formation, south side of Yukon River, Yukon									
402	Linoproductus sp.	3.8	-5.5	1927	1403	15	4903	959	83.57
Acheson watershed west, NWT									
403	Spirifer sp.	4.1	-4.6	3709	863	5	2313	848	19.50
Dry Canyon, Wasatch Mtns., Utah									
422	Pustula subhorrida	1.5	-7.9	4936	342	69	1020	338	48.81
Kandik, Alaska									
414	Echinoconchus sp.	3.3	-4.1						
416	Linoproductus sp.	1.4	-4.7	5989	1637	129	6957	984	27.91
Northern Yukon									
419	Dictyoclostus cf. depressus	2.4	-1.0	3657	1196	5	427	1008	7.08
420	Waagenochonchia sp.	-2.5	-3.2	3537	880	55	2182	759	8.52
428	Dictyoclostus uralicus	0.9	-2.6	2222	1186	12	125	834	13.66
Ogilvie Mtns., Jungle Creek, NWT									
423	Dictyoclostus sp.	3.3	-7.6						
Peace River, La Biche River, Alberta									
405	Spirifer sp.	-0.3	-7.6	1264	344	115	464	401	10.99
424	Dictyoclostus sp.	-0.9	-2.9	2288	734	155	271	532	1.07
425	Spirifer sp.	-3.6	-5.1	2168	303	192	240	375	0.54
Peel Plateau, Mt. Effie, NWT									
427	Indet. terebratulid	0.4	-7.8	826	163	47	326	656	0.10
Peel Plateau, Peel River, NWT									
408	Dictyoclostus sp.	2.2	-2.7	2286	1675	41	820	945	50.31
409	Dictyoclostus sp.	1.3	-1.4	2893	1280	17	1394	899	19.60
412	Spirifer sp.	3.0	-1.2	1638	2012	5	928	1290	12.01
413	Dictyoclostus sp.	1.8	-2.6	2365	1091	42	433	952	24.90
415	Dictyoclostus sp.	2.2	-1.2	2842	1205	16	1022	2357	32.68
417	Indet. terebratulid	3.3	-1.6	708	683	5	875	677	4.96
418	Indet. rhynconellid	0.7	-10.6	1308	118	26	69	352	0.29
426	Dictyoclostus sp.	2.1	-2.9	2566	1162	27	2569	1215	25.23
Sheep Creek, NWT									
404	Spirifer sp.	3.5	-10.1	1579	558	10	468	972	57.94
West of Bear Creek, NWT									
406	Spirifer sp.	4.5	-6.8	491	1234	5	129	1405	1.33
407	Spirifer sp.	5.2	-5.3	736	1127	5	1247	1305	10.40
locality unknown									
400	Linoproductus cf. lineatus	0.4	-6.1	9148	276	182	641	437	0.52
401	Dictyoclostus cf. neoinflatus	4.2	-4.4	2245	1231	53	1441	837	54.11
CARBONIFEROUS									
Banff Formation, Beaver River, NWT									
310	Choristites esplanadensis	1.5	-4.9	2507	690	157	35	693	30.94
Banff Formation, Wapiti Lake, BC									
323	Spirifer esplanadensis	-1.2	-7.1						
Boggy Shale Formation, Stonewall, Oklahoma									
429	Marginifera muricatina	1.3	-3.8	3502	1620	564	2067	1116	4.90
Mt. Head Formation, Lizard Range, NWT									
318	Gigantoproductus sp.	-1.5	-6.7	6168	462	5	32	1154	0.01
Mt. Head Formation									
314	Gigantoproductus brazeriarus	-0.2	-5.6	1902	788	27	217	944	38.39
Pekisko Formation, Jockfish, Yukon									
329	Spirifer sp.	2.7	-4.2	3493	1066	16	337	945	6.56
Pekisko Formation, Liard River, Nahanni Butte, NWT									
309	Spirifer centronatus	2.6	-4.1	1535	271	33	643	1198	4.20
Pekisko Formation, Monoghan Creek									
306	Spirifer centronatus	3.0	-4.6	4121	1077	10	626	803	0.32
Pekisko Formation, Moose Dome area, BC									
302	Spirifer minnewankensis	1.7	-4.2	4711	1099	11	130	1082	0.82
Pekisko Formation, Mt. Rundle, Alberta									
320	Brachythyris sp.	3.2	-3.6	7230	316	14	164	921	0.58
Pekisko Formation, Nahanni Range, NWT									
311	Spirifer cf. striatus	-2.6	-5.3	1701	1041	16	290	1124	67.94
Pekisko Formation, Wapiti Lake, BC									
328	Spirifer striatus	2.9	-5.8	3327	603	23	108	1237	0.25
Pekisko Formation									
313	Syringothyris sp.	2.1	-5.6	1517	721	10	117	1269	32.28
Rundle Formation, Slate Creek, BC									
325	Rhipidomella sp.	0.6	-6.2						
Shunda Formation, Ant Creek, Yukon									
305	Spirifer aff. rowleyi	2.3	-5.0	1577	1307	26	602	957	23.40
331	Spirifer aff. rowleyi	2.5	-4.1	971	966	5	166	1015	18.31
Shunda Formation, Nahanni Ridge, NWT									
300	Spirifer aff. rowleyi	1.5	-5.0	1243	519	13	139	1219	25.66
315	Spirifer aff. rowleyi	1.7	-4.3	828	527	16	15	750	31.86
317	Buxtonia sp.	0.6	-6.5	3144	462	54	190	485	38.84
Shunda Formation									
330	Spirifer rowleyi	1.6	-5.6	1464	287	26	187	867	18.44

SAMPLE NO.	SPECIES	PDB C 13	PDB O 18	PPM MG	PPM NA	PPM MN	PPM FE	PPM SR	% I.R.
Wetumka Formation, near Ada, Oklahoma									
431	Mesolobus mesolobus	0.7	−4.8	5067	2239	180	940	949	10.95
Beaver Dam, BC									
327	Martinia rostrata	−1.4	−8.6	4050	813	85	399	947	2.86
Canyon Creek, Moose Dome, BC									
307	Syringothyris cf. hannibalensis	5.7	−3.1	1707	134	44	684	1505	4.87
Captain Creek Island, Ottawa, Kansas									
433	Enteletes hemiplicata	2.0	−7.4	2153	193	778	2590	1338	0.33
Moose Lake, BC									
321	Spirifer esplanadensis	−0.6	−6.7	3900	474	152	1072	1469	1.15
326	Spirifer sp.	1.5	−5.9	2990	584	89	1126	1276	1.16
Mt. Greenock, Alberta									
301	Cleiothyridina lata	1.1	−5.3	7417	1187	35	714	1430	3.98
Mt. Hannington, BC									
322	Spirifer sp.	2.7	−3.4	1518	203	29	701	151	10.10
324	Spirifer esplanadensis	1.8	−5.7	2570	295	57	835	667	54.17
Nahanni Ridge area, NWT									
312	Spirifer aff. rowleyi	1.5	−4.6	865	420	12	69	907	16.78
Ogilvie Mtns., Jungle Creek, NWT									
430	Indet. brachiopod	4.3	−7.5	3189	1369	388	5394	1244	29.77
432	Indet. brachiopod	4.5	−5.6	1616	769	10	713	545	31.34
Pekisko Lake, Nahanni Ridge, NWT									
316	Cleiothyridina sp.	2.1	−5.8	5599	359	38	490	589	33.56
Slate Creek, BC									
303	Spirifer minnewankensis	1.8	−6.4	5320	260	16	10	552	0.15
Wapiti Lake, BC									
319	Punctospirifer sp.	2.0	−6.8	2408	661	96	352	1236	0.20
Wapiti Pass, BC									
304	Setigerites setigerus	1.0	−5.9	5658	349	60	1294	473	43.74
308	Maginata sp.	1.2	−5.9	2216	632	54	1134	562	58.02
U.DEVONIAN									
Hay River Formation, Hay River, NWT									
HR-1A	Atrypa cosmeta	1.4	−5.9	1010	272	86	429	425	19.61
HR-1B	Atrypa cosmeta	0.8	−6.2	1421	667	151	914	700	5.36
HR-1C	Atrypa cosmeta	0.9	−5.6	1512	538	185	923	659	5.37
HR-2A	Atrypa cosmeta	1.0	−6.3	1955	430	215	1434	618	4.09
HR-2B	Atrypa cosmeta	1.0	−6.4	1571	441	172	865	628	5.94
HR-3	Atrypa cosmeta	0.4	−6.3	2662	742	291	2238	738	6.48
M.DEVONIAN									
Bird Fiord Formation, Bathurst Island, NWT									
7	Anatrypa (Variatrypa) arctica	0.7	−5.8	2022	358	194	1577	733	1.63
8	Spinatrypa (Spinatrypa) borealis	0.7	−6.1	2258	323	184	599	550	1.65
9	Anatrypa (Variatrypa) arctica	0.5	−6.5	1330	273	359	2604	455	0.88
10	Spinatrypa (Spinatrypa) borealis	0.8	−6.3	2693	192	208	396	984	1.27
11	Anatrypa (Variatrypa) arctica	1.8	−7.6	1443	297	161	2603	433	3.99
12	Schizophoria sulcata	0.4	−6.4	4499	1436	325	1077	1002	2.29
13	Spinatrypa sp.	0.1	−6.2	3053	562	577	286	1093	5.54
14	Atrypa sp.	1.0	−6.3	1391	317	186	1222	513	1.89
15	Cupularostrum sp.	−1.9	−8.9	2698	138	1190	5811	722	0.17
16	Anatrypa (Variatrypa) arctica	0.4	−5.5	1692	390	155	1246	611	0.30
17	Anatrypa (Variatrypa) arctica	0.7	−6.0	1527	323	173	1597	437	1.61
18	Spinatrypa (Spinatrypa) borealis	0.9	−6.7	2723	622	200	790	937	3.87
19	Anatrypa (Variatrypa) arctica	0.7	−6.1	1864	279	248	2703	448	2.26
20	Cupularostrum repetitor	1.6	−6.5						
21	Schizophoria sulcata	0.3	−5.9	5260	1377	328	2770	929	1.80
22	Cupularostrum repetitor	−1.5	−7.4	1703	76	1250	7764	487	0.36
23	Anatrypa (Variatrypa) arctica	0.7	−5.0	1078	363	138	2346	509	2.08
24	Cupularostrum repetitor	1.3	−6.9						
25	Schizophoria sulcata	0.1	−5.7	4514	2344	106	872	1161	1.23
26	Spinatrypa (Spinatrypa) borealis	0.6	−5.6	1437	617	76	353	1263	12.67
27	Anatrypa (Variatrypa) arctica	0.5	−6.1	2348	288	288	2021	767	1.73
28	Cupularostrum repetitor	−0.2	−6.6						
29	Anatrypa (Variatrypa) arctica	0.8	−6.6	1807	253	258	2070	1069	9.35
30	Cupularostrum repetitor	1.7	−7.4	3204	528	181	2476	866	6.34
31	Anatrypa (Variatrypa) arctica	1.1	−6.4	2143	298	106	720	656	1.73
32	Schizophoria sulcata	−0.1	−6.7						
33	Anatrypa (Variatrypa) arctica	1.0	−6.4						
34	Spinatrypa (Spinatrypa) borealis	0.2	−5.7	3049	814	347	913	1147	8.52
35	Anatrypa (Variatrypa) arctica	1.1	−6.8	2866	576	274	2132	798	4.59
36	Spinatrypa (Spinatrypa) borealis	0.4	−6.4	1420	427	363	3419	603	1.49
37	Cupularostrum repetitor	2.7	−8.6						
38	Schizophoria sulcata	0.2	−6.6	5138	1408	253	2717	997	3.37
39	Atrypa arctica	0.4	−6.3	2174	282	249	1581	1006	1.42
40	Cupularostrum repetitor	−0.9	−7.4	2663	204	949	2169	670	5.64
41	Schizophoria sulcata	0.1	−7.2	5113	1464	402	3550	958	5.19
42	Spinatrypa sp.	−0.3	−6.2						
43	Schizophoria sulcata	−0.4	−6.0	3927	1507	278	1151	1087	0.44
44	Atrypa arctica	0.8	−7.8						
45	Schizophoria sulcata	−0.1	−6.9	4460	2114	137	833	1296	2.20
46	Spinatrypa (Spinatrypa) borealis	0.4	−7.1	2457	498	241	371	899	21.27
47	Cupularostrum repetitor	−0.4	−7.7	2681	127	545	4351	503	4.58

SAMPLE NO.	SPECIES	PDB C 13	PDB O 18	PPM MG	PPM NA	PPM MN	PPM FE	PPM SR	% I.R.
48	Cupularostrum repetitor	0.6	-6.1	4667	279	630	5702	816	3.54
49	Schizophoria sulcata	0.2	-6.7	5563	845	162	1269	1171	1.97
50	Cupularostrum repetitor	2.2	-7.6						
51	Spinatrypa (Spinatrypa) borealis	0.2	-6.7	3506	575	344	782	881	6.26
52	Spinatrypa sp.	-0.5	-7.4	2194	1108	529	1353	1153	1.25
54	Spinatrypa sp.	-0.7	-6.4	1612	319	511	5313	917	2.08
55	Spinatrypa sp.	-0.4	-7.6	3152	579	418	4047	1841	2.06
56	Schizophoria sulcata	-0.7	-6.2						
57	Atrypa sp.	0.6	-6.9	2396	348	204	1489	758	0.25
58	Warrenella sp.	0.3	-5.4	1082	2140	26	94	1684	20.48
59	Anatrypa (Variatrypa) arctica	0.5	-6.3	2193	347	169	701	2944	1.14
60	Cupularostrum sp.	-1.0	-7.9						
61	Atrypa sp. A	0.2	-6.0	4016	419	187	1934	1246	0.69
62	Cupularostrum sp.	4.4	-10.7						
Bird Fiord Formation, Devon Island, NWT									
110	Atrypa sp.	0.7	-5.4	1884	283	192	1197	560	1.25
111	Schizophoria sulcata	-0.1	-6.0	6390	2344	200	1984	957	0.32
112	Atrypa sp.	0.6	-5.5	2028	277	156	2202	585	0.97
120	Schizophoria sulcata	-0.4	-5.0	3942	405	22	141	1067	2.94
127	Atrypa sp.	0.5	-5.0	1469	396	82	989	651	2.95
128	Spinulicosta sp.	0.6	-5.1						
129	Cupularostrum sp. A	1.1	-6.6						
Bird Fiord Formation, Ellesmere Island,									
1	Atrypa sp.	0.5	-5.9	2464	348	222	2613	586	2.40
2	Atrypa sp.	-0.1	-6.1	1300	349	221	3786	436	1.23
3	Spinatrypa (Spinatrypa) borealis	0.3	-6.3	1452	428	200	2708	405	0.33
4	Atrypa sp.	0.3	-5.4	1193	430	110	2301	540	1.24
5	Atrypa sp.	0.4	-6.4	1129	373	123	2584	493	1.53
6	Cupularostrum repetitor	0.2	-6.4						
63	Atrypa sp.	0.6	-4.9	1998	304	145	1943	590	2.03
64	Schizophoria sulcata	0.0	-6.4						
65	Spinulicosta sp.	0.1	-7.2						
84	Cupularostrum sp.	1.6	-6.1	2609	316	181	2537	2121	4.12
85	Atrypa sp. B	0.3	-5.8	1583	395	85	506	804	2.78
86	Atrypa sp. B	0.1	-6.5	2470	494	119	1328	837	1.72
104	Atrypa sp. C	0.4	-6.6	1866	465	236	986	576	1.72
105	Atrypa sp.	-0.2	-5.9	3599	916	10	1240	681	1.36
106	Atrypa sp.	0.2	-6.4	2437	590	143	1770	763	6.67
107	Atrypa sp.	-0.5	-5.1	1605	1544	57	416	1054	0.16
108	Atrypa sp. B	2.5	-7.3	3957	422	82	538	457	0.51
109	Atrypa sp.	0.9	-5.4	1900	348	180	52	902	17.26
116	Elythyna sverdrupi	-0.3	-4.6						
117	Atrypa sp.	-0.1	-6.0	2587	235	252	397	580	6.45
118	Schizophoria sulcata	-0.3	-6.9	4416	1077	453	2651	628	4.27
123	Atrypa sp. B	0.2	-5.7						
125	Schizophoria sulcata	-0.5	-6.3	3768	397	101	34	1078	3.50
126	Atrypa sp. B	0.4	-5.5	1478	479	79	36	675	13.38
134	Cupularostrum sp.	0.8	-6.0						
135	Atrypa sp. C	0.2	-6.0	1645	328	18	170	678	0.39
136	Schizophoria sulcata	-0.7	-6.0	3441	1358	33	297	867	0.73
137	Spinatrypa (Spinatrypa) borealis	0.6	-6.3	2267	552	105	1105	744	1.25
142	Atrypa sp. B	0.0	-6.6						
143	Atrypa sp. B	0.8	-5.1	3573	603	220	2004	712	4.34
144	Atrypa sp. B	0.6	-5.5	993	396	36	179	697	0.79
145	Perryspirifer scheii	0.0	-6.9	1996	2139	80	628	1217	0.52
146	Schizophoria sulcata	-0.5	-6.7	5237	1758	72	821	1080	0.27
Bird Fiord Formation, Norfolk Island, NWT									
119	Elythyna sverdrupi	-0.2	-4.8						
121	Atrypa sp. B	0.6	-5.6	1822	324	35	937	535	0.65
122	Atrypa sp. B	0.6	-6.2						
124	Atrypa sp. B	0.2	-6.4	1470	485	87	1303	704	2.51
130	Atrypa sp. B	-0.2	-6.2	1757	521	165	415	723	0.14
131	Warrenella sp.	-0.2	-5.8	1269	1824	23	102	1330	0.01
132	Perryspirifer scheii	-0.3	-5.5	1703	2024	27	43	1378	8.70
133	Schizophoria sulcata	-0.8	-5.9						
138	Perryspirifer scheii	-0.5	-6.4	2007	2588	38	238	1414	0.58
139	Schizophoria sulcata	-0.6	-6.6						
140	Warrenella sp.	-0.2	-5.8	945	1823	13	42	1215	3.76
141	Atrypa sp. B	-0.1	-4.7	1892	1476	62	632	1134	0.90
M./L.DEVONIAN									
Bird Fiord Formation, Devon Island, NWT									
66	Atrypa sp. B	0.3	-6.1	2057	368	37	383	733	2.25
67	Ivdelinia grinnellensis	0.8	-4.9	1118	183	10	20	573	18.07
68	Warrenella sp.	0.2	-4.4	1456	2128	14	34	1206	25.88
78	Atrypa sp.	0.6	-5.5	1647	425	109	322	656	12.13
79	Spinulicosta sp.	0.2	-6.0						
82	Spinatrypa sp.	1.6	-6.2	1717	757	269	2246	831	0.60
83	Schizophoria sulcata	0.4	-6.0						
147	Warrenella sp.	-0.4	-5.5	3701	4486	70	1200	1077	1.63
148	Cupularostrum sp. B	0.8	-5.9						

SAMPLE NO.	SPECIES	PDB C 13	PDB O 18	PPM MG	PPM NA	PPM MN	PPM FE	PPM SR	% I.R.
Bird Fiord Formation, Ellesmere Island, NWT									
69	Spinatrypa sp.	0.0	-5.8	1737	812	189	4048	804	2.65
70	Atrypa sp.	0.9	-5.3	1111	526	122	262	724	28.26
71	Schizophoria sulcata	-0.2	-5.7						
72	Spinulicosta sp.	-0.9	-6.5	7399	1243	456	8975	900	6.51
75	Atrypa sp.	1.5	-7.1	2630	338	164	1360	575	3.37
76	Warrenella sp.	0.1	-5.0	2767	1099	51	672	918	3.34
77	Nucleospira sp.	-0.1	-6.1						
80	Atrypa sp.	0.8	-5.8	1766	395	101	302	606	3.03
81	Atrypa sp.	1.1	-6.2	1346	418	88	1295	576	0.76
88	Atrypa sp. B	0.7	-6.8	4344	523	227	4512	707	4.11
89	Perryspirifer scheii	-0.7	-5.6	1809	2097	54	248	1309	24.91
90	Warrenella sp.	-0.1	-5.0	943	1592	11	177	1144	16.45
91	Atrypa sp. B	0.2	-4.7						
92	Atrypa sp.	1.2	-6.6	3852	296	224	1890	556	7.88
93	Atrypa sp.	-0.4	-8.3	2746	1664	203	533	1118	14.32
94	Atrypa sp.	-0.8	-7.5	2135	1927	118	568	1095	0.17
95	Elythyna sverdrupi	0.5	-5.8	2951	507	34	821	650	0.36
96	Atrypa sp. B	-0.2	-7.3	1639	583	165	503	730	0.41
97	Atrypa sp.	0.2	-6.7	2922	661	165	2452	739	6.09
98	Atrypa sp.	-0.7	-7.8	1477	468	58	517	580	0.93
100	Atrypa sp. C	-0.6	-6.4						
101	Elythyna sverdrupi	-0.7	-6.7	2449	1325	88	505	1106	1.96
102	Atrypa sp.	0.1	-6.1	2594	481	159	1212	638	3.92
103	Atrypa sp. C	0.2	-6.2	1212	520	84	492	889	0.48
Bird Fiord Formation, Norfolk Island, NWT									
73	Spinatrypa sp.	-0.2	-5.3						
74	Schizophoria sp.	-0.5	-5.5	4514	1532	57	1152	1015	0.33
L.DEVONIAN									
Bird Fiord Formation, Ellesmere Island, NWT									
113	Elythyna sverdrupi	0.4	-5.6	2263	793	46	210	1119	1.06
114	Elythyna sverdrupi	0.1	-6.1	1628	471	53	227	683	0.30
115	Elythyna sverdrupi	-0.1	-5.2	1515	1291	50	351	1133	5.52
Eids Formation, Ellesmere Island, NWT									
EO-1	Eoschuchertella n. sp.	-0.4	-6.4	2732	716	97	314	1010	23.37
EO-2	Eoschuchertella n. sp.	-0.3	-4.6	3690	1478	56	214	1296	7.78
EO-3	Eoschuchertella n. sp.	-0.1	-4.5	3588	1239	128	454	1063	11.22
EO-4	Eoschuchertella n. sp.	-0.1	-5.0	4076	1089	148	575	1369	8.02
EO-5	Eoschuchertella n. sp.	-0.1	-4.6	3502	1752	59	312	1251	2.00
EO-6	Eoschuchertella n. sp.	-0.1	-4.9	3291	641	110	219	1014	27.74
EO-7	Eoschuchertella n. sp.	-0.2	-4.5	4784	1034	185	405	1168	2.02
EO-8	Eoschuchertella n. sp.	-0.4	-4.5	3082	1863	64	273	1384	1.56
EO-9	Eoschuchertella n. sp.	0.3	-4.1	4588	1083	152	624	1203	10.14
EO-10	Eoschuchertella n. sp.	0.0	-5.2	3348	973	88	225	1083	13.79
EO-11	Eoschuchertella n. sp.	-0.3	-5.6	3379	1584	101	288	1294	2.36
EO-12	Eoschuchertella n. sp.	-0.4	-5.0	4186	1555	85	449	1306	4.06
PER-1	Perryspirifer scheii	0.2	-4.8	1477	1729	27	255	1052	5.31
PER-2	Perryspirifer scheii	-1.2	-13.4	4079	134	165	416	785	7.49
PER-3	Perryspirifer scheii	0.3	-5.1	1736	1954	35	154	1219	1.28
PER-4	Perryspirifer scheii	0.1	-6.0	744	1121	22	46	1545	24.78
PER-5	Perryspirifer scheii	0.4	-4.5	1570	1548	29	108	1022	6.01
PER-6	Perryspirifer scheii	0.2	-4.7	1229	1254	28	176	773	19.72
PH-1	Phragmostrophia sp.	-0.6	-10.7	3309	767	309	1982	1126	6.83
PH-2	Phragmostrophia sp.	-0.6	-6.6	3315	1004	161	1391	895	17.48
PH-3	Phragmostrophia sp.	-0.4	-6.8	4998	1257	292	3051	1095	3.69
PH-4	Phragmostrophia sp.	-1.3	-9.1	3625	991	217	716	1871	8.22
PH-5	Phragmostrophia sp.	-0.1	-5.8	4705	1276	209	2621	989	6.76
PH-6	Phragmostrophia sp.	-0.5	-5.6	5523	1652	195	1862	1095	8.22
PH-7	Phragmostrophia sp.	0.1	-5.8	4852	1424	250	2832	1073	4.05
PH-8	Phragmostrophia sp.	-0.5	-7.3	2545	869	162	1087	789	25.79
PH-9	Phragmostrophia sp.	-0.3	-5.9	4914	1372	275	3148	1105	3.78
SILURIAN									
Barlow Inlet Formation, Cornwallis Island, NWT									
BI-1A	Atrypoidea polaris	0.9	-6.3	6269	164	65	601	542	3.26
BI-1B	Atrypoidea polaris	0.8	-6.4	7257	184	70	417	852	4.22
BI-1C	Atrypoidea polaris	1.2	-6.4	6475	223	57	475	704	7.12
BI-1D	Atrypoidea polaris	1.7	-6.4	6627	239	58	395	667	4.89
BI-1E	Atrypoidea polaris	0.4	-6.8	19626	136	79	1187	587	6.26
BI-1	Atrypoidea polaris	1.2	-4.9	3468	267	98	2010	669	8.47
BI-2	Atrypoidea polaris	0.7	-5.6						
BI-3	Atrypoidea polaris	0.8	-6.0	6127	145	108	1948	705	3.04
BI-4	Atrypoidea polaris	0.3	-6.0						
BI-5	Atrypoidea polaris	2.0	-6.4						
BI-6	Atrypoidea polaris	1.4	-6.1						
BI-7	Atrypoidea polaris	1.2	-5.7	6245	143	60	621	965	3.76
BI-8	Atrypoidea polaris	1.0	-5.5	11202	159	60	643	669	10.98
BI-9	Atrypoidea polaris	0.9	-6.2	3185	136	70	493	741	2.21
BI-10	Atrypoidea polaris	0.8	-5.6	8385	181	75	700	897	8.66
222	Fardenia sp.	3.1	-6.5	9844	607	209	2567	850	6.93
Douro Formation, Cornwallis Island, NWT									
211	Atrypoidea foxi f. A	3.8	-6.7	2576	350	149	521	902	2.09
213	Nanukidium sp.	1.2	-6.7	6464	1300	12	116	1736	0.01

SAMPLE NO.	SPECIES	PDB C 13	PDB O 18	PPM MG	PPM NA	PPM MN	PPM FE	PPM SR	% I.R.
Douro Formation, Ellesmere Island, NWT									
223	Atrypoidea gigantus	0.1	-6.9	1030	154	28	45	792	0.11
Douro Formation, Prince of Wales Island, NWT									
200	Atrypoidea phoca	-0.2	-7.3	2995	221	60	10	454	0.66
202	Atrypoidea phoca	0.0	-6.6	11229	310	46	1103	660	13.96
203	Atrypoidea foxi f. A	0.8	-6.8	3649	299	5	376	803	0.30
204	Atrypoidea netserki	-2.2	-6.7	3996	349	49	234	801	0.40
206	Gypidula sp.	-0.2	-7.8	4119	955	39	639	1105	0.76
207	Protathyris praecursor	-1.0	-6.7	3753	849	38	144	1043	6.55
209	Atrypoidea netserki	-1.1	-7.2	7623	278	28	492	558	1.95
214	Atrypoidea netserki	-1.6	-6.8	4121	477	27	126	858	0.98
216	Atrypoidea erebus	-3.1	-6.6	30191	140	52	2252	157	7.05
219	Atrypoidea foxi f. B	-0.8	-7.2	6279	129	133	1001	377	0.11
220	Atrypoidea phoca	1.2	-7.8	3773	220	33	183	560	6.62
224	Protathyris praecursor	0.2	-7.8	3484	1425	20	145	1385	0.44
225	Atrypoidea foxi f. A	0.3	-7.5	3232	335	22	406	703	0.42
Douro Formation, Somerset Island, NWT									
FA-A1	Atrypoidea foxi	0.2	-5.7	2334	78	91	557	655	15.70
FA-A2	Atrypoidea foxi	0.4	-6.2	2791	77	89	489	691	15.00
FA-A4	Atrypoidea foxi	0.2	-5.8	3685	96	116	686	869	2.72
FA-A5	Atrypoidea foxi	0.7	-6.2	2599	115	27	96	432	25.95
FA-B1	Atrypoidea foxi	0.6	-6.6	5248	345	102	1835	694	13.98
FA-B2	Atrypoidea foxi	0.8	-6.4	8472	403	78	3287	554	22.41
FA-D1	Atrypoidea foxi	1.0	-5.9	1864	215	17	291	667	2.96
FA-D3	Atrypoidea foxi	0.5	-6.4	5627	312	105	1903	530	17.54
FA-D4	Atrypoidea foxi	0.6	-6.7	6821	477	59	2115	729	14.90
FA-L	Atrypoidea foxi	0.3	-6.3						
NONE	Atrypoidea foxi	0.6	-6.6	2849	462	54	1053	826	5.62
53	Atrypoidea bioherma	0.9	-7.0	3478	285	17	474	750	0.59
201	Atrypoidea erebus	-0.2	-6.7	3842	922	25	20	536	1.98
205	Atrypoidea foxi f. B	0.6	-7.1	3357	380	34	523	923	3.50
208	Atrypoidea foxi f. B	0.5	-7.3	3564	324	61	1104	754	4.32
210	Protathyris praecursor	-0.4	-7.2	10929	2348	66	3949	1540	5.75
212	Atrypoidea foxi f. A	0.7	-7.5	10760	195	29	869	594	29.11
217	Atrypoidea foxi f. A	-0.7	-6.9	12113	238	27	779	729	2.50
226	Protathyris praecursor	-0.1	-7.0	3978	865	65	719	1475	0.21
Ellis Bay Formation, Anticosti Island, Quebec									
215	Hindella umbonata	0.7	-4.7	2586	1079	160	1197	1056	0.93
218	Hindella primstana	-0.3	-7.4						
221	Hindella sp.	-1.0	-4.4	3972	1587	245	2025	1152	3.46
ORDOVICIAN									
Ellis Bay Formation, Anticosti Island, Quebec									
X1Z1	Dinorthis anticostiensis	0.7	-5.3	4906	1205	136	1090	1258	4.44
X3Z1	Dinorthis anticostiensis	0.8	-4.8	4006	1294	155	807	1294	3.26
X4Z1	Dinorthis anticostiensis	1.1	-4.9	4390	1321	183	752	1270	1.56
X6Z1	Dinorthis anticostiensis	0.9	-4.7	4859	1425	140	1101	1835	7.26
2Z1	Dinorthis anticostiensis	0.9	-4.6	4304	907	130	660	1049	2.02
3Z1	Dinorthis anticostiensis	0.8	-4.9	4491	660	108	1163	1234	7.64
4Z1	Dinorthis anticostiensis	1.0	-4.8	3649	585	166	787	1056	3.40
5XZ1	Dinorthis anticostiensis	0.8	-5.1	3981	1028	216	936	1060	2.72
5Z1	Dinorthis anticostiensis	0.5	-5.5	4665	839	115	996	1069	4.66
6Z1	Dinorthis anticostiensis	0.7	-4.8	4046	591	137	788	1084	3.54
7Z2	Dinorthis anticostiensis	0.9	-5.0	4294	665	102	665	1125	2.14
8Z2	Dinorthis anticostiensis	1.1	-4.8	3941	616	130	994	1190	4.20
9XZ1	Dinorthis anticostiensis	0.9	-4.5	4223	1139	150	848	1128	3.22
9Z2	Dinorthis anticostiensis	1.1	-4.8	3549	828	144	674	1013	2.72
10XZ2	Dinorthis anticostiensis	1.2	-5.0	4825	1355	144	706	1247	2.92
10Z2	Dinorthis anticostiensis	1.0	-4.8	3720	759	121	592	1093	1.22
14Z1	Dinorthis anticostiensis	0.9	-5.0	4662	1309	133	736	1319	2.14
227	Dinorthis anticostiensis	0.9	-4.9	4850	1760	145	953	1279	1.87
228	Dinorthis anticostiensis	0.8	-4.8	5219	1719	176	1103	1261	2.04
229	Dinorthis anticostiensis	0.7	-5.1	4468	1665	126	403	1117	0.17
230	Dinorthis anticostiensis	0.9	-5.0	4030	1634	113	1485	1131	0.30