Pergamon

Geochimica et Cosmochimica Acta, Vol. 58, No. 20, pp. 4429–4442, 1994

0016-7037/94 $6.00 + .00

0016-7037(94)00218-5

Oxygen and carbon isotopic composition of Ordovician brachiopods: Implications for coeval seawater

HAIRUO QING[1,*] and JAN VEIZER[1,2]

[1]Derry/Rust Research Unit, Ottawa-Carleton Geoscience Centre, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5
[2]Institut fur Geologie, Ruhr Universitat, 44780 Bochum, Federal Republic of Germany

(*Received July* 7, 1993; *accepted in revised form April* 21, 1994)

Abstract—One hundred and two articulate brachiopods and twenty-one marine cements from Ordovician strata were analyzed for oxygen and carbon isotopes. These, together with 200 previously published analyses of Ordovician brachiopods (mostly of Upper Ordovician age), define a general trend of increasing $\delta^{18}O$ values with decreasing age, from a minimum of −10.5‰ in the earliest Ordovician to a maximum of −1.5‰ at the Ordovician/Silurian boundary. The $\delta^{13}C$ values show a general positive correlation with $\delta^{18}O$ and increase from −2.5‰ in the earliest Ordovician to as high as +7‰ at the Ordovician/Silurian boundary. The magnitudes of Ordovician excursions for both $\delta^{18}O$ and $\delta^{13}C$ are similar to those reported previously for the entire Phanerozoic.

Different genera of brachiopods from the same stratigraphic level did not yield any large differences in their isotopic compositions, suggesting that vital effects did not influence decisively the isotope values of the studied skeletal parts. Petrographic examination and trace element analyses indicate that brachiopod shells from Llandeilo to Ashgill strata are well preserved and thus, may have retained their primary isotopic signatures. The same criteria for the Tremadoc, Arenig, and some Llanvirn brachiopods suggest partial diagenetic alteration of $\delta^{18}O$ values in these samples, but this does not preclude their utility as a recorder of a primary $\delta^{13}C$ signal.

The observed $\delta^{18}O$ trend for the well preserved portion of the record may reflect progressive cooling during Ordovician, perhaps complemented by a changing $\delta^{18}O$ values of seawater. The latter could have been a consequence of a net increase in the rate of high-temperature water/rock interaction relative to its low-temperature counterpart, as indicated also by the large coeval decrease of marine $^{87}Sr/^{86}Sr$. Superimposed on the above long-term $\delta^{18}O$ trend is a positive excursion of about 2‰ at the end of the Ordovician, probably reflecting a large expansion of polar ice caps. The magnitude of this excursion indicates a degree of glaciation comparable to that at the height of the Quaternary glacial episodes.

The secular $\delta^{13}C$ trend may reflect a progressive increase in marine organic productivity and/or enhanced organic deposition in the Ordovician oceans, particularly noticeable at the time of the terminal Ordovician glaciation.

INTRODUCTION

THE CHEMICAL AND ISOTOPIC composition of seawater is controlled by kinetic steady-states, reflecting the following major fluxes: (1) continental input, principally the dissolved load of rivers; (2) oceanic crust/seawater exchange at mid-oceanic ridges, and (3) removal of chemical species via sedimentation (e.g., HOLLAND, 1984). Although the chemical composition of seawater may have been relatively stable during geological history, this was not the case for many isotopes (e.g., BURKE et al., 1982; STILLE et al., 1992; VEIZER, 1992a). Isotopes can, therefore, serve as a valuable tracer for understanding the dynamics of the Earth system. In addition, quantification of isotopic composition of ancient seawater is crucial for deconvolution of sedimentary, diagenetic, and thermal maturation histories of sedimentary basins. This is because the resulting isotopic curves can be utilized (1) as a dating and correlation tool (the so-called isotopic stratigraphy) that is global in scope and applicable to nonfossiliferous sequences (ELDERFIELD, 1986; WILLIAMS et al., 1988), (2) as a reference base for potential oxygen isotopic paleothermometer (EPSTEIN et al., 1951; ANDERSON and ARTHUR, 1983), and (3) as a paleoceanographic tracer of circulation patterns in ancient oceans (SAVIN and YEH, 1981). Such information, in turn, can help to interpret geologic events, such as dolomitization and mineralization in sedimentary basins (LAND, 1980, 1983; QING and MOUNTJOY, 1989, 1994; VEIZER, 1992a).

Previous systematic studies of sedimentary carbonates delineated the first order secular trends for oxygen and carbon isotopes during geologic history (DEGENS and EPSTEIN, 1962; WEBER, 1965a,b; SCHIDLOWSKI et al., 1975; VEIZER and HOEFS, 1976; POPP et al., 1986; VEIZER et al., 1986; BRAND and MORRISON, 1987; LOHMANN and WALKER, 1989; WADLEIGH and VEIZER, 1992), with resolution of higher order features in these trends available only for the younger time intervals. For the Ordovician, the subject of the present study, the existing database is relatively sparse and covers mostly the Upper Ordovician. For example, the $\delta^{18}O$ and $\delta^{13}C$ curves of VEIZER et al. (1986) were based on samples from one, and those of POPP et al. (1986) from two Upper Ordovician formations. The recent work of WADLEIGH and VEIZER (1992) includes brachiopod samples from a variety of Ordovician strata, but even these are mostly of Upper

* *Present address:* Institute of Sedimentary and Petroleum Geology, Geological Survey of Canada, 3303-33rd St. NW, Calgary, Alberta, Canada T2L 2A7.

Ordovician age. Therefore, the main objectives of this paper are to establish secular $\delta^{18}O$ and $\delta^{13}C$ curves for the Ordovician based on brachiopods and marine cements, to compare these results with previously published data, and to search for possible causes that could have generated the observed isotopic patterns.

The isotopic composition of ancient oceans can be deciphered from attributes of ancient chemical and biochemical carbonate precipitates. For the Paleozoic, the most common biochemical carbonates used for the reconstruction of the first order isotopic variations are the well preserved interior "secondary" layers of brachiopod shells, which are composed of stable low-Mg calcite (POPP et al., 1986; VEIZER et al., 1986; BRAND and MORRISON, 1987; ADLIS et al., 1988; GROSSMAN et al., 1991; BRAND, 1989; WADLEIGH and VEIZER, 1992). Marine cements, precipitated in equilibrium with ambient seawater, can also be utilized for the intervals where they are available (GONZALEZ and LOHMANN, 1985; CARPENTER et al., 1991). Marine calcite cements may have been precipitated as original low-Mg calcite (CARPENTER et al., 1991; JOHNSON and GOLDSTEIN, 1993), but in most cases they were originally aragonite or high Mg-calcite that must have been diagenetically altered to more stable low-Mg calcite. Nevertheless, their original $\delta^{18}O$ and $\delta^{13}C$ values can apparently be inferred from isotopic trends, as demonstrated by the studies of MEYERS and LOHMANN (1985), GIVEN and LOHMANN (1985), CARPENTER and LOHMANN (1989), and CARPENTER et al. (1991). The overall agreement of Phanerozoic secular trends, regardless of whether generated from studies of marine cements or brachiopod shells (see Fig. 7 in POPP et al., 1986), suggests that either or both these approaches can be employed to delineate secular isotopic curves.

In this study we utilize both approaches, but the bulk of the samples is represented by Ordovician articulate brachiopods. These samples have been collected from various localities that were in a paleolatitude below 30° in Laurentia (Fig. 1). Their location, stratigraphic assignment, host lithology, and generic identification are summarized in Appendix. The bulk of the brachiopods from the Arenig to Llandeilo were collected in the field by H. Qing or donated by J. F. Miller (SW Missouri State University, Springfield). Additional brachiopod samples were donated by T. E. Bolton (Geological Survey of Canada, Ottawa), H. J. Hoffman (University of Montreal, Montreal), E. Landing (New York Geological Survey, Albany), and J. B. Waddington (Royal Ontario Museum, Toronto). Marine cements were collected at Meiklejohn Peak, southern Nevada by H. Qing.

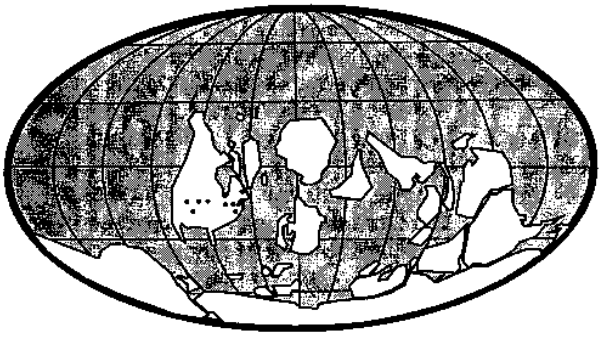

FIG. 1. Paleogeographic reconstruction for the Middle Ordovician (modified after SCOTESE and MCKERROW, 1990). Black dots represent sample locations.

METHODS

The collected Ordovician brachiopod shells are small (0.5–2 cm) and have thin shells (0.1–1 mm), particularly the early Ordovician ones. In order to avoid contamination from surrounding rock matrix, bulk rocks that contained brachiopods were crushed by hammer. In most cases, the outer "primary" layers of the shells, often diagenetically altered, remained in the molds of the rock matrix, while pieces of the well preserved "secondary" layers were cleanly separated. These shell materials were handpicked and examined by binocular microscope, and pieces that still contained rock matrix were eliminated. In addition, the selected brachiopod shells were thin-sectioned, in order to examine their state of preservation under transmitted light and by cathodoluminescence (CL). The equipment used was a Technosyn 8200 MKII model, with settings at 10 kV and 0.5 mA. Some shell fragments were also studied by scanning electron microscopy (SEM).

Complementary to textural evaluation, the state of preservation of the shells was also examined by chemical criteria. From the total of 123 samples analyzed for oxygen and carbon isotopes, eighty-nine yielded enough material for determination of their calcium, magnesium, and trace element (strontium, sodium, potassium, iron, and manganese) contents. This analytical work has been performed in the laboratories of the Ottawa-Carleton Geoscience Centre, utilizing Thermal-Jarrell Ash ATOMSCAN25 inductively coupled argon plasma sequential spectroscopy (ICP-AES). Fifteen to 20 mg of sample were digested in 15 mL of 8% HCl. The solution was filtered through ashless paper if the samples contained noticeable insoluble residue. The detection limits for strontium, sodium, manganese, and iron were 1, 50, 1, and 60 ppm, respectively. The reproducibility for duplicates was better than three relative percent. The results are listed in Appendix.

In total, 102 brachiopod shell and twenty-one marine cements were analyzed for oxygen and carbon isotopes. Five to 10 mg of sample was reacted overnight with 100% phosphoric acid at 25°C. The produced carbon dioxide was analyzed on a VG-602E mass spectrometer at the Ottawa-Carleton Geoscience Centre. The reproducibility for both oxygen and carbon isotopes was within 0.1‰. The analytical results, reported relative to PDB, are summarized in Appendix.

TEMPORAL TRENDS

The overall temporal trends for $\delta^{18}O$ and $\delta^{13}C$ of Ordovician brachiopods and marine cements are presented in Figs. 2 and 3. These figures include all present as well as previously published Ordovician data (323 samples). In general, $\delta^{18}O$ values increase with decreasing age (Fig. 2), in accord with the previously documented Paleozoic trends based on brachiopods and marine calcites (POPP et al., 1986; VEIZER et al., 1986; HUDSON and ANDERSON, 1989; LOHMANN and WALKER, 1989; BRAND, 1989; WADLEIGH and VEIZER, 1992). However, it appears that the $\delta^{18}O$ increase did not occur at an uniform rate. Instead, major jumps are indicated near the Tremadoc/Arenig and Arenig/Llanvirn transitions, in the late Llandeilo, and in the latest Ashgill, respectively (Fig. 2).

For carbon isotopes, the overall trend resembles that of $\delta^{18}O$ (Fig. 3), with $\delta^{13}C$ values increasing from a minimum of −2.5‰ in the earliest Ordovician to as much as +7‰ at the Ordovician/Silurian boundary. As with oxygen isotopes, the $\delta^{13}C$ increase was not gradual. Sudden changes in $\delta^{13}C$

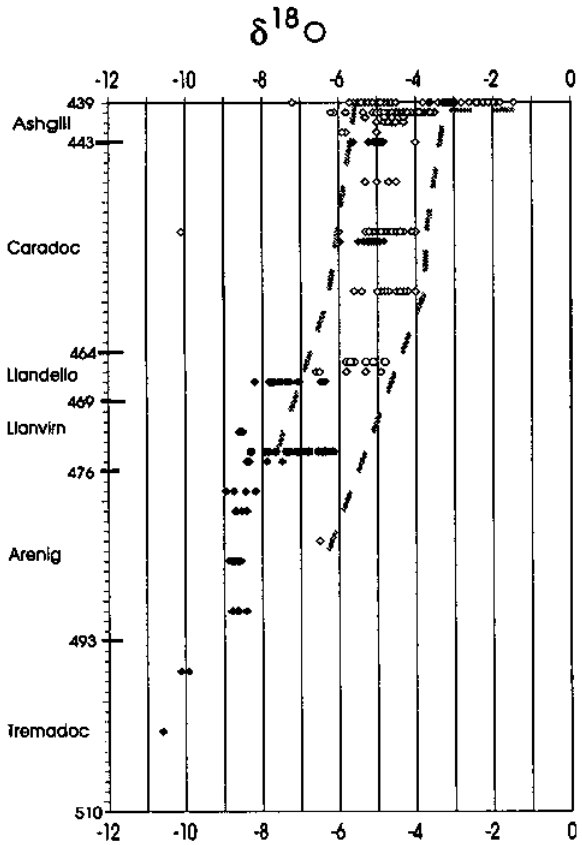

FIG. 2. $\delta^{18}O$ of Ordovician brachiopods and marine cements plotted according to the best available stratigraphic information. The time-scale of HARLAND et al. (1990) is used. Samples with $\delta^{18}O$ less than −12‰ are excluded from the plot. Solid diamonds, brachiopods from this study; open diamonds, brachiopods from VEIZER et al. (1986), RAILSBACK (1990), MIDDLETON et al. (1991), and WADLEIGH and VEIZER (1992); dots, marine cements from this study; and circles, marine cements from GROVER (1981). The contours enclose the "best-preserved" samples as discussed in the text.

are indicated at the Tremadoc/Arenig and Arenig/Llanvirn transitions and in the latest Ashgill (Fig. 3), all accompanied by $\delta^{18}O$ shifts (Figs. 2, 3). The general increase in $\delta^{13}C$ is similar to the previously documented carbon isotopic age trend (VEIZER et al., 1980; HOLSER et al., 1988; WADLEIGH and VEIZER, 1992).

DISCUSSION

The results presented above demonstrate convincingly the shifts towards ^{18}O and ^{13}C enrichments in the course of the Ordovician. In an optimal case, the $\delta^{18}O$ may reflect oxygen isotopic composition and temperature of the Ordovician seawater and the $\delta^{13}C$ of its dissolved inorganic carbon. Alternatively, the data may reflect superimposed vital fractionation effects, or postdepositional alteration patterns, or any combination of the above. It is, therefore, essential to evaluate factors that may have played a role in the observed isotopic trends.

Vital Effect

Vital effects refer to disequilibrium precipitation of biogenic carbonate. Some organisms, such as corals and echinoderms, precipitate skeletal calcites out of equilibrium with respect to ambient water (MCCONNAUGHEY, 1990a,b; WEFER and BERGER, 1991). For brachiopods, the role of "vital effects" is not entirely clarified. POPP et al. (1986) and VEIZER et al. (1986) suggested that some genera of Paleozoic brachiopods may have been involved in fractionation of carbon isotopes. Other authors (LOWENSTAM, 1961; BRAND, 1989; GROSSMAN et al., 1991) maintained that brachiopods secreted their shells in oxygen isotopic equilibrium with ambient water. Based on experimental work on living brachiopods, HEIBERT et al. (1988) suggested variations of ±1‰ in $\delta^{18}O$ and $\delta^{13}C$ within single brachiopod shells and cautioned that the brachiopods should not be utilized as precise recorders of seawater isotopic signature.

Extensive optical and chemical studies on recent brachiopods show that the exterior "primary" layer frequently contains disequilibrium isotopic signals (CARPENTER and LOHMANN, 1994) and is susceptible to postdepositional alteration (DIENER, 1992). However, the isotopic values for the interior "secondary" layer of these recent brachiopods are more complicated. The data from CARPENTER and LOHMANN

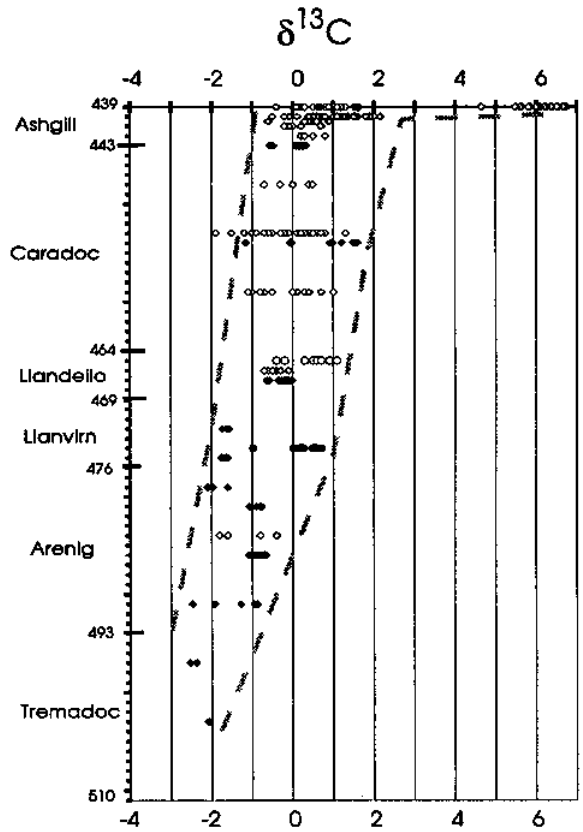

FIG. 3. $\delta^{13}C$ of Ordovician brachiopods and marine cements plotted according to the best available stratigraphic information. See Fig. 2 for further details.

(1994) show that those from latitudes lower than 40° have $\delta^{18}O$ values mostly within 1‰ of the equilibrium values calculated from seasonal temperature variations and from the $\delta^{18}O$ value of ambient seawater. In contrast, brachiopods from higher latitudes have more variable $\delta^{18}O$ values that are generally less than the calculated equilibrium values (see Fig. 9 in CARPENTER and LOHMANN, 1994). It appears, therefore, that the unaltered interior "secondary" layers from latitudes lower than 40° can be utilized for studies of the first order isotopic variations that are in excess of 1‰. This is the case for our Ordovician brachiopod samples, all collected from paleolatitudes lower than 30° (Fig. 1).

The isotopic compositions of multiple brachiopod genera for a given stratigraphic unit are summarized in Fig. 4 and no noticeable differences have been observed within a single stratigraphic unit. Only the *Sowerbylla* sp. (Hirnantian, Ashgill) has $\delta^{13}C$ values about 1‰ lighter than those of other coeval genera. This suggests that vital effects did not play a decisive role in determining the isotopic composition of the studied Ordovician brachiopods. A similar conclusion has been reached also by BATES and BRAND (1991), who observed no significant differences in $\delta^{18}O$ and $\delta^{13}C$ values between two Devonian brachiopod species from the same stratigraphic unit, and by WADLEIGH and VEIZER (1992), who found no isotopic differences between Ordovician *Platystrophia* sp. and other Ordovician genera, despite the fact that the latter originated from different environments and localities. Based on all these results, we conclude that the studied Ordovician brachiopods did not exert significant biological control over $\delta^{18}O$ and $\delta^{13}C$ values in the "secondary" layer of their shells.

Diagenetic Alteration

In order to select the "best preserved" brachiopod shells, thin sections of brachiopods were examined under transmitted light and subsequently by cathodoluminescence (CL). As a rule, the unaltered shells should consist of nonluminescent fibrous layers with no visible dissolution and cementation features (cf. POPP et al., 1986). In addition, scanning electron microscope (SEM) studies showed a general good preservation of the original brachiopod fabric, although dissolution features are found in some nonluminescent samples (Fig. 5), indicating that nonluminescent brachiopods too may have experienced some diagenetic alteration (cf. RUSH and CHAFETZ, 1990). Whether a partial alteration that is visible by SEM, while undetectable optically and by CL, can reset entirely the isotopic composition is another matter. Previous studies indicated that diagenetic alteration of brachiopod shells is most severe in the "primary" prismatic layer at its surface, while the volumetrically dominant "secondary" layer usually remains well preserved (e.g., ADLIS et al., 1988; GROSSMAN et al., 1991; DIENER, 1992). Even occurrences of a relatively large percentage of diagenetic calcite within the primary shell structure may only result in a fractional isotopic shift, possibly because the well preserved "secondary" layers accounted for the bulk of samples (WADLEIGH and VEIZER, 1992). Only a substantial dissolution/reprecipitation, usually detectable by SEM, can result in large-scale resetting of the original isotopic signal. In order to minimize the role of diagenetic alteration, we employed all the above techniques for sample selection and analyzed only the nonluminescent "secondary" layer of the selected shells with no visible diagenetic alterations such as dissolution and recrystallization.

In addition to textural evaluation, trace elements were utilized as supplementary criteria of secondary alteration of the brachiopods. Recent brachiopod shells have strontium contents from 800 to 2,000 ppm; Na, 500–3,700 ppm; Mn, 5–500 ppm; and Fe, 20–800 ppm (MORRISON and BRAND, 1986). Diagenetic alteration, in general, leads to depletions in strontium and sodium and enrichments in manganese and iron (Figs. 6, 7). These trends are often associated with depletions in ^{18}O and ^{13}C (Figs. 8,9). While the bulk of our samples has strontium and sodium contents similar to those of recent brachiopods (Figs. 6,8), the iron and manganese contents in the Llanvirn and in some Ashgill and Llandeilo specimens are much higher than those of recent brachiopods (Figs. 7,9), suggesting possible alteration by late-stage diagenetic processes. Yet, for a given stratigraphic unit, $\delta^{18}O$

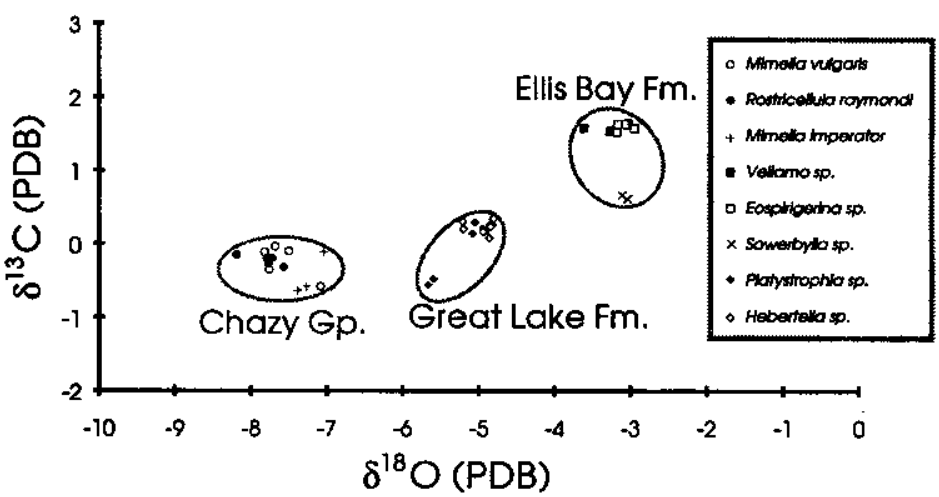

FIG. 4. $\delta^{18}O$ and $\delta^{13}C$ of different brachiopod genera from the same stratigraphic unit.

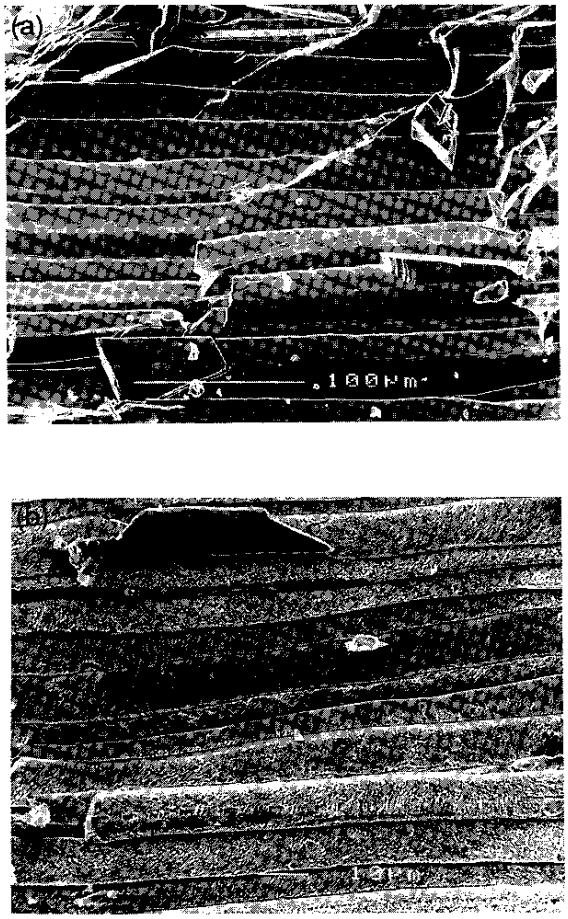

FIG. 5. SEM of brachiopod shell fragments. (a) Well-preserved secondary fibrous layer of brachiopod shell from the Ellis Bay Formation (Hirnantian), Anticosti Island. (b) Slightly altered brachiopod shell with micro dissolution vugs from the Laval Formation (Llandeilo), Ontario.

values decrease only slightly despite large variations in trace element contents (Fig. 9). This is probably caused by partial recrystallization, which could have resulted in large shifts in trace element content while hardly affecting the $\delta^{18}O$ or $\delta^{13}C$ signals (cf. WADLEIGH and VEIZER, 1992). Note also, that the pattern is preserved even at the level of formations. For example, the two parallel trends for the Ashgill samples (Figs. 8,9) represent the Ellis Bay and the Great Lake Formations, respectively. This type of covariance can be generated if the samples were subjected to only a minor partial recrystallization or to a minor contamination by diagenetic calcite.

Due to the limited collection and small sample size of the early Ordovician (Tremadoc and early Arenig) brachiopods, we did not have enough shell material for SEM study or trace element analyses. As a result, their diagenetic alteration cannot be evaluated using the above discussed criteria. However, the $\delta^{18}O$ values of the Tremadoc and the early Arenig samples (−10.5 to −8.5‰) (Fig. 2) are much lower than the $\delta^{18}O$ of the contemporary marine calcite cements (−5 to −6.5‰; LOHMANN and WALKER, 1989; JOHNSON and GOLDSTEIN, 1993) or the early Ordovician limestones that have undergone meteoric diagenesis (−7‰) (GAO and LAND, 1991). This indicates that these brachiopod shells have been diagenetically altered. Optical evaluation of the shell material confirms its recrystallized nature, since no primary fibrous structures were observed. In addition, the lime matrix in which the brachiopods were embedded is also strongly recrystallized. The late Arenig samples, on the other hand, appear to be well preserved in terms of their optical and trace elements characteristics, yet their $\delta^{18}O$ values are less than −8‰ (Fig. 2). We have no satisfactory explanation for this anomaly, but as a precautionary step, we prefer to exclude these results pending additional studies. Note also that one half of the Tremadoc and all of the Arenig and Llanvirn brachiopod samples are from Utah (Appendix), an area where conodont alteration index of 3–5 has been documented (ETHINGTON and CLARK, 1981), suggesting a considerable thermal overprint. Based on the above criteria, our $\delta^{18}O$ database for early Ordovician samples is clearly unsatisfactory and requires additional sampling and analytical work.

The Llanvirn brachiopod samples have excessive manganese and iron contents (Figs. 7,9) and their $\delta^{18}O$ and $\delta^{13}C$ are lighter than those of the contemporaneous marine cements (Figs. 2,3), but comparable to the Llandeilo brachiopods (Fig. 9). Taking a conservative attitude, we shall con-

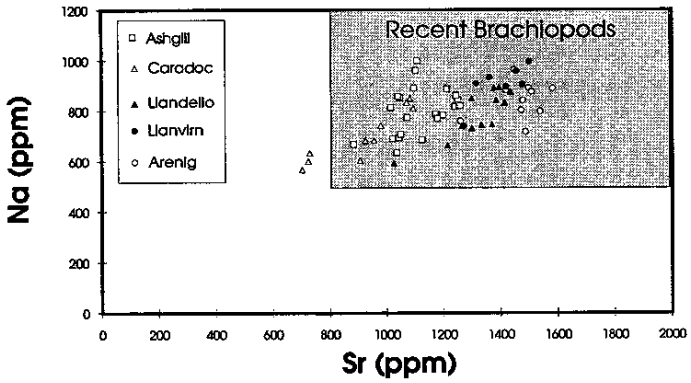

FIG. 6. Scatter diagram of strontium and sodium concentrations in Ordovician brachiopods. Shaded area for recent brachiopods from MORRISON and BRAND (1986).

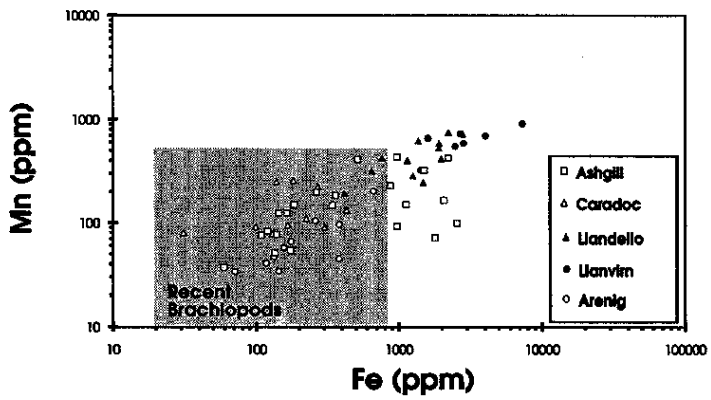

FIG. 7. Scatter diagram of manganese and iron concentrations in Ordovician brachiopods. Shaded area for recent brachiopods from MORRISON and BRAND (1986).

sider these samples as altered. On the other hand, petrographic and trace element evaluation suggest that some of the Llanvirn marine cements have been well preserved and their heaviest $\delta^{18}O$ values (around −6‰) are used as a substitute for the brachiopod data. In contrast to the above, the younger, post-Llanvirn, temporal trend for $\delta^{18}O$ appears to be a real primary feature of the geologic record, with $\delta^{18}O$ forming a band of ±1.5‰ around a mean that is increasing from about −5.5‰ to −4.5‰ (Fig. 2). In the latest Ashgill, there appears a sudden ^{18}O spike of about 2‰ that will be discussed later in the text.

The $\delta^{13}C$ temporal trend, on the other hand, may approximate the real marine record for the entire Ordovician (Fig. 3), because the carbon budget in a diagenetic system is usually dominated by the dissolving precursor carbonate and its $\delta^{13}C$ is thus transposed into the successor phase. This may even be the case for the diagenetically altered Tremadoc and early Arenig samples, with $\delta^{13}C$ values similar to coeval brachiopods (WADLEIGH and VEIZER, 1992) and marine limestones (GAO and LAND, 1991). As with oxygen, the latest Ashgill is also characterized by a sudden ^{13}C enrichment of about 5‰.

The large positive $\delta^{18}O$ and $\delta^{13}C$ excursions at the end of Ordovician have occurred synchronously on Anticosti Island (Canada), in central Sweden and in Baltic States (cf. Fig. 2 in BRENCHLEY et al., 1994a). Such a synchronization over large geographic spread suggests that the signal is not simply a consequence of local vital, postdepositional or environmental effects. Instead, it may be of global significance and reflect secular variations in isotopic composition of seawater (BRENCHLEY et al., 1994a,b).

Factors Controlling $\delta^{18}O$ values of Brachiopods and Marine Cements

Accepting the validity of the Ordovician database, what could cause (1) the overall increase in $\delta^{18}O$ and $\delta^{13}C$ in the course of the Ordovician, (2) the approximate 5‰ ^{18}O depletion relative to Quaternary calcites, and (3) the sudden spike in $\delta^{18}O$ and $\delta^{13}C$ in the latest Ashgill? These points will be discussed in the subsequent sections.

Change in seawater temperature

Interpretation of the secular $\delta^{18}O$ trends as temperature variations has previously been advocated by one school of researchers (e.g., KNAUTH and EPSTEIN, 1976; KNAUTH and LOWE, 1978; KOLODNY and EPSTEIN, 1976; HOLMDEN and

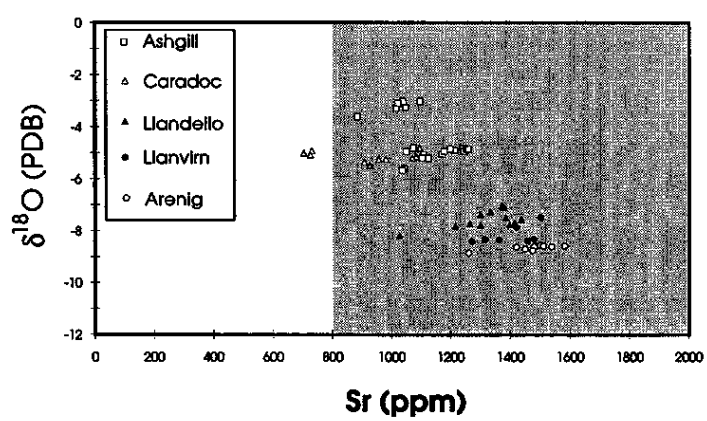

FIG. 8. Scatter diagram of $\delta^{18}O$ and strontium concentrations in Ordovician brachiopods. Shaded area denotes strontium concentrations for recent brachiopods (MORRISON and BRAND, 1986).

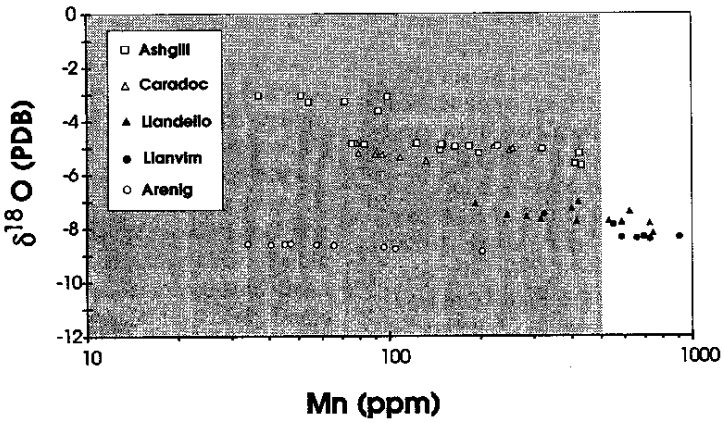

FIG. 9. Scatter diagram of $\delta^{18}O$ and manganese concentrations in Ordovician brachiopods. Shaded area denotes manganese concentrations for recent brachiopods (MORRISON and BRAND, 1986).

MUEHLENBACHS, 1993). Utilizing coexisting chert/phosphorite pairs and assuming that seawater $\delta^{18}O$ was constant during geologic history at about −1‰ (SMOW), KARHU and EPSTEIN (1986) suggested that seawater temperature was about 45°C during the Cambrian, dropped to about 22°C during Ordovician, and rose again to about 40°C in the Devonian.

It appears unlikely that the gradual increase in $\delta^{18}O$ values of brachiopods (Fig. 2) can be attributed entirely to a progressive cooling of the epeiric Ordovician seas. Assuming a $\delta^{18}O$ values of −1‰ (SMOW) for seawater in an "ice free' Ordovician, and accepting that the Llandeilo to Ashgill brachiopods have near primary $\delta^{18}O$ values at about −5.5 ± 1‰ to −4.5 ± 1‰ (Fig. 2), the seawater temperature would have decreased from 37 ± 6°C to about 31 ± 5°C (arrow A in Fig. 10). An assumption that the $\delta^{18}O$ of Ordovician sea water was as today, 0‰ SMOW, is even less palatable since it would increase the calculated temperatures by about 5°C. To complicate the issue, the peak in the latest Ashgill (Fig. 2) would require complementary and instantaneous cooling, of up to 10°C, for the low latitude epeiric seas (cf. Fig. 1). As already discussed in VEIZER et al. (1986), it is unlikely that identical Paleozoic faunal assemblages would tolerate such hot habitats and/or the large and rapid temperature swings. It seems, therefore, unlikely that ocean water temperature was the sole agent that resulted in $\delta^{18}O$ shifts observed in the Ordovician brachiopods. However, we do not discount the role of temperature as a complementary factor and we shall discuss this point later.

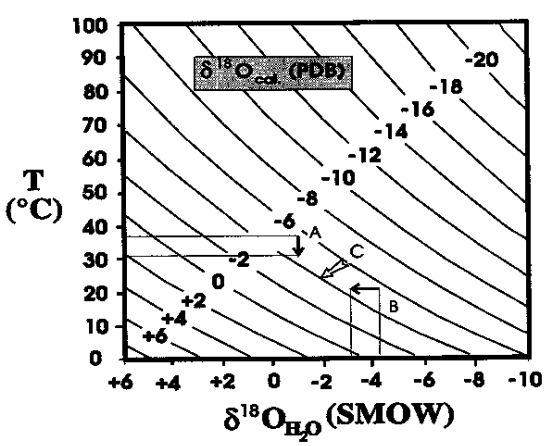

FIG. 10. Temperature vs. $\delta^{18}O_{H_2O}$ for various $\delta^{18}O_{cal.}$ values. Arrow A indicates the changes of brachiopod $\delta^{18}O$ as a result of seawater temperature changes, arrow B as a result of seawater $\delta^{18}O$ changes, and arrow C as a combined result of temperature and $\delta^{18}O$ changes.

Change of seawater $\delta^{18}O$

An alternative, or more likely complementary, explanation maintains that the isotopic composition of global ocean may have changed through time (see WEBER, 1965a,b; PERRY, 1967; DONTSOVA, 1970; FRITZ, 1971; PERRY and TAN, 1972; VEIZER and HOEFS, 1976; POPP et al., 1986; VEIZER et al., 1986; BRAND and MORRISON, 1987; LOHMANN and WALKER, 1989; CARPENTER et al., 1991; WADLEIGH and VEIZER, 1992). For the Ordovician, this would require an average ^{18}O enrichment of about 1‰ between average Llandeilo and the bulk of Ashgill (Arrow B in Fig. 10), with a superimposed spike of about 2‰ in the latest Ashgill (Fig. 2). A change in $\delta^{18}O$ value of global seawater can be caused by (1) major changes in water storage between hydrosphere and cryosphere, and/or (2) exchange of oxygen between seawater and the lithosphere.

Increases in the storage of water as continental glaciers can cause an increase $\delta^{18}O$ in seawater, because high latitude precipitation is significantly depleted in ^{18}O. The glacial-interglacial fluctuations in $\delta^{18}O$ of Quaternary seawater were estimated to have been within a 0.8‰ to 1.3‰ range (SAVIN and YEH, 1981). A polar ice cap in North Africa existed continuously from Arenig to latest Ordovician (SPJELDNAES, 1981; WEBBY, 1984). A major expansion of glaciation during the terminal Ordovician resulted in an onset of global cooling and in a drastic lowering of sea level. The collected $\delta^{18}O$ data show a jump towards the end of the Ashgill (Fig. 2). This excursion is also marked by the $\delta^{18}O$ shift, on the average

from −4.5‰ to −2.5‰, for the brachiopods in the latest Ashgill mud mounds in Sweden (MIDDLETON et al., 1991) and with even larger increase of about 5‰ in Latvian brachiopods (BRENCHLEY et al., 1992). Such synchronous increases in $\delta^{18}O$ in several widely spaced localities can be tentatively interpreted as secular variation in $\delta^{18}O$ of seawater. If so, a change of this rapidity and magnitude is best explained by "ice-volume" effect (MARSHALL and MIDDLETON, 1990; MIDDLETON et al., 1991; WADLEIGH and VEIZER, 1992; BRENCHLEY et al., 1994a,b). Similar to the Quaternary studies, it is difficult to separate the portion of the signal that may have been due to ice formation as opposed to temperature. Nonetheless, the latest Ashgill ^{18}O enrichment of about 2‰ suggests that the magnitude of the terminal Ordovician glaciation(s) would have been comparable to the ice volume at the height of the Quaternary glaciation. In order to explain the long-term $\delta^{18}O$ Ordovician gradient of about 1–1.5‰ (Fig. 2) as an interplay of ice buildup and temperature, a progressive growth of yet another Quaternary-size ice cap from Llandeilo to Ashgill would have to be postulated, a proposition not supported by the geologic record. An acceptance of such a proposition would also require that the $\delta^{18}O_{water}$ in the ocean during ice-free times would have to be considerably less than the −1‰ SMOW suggested from Quaternary studies.

An alternative interpretation for the long-term ^{18}O enrichment in the course of the Ordovician may be based on the proposition that the $\delta^{18}O$ of seawater is ultimately controlled by exchange of oxygen between seawater and lithosphere, particularly via interactions with basalt in hydrothermal systems at mid-oceanic ridges (HOLLAND, 1984). At high temperatures (e.g., ridge circulation), ^{18}O in the rocks is preferentially released into seawater, whereas at low temperatures (e.g., weathering) the opposite happens. The increase in ^{18}O during the Ordovician (and Paleozoic) may have then resulted from increasing rates of high-temperature exchange, relative to low-temperature processes. The concomitant decrease in seawater $^{87}Sr/^{86}Sr$ during the Ordovician (from 0.7090 to 0.7077, BURKE et al., 1982) is consistent with the proposition of increasing high-temperature water/rock interaction associated with global tectonism. Unfortunately, it is difficult to test this scenario experimentally, since neither the available isotope data nor the existing Paleozoic time scale (HARLAND et al., 1990) provide a resolution that would enable correlation of higher order $\delta^{18}O$ oscillations with specific tectonic events during the Ordovician. We are aware that model calculations based on the $\delta^{18}O$ depth profiles in recent and ancient oceanic crusts suggest that seawater/rock interaction at high and low temperatures about balance each other and buffer the seawater $\delta^{18}O$ at about 0‰ SMOW (e.g., MUEHLENBACHS and CLAYTON, 1976; GREGORY and TAYLOR, 1981; HOLLAND, 1984; HOLMDEN and MUEHLENBACHS, 1993). Nonetheless, the mass balance calculations of GREGORY (1991) do not preclude moderate changes in $\delta^{18}O$ of seawater over geologic timescales. Doubling of seafloor spreading rate can result in about 2‰ increase in $\delta^{18}O$ of seawater over 15 Ma (Fig. 4 in GREGORY, 1991), comparable to our post-Llanvirn background gradient from about −5.5‰ to −4.5‰ over 30 Ma (Fig. 2).

Stratified oceans

Another explanation that may conceivably explain the observed features of the isotopic record is based on the proposition of stratified oceans (WILDE and BERRY, 1984; GRUSZCZYNSKI et al., 1992). In this instance, it is hypothesized that during ice-free times, oceanic deep waters are generated by sinking brines due to extensive evaporation at low latitudes, leaving the waters above thermocline, the habitant of most brachiopods, depleted in ^{18}O. The present-day oceans are thermally stratified with a surface water temperature of approximately 15°C, and bottom temperature of about 5°C. These temperature differences are the cause of the nearly 2.5‰ difference in $\delta^{18}O$ between planktonic and benthic foraminifera (SAVIN, 1977; PRENTICE and MATTHEWS, 1988). For the same reason, brachiopods that lived at different water depths should have different $\delta^{18}O$ values, providing the thermal structure of the Ordovician ocean was comparable to its present-day counterpart.

RAILSBACK (1990) suggested that the Late Ordovician (Caradoc) ocean, in contrast to its thermally stratified modern counterpart, was salinity stratified and that this could have resulted in $\delta^{18}O$ variations from −8‰ to −5.5‰ in the contemporaneous brachiopods. However, the perpetuity of Gondwana glaciation during most of the Ordovician (WEBBY, 1984) does not support the rationale for such mode of oceanic circulation, even leaving aside the question of the theoretical feasibility of this model. Furthermore, as argued by VEIZER (1992b), gradual trends that span 10^7–10^8 years time intervals cannot be generated by ocean circulation processes that operate on a timescale of 10^3 years. Any changes caused by such circulation phenomena must appear as instantaneous step functions in the secular pattern that has geological resolution no better than 10^6–10^7 years.

Factors Controlling the $\delta^{13}C$ of Brachiopods and Marine Cements

The secular $\delta^{13}C$ trend can be caused by changes in the balance of fluxes in the marine carbon cycle, with inputs from degassing, rivers, and oxidation of organic matter and outputs that include production of marine carbonates and organic matter (ANDERSON and ARTHUR, 1983). The general increase in $\delta^{13}C$ of Ordovician seawater could have resulted from enhanced organic productivity and/or storage of C_{org} in sediments, both preferentially consuming ^{12}C and leaving sea water enriched in ^{13}C.

A large positive shift in $\delta^{13}C$, from 1.8‰ to 6.3‰, appears in brachiopods from the latest Ordovician mud mounds from central Sweden (MIDDLETON et al., 1991; Fig. 3). The latest Ordovician peak seems to have been of global significance, because it was observed also in Laurentia (YAPP and POTHS, 1992; LONG, 1993; WANG et al., 1993a), in south China (WANG et al., 1993b), and in Baltica (BRENCHLEY et al., 1992). However, the magnitude of this shift appears variable for different materials and geographic regions. For Laurentia, the bulk micritic carbonates from the Mackenzie Mountains (Northwest Territories, Canada) yielded a 2‰ increase (WANG et al., 1993a), those from Anticosti Island (Quebec, Canada) a 4‰ increase (LONG, 1993), and natural goethites

from Wisconsin (USA) a 3‰ increase (YAPP and POTHS, 1992). For south China, the increase in organic carbon $\delta^{13}C$ values in the latest shales was 5–6‰ (WANG et al., 1993b). Finally, for Baltica the unaltered brachiopod shells from Latvia yielded a 5‰ jump at latest Ordovician (BRENCHLEY et al., 1992). The secular $\delta^{13}C$ trend could reflect a progressive increase in organic productivity and/or enhanced organic deposition in the Ordovician oceans. The latter was interpreted to have caused the major positive shift in $\delta^{13}C$ at the end of the Ordovician (MIDDLETON et al., 1991; BRENCHLEY et al., 1992). This interpretation is also supported by a recent modeling of $\delta^{13}C$ change during glacial and interglacial time (KU and LUO, 1992), which suggests that marine deposition of organic carbon in glacial oceans increased by 3–10%, in spite of a reduction in terrestrial biomass during ice ages.

It has been suggested that increased storage of organic carbon in sedimentary rocks could lower P_{CO_2} in the ocean and atmosphere, which, in turn, could diminish the greenhouse effect and stimulate the glaciation at the end of the Ordovician (cf. MARSHALL and MIDDLETON, 1990; MIDDLETON et al., 1991). We consider it premature to speculate on atmospheric CO_2 and climate during the terminal Ordovician glaciation because the relationship between burial of organic matter and P_{CO_2} is not a simple feedback situation, but depends on a plethora of factors such as nutrient supply, sedimentary rate, etc. (CALDEIRA et al., 1993).

In addition to $\delta^{13}C$ secular variations in the entire ocean, the seawater column is characterized also by a depth gradient due to removal of carbon from surface water via organic matter and its progressive oxidation with depth. This results in a $\delta^{13}C$ decrease of up to 2‰ with depth, depending on the productivity of surface water and circulation patterns of the oceans. Consequently, brachiopods living at different water depths could have different $\delta^{13}C$ values. This could partially explain the spread in $\delta^{13}C$ observed in the contemporaneous brachiopods (Fig. 3), although most of our samples were from shallow marine sediments. Potentially, it may be desirable to concentrate on single genera that lived at a known water depth to selfcorrect for these environmental factors.

CONCLUSIONS

A new set of $\delta^{18}O$ and $\delta^{13}C$ measurements on 102 Ordovician brachiopods and twenty-one marine cements, combined with 200 previously published data for coeval brachiopods, demonstrates a general enrichment in ^{18}O and ^{13}C with decreasing age. The magnitudes of these Ordovician isotopic excursions are similar to those reported previously for the entire Phanerozoic.

Since no noticeable differences were observed in the isotopic compositions of different genera at the same stratigraphic level, vital effects do not appear to have contributed significantly to these secular trends. Petrographic examination indicates that the Tremadoc and early Arenig brachiopods contain features of diagenetic recrystallization. Although strontium and sodium contents for the Llanvirn samples are similar to those of recent brachiopods, their iron and manganese contents are much higher, suggesting their diagenetic alteration. Petrographic examination and trace element analyses indicate that brachiopod shells from Llandeilo to Ashgill are generally well preserved.

Presently, we accept an average $\delta^{18}O$ change from −5.5‰ for the Llandeilo to −4.5‰ for the Ashgill as reflecting the primary isotopic composition of the shells. Superimposed on the above long-term trend is a large positive excursion of about 2‰ at the latest Ordovician, probably reflecting a large expansion of polar ice caps. The magnitude of this excursion indicates a degree of glaciation comparable to that at the height of the Quaternary glacial episodes.

The observed increase in $\delta^{18}O$ with decreasing age can be attributed to an increasing enrichment of Ordovician seawater in ^{18}O combined with progressive cooling of shallow waters, particularly evident towards the end of the Ordovician. The former may have been a response to global tectonic evolution that led to a relative increase in the proportion of high to low temperature water/rock interaction in the crust, as indicated also by the concomitant rapid enhancement of "mantle" components in isotopic signal of marine strontium.

Although diagenetic alteration may render the $\delta^{18}O$ signals from Tremadoc to Llanvirn suspect, their $\delta^{13}C$ values may still be preserved. The observed average $\delta^{13}C$ values for Ordovician brachiopods increase from −2‰ in Tremadoc to about +2‰ in Ashgill and, similar to $\delta^{18}O$, there is a major positive shift at the end of Ordovician. The general increase in $\delta^{13}C$ of Ordovician seawater could have resulted from an increased organic productivity and/or enhanced organic deposition in the ocean. The latter could have been also responsible for the global positive shift in $\delta^{13}C$ at the end of the Ordovician.

Acknowledgments—We acknowledge donation of samples by T. E. Bolton (Geological Survey of Canada, Ottawa), H. J. Hoffman (University of Montreal, Montreal), E. Landing (New York Geological Survey, Albany), J. F. Miller (S.W. Missouri State University, Springfield), and J. B. Waddington (Royal Ontario Museum, Toronto), technical assistance in the laboratory by G. St-Jean, J. Loop, and M. MacLean, and discussions with F. Brunton, A. Desrochers, R. J. Ross Jr., and K. Wang. Constructive comments by the journal reviewers, U. Brand, S. Carpenter, and E. Grossman greatly improved the manuscript. This study was financially supported by the Natural Sciences and Engineering Research Council of Canada.

Editorial handling: H. P. Schwarcz

REFERENCES

ADLIS D. S., GROSSMAN E. L., YANCEY T. E., and MCLERRAN, R. D. (1988) Isotope stratigraphy and paleodepth changes of Pennsylvanian cyclical sedimentary deposits. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **59**, 487–506.

ANDERSON T. F. and ARTHUR M. A. (1983) Stable isotopes of oxygen and carbon and their application to sedimentologic and paleoenvironmental problems. In *Stable Isotopes in Sedimentary Geology* (ed. M. A. ARTHUR et al.); *SEPM Short Course 10*, pp. 1.1–1.151.

BATES N. R. and BRAND U. (1991) Environmental and physiological influences on isotopic and elemental compositions of brachiopod shell calcite: implications for the isotopic evolution of Paleozoic oceans. *Chem. Geol.* **94**, 67–78.

BRAND U. (1989) Biogeochemistry of Late Paleozoic North American brachiopods and secular variation of seawater composition. *Biogeochemistry* **7**, 159–193.

BRAND U. and MORRISON J. O. (1987) Biogeochemistry of fossil marine invertebrate. *Geosci. Canada* **14**, 85–107.

BRENCHLEY P. J., MARSHALL J. D., ROBERSTON D. B. R., HINTS L., and CARDEN G. A. F. (1992) Climatic-biotic interactions in the Late Ordovician mass extinction. In *Fifth International Conf. Global Bioevents, Gottingen, Germany; Abstract Vol.* pp. 22–23.

BRENCHLEY P. J. et al. (1994a) Bathymetric and isotopic evidence for a short-lived late Ordovician glaciation in a greenhouse period. *Geology* **22**, 295–298.

BRENCHLEY P. J., CARDEN G. A. F., and MARSHALL J. D. (1994b) Environmental changes associated with the "first strike" of the late Ordovician mass extinction. *Modern Geol.* (in press).

BURKE W. H., DENISON R. E., HETHERINGTON E. A., KOEPINCK R. B., NELSON H. F., and OTTO J. B. (1982) Variation of seawater $^{87}Sr/^{86}Sr$ throughout Phanerozoic time. *Geology* **10**, 516–519.

CALDEIRA K., ARTHUR M. A., BERNER R. A., and LASAGA A. C. (1993) Cooling in the late Cenozoic. *Nature* **361**, 123–124.

CARPENTER S. J. (1991) Isotopic and minor element chemistry of Devonian-Carboniferous abiotic marine calcite. Ph.D. thesis, Univ. of Michigan.

CARPENTER S. J. and LOHMANN K. C. (1989) $\delta^{18}O$ and $\delta^{13}C$ variations in Lake Devonian marine elements from Golden Spike and Nevis reefs, Alberta, Canada. *J. Sediment. Petrol.* **59**, 792–814.

CARPENTER S. J. and LOHMANN K. C. (1992) Sr/Mg ratios of modern marine calcite: empirical indicators of ocean chemistry and precipitation rate. *Geochim. Cosmochim. Acta* **56**, 1837–1849.

CARPENTER S. J. and LOHMANN K. C. (1994) $\delta^{18}O$ and $\delta^{13}C$ values of modern brachiopod shells. *Geochim. Cosmochim. Acta* (in press).

CARPENTER S. J., LOHMANN K. C., HOLDEN P., WALTER L. M., HUSTON T. J., and HALLIDAY A. N. (1991) $\delta^{18}O$ values, $^{87}Sr/^{86}Sr$ and Sr/Mg ratios of Late Devonian abiotic marine calcite: implications for the composition of ancient seawater. *Geochim. Cosmochim. Acta* **55**, 1991–2010.

DEGENS E. T. and EPSTEIN S. (1962) Relationship between O^{18}/O^{16} ratios in coexisting carbonates, cherts and diatomites. *Amer. Assoc. Petrol. Geol. Bull.* **46**, 534–542.

DIENER A. (1992) Variation im Verhaltnis von $^{87}Sr/^{86}Sr$ in Brachiopodenschalen aus dem Devon der Eifel. Diplomarbeit, Ruhr-Universitat Bochum.

DONTSOVA E. I. (1970) Oxygen isotope exchange in rock forming processes. *Geochem. Intl.* **7**, 624–636.

ELDERFIELD H. (1986) Strontium isotope stratigraphy. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **57**, 71–90.

EPSTEIN S., BUCHSBAUM R., LOWENSTAM H. A., and UREY H. C. (1951) Carbonate-water isotopic temperature scale. *GSA Bull.* **62**, 417–426.

ETHINGTON R. L. and CLARK D. L. (1981) Lower and Middle Ordovician conodonts from the Ibex area, western Millard County, Utah. *Brigham Young Univ. Geol. Studies 28* (pt. 2), p. 115.

FRITZ P. (1971) Geochemical characteristics of dolomites and $\delta^{18}O$ content of Middle Devonian oceans. *Earth Planet. Sci. Lett.* **11**, 277–282.

GAO G. and LAND S. L. (1991) Geochemistry of Cambro-Ordovician Arbuckle limestone, Oklahoma: implications for diagenetic $\delta^{18}O$ alteration and secular $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ variation. *Geochim. Cosmochim. Acta* **55**, 2911–2920.

GIVEN R. K. and LOHMANN K. C. (1986) Isotopic evidence for the early diagenesis of the reef facies, Permian reef complex of west Texas and New Mexico. *J. Sediment Petrol.* **56**, 183–193.

GONZALEZ L. A. and LOHMANN K. C. (1985) Carbon and oxygen isotopic composition of Holocene reefal carbonates. *Geology* **13**, 811–814.

GREGORY R. T. (1991) Oxygen isotope history of seawater revisited: Timescales for boundary event changes in the oxygen isotope composition of seawater. In *Stable Isotope Geochemistry: A Tribute to Samuel Epstein* (ed. H. P. TAYLOR JR. et al.); *Geochem. Soc. Spec. Publ. 3*, pp. 65–76.

GREGORY R. T. and TAYLOR H. P. (1981) An oxygen isotope profile in a section of Cretaceous oceanic crust, Samail Ophiolite, Oman: evidence for $\delta^{18}O$ buffering of the oceans by deep (5 km) seawater-hydrothermal circulation at midocean ridges. *J. Geophys. Res.* **86**, 2737–2755.

GROSSMAN E. L., ZHANG C., and YANCEY T. E. (1991) Stable-isotope stratigraphy of brachiopods from Pennsylvanian shales in Texas. *GSA Bull.* **103**, 953–965.

GROVER G. A., JR. (1981) Cement types and cementation patterns of Middle Ordovician ramp-to-basin carbonates, Virginia. Ph.D. thesis, Virginia Polytechnic Inst. and State Univ.

GRUSZCZYNSKI M., HOFFMAN A., MALKOWSKI K., and VEIZER J. (1992) Seawater strontium isotopic perturbation at the Permian-Triassic boundary, West Spitsbergen, and its implications for the interpretation of strontium isotopic data. *Geology* **20**, 779–782.

HARLAND W. B., ARMSTRONG R. L., COX A. V., CRAIG L. E., SMITH A. G., and SMITH D. G. (1990) *A Geological Time Scale 1989.* Cambridge Univ. Press.

HEIBERT R. N., CARPENTER S. J., and LOHMANN K. C. (1988) $\delta^{18}O$ and $\delta^{13}C$ variation in recent brachiopods: implications for the use of brachiopods as indicators of paleo-ocean chemistry. *SEPM Annual Midyear Mtg.* **5**, p. 25. (Abstr.).

HOLLAND H. D. (1984) *The Chemical Evolution of the Atmosphere and Oceans.* Princeton Univ. Press.

HOLMDEN C. and MUEHLENBACHS K. (1993) The $^{18}O/^{16}O$ ratio of 2-billion-year-old seawater inferred from ancient oceanic crust. *Science* **259**, 1733–1736.

HOLSER W. T., SCHIDLOWSKI M., MACKENZIE F. T., and MAYNARD J. B. (1988) Biogeochemical cycles of carbon and sulfur. In *Chemical Cycles in the Evolution of the Earth* (ed. C. B. GREGOR et al.), pp. 105–174. Wiley Interscience.

HUDSON J. D. and ANDERSON T. F. (1989) Ocean temperatures and isotopic compositions through time. *Roy. Soc. Edinburgh Trans.* **80**, 183–192.

JOHNSON W. J. and GOLDSTEIN R. H. (1993) Cambrian seawater preserved as inclusions in marine low-magnesium calcite cement. *Nature* **232**, 335–337.

KARHU J. and EPSTEIN S. (1986) The implication of the oxygen isotope records in coexisting cherts and phosphates. *Geochim. Cosmochim. Acta* **50**, 1745–1756.

KNAUTH L. P. and EPSTEIN S. (1976) Hydrogen and oxygen isotope ratios in nodular and bedded charts. *Geochim. Cosmochim. Acta* **40**, 1095–1108.

KNAUTH L. P. and LOWE D. R. (1978) Oxygen isotope geochemistry of cherts from the Onverwacht Group (3.4 Billion years), Transvaal, South Africa, with implications for secular variations in the isotopic composition of cherts. *Earth Planet. Sci. Lett.* **64**, 398–404.

KOLODNY Y. and EPSTEIN S. (1976) Stable isotope geochemistry of deep sea cherts. *Geochim. Cosmochim. Acta* **40**, 1195–1209.

KU T. L. and LUO S. (1992) Carbon isotopic variations on glacial-to-interglacial time scales in the ocean: modeling and implications. *Paleoceanography* **7**, 543–562.

LAND L. S. (1980) The isotopic and trace element geochemistry of dolomite: The state of the art. In *Concepts of Models of Dolomitization* (ed. D. H. ZENGER et al.); *SEPM Spec. Publ. 28*, pp. 87–110.

LAND L. S. (1983) The application of stable isotopes to studies of the origin of dolomite and to problems of diagenesis of clastic sediments. In *Stable Isotopes in Sedimentary Geology* (ed. M. A. ARTHUR et al.); *SEPM Short Course 10*, pp. 4.1–4.22.

LOHMANN K. C. and WALKER J. G. C. (1989) The $\delta^{18}O$ record of Phanerozoic abiotic marine calcite cements. *Geophys. Res. Lett.* **16**, 319–322.

LONG D. G. F. (1993) Oxygen and carbon isotopes and event stratigraphy near the Ordovician-Silurian boundary, Anticosti Island, Quebec. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **104**, 49–59.

LOWENSTAM H. A. (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. *J. Geol.* **69**, 241–260.

MARSHALL J. D. and MIDDLETON J. D. (1990) Changes in marine isotopic composition and the late Ordovician glaciation. *J. Geol. Soc. London* **147**, 1–4.

MCCONNAUGHEY T. (1989a) ^{13}C and ^{18}O isotopic disequilibrium in biological carbonates: I Patterns. *Geochim. Cosmochim. Acta* **53**, 151–162.

McConnaughey T. (1989b) ^{13}C and ^{18}O isotopic disequilibrium in biological carbonates: II. In vitro simulation of kinetic isotope effects. *Geochim. Cosmochim. Acta* **53**, 163–171.

Meyers W. J. and Lohmann K. C. (1985) Isotope geochemistry of regionally extensive calcite cement zones and marine components in Mississippian limestones, New Mexico. *SEPM Spec. Publ. 36*, pp. 223–240.

Middleton P. D., Marshall J. D., and Brenchley P. J. (1991) Evidence for isotopic changes associated with Late Ordovician glaciation from brachiopod and marine cements of central Sweden. *Geol. Surv. Canada Pap. 90-9*, pp. 313–321.

Morrison J. O. and Brand U. (1986) Geochemistry of recent marine invertebrates. *Geosci. Canada* **13**, 237–254.

Muehlenbachs K. and Clayton R. N. (1976) Oxygen isotope composition of the oceanic crust and its bearing on seawater. *J. Geophys. Res.* **81**, 4365–4369.

Perry E. C. (1967) The oxygen isotope chemistry of ancient cherts. *Earth Planet. Sci. Lett.* **3**, 62–66.

Perry E. C. and Tan F. C. (1972) Significance of oxygen and carbon isotope variations in Early Precambrian cherts and carbonate rocks of southern Africa. *GSA Bull.* **83**, 647–664.

Popp B. N., Anderson T. F., and Sandberg P. A. (1986) Textural, elemental, and isotopic variations among constituents in Middle Devonian limestones, North America. *J. Sediment Petrol.* **56**, 715–727.

Prentice M. L. and Matthews R. K. (1988) Cenozoic ice-volume history: development of a composite oxygen isotope record. *Geology* **16**, 963–966.

Qing H. and Mountjoy E. W. (1989) Multistage dolomitization in Rainbow buildups, Middle Devonian Keg River Formation, Alberta, Canada. *J. Sediment Petrol.* **59**, 114–126.

Qing H. and Mountjoy E. W. (1994) Formation of coarsely crystalline, hydrothermal dolomite reservoirs in the Presqu'ile barrier, Western Canada Sedimentary Basin. *Amer. Assoc. Petrol. Geol. Bull.* **78**, 55–77.

Railsback L. B. (1990) Influence of changing deep ocean circulation on the Phanerozoic oxygen isotope record. *Geochim. Cosmochim. Acta* **54**, 1501–1509.

Rush P. F. and Chafetz H. S. (1990) Fabric-retentive, non-luminescent brachiopods as indicators of original $\delta^{13}C$ and $\delta^{18}O$ composition: A test. *J. Sediment Petrol.* **60**, 968–981.

Savin S. M. (1977) The history of the Earth's surface temperature during the past 100 million years. *Ann. Rev. Earth Planet. Sci.* **5**, 319–355.

Savin S. M. and Yeh H. W. (1981) Stable isotopes in ocean sediments. In *The Sea*, Vol. 7 (ed. C. Emiliani), pp. 1521–1554. Wiley-Interscience.

Scotese C. R. and McKerrow W. S. (1990) Revised world maps and introduction. In *Palaeozoic Palaeogeography and Biogeography; Geol. Soc. London Mem. 12*, pp. 1–21.

Schidlowski M., Eichmann R., and Junge C. E. (1975) Precambrian sedimentary carbonates; carbon and oxygen isotope geochemistry and implications for the terrestrial oxygen budget. *Precambrian Res.* **2**, 1–69.

Spjeldnaes N. (1981) Lower Paleozoic paleoclimatology. In *Lower Paleozoic of the Middle East, Eastern and Southern Africa, and Antarctica* (ed. C. H. Holland), pp. 199–256. Wiley.

Stille P., Chaudhuri S., Kharaka Y. K., and Clauer N. (1992) Neodymium, strontium, oxygen and hydrogen isotope compositions of waters in present and past oceans: a review. In *Isotopic Signatures and Sedimentary Records* (ed. N. Clauer and S. Chaudhuri); *Springer Lecture Notes in Earth Sciences 43*, pp. 389–410.

Veizer J. (1983) Chemical diagenesis of carbonates: Theory and application of trace element technique. In *Stable Isotopes in Sedimentary Geology* (ed. M. A. Arthur et al.); *SEPM Short Course 10*, pp. 3.1–3.100.

Veizer J. (1992a) Depositional and diagenetic history of limestones: stable and radiogenic isotopes. In *Isotopic Signatures and Sedimentary Records* (ed. N. Clauer and S. Chaudhuri); *Springer Lecture Notes in Earth Sciences 43*, pp. 13–48.

Veizer J. (1992b) Atmospheric evolution: Life and the rock cycle. *Nature* **359**, 587–588.

Veizer J. and Hoefs J. (1976) The nature of O^{18}/O^{16} and C^{13}/C^{12} secular trends in sedimentary carbonate rocks. *Geochim. Cosmochim. Acta* **40**, 1387–1395.

Veizer J., Holser W. T., and Wilgus C. K. (1980) Correlation of $^{13}C/^{13}C$ and $^{34}S/^{32}S$ secular variations. *Geochim. Cosmochim. Acta* **44**, 579–587.

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

Wadleigh M. A. and Veizer J. (1992) $^{18}O/^{16}O$ and $^{13}C/^{12}C$ in lower Paleozoic articulate brachiopods: Implication for the isotopic composition of seawater. *Geochim. Cosmochim. Acta* **56**, 431–443.

Wang K., Chatterton B. D. E., Attrep M., Jr., and Orth C. J. (1993a) Late Ordovician mass extinction event on northwestern Laurentia: geochemical, paleontological and sedimentological analyses of the Ordovician-Silurian boundary interval, Mackenzie Mountains, N.W.T. *Canadian J. Earth Sci.* **30**, 1870–1880.

Wang K., Orth C. J., Attrep M., Jr., Chatterton B. D. E., Wang X., and Li J. (1993b) The great latest Ordovician extinction on the South China Plate: chemostratigraphic studies of the Ordovician boundary interval on the Yangtze Platform. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **104**, 61–97.

Webby B. D. (1984) Ordovician reefs and climate: a review. In *Aspects of the Ordovician System* (ed. D. L. Bruton), pp. 89–100. Universitetsforlaget.

Weber J. N. (1965a) The O^{18}/O^{16} ratio in ancient oceans. *Geokhimija* **6**, 674–680.

Weber J. N. (1965b) Evolution of the ocean and the origin of fine-grained dolomites. *Nature* **207**, 930–933.

Wefer G. and Berger W. H. (1991) Isotope paleontology: growth and composition of extent calcareous species. *Mar. Geol.* **100**, 207–248.

Wilde P. and Berry W. B. N. (1984) Progressive ventilation of the oceans—potential for return to anoxic conditions in the post-Paleozoic. In *Nature and Origin of Cretaceous Carbon Rich Facies* (ed. S. O. Schlanger and M. B. Cita), pp. 209–224. Academic Press.

Williams D. F., Lerche I., and Full W. E. (1988) *Isotope Chronostratigraphy: Theory and Methods*. Academic Press.

Witzke B. J. and Heckel P. H. (1988) Paleoclimatic indicators and inferred Devonian paleolatitudes of Euramerica: In *Devonian of the World* (ed. N. J. McMillan et al.); *Proc. Second Intl. Symp. Devonian System, Canadian Soc. Petrol. Geol.*, Vol. 1, pp. 49–63.

Yapp C. J. and Poths H. (1992) Ancient atmospheric CO_2 pressures inferred from natural goethites. *Nature* **355**, 342–355.

Appendix List of samples and analytical data. Ca and I.R. in%, others in ppm; $\delta^{18}O$ and $\delta^{13}C$ in % PDB. Lithology: S - shales; L - limestones. BDL - below the detection limit. Approximate ages estimated by linear interpolation from Harland et al (1990).

No.	Strat.	Fm.	Description	lith.	locality	Ma.	$\delta^{18}O$	$\delta^{13}C$	Ca	Mg	Mn	Fe	K	Na	Sr	I.R.
18-1	Ash	Ellis Bay	*Vellamo sp.*	S	Anticosti Is	439	-3.03	1.61	39.22	3600	37	59	30	890	1097	BDL
18-2	Ash	Ellis Bay	*Vellamo sp.*	S	Anticosti Is	439	-3.26	1.55	39.70	3370	72	1785	219	851	1048	BDL
18-3	Ash	Ellis Bay	*Vellamo sp.*	S	Anticosti Is	439	-3.28	1.53	38.16	3563	54	174	325	813	1016	BDL
18-4	Ash	Ellis Bay	*Vellamo sp.*	S	Anticosti Is	439	-3.03	1.64	42.22	3904	51	135	247	856	1040	BDL
18-5	Ash	Ellis Bay	*Vellamo sp.*	S	Anticosti Is	439	-3.61	1.57	38.30	4619	93	967	185	668	884	0.02
19-1	Ash	Ellis Bay	*Eospirigerina sp.*	S	Anticosti Is	439	-3.08	1.63	40.19	1584	99	2544	342	689	1022	BDL
19-2	Ash	Ellis Bay	*Eospirigerina sp.*	S	Anticosti Is	439	-3.17	1.63								
19-3	Ash	Ellis Bay	*Eospirigerina sp.*	S	Anticosti Is	439	-2.95	1.57								
19-4	Ash	Ellis Bay	*Eospirigerina sp.*	S	Anticosti Is	439	-3.18	1.52								
20-1	Ash	Ellis Bay	*Sowerbylla sp.*	S	Anticosti Is	439	-3.04	0.61								
20-2	Ash	Ellis Bay	*Sowerbylla sp.*	S	Anticosti Is	439	-3.11	0.66								
17-1	Ash	Great Lake	*Sowerbylla sp.*	S	Ohio	443	-5.60	-0.48	41.83	2693	412	516	251	693	1045	BDL
17-2	Ash	Great Lake	*Platystrophia sp.*	S	Ohio	443	-5.67	-0.56	40.63	2892	432	967	225	634	1037	BDL
17-3	Ash	Great Lake	*Platystrophia sp.*	S	Ohio	443	-5.08	0.14	38.96	2447	148	342	229	998	1109	BDL
17-5	Ash	Great Lake	*Platystrophia sp.*	S	Ohio	443	-4.90	0.18	40.90	3904	150	1119	416	886	1213	BDL
17-6	Ash	Great Lake	*Platystrophia sp.*	S	Ohio	443	-4.86	0.24	41.58	3111	149	184	244	844	1252	BDL
17-7	Ash	Great Lake	*Platystrophia sp.*	S	Ohio	443	-4.84	0.27	41.68	3246	123	164	379	782	1199	BDL
17-8	Ash	Great Lake	*Platystrophia sp.*	S	Ohio	443	-5.05	0.29	41.73	3116	321	1499	227	787	1172	0.04
17-9	Ash	Great Lake	*Platystrophia sp.*	S	Ohio	443	-4.95	0.20	37.71	3422	165	2071	308	707	1051	0.05
17-10	Ash	Great Lake	*Hebertella*	S	Ohio	443	-4.82	0.26	42.15	3376	124	143	451	817	1242	BDL
17-11	Ash	Great Lake	*Hebertella*	S	Ohio	443	-5.20	0.20	39.69	2503	198	264	369	960	1104	BDL
17-12	Ash	Great Lake	*Hebertella*	S	Ohio	443	-5.21	0.30	43.75	3545	425	2213	354	684	1126	0.05
17-14	Ash	Great Lake	*Hebertella*	S	Ohio	443	-4.81	0.34	39.02	2800	77	139	175	774	1073	BDL
17-15	Ash	Great Lake	*Hebertella*	S	Ohio	443	-4.94	0.16	43.02	3115	184	359	277	861	1245	BDL
17-16	Ash	Great Lake	*Hebertella*	S	Ohio	443	-4.94	0.16	42.65	3054	229	869	250	770	1179	BDL
17-17	Ash	Great Lake	*Hebertella*	S	Ohio	443	-4.84	0.23	41.45	2996	76	108		821	1255	BDL
17-18	Ash	Great Lake	*Hebertella*	S	Ohio	443	-4.86	0.08	42.16	2986	83	119	261	820	1260	BDL
15-1	Crd	Trenton	*Strophomena*	L	Ontario	453	-5.35	0.99	38.29	3273	109	225	178	603	908	0.02
15-2	Crd	Trenton	*Strophomena*	L	Ontario	453	-5.49	0.93	40.39	3739	133	430	414	683	926	BDL
15-3	Crd	Trenton	*Strophomena*	L	Ontario	453	-5.25	1.52	38.65	2976	95	166	101	684	957	BDL
15-4	Crd	Trenton	*Strophomena*	L	Ontario	453	-5.14	1.49	41.06	2915	91	99	382	848	1083	BDL
15-5	Crd	Trenton	*Strophomena*	L	Ontario	453	-5.24	1.56	38.51	3302	91	302	266	742	961	BDL
15-6	Crd	Trenton	*Strophomena*	L	Ontario	453	-5.20	1.59	39.55	2538	80	31	232	832	1071	BDL
15-8	Crd	Trenton	*Strophomena*	L	Ontario	453	-4.82	1.21	40.31	3000	79	130	189	811	1095	BDL
16.1-1	Crd	Trenton			Tennessee	453	-4.93	-0.03	40.22	2934	222	272	328	633	730	0.22
16.1-2	Crd	Trenton			Tennessee	453	-5.09	-0.05	40.81	2815	250	139	180	601	725	BDL
16.1-3	Crd	Trenton			Tennessee	453	-5.02	-0.06	40.18	2774	256	182	423	567	703	BDL
16.2-1	Crd	Trenton			Tennessee	453	-5.96	-1.15								
12-1	Llo	Laval Fm	*Mimella vulgaris*	L	Ontario	467	-7.08	-0.58	39.78	3022	192	415	291	891	1379	BDL
12-4	Llo	Laval Fm	*Mimella vulgaris*	L	Ontario	467	-7.82	-0.11	40.53	6038	727	2782	146	663	1216	0.02

Appendix (Continued)

No.	Strat.	Fm.	Description	lith.	locality	Ma.	$\delta^{18}O$	$\delta^{13}C$	Ca	Mg	Mn	Fe	K	Na	Sr	I.R.
12-5	Llo	Laval Fm	*Mimella vulgaris*	L	Ontario	467	-7.50	-0.10	39.55	3768	244	1476	360	842	1386	BDL
12-6	Llo	Laval Fm	*Mimella vulgaris*	L	Ontario	467	-7.76	-0.35	40.70	4235	415	1985	417	893	1398	0.04
12-7	Llo	Laval Fm	*Mimella vulgaris*	L	Ontario	467	-7.68	-0.04	42.44	2955	316	647	300	832	1415	0.05
12-8	Llo	Laval Fm	*Rostricellula raymondi*	L	Ontario	467	-8.19	-0.15	40.49	4419	743	2220	251	592	1026	0.01
12-9	Llo	Laval Fm	*Rostricellula raymondi*	L	Ontario	467	-7.77	-0.27	41.16	5325	587	1908	389	850	1301	0.04
12-10	Llo	Laval Fm	*Rostricellula raymondi*	L	Ontario	467	-7.57	-0.32	41.02	3995	284	1253	230	875	1437	0.02
12-11	Llo	Laval Fm	*Rostricellula raymondi*	L	Ontario	467	-7.72	-0.20	39.26	4359	532	1904	300	738	1265	0.02
12-12	Llo	Laval Fm	*Rostricellula raymondi*	L	Ontario	467	-7.79	-0.20	41.16	5325	587	1908	389	850	1301	0.04
21-2	Llo	Chazy	*Hebertella imperator*	L	Quebec	467	-6.36	-0.02								
21-3	Llo	Chazy	*Hebertella imperator*	L	Quebec	467	-6.48	-0.36								
22-1	Llo	Chazy	*Mimella imperator*	L	Ontario	467	-7.27	-0.58	38.68	4360	400	1149	266	745	1334	BDL
22-2	Llo	Chazy	*Mimella imperator*	L	Ontario	467	-7.04	-0.11	39.08	3525	421	759	4	745	1372	0.02
22-3	Llo	Chazy	*Mimella imperator*	L	Ontario	467	-7.38	-0.64	38.84	4221	623	1366	212	730	1301	0.02
26-1	Lln	t-Kanosh	*Anomalorthis sp.*	S	Utah	472	-8.61	-1.74								
26-2	Lln	t-Kanosh	*Anomalorthis sp.*	S	Utah	472	-8.53	-1.60								
26-3	Lln	t-Kanosh	*Anomalorthis sp.*	S	Utah	472	-8.51	-1.63								
26-4	Lln	t-Kanosh	*Anomalorthis sp.*	S	Utah	472	-8.59	-1.57								
MC-1	Lln	Antelope Valley Ls.	Marine cement	L	Nevada	474	-6.43	0.55	40.38		150	105		164	275	BDL
MC-2	Lln	Antelope Valley Ls.	Marine cement	L	Nevada	474	-6.15	0.58								BDL
MC-3	Lln	Antelope Valley Ls.	Marine cement	L	Nevada	474	-6.36	0.25	40.39		100	123	74	205	344	BDL
MC-4	Lln	Antelope Valley Ls.	Marine cement	L	Nevada	474	-7.28	0.54	41.17		87	258	22	122	384	BDL
MC-5	Lln	Antelope Valley Ls.	Marine cement	L	Nevada	474	-7.02	0.48	39.62		66	228	109	280	377	BDL
MC-6	Lln	Antelope Valley Ls.	Marine cement	L	Nevada	474	-7.33	0.49	40.45		75	235	202	245	360	BDL
MC-7	Lln	Antelope Valley Ls.	Marine cement	L	Nevada	474	-7.29	0.71	40.48		65	101	345	302	414	BDL
MC-8	Lln	Antelope Valley Ls.	Marine cement	L	Nevada	474	-6.53	0.57	40.43		68		12	206	328	BDL
MC-9	Lln	Antelope Valley Ls.	Marine cement	L	Nevada	474	-6.33	0.55	41.91		83	115		289	379	BDL
MC-10	Lln	Antelope Valley Ls.	Marine cement	L	Nevada	474	-6.79	0.56	41.23		84	65	201	259	336	BDL
MC-11	Lln	Antelope Valley Ls.	Marine cement	L	Nevada	474	-6.83	0.49	40.67		307	1038	633	297	436	BDL
MC-12	Lln	Antelope Valley Ls.	Marine cement	L	Nevada	474	-8.30	-0.98	40.33		290	804	550	215	434	BDL
MC-13	Lln	Antelope Valley Ls.	Marine cement	L	Nevada	474	-7.65	0.22	38.94		499	857	591	164	405	BDL
MC-14	Lln	Antelope Valley Ls.	Marine cement	L	Nevada	474	-7.85	0.50	42.43		80	41	271	218	334	BDL
MC-15	Lln	Antelope Valley Ls.	Marine cement	L	Nevada	474	-7.93	0.17	40.97		29	43		186	526	BDL
MC-16	Lln	Antelope Valley Ls.	Marine cement	L	Nevada	474	-7.10	0.01	40.89		27	33	339	191	387	BDL
MC-17	Lln	Antelope Valley Ls.	Marine cement	L	Nevada	474	-7.86	0.14	43.11		46	337	416	169	642	BDL
MC-18	Lln	Antelope Valley Ls.	Marine cement	L	Nevada	474	-6.78	0.21	43.55		27	109	161	177	357	BDL
MC-19	Lln	Antelope Valley Ls.	Marine cement	L	Nevada	474	-6.94	0.07	42.26		32	110	133	175	362	BDL
MC-20	Lln	Antelope Valley Ls.	Marine cement	L	Nevada	474	-6.40	0.72	40.38		256	845	913	127	343	BDL
MC-21	Lln	Antelope Valley Ls.	Marine cement	L	Nevada	474	-7.38	0.17	40.79		194	169	200	147	341	BDL
10-1	Lln	m-Kanosh	*Anomalorthis sp.*	S	Utah	475	-7.88	-1.65	40.15	3949	549	2477	545	896	1421	0.04
10-2	Lln	m-Kanosh	*Anomalorthis sp.*	S	Utah	475	-7.48	-1.61	40.15	3218	324	1424	532	995	1501	BDL
10-3	Lln	m-Kanosh	*Anomalorthis sp.*	S	Utah	475	-8.35	-1.70	40.22	4150	586	2839	312	932	1363	0.03
10-4	Lln	m-Kanosh	*Anomalorthis sp.*	S	Utah	475	-8.33	-1.64	40.60	3974	695	4031	239	905	1479	0.05
10-5	Lln	m-Kanosh	*Anomalorthis sp.*	S	Utah	475	-8.41	-1.75	41.02	4079	726	2690	288	738	1273	0.03
10-6	Lln	m-Kanosh	*Anomalorthis sp.*	S	Utah	475	-8.34	-5.55	40.93	5120	908	7267	430	908	1316	0.07
10-7	Lln	m-Kanosh	*Anomalorthis sp.*	S	Utah	475	-8.38	-1.60	42.70	4276	657	1597	588	957	1457	0.04
25-1	Lln	b-Kanosh	*Anomalorthis sp.*	S	Utah	478	-8.43	-1.60								
25-2	Lln	b-Kanosh	*Anomalorthis sp.*	S	Utah	478	-8.95	-1.61								

Appendix (Continued)

No.	Strat.	Fm.	Description	lith.	locality	Ma.	$\delta^{18}O$	$\delta^{13}C$	Ca	Mg	Mn	Fe	K	Na	Sr	I.R.
25-3	Lln	b-Kanosh	*Anomalorthis sp.*	S	Utah	478	-8.16	-1.99								
25-4	Lln	b-Kanosh	*Anomalorthis sp.*	S	Utah	478	-8.18	-2.10								
25-5	Lln	b-Kanosh	*Anomalorthis sp.*	S	Utah	478	-8.74	-1.98								
23-1	Arg	Juab	*Orthambonites sp.*	L	Utah	480	-8.54	-0.79								
23-2	Arg	Juab	*Orthambonites sp.*	L	Utah	480	-8.40	-1.07								
23-3	Arg	Juab	*Orthambonites sp.*	L	Utah	480	-8.67	-0.77								
23-5	Arg	Juab	*Orthambonites sp.*	L	Utah	480	-8.67	-0.79								
23-6	Arg	Juab	*Orthambonites sp.*	L	Utah	480	-8.69	-0.78								
23-7	Arg	Juab	*Orthambonites sp.*	L	Utah	480	-8.71	-0.91								
24-1	Arg	Wahwah	*Hesperonomia sp.*	L	Utah	485	-8.80	-0.97								
24-2	Arg	Wahwah	*Hesperonomia sp.*	L	Utah	485	-8.61	-1.02								
24-3	Arg	Wahwah	*Hesperonomia sp.*	L	Utah	485	-8.74	-1.10								
24-4	Arg	Wahwah	*Hesperonomia sp.*	L	Utah	485	-8.62	-0.97								
24-5	Arg	Wahwah	*Hesperonomia sp.*	L	Utah	485	-8.65	-0.79								
9-1	Arg	Wahwah	*Hesperonomia sp.*	L	Utah	485	-8.58	-0.96	40.34	3203	47	133	125	717	1489	BDL
9-2	Arg	Wahwah	*Hesperonomia sp.*	L	Utah	485	-8.61	-0.82	39.72	3875	41	117	267	841	1480	BDL
9-3	Arg	Wahwah	*Hesperonomia sp.*	L	Utah	485	-8.56	-0.81	40.88	3502	34	143	365	890	1500	BDL
9-4	Arg	Wahwah	*Hesperonomia sp.*	L	Utah	485	-8.58	-0.67	40.77	4079	34	71	184	888	1583	BDL
9-6	Arg	Wahwah	*Hesperonomia sp.*	L	Utah	485	-8.71	-0.85	40.17	3885	96	380	466	962	1450	BDL
9-7	Arg	Wahwah	*Hesperonomia sp.*	L	Utah	485	-8.86	-0.77	39.76	3768	202	663	277	759	1262	BDL
9-8	Arg	Wahwah	*Hesperonomia sp.*	L	Utah	485	-8.81	-0.91								
9-9	Arg	Wahwah	*Hesperonomia sp.*	L	Utah	485	-8.61	-0.85	39.87	3667	58	156	233	798	1539	BDL
9-10	Arg	Wahwah	*Hesperonomia sp.*	L	Utah	485	-8.70	-1.05								
9-11	Arg	Wahwah	*Hesperonomia sp.*	L	Utah	485	-8.76	-0.69	40.27	2840	105	260	395	802	1475	BDL
9-12	Arg	Wahwah	*Hesperonomia sp.*	L	Utah	485	-8.63	-0.77	40.78	3953	66	175	330	882	1421	BDL
9-13	Arg	Wahwah	*Hesperonomia sp.*	L	Utah	485	-8.59	-0.96	40.42	3848	45	378	278	876	1510	BDL
5-1	Tre	Fillmore	*Hesperonomia sp.*	L	Utah	490	-8.66	-1.28								
5-2	Tre	Fillmore	*Hesperonomia sp.*	L	Utah	490	-8.62	-0.95								
5-3	Tre	Fillmore	*Hesperonomia sp.*	L	Utah	490	-8.78	-2.47								
5-4	Tre	Fillmore	*Hesperonomia sp.*	L	Utah	490	-8.65	-0.91								
5a-1	Tre	Fillmore	*Hesperonomia sp.*	L	Utah	490	-8.41	-1.92								
5b-1	Tre	Fillmore	*Hesperonomia sp.*	L	Utah	490	-8.79	-0.87								
3-1	Tre	Spellman			New York	496	-9.92	-2.53								
3-2	Tre	Spellman			New York	496	-10.12	-2.37								
1-1	Tre	Tribes Hill	*Tetralobula palmata*		New York	502	-10.61	-2.05								
1-2	Tre	Tribes Hill	*Tetralobula palmata*		New York	502	-10.60	-2.09								