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

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ABSTRACT

We collected 236 calcitic brachiopod shells, covering the entire Silurian Period (~ 30 m.y.), at high temporal resolution from stratotype sections from Anticosti Island (Canada), Wales (United Kingdom), the Oslo region (Norway), Gotland (Sweden), and Podolia (Ukraine), Estonia, Latvia, and Lithuania. Data from petrography, scanning electron microscopy, cathodoluminescence, isotopes, and trace elements all confirmed that there was excellent preservation in most shells, thus arguing for retention of primary isotope signals; exceptions were samples from the Oslo region.

The $\delta^{18}O$ and $\delta^{13}C$ values for the well-preserved samples range from –2‰ to –6.5‰ and from –1‰ to 7.5‰ (Peedee belemnite), respectively. In terms of temporal trends, oxygen and carbon isotopes vary in parallel, with a slight decrease with declining age of ~1‰ through Silurian time, with superimposed short-term oscillations that are negatively correlated with sea-level changes. Three successive positive $\delta^{18}O$ shifts in early Aeronian, latest Aeronian, and early Wenlock time correlate with sea-level lowstands and with glacial diamictite deposits in the Amazon Basin and in Africa. The high $\delta^{18}O$ and $\delta^{13}C$ values are attributed to cold episodes with low sea levels and low values to warm episodes with high sea levels. During warm Silurian episodes, the $\delta^{18}O$ value of seawater is suggested to have been about –3.5‰ standard mean ocean water (SMOW) and the global tropical temperatures of about 20–30 °C, similar to the present-day values in summer. During glacial episodes, seawater is proposed to have had a $\delta^{18}O$ value of ~–2.5‰ (SMOW) and temperature of about 14–23 °C, comparable to tropical temperatures proposed for the last glacial episode (14 to 28 °C). Three positive $\delta^{13}C$ peaks, in early and late Wenlock and late Ludlow time, likely of regional to global significance, appear to coincide with sea-level lowstands, but we are as yet unable to propose a convincing causative geologic scenario that would explain their origin.

INTRODUCTION

Studies of the isotopic composition of Paleozoic seawater have relied on brachiopod shells (e.g., Popp et al., 1986; Veizer et al., 1986, 1997; Wadleigh and Veizer, 1992; Grossman, 1994) because (1) brachiopods are abundant in marine successions, (2) they precipitate shells composed of low-Mg calcite in apparent isotopic equilibrium with the ambient seawater, and (3) the low-Mg calcite shells tend to resist diagenesis, thus retaining primary isotopic signals. Furthermore, petrographic and chemical techniques, such as transmitted light microscopy, cathodoluminescence, scanning electron microscope (SEM), and trace element analysis make it possible to evaluate diagenetic alteration of the shell ultrastructure (e.g., Wadleigh and Veizer, 1992; Grossman, 1994).

Previous studies of Paleozoic brachiopods included only partial coverage for Silurian time. The main objectives of this study are to construct detailed isotope curves for the entire Silurian Period and to interpret these curves in terms of paleoclimate and paleoceanography. We examine isotopic variations in brachiopod shells sampled from stratotype sections at a resolution (<1 m.y.) higher than previous studies. Furthermore, we discuss the significance of a contentious issue (cf. Land, 1995, vs. Veizer, 1995): the fact that early–middle Paleozoic brachiopods are generally depleted in ^{18}O compared with their Holocene counterparts (Popp et al., 1986; Veizer et al., 1986).

STUDY AREAS

This study includes samples from diverse sedimentary basins and from different continents (cf. Azmy, 1996, for details). All represent low paleolatitudes, between 30°N and 30°S (Fig. 1). Sample localities are Anticosti Island, Québec, Canada (Laurentia), England, Norway, Sweden, Estonia, Lithuania, Latvia, and Podolia in the Ukraine (Baltica) (Fig. 2). Samples were collected from limestones deposited on shallow shelves or ramps, commonly associated with reefs (Copper and Brunton, 1991).

METHODOLOGY

Brachiopods were collected from exposed successions (Podolia, Ukraine), from borehole materials (Lithuania and Latvia), or obtained from collections at the Natural Museum of Wales (Britain, Norway and Sweden) and at the Department of Earth Sciences, Laurentian University (Anticosti Island, Québec). In addition to brachiopods, samples include some carbonate cements and matrix.

Only apparently well-preserved brachiopod shells were selected for further studies. For these, two identical slabs, passing through the umbo (each about 1.5 mm thick), were cut using a microsaw cutting machine and each

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Data Repository item 9880 contains additional material related to this article.

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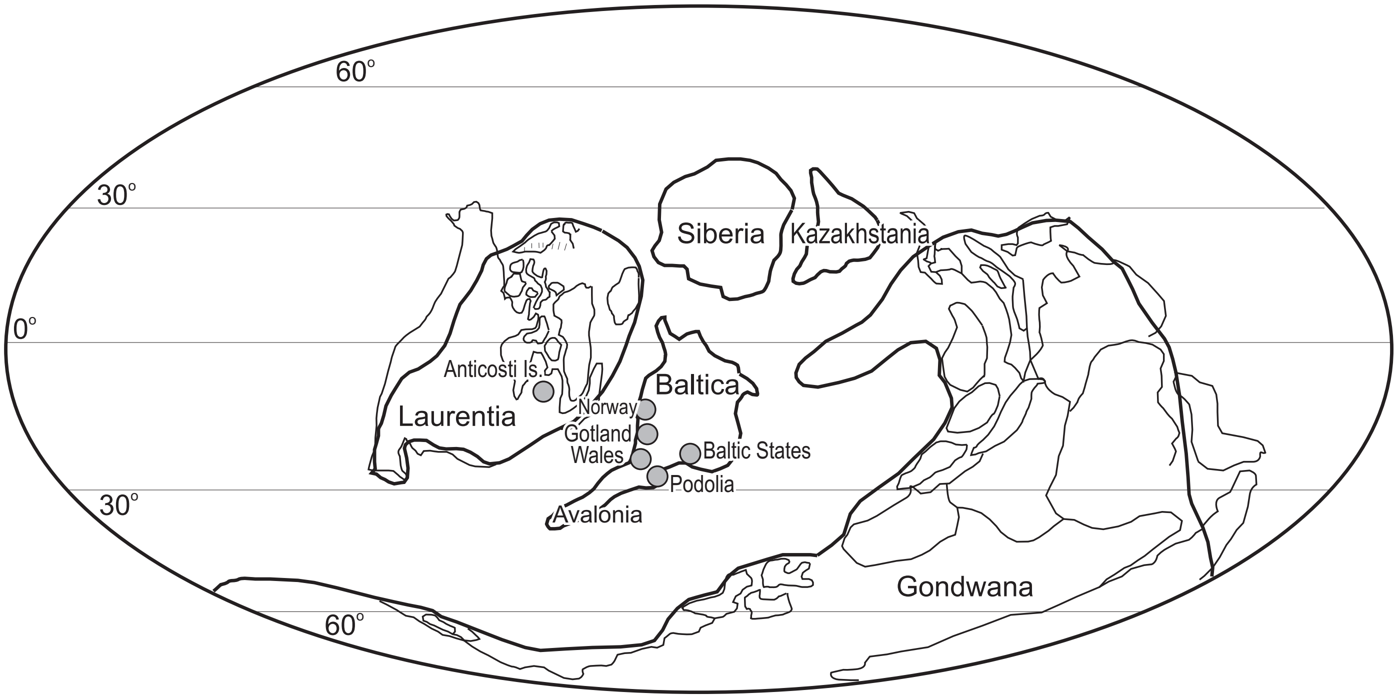

Figure 1. Paleogeographic map of the world during Early Silurian time (Llandovery), showing relative positions of paleocontinents (from Cocks and Scotese, 1991) and approximate locations of studied sections (highlighted circles).

slab was gently polished on a glass plate using Al_2O_3 powder (size 9.5 µm). One of the slabs was prepared as a thin section and studied under polarizing microscope and luminoscope (Technosyn cold cathode luminoscope) to examine the preservation of the calcite fibers.

The carbonate material from the nonluminescent portions of the secondary layer was microsampled from the other slab by breaking the shell under binocular microscope with a stainless steel dental pick (cf. Diener et al., 1996). The fragments were picked by forceps, submerged in deionized water, and cleaned in an ultrasonic bath. Samples were dried overnight at room temperature.

A fragment of dry sample was coated with gold and examined by SEM (JEOL 6400), and the rest was ground in a previously acid-washed small agate mortar.

About 3 mg of the powdered sample was reacted under vacuum overnight with ~1.5 ml of ultrapure orthophosphoric acid at 25 °C in a water bath. Produced CO_2 was analyzed using the VG Isogas SIRA-12 triple collecting mass spectrometer at the G. G. Hatch Isotope Laboratories of the University of Ottawa. The results are reported in per mil relative to Peedee belemnite (PDB). The laboratory standards were NBS-18 ($\delta^{18}O$ = –23.00‰ and $\delta^{13}C$ = –5.00‰ PDB) and NBS-19 ($\delta^{18}O$ = –2.20‰ and $\delta^{13}C$ = +1.95‰ PDB). The routine precision (2σ) for $\delta^{18}O$ and for $\delta^{13}C$ was 0.1‰.

The residual H_3PO_4 left after the preparation of CO_2 gas for C and O isotope measurements was analyzed for Ca, Mg, Sr and Mn (Coleman et al., 1989) using a Thermo Jarrell Ash–AtomScan 25 inductively coupled plasma source spectrometer at the University of Ottawa. The chemical data were recalculated on an insoluble residue–free basis (100% soluble carbonate). The analytical precision and accuracy, in relative percent, are 0.4 and 0.3 for Ca, 10 and 11.1 for Mg, 8 and 13 for Mn and 5.6 and 14 for Sr.

SHELL PRESERVATION

Three shell layers can be distinguished in articulate brachiopods (terebratulids, rhynchonellids): an outer noncalcareous periostracum, a middle very thin granular calcareous primary layer, and a thicker inner prismatic calcareous secondary layer. The calcareous layers are secreted as low-Mg calcite, near or in isotopic equilibrium with ambient seawater (Lowenstam, 1961; Carpenter and Lohmann, 1995; James et al., 1997). In fossil articulate brachiopods, the outermost layer (periostracum) is nearly always absent. In some pentamerids, atrypids, and spiriferids an additional tertiary prismatic layer may be secreted (McKinnon, 1974). Some shells of articulate brachiopods (orthids, terebratulids, atrypids, spiriferids) are penetrated by punctae, at 0.05 to 0.1 mm intervals, arranged normal to the shell surface. The majority of brachiopods analyzed in this study were selected for their impunctate shells in order to avoid any postdepositional contamination by secondary calcite filling punctae, but some punctate shells were examined for comparative purposes.

In order to evaluate the preservation state of the brachiopod shells, we used a combination of criteria based on their optical microscope, cathodoluminescence, SEM, and trace element characteristics. Since all Silurian samples, in the previously published as well the present sets, are depleted in ^{18}O by several per mil relative to modern marine carbonate minerals (see Table DR1 in Data Repository[1]), one advocated interpretation maintains

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[1] GSA Data Repository item 9880, Table DR1—samples, description, localities, stratigraphy, isotopic composition ($\delta^{18}O$ and $\delta^{13}C$ in per mil PDB) and trace element contents, is available on request from Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301. E-mail: editing@geosociety.org. Table DR1 is also available in Azmy (1996) or from the authors on request.

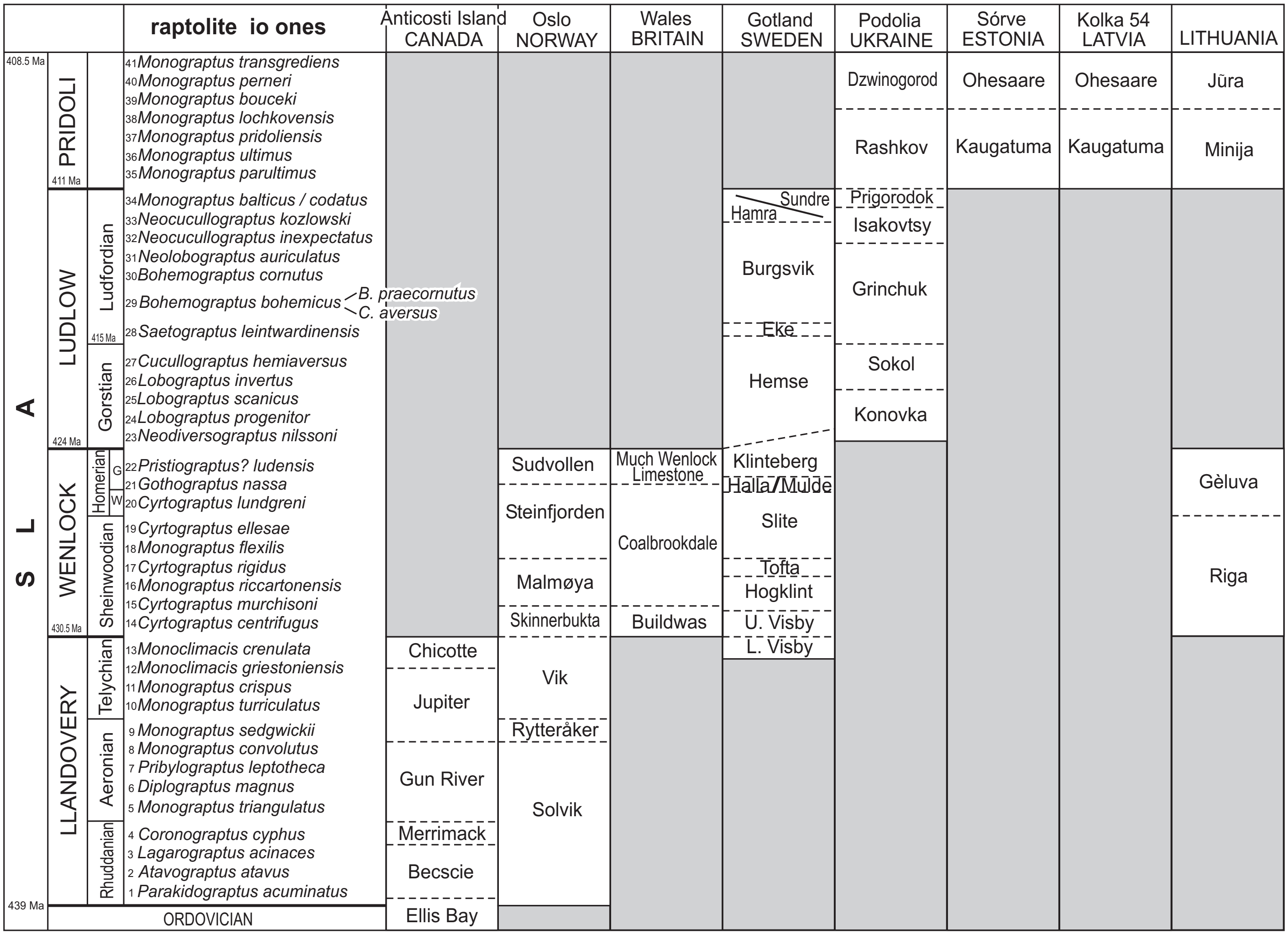

Figure 2. Nomenclature and correlation of Silurian lithostratigraphic and chronostratigraphic units for the studied sections (from Worsley et al., 1983; Bassett et al., 1989; Koren et al., 1989; Siveter et al., 1989; Worsley, 1989; Jin et al., 1990; Kaminskas and Musteikis, 1994).

that they all must be postdepositionally altered (Land, 1995). In order to demonstrate that this is not the case, we shall concentrate on documentation of the excellent preservation of few representative specimens rather than on description of textural, chemical and isotopic trends that reflect postdepositional recrystallization phenomena. (For details of such descriptions, see Azmy, 1996).

As a general rule, the secondary layers of the selected brachiopod shells were nonluminescent (Fig. 3A). The boundaries to brightly luminescent internal sediment or to interspersed veinlets are sharp. Such luminescent veinlets account for only a negligible portion of the shell; they can be avoided during sampling, and even if included should not influence the overall analytical result. Furthermore, in the case of sample A800 (Fig. 3A), the brightly luminescent bands are likely not a result of postdepositional recrystallization phenomena, since similar luminescent bands have been observed in some modern brachiopods (Barbin and Gaspard, 1995) where they are related to periods of slow growth. The excellent preservation of many shells can also be demonstrated by SEM photomicrographs, which show regularly stacked calcite prisms with smooth clean and straight boundaries (Fig. 3, B and C). Note the absence of any signs of textural disruption at <1 μm resolution (Fig. 3) and the compatibility of chemical and isotopic attributes with those of a Silurian marine precipitate. Transmission electron microscopy (TEM) studies of this sample in progress also support the preservation of the primary textures of the shell.

We do not claim that the entire sample set was as well-preserved as the examples herein, but the textural preservation of the studied brachiopod shells, excluding the samples from Norway, was exceptional. Diagenetic recrystallization, if present, was clearly recognizable in SEM images as dissolution pits and crystal coarsening (Fig. 3D), proceeding from crystal boundaries into crystal interior with increasing degrees of alteration (Azmy, 1996). The samples from Oslo region were strongly recrystallized (Fig. 4, A and B) at elevated temperatures to 400 °C, as indicated by conodonts with color alteration indices (CAI) of 3 to 5 (Aldridge, 1984). These samples are therefore not considered further, although their isotopic and chemical attributes are listed in Table DR1 (see footnote 1).

Earlier SEM studies of comparably well-preserved textures in brachiopod shells from diverse localities and sequences (e.g., Wadleigh and Veizer, 1992; Qing and Veizer, 1994; Bruhn et al., 1994; Carden, 1994; Copper, 1995; Wenzel and Joachimski, 1996; Samtleben et al., 1996; Wenzel, 1997) lend additional support to our claim that retention of original textures (and chemistry) in low-Mg calcites is not a rarity of the geologic record.

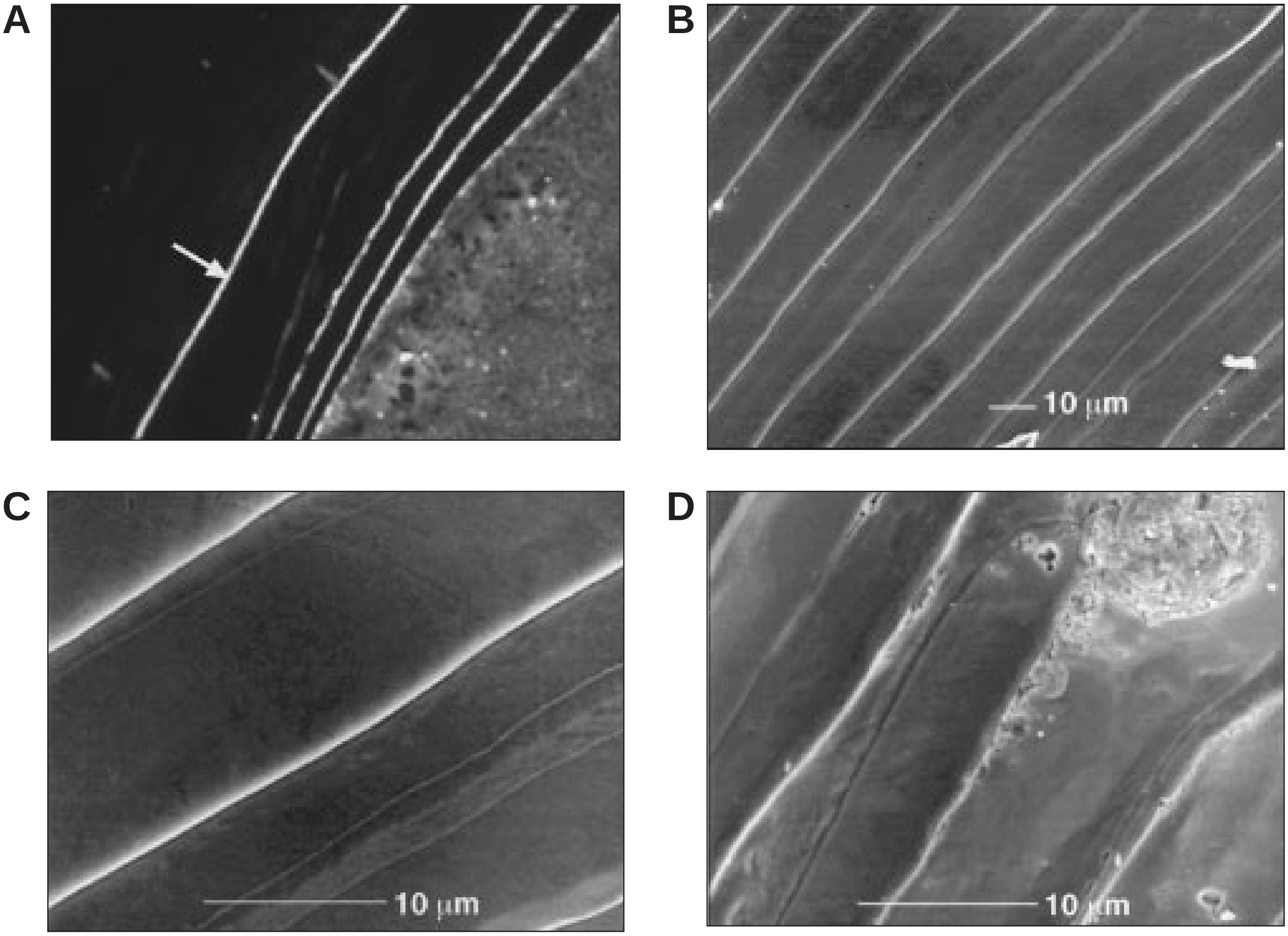

Figure 3. (A) Photomicrograph of a thin section of a well-preserved nonluminescent secondary layer in a shell of sample A800, *Gotatrypa* sp., Jupiter Formation, Anticosti Island (Sr = 1067 ppm, Mn = 29 ppm, Mg = 1100 ppm, δ^{18}O = –4.86‰, δ^{13}C = 0.59‰, ^{87}Sr/^{86}Sr = 0.708197), interspersed with brightly luminescent veinlets (arrow). The lower right-hand corner is a brightly luminescing internal sediment. Field of view is 1 mm across. (B and C) scanning electron microscope (SEM) photomicrographs of the secondary layer of sample A916, *Joviatrypa brabyla*, Jupiter Formation, Anticosti Island, with excellent preservation and clean crystal boundaries; C is a close-up of B. The sample has the following chemical and isotopic attributes: Sr = 1226 ppm, Mn = 70 ppm, Mg = 1500 ppm, δ^{18}O = –5.28‰, δ^{13}C = 0.69‰. (D) SEM photomicrographs of sample EK3, *Delthyris magna*, Kaugatuma Formation, Latvia, with well-preserved secondary layer containing a recrystallized puncta. Its chemical and isotope attributes are Sr = 1744 ppm, Mn = 48 ppm, Mg = 3100 ppm, δ^{18}O = –5.38‰, δ^{13}C = –0.52‰, ^{87}Sr/^{86}Sr = 0.708685.

TRACE ELEMENTS AND CHEMICAL PRESERVATION

The bulk of the studied Silurian brachiopods have Sr and Mn contents similar to those of Holocene brachiopods (Fig. 5 and Table DR1, see footnote 1). Except for a few samples with Sr contents >2000 ppm, and some with Mn contents to about 500 ppm, the majority of samples (~90%) are within the anticipated 1000–2000 ppm Sr and 4–200 ppm Mn ranges (Table 1). Some strophomenids and a few atrypids have Sr contents that are slightly higher than 2000 ppm. This is likely a primary feature, because alteration would likely lower Sr concentrations. These high concentrations and the residual differences in Sr contents among different orders may be a result of varying growth rates (cf. Bates and Brand, 1991) that may reflect temperature variations (Mii and Grossman, 1994; Grossman et al., 1996). In a similar manner, a few atrypids show a slightly higher content of Mn, to 500 ppm. Note also that the scatter diagram (Fig. 5) shows no correlation between Mn and Sr, attesting to preservation of the original signals, with the scatter reflecting ambient physiological and environmental variability.

The Sr and Mn contents of cement and matrix plot clearly outside the ranges of Holocene brachiopods. As anticipated from the diagenetic repartitioning concept (Veizer, 1983a, 1983b), they contain significantly higher Mn and lower Sr contents (Fig. 5). The clear dichotomy indicates that the sampled shells contain no significant matrix contamination and minimal or no inclusions of cements. Note also that despite the risk of contamination increasing with thin shells, the strophomenids exhibit Mn and Sr contents typical of well-preserved shells (Table 1) (attesting again to clean and efficient experimental work).

REVIEW OF SILURIAN OXYGEN AND CARBON ISOTOPE DATA

The mean values of 194 early measurements of δ^{13}C and δ^{18}O from Silurian brachiopod shells (Popp et al., 1986; Veizer et al., 1986; Wadleigh and Veizer, 1992) are reproduced here (Fig. 6) in an attempt to reconstruct the pattern of isotopic variations during the Silurian Period. These samples did not provide temporal resolution that would permit delineation of detailed trends and most of them are from North America. Such data show parallel δ^{13}C and δ^{18}O trends, with a minimum in early Ludlow time, and the earlier discussed overall depletion of all samples in ^{18}O. Studies by Wenzel and Joachimski (1996), Samtleben et al. (1996), Wenzel (1997), and Bickert et al. (1997) on Silurian brachiopods from Gotland have provided much better resolution (Fig. 6), with positive isotope shifts in δ^{13}C and δ^{18}O during early and late Wenlock time (cf. Heath et al., 1996) and particularly in late Ludlow time. These curves hint at a reciprocal relationship with sea-level stands of Johnson et al. (1991).

Isotope compositions for whole-rock samples may not represent the original signals due to diagenetic alteration, but may retain general features of isotopic variations through time. Such data from the Anglo-Welsh area (Corfield et al., 1992) reveal a recognizable negative shift in δ^{13}C values (~2‰) around the Wenlock-Ludlow boundary (*nassa-ludensis* biozones) that coincides with a sea-level fall (Johnson et al., 1991) and with a decline in graptolite diversity (Koren and Rickards, 1980; Kemp, 1991). The whole-rock data from Estonia (Kaljo et al., 1994, 1997) show, however, positive δ^{13}C shifts with magnitudes of 4.2‰ and 4.6‰, during early and late Wenlock time (*riccartonensis* and *nassa* biozones), respectively. A very large increase in δ^{13}C values, with a magnitude of 12‰, was recorded in upper Ludlow strata at the Brocker River section in Queensland, Australia (Andrew et al., 1994a, 1994b). This section contains also a minor ^{13}C enrichment across the Llandovery-Wenlock boundary.

OXYGEN AND CARBON ISOTOPE DATA

The δ^{18}O and δ^{13}C measurements for 237 Silurian brachiopod shells (Table DR1, see footnote 1) are plotted in Figure 7: they range from –6.4‰ to –2.0‰ and from –1.0‰ to 7.5‰, respectively. Compared with modern brachiopods from comparable warm shallow-water habitats, the Silurian brachiopod samples are consistently depleted in ^{18}O.

The total sample population only shows an indistinct, although statistically significant, correlation ($R^2 = 0.16$) between δ^{18}O and δ^{13}C (cf. Davis, 1986). This is consistent with the proposition that the shells reflect mostly an original scatter that was not strongly affected by postdepositional resetting. A similar picture emerges even if samples for every locality are considered independently. Note also that there is no correlation between δ^{18}O and Mn or Sr in the studied brachiopod shells (Fig. 8, A and B), even if samples are subdivided into groups by localities.

Vital Effects—Interspecies and Intraspecies Isotopic Variations

Variations in the mean δ^{18}O and δ^{13}C values for different brachiopod orders (±0.3‰) from the same graptolite biozone (*M. ludensis*) appear to be negligible (Table 2). Such small variations between the orders for both isotopes imply that these brachiopod shells do not possess any significant interspecies vital isotope fractionation effect (cf. Bates and Brand, 1991; Wadleigh and Veizer, 1992; Qing and Veizer, 1994). Modern brachiopods, from latitudes less than 40°, also display similar small δ^{18}O variations, to ±1‰ (Carpenter and Lohmann, 1995).

In order to test for intraspecies isotope variations, 12 samples of *Atrypa* sp. from the same formation (Much Wenlock, Wales) and the same biozone were analyzed. Their δ^{18}O and δ^{13}C values (–5.11‰ ± 0.47‰ and –1.00‰ ± 0.44‰, respectively) show less than 0.5‰ standard deviation. This is again comparable to the 0.5‰ range reported for intraspecimen variations in modern brachiopods (cf. Carpenter and Lohmann, 1995). We conclude, therefore, that intraspecies and interspecies isotope effects are not important factors for the observed temporal isotope variations.

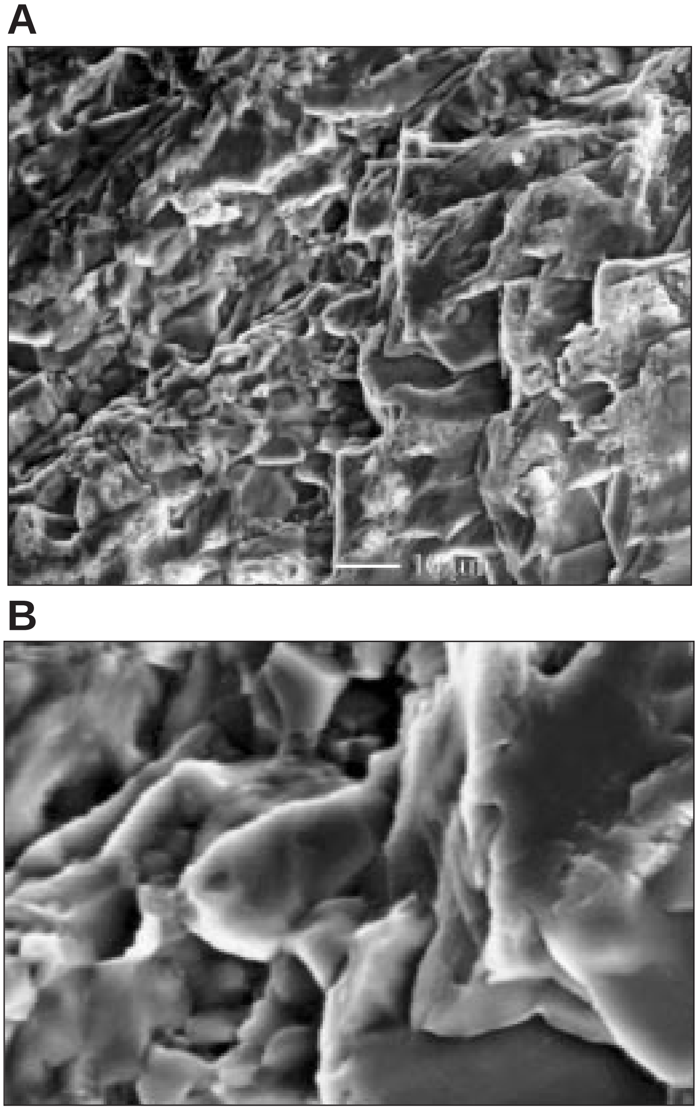

Figure 4. (A) Scanning electron microscope photomicrographs of sample N3, *Eocoelia angelini*, Steinfjorden Formation, Oslo (Norway), showing total recrystallization of the original structure. B is a close-up of A. Its chemical and isotope attributes are Sr = 1773 ppm, Mn = 54 ppm, Mg = 2400 ppm, δ^{18}O = –10.40‰, δ^{13}C = 4.46‰.

Temporal Trends and Regional Variations

On the basis of the above criteria, we believe that these carefully selected brachiopod shells retained their primary (or only slightly modified) isotopic characteristics. We also believe that the bulk of the observed scatter of any given time interval reflects chiefly the variability of natural habitats (in terms of their physical as well as biological parameters), today as in the past. For this reason, we decided to plot temporal trends as boxes of ±1 standard

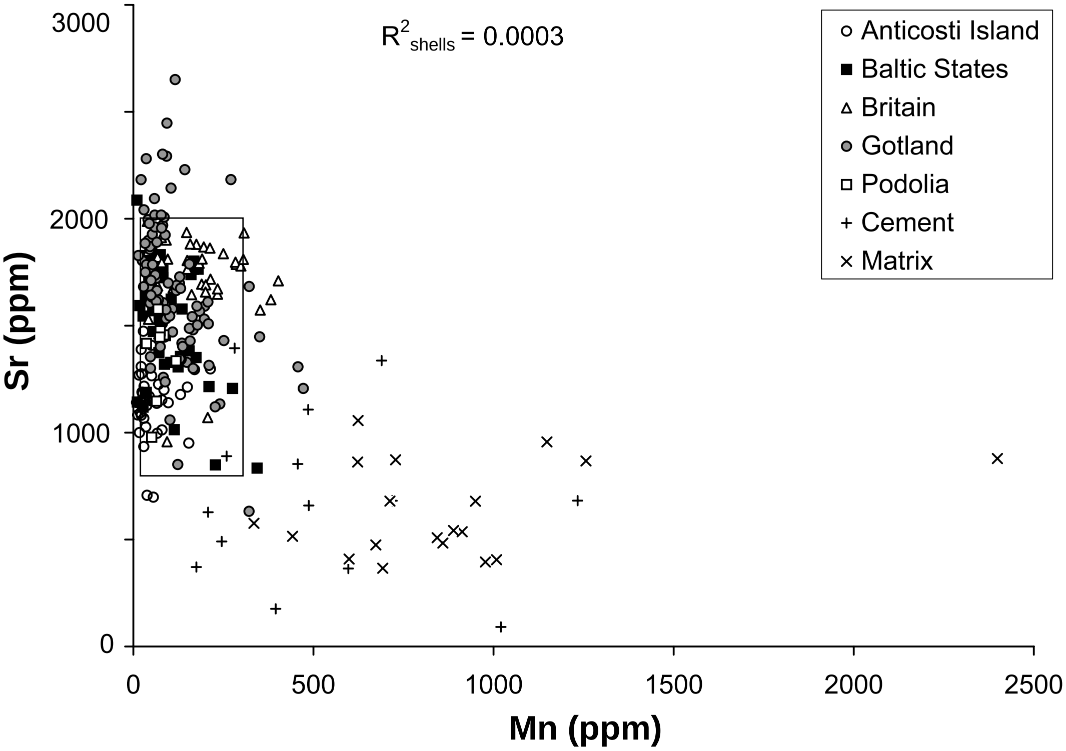

Figure 5. Scatter diagram of Mn vs. Sr for brachiopod shells, cements, and matrix from all sections. The box represents the trace element ranges for Holocene brachiopods based on the data of Lowenstam (1961), Lepzelter et al. (1983), Dittmar and Vogel (1968), Frank et al. (1982), and Grossman (1994).

deviation around the mean for the smallest globally to regionally correlatable unit, the biozone (Fig. 9; Table 3).

The first-order feature of the figure is the parallelism of δ^{13}C and δ^{18}O trends, particularly the pronounced peaks during early and late Wenlock and late Ludlow time. The second observation is the coincidence of δ^{18}O peaks in the latest Ordovician and Llandovery with episodes of glaciation. The third feature is the apparent coincidence of positive isotopic peaks with sea-level lowstands and the fourth, and most prominent, is the 2‰ to 5‰ ^{18}O depletion of all samples relative to modern marine carbonates. In the subsequent text, we review the possible causes of these oxygen and carbon isotopic patterns, but prior to such discussion it is essential to consider the issue of regional variability.

Brachiopod isotope data from diverse Silurian regions that satisfy quantitative and qualitative requirements of our approach exist at present only for Wenlock time, with samples from Great Britain, Gotland, and Lithuania (Fig. 10). These data demonstrate the coherency of isotopic trends for all three regions. For δ^{13}C, it is a trend of decreasing values from biozone 14 to 18-19, followed by an increase to biozone 22. For δ^{18}O, all data define a band of about 1.5‰ width in the vicinity of –4.5‰ ± 1.0‰ values. Hence, all values are depleted in ^{18}O relative to modern marine shells, by some 2‰ to 5‰, and the width of this band likely reflects differing environmental conditions.

The association of coral-algal-sponge reefs with the studied successions is a clear indication of shallow-water environmental conditions. Comparison of δ^{18}O values for shells from such successions with those from deeper subtidal environments may provide clues about the paleodepth control on the δ^{18}O values. Comparison of $\delta^{18}O_{shell}$ from Gotland and Britain (mostly reef-associated atrypids) with those from Lithuania (non reef-associated, deeper subtidal) during Wenlock time (Fig. 10) shows that the δ^{18}O values of shells from Lithuania (–4.1‰ ± 0.4‰) are almost always higher than those from Gotland (–4.8‰ ± 0.5‰) and Britain (–4.9‰ ± 0.4‰). The difference, on average about 0.8‰, may reflect a temperature gradient of about 4 °C, with the deeper water being somewhat cooler.

The coherency of Wenlock δ^{18}O and δ^{13}C isotope data from various regions and the indication that the observed δ^{18}O spread may reflect environmental differences at the time of deposition of these strata strongly support our proposition that the brachiopod shells retained their primary isotope signatures.

FACTORS CONTROLLING ISOTOPIC COMPOSITION OF SILURIAN BRACHIOPODS

The observed temporal isotope trends (Fig. 9) are likely a result of a combination of factors, with some being more important than others. We shall review these factors first for oxygen and subsequently for carbon.

TABLE 1. Mn, Sr, ^{18}O AND ^{13}C STATISTICS FOR BRACHIOPOD ORDERS FROM ALL STUDIED SECTIONS

Order	Atrypida				Orthida				Pentamerida				Rhynchonellida				Spiriferida				Strophomenida			
Parameter	Mn	Sr	δ^{18}O	δ^{13}C	Mn	Sr	δ^{18}O	δ^{13}C	Mn	Sr	δ^{18}O	δ^{13}C	Mn	Sr	δ^{18}O	δ^{13}C	Mn	Sr	δ^{18}O	δ^{13}C	Mn	Sr	δ^{18}O	δ^{13}C
Mean	98	1532	–5.0	1.1	153	1599	–5.2	1.5	81	1502	–4.5	0.7	143	1446	–5.1	1.5	84	1554	–5.1	1.4	134	1870	–5.0	1.5
Standard deviation	91	317	0.8	1.3	79	373	0.8	1.7	63	173	0.7	0.7	70	243	0.7	1.8	62	372	1.1	2.2	75	422	0.6	1.7
Minimum	9	435	–6.6	–1.0	36	632	–6.1	–0.9	22	1137	–5.1	1.5	51	1014	–6.6	5.4	12	684	–6.4	–1.1	33	1134	–5.7	–0.5
Maximum	471	2094	–3.4	4.4	321	2007	–3.6	4.4	234	1686	–2.7	–0.6	352	1836	–3.9	–0.2	239	2021	–1.9	6.4	322	2651	–4.2	4.9
Number of samples	96	96	94	95	21	21	21	21	9	9	9	9	22	22	22	22	27	27	28	28	19	19	14	14

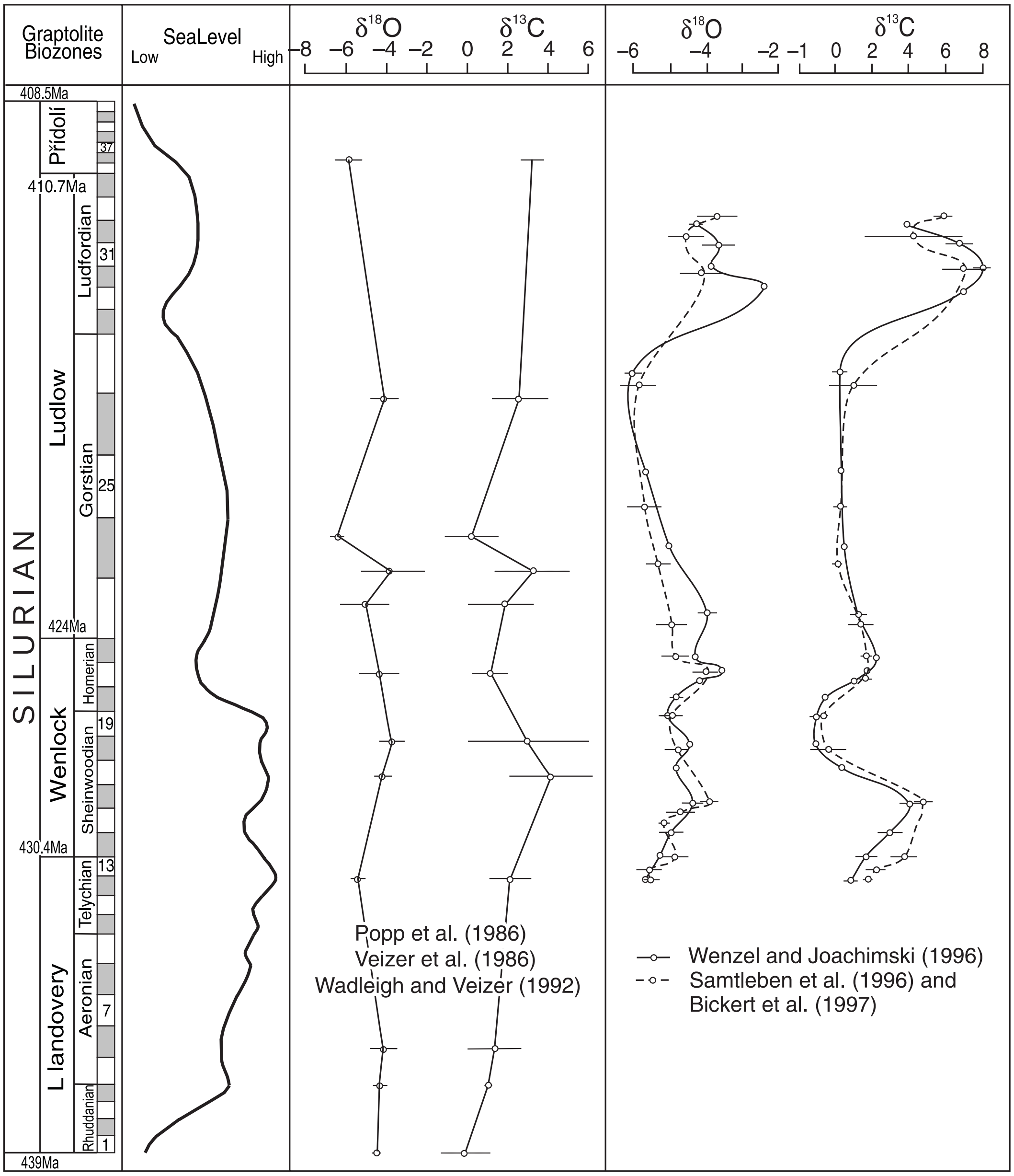

Figure 6. Mean variations in δ^{18}O and δ^{13}C values (in ‰ Peedee belemnite) for Silurian brachiopods and of sea-level changes. Bars represent 2σ values. The estimated absolute ages follow the scale of Harland et al. (1990), and the numbers in the biozonation bar refer to the graptolite biozones in Figure 2.

Oxygen Isotopes

1. Temperature. In modern environments, tropical sea-surface temperatures range from 23 to 27 °C, the optimum condition for reef growth (Milliman, 1974). Since the sampled successions (Anticosti, Wales, Gotland, Baltic states, and Podolia) were all located in tropical paleolatitudes of less than 30°S (cf. Scotese and McKerrow, 1990; McKerrow et al., 1991), and most were associated with reefal facies, it is reasonable to assume comparable range of temperatures for the tropical Silurian seas. Assuming that the ^{18}O of seawater was constant during geologic history, at about −1‰ standard mean ocean water (SMOW) (Karhu and Epstein, 1986), and utilizing the temperature equation of Hays and Grossman (1991), the calculated temperatures for the Silurian seawater would have ranged between 20.2 °C and 42.7 °C. This is not a realistic scenario considering that protein molecules cannot withstand continuous temperature stress in excess of 37 °C (cf. Milliman, 1974; Brock, 1985) and that such "warm" oceans would have had to exist during glacial times (Fig. 9). Assuming a δ^{18}O for Silurian seawater of 0‰ SMOW, as today, would only compound the difficulty by increasing the estimated temperatures by about 5 °C. Furthermore, such a large range of temperatures (~22 °C) is atypical for the equatorial zone, where even the postglacial increase in temperature was estimated to be no more than about 5 or 6 °C (Crowley, 1994; Guilderson et al., 1994). We conclude, therefore, that the "warm" ocean scenario, if taken as a sole causative factor, cannot explain the low Silurian δ^{18}O values.

2. Salinity. Although some authors suggest a slope between δ^{18}O and salinity (S) of ~ 0.5 (e.g., Samtleben et al., 1996), the $\Delta\delta^{18}$ O/ΔS calculated from a broad spectrum of modern brachiopod data (cf. Carpenter and Lohmann, 1995) provide a value of ~ 0.14. Assuming a comparable Silurian $\Delta\delta^{18}$ O/ΔS gradient and considering salinity to be the sole factor that controlled the $\delta^{18}O_{shell}$ (e.g., Samtleben et al., 1996; Bickert et al., 1997), the shift of ~2‰, as observed for the ^{29}*nassa-bohemicus* biozone (zone 29 in Fig. 9),

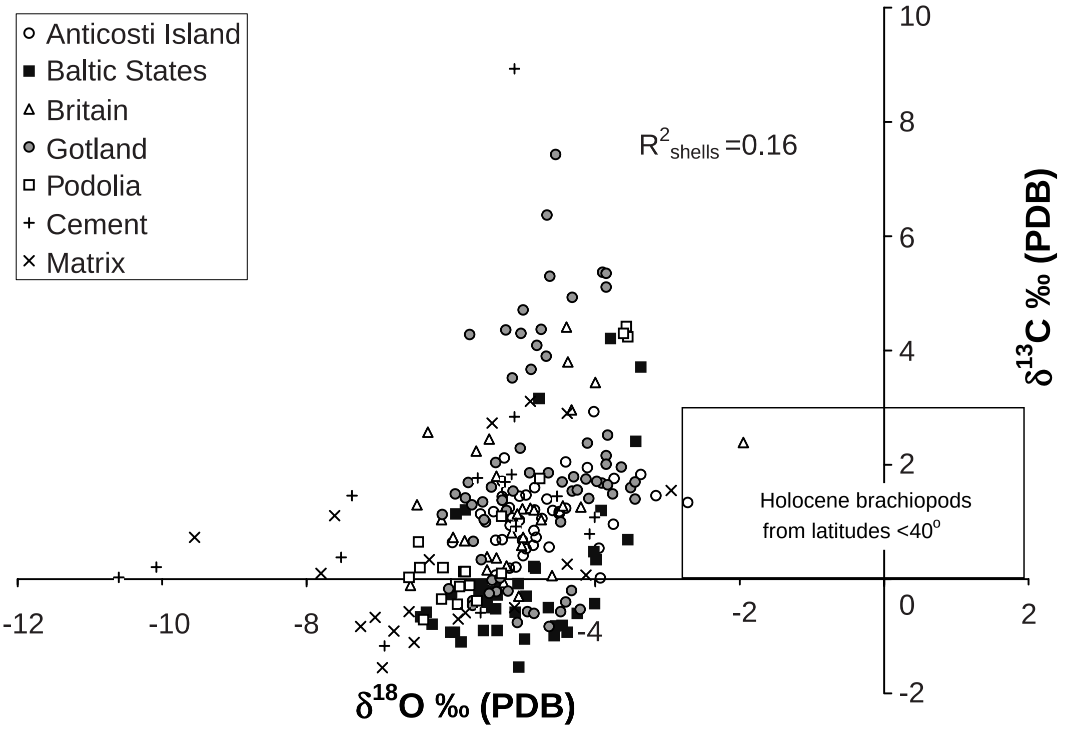

Figure 7. Oxygen vs. carbon isotope values for all studied Silurian brachiopods as well as cements and matrix from different localities (PDB—Peedee belemnite). The samples from Norway (Oslo region) that have very poor textural preservation (Fig. 4) and δ^{18}O signals highly depleted, as low as –20.7‰ (Table DR1, see footnote 1), are excluded. The box for Holocene low-latitude brachiopods is from Carpenter and Lohmann (1995).

would require a salinity change of ~14‰. This is an unrealistic alternative since the brachiopods, and the associated fossils (e.g., corals), are relatively stenohaline fauna that cannot tolerate such large salinity variations. We therefore conclude that salinity gradients can be only a marginal factor among those controlling the δ^{18}O signal of Silurian brachiopods.

3. Paleodepth. Comparison of samples from Gotland and Britain (reef associated) with those from deeper water sections in Lithuania (Fig. 10) shows that depth alone cannot explain more than about 1‰ gradient in the overall spread of values (cf. Grossman, 1994).

4. Stratified Oceans. The distribution of Silurian landmasses and lithofacies (McKerrow et al., 1991; Cocks and Scotese, 1991) suggests the existence of expansive, possibly salinity-stratified (Wilde et al., 1991; Cotter, 1988) epeiric seas with restricted connection to the open ocean. During evaporative episodes and sea-level highstands, dense warm saline ^{18}O-rich water would circulate downslope, feeding deep water (warm saline deep water, WSDW) and leaving the surface water enriched in ^{16}O.

Railsback (1990), Railsback et al. (1990), Wenzel and Joachimski (1996), and Bickert et al. (1997) invoked this model to explain those short-term negative δ^{18}O shifts that correlate with sea-level highstands. They estimated that the drop in δ^{18}O signal for surface water caused by WSDW circulation would have been about 0.5‰ to 1.5‰ SMOW, comparable to the δ^{18}O oscillations exhibited by the Silurian oxygen-isotope curve (Fig. 9). Theoretically, the stratified ocean scenario could, therefore, account for at least some of the detailed isotope pattern, but the physical feasibility of the WSDW oceanic circulation pattern has yet to be demonstrated.

5. Glacial and Short-Term Secular Changes of Seawater δ^{18}O. Glaciation is the best documented mechanism for generation of short-term oscillations in δ^{18}O composition of seawater and its precipitates. The waning of ice sheets that followed the latest Quaternary glacial maximum depleted the δ^{18}O of seawater by ≤1‰. The simultaneous temperature rise of equatorial seawater, of about 6 °C (cf. Guilderson et al., 1994; Crowley, 1994), enhanced the signal in shells by a comparable magnitude.

The well-documented terminal Ordovician glaciation was followed by three successive Silurian glaciations, indicated by diamictites, that have been recognized in the Amazon basin (Grahn and Caputo, 1992). These were during early Aeronian time (early–middle Llandovery, *C. gregarius*), latest Aeronian time (middle Llandovery), and earliest Wenlock time. Comparable glacial phases were also documented in the Silurian deposits of north and south Africa (Grahn and Caputo, 1992). The estimated duration of each glacial phase was about 2.5 m.y. (Johnson et al., 1991; Cotter, 1988), comparable to the third-order cycles of eustatic sea-level changes (Plint et al., 1992). Each of these glacial episodes is accompanied, within the uncertainty limit of a single biozone, by a δ^{18}O peak of 1‰ magnitude (Fig. 9) and by a sea-level lowstand, fully consistent with the comparable Quaternary scenarios. The earliest Wenlock positive δ^{18}O shift at Gotland was also documented by Wenzel and Joachimski (1996).

No Silurian glacial deposits or evidence of cool climatic conditions younger than earliest Wenlock time are as yet known from Gondwana, and it is therefore difficult to assign the observed younger ^{18}O enrichments to such a cause. It is still possible that the glacial record has been lost, but such a scenario is not very plausible in view of the generally warm climate that dominated later Silurian time (Frakes et al., 1992).

Except for the earliest Wenlock glacial episode, which may conceivably have coincided with the Ireviken event (Jeppson et al., 1995), none of these glacial phases appears to have coincided with extinction events. This is similar to the Quaternary, where large eustatic sea-level changes do not appear to have resulted in large-scale mass extinctions in marine biota (cf. Eckert, 1988).

In summary, correlation of positive δ^{18}O shifts with glacial episodes is consistent with the primary nature and ice-volume control of the observed isotope signal. None of the above scenarios, however, can explain the overall 4‰ ± 1‰ depletion in the entire Silurian δ^{18}O values, relative to Quaternary counterparts. This brings us to the most contentious issue of oxygen isotope stratigraphy, the long-term stability of seawater δ^{18}O.

6. Long-Term Evolution of Seawater δ^{18}O. The isotope record of marine chemical sediments shows a general trend of decreasing δ^{18}O values with in-

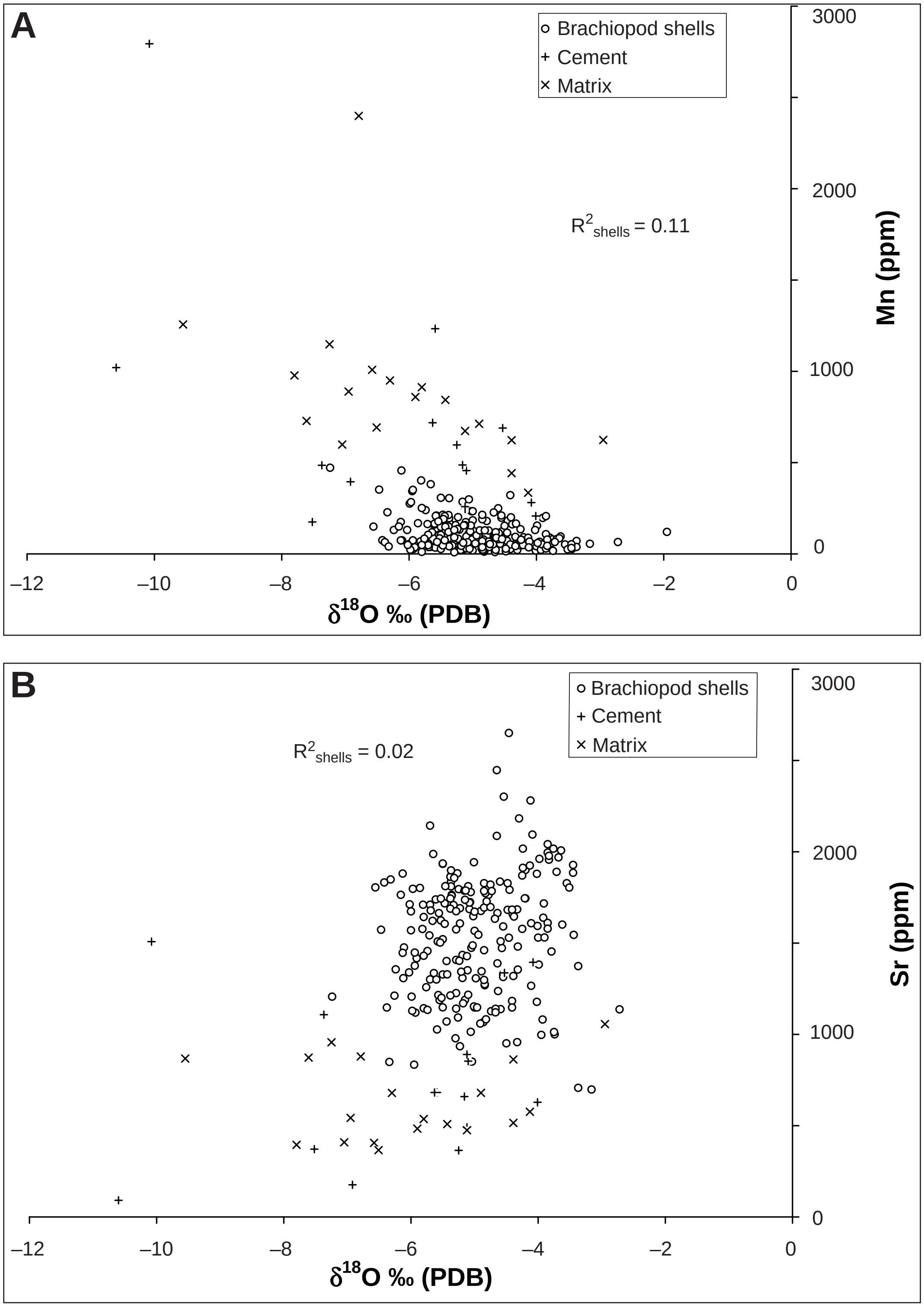

Figure 8. Scatter diagram of δ^{18}O with (A) Mn and (B) Sr for brachiopod shells, cement, and matrix from all settings. Norwegian data are excluded. PDB—Peedee belemnite.

creasing age. Such trends have been observed in carbonates (e.g., Keith and Weber, 1964; Veizer and Hoefs, 1976), cherts (e.g., Degens and Epstein, 1962; Knauth and Lowe, 1978), and glauconites (Friedrichsen, 1984). In accord with this, all δ^{18}O values for the Silurian brachiopods are about 4‰ ± 1‰ depleted in δ^{18}O compared with their Holocene counterparts.

The reality of this long-term δ^{18}O trend is not questioned, but the stable isotope community is strongly polarized as to its implications (cf. Hoefs, 1997, p. 117). One camp considers the trend to be predominantly postdepositional alteration phenomenon (e.g., Land, 1995), while the other (e.g., Veizer, 1995) maintains that it is essentially a primary feature of the geologic record.

The proposition that one is dealing essentially with a record of alteration is difficult to reconcile with all the above textural, chemical, and isotopic observations. Geological arguments also point to the same conclusion. Considering the diverse geologic histories of different crustal blocks, it is highly un-

TABLE 2. MEAN $\delta^{18}O$ AND $\delta^{13}C$ VALUES OF BRACHIOPOD SAMPLES FROM THE *M. ludensis* BIOZONE

Order	n	$\delta^{18}O \pm 1\sigma$	$\delta^{13}C \pm 1\sigma$
Orthida	3	–5.70 ± 0.37	1.29 ± 1.05
Rhynchonellida	3	–5.61 ± 0.85	0.71 ± 1.03
Pentamerida	2	–5.05 ± 0.04	0.86 ± 0.39
Atrypida	113	–5.04 ± 0.64	1.03 ± 0.46
Biozone	221	–5.35 ± 0.34	1.02 ± 0.31

Note: n = number of samples.

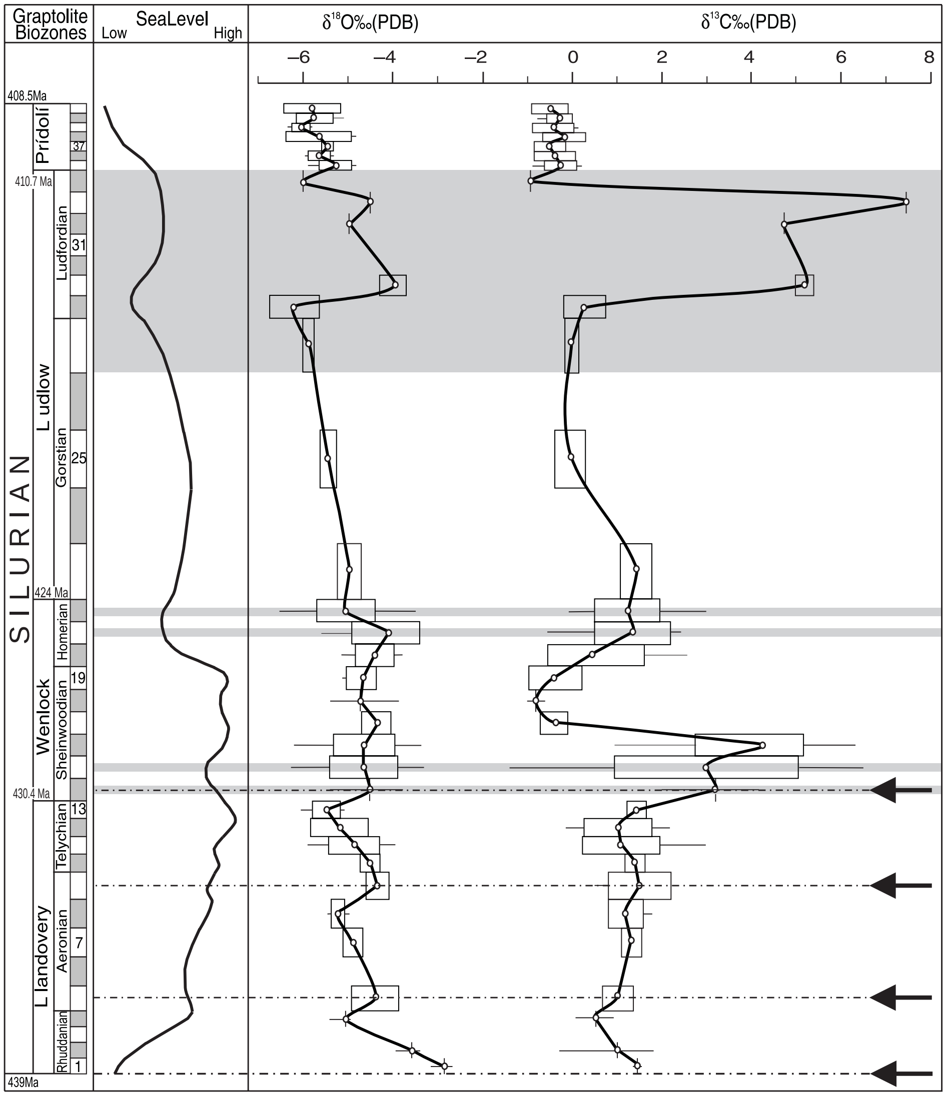

Figure 9. Silurian isotope curves showing the variations in $\delta^{18}O$ and $\delta^{13}C$ (PDB—Peedee belemnite) values for brachiopods and sea-level changes, the latter after Johnson et al. (1991). The black lines connect the means for each graptolite biozone. Boxes represent 2σ values and bars refer to maximum and minimum values. The estimated absolute ages follow the scale suggested by Harland et al. (1990). The highlighted bands represent ventilation episodes, as suggested for Wenlock time by Kemp (1991) and for Ludlow time by Jaeger (1979). Arrows refer to glacial episodes, as suggested by Grahn and Caputo (1992), with the oldest arrow relating to terminal Ordovician glaciation. The numbers on the biozonation bar refer to graptolite biozones in Figure 2. The samples from Norway are excluded. The full list of data is in Table DR1 (see footnote 1).

TABLE 3. MEAN, STANDARD DEVIATION, MAXIMUM AND MINIMUM ISOTOPE VALUES CALCULATED FOR EACH GRAPTOLITE BIOZONE IN THE BIOCORRELATION OF SILURIAN PERIOD

Biozone	$n_{c,o}$	$\delta^{18}O_{mean} \pm 1\sigma$	Maximum	Minimum	$\delta^{13}C_{mean} \pm 1\sigma$	Maximum	Minimum
^{41} *transgrediens*	3	–5.8 ± 0.5	–5.4	–6.3	–0.4 ± 0.4	–0.1	–0.8
^{40} *perneri*	8	–5.7 ± 0.5	–4.9	–6.4	–0.3 ± 0.3	–0.2	–0.7
^{39} *bouceki*	3	–6.0 ± 0.2	–5.8	–6.1	–0.4 ± 0.5	0.1	–0.9
^{38} *lochkovensis*	3	–6.1 ± 0.4	–4.7	–6.4	–0.5 ± 0.3	0.1	–0.7
^{37} *pridoliensis*	3	–5.5 ± 0.1	–5.4	–5.6	–0.5 ± 0.3	–0.3	–0.9
^{36} *ultimus*	4	–5.8 ± 0.3	–5.5	–6.0	–0.5 ± 0.5	–0.2	–1.1
^{35} *parultimus*	7	–5.3 ± 0.3	–4.8	–5.9	–0.2 ± 0.3	0.2	–0.5
^{34} *balticus*	1	–5.6			–0.9		
^{33} *kozlowskii*	1	–4.6			7.4		
^{32} *inexpectatus*	1	–5.0			4.7		
^{29} *bohemicus*	3	–4.0 ± 0.3	–3.9	–4.3	5.1 ± 0.2	5.4	4.9
^{28} *leintwardinensis*	6	–6.1 ± 0.4	–5.7	–6.6	0.2 ± 0.4	0.7	–0.4
^{27} *hemiavesus*	3	–5.7 ± 0.2	–5.4	–5.9	0.0 ± 0.1	0.1	–0.1
^{25} *scanicus*	4	–5.5 ± 0.2	–5.3	–5.7	–0.1 ± 0.3	0.3	–0.5
^{23} *nilssoni*	3	–5.0 ± 0.3	–4.8	–5.3	–1.4 ± 0.4	1.8	1.1
^{22} *ludensis*	26	–5.1 ± 0.7	–3.6	–6.6	1.2 ± 0.7	3.0	–0.1
^{21} *nassa*	24	–4.3 ± 0.7	–3.5	–5.7	1.4 ± 0.8	2.4	–0.3
^{20} *lundgreni*	10	–4.6 ± 0.6	–3.8	–5.5	0.4 ± 1.2	2.5	–0.8
^{19} *ellesae*	6	–4.6 ± 0.3	–4.2	–5.0	–0.6 ± 0.3	0.2	–1.1
^{18} *flexilis*	2	–4.7	–4.6	–4.9	–0.8	–0.6	–1.0
^{17} *rigidus*	3	–4.5 ± 0.1	–4.4	–4.6	–0.9 ± 0.1	4.4	–0.9
^{16} *riccartonensis*	11	–4.4 ± 0.7	–3.6	–5.7	4.0 ± 1.3	5.3	0.3
^{15} *murchisoni*	12	–4.6 ± 0.8	–3.4	–6.3	2.9 ± 2.1	6.4	–1.5
^{14} *centrifugus*	2	–4.6	–3.8	–5.4	3.1	4.2	2.0
^{13} *crenulata*	12	–5.6 ± 0.3	–5.1	–6.1	1.4 ± 0.2	1.6	1.0
^{11} *crispus*	7	–4.9 ± 0.6	–4.0	–6.0	1.0 ± 0.9	2.9	0.4
^{10} *turriculatus*	3	–4.6 ± 0.2	–4.4	–4.8	1.3 ± 0.2	1.6	1.1
^{9} *sedgwickii*	4	–4.4 ± 0.2	–4.1	–4.6	1.4 ± 0.7	2.1	0.6
^{8} *convolutus*	8	–5.3 ± 0.1	–5.1	–5.5	1.1 ± 0.4	1.7	0.7
^{7} *leptotheca*	3	–5.0 ± 0.2	–4.7	–5.2	1.3 ± 0.2	1.5	1.1
^{5} *triangulatus*	6	–4.5 ± 0.5	–3.8	–5.1	0.9 ± 0.4	1.4	0.5
^{4} *cyphus*	2	–5.1	–4.9	–5.4	0.5	0.9	0.1
^{2} *avatus*	2	–3.7	–3.4	–3.9	0.9	1.8	0.0
^{1} *acuminatus*	2	–2.9	–2.7	–3.2	1.4	1.5	1.3

likely that their $\delta^{18}O$ would have been shifted in such a way that they all fall within the same overall range (see Fig. 10). This would require coincident diagenetic history in multiple basins. Similar inferences can be drawn also from a more detailed scale. The coincidence of the positive $\delta^{18}O$ excursions in latest Ordovician time (a global feature observed in Laurentia, Baltica and Gondwana; Middleton et al., 1991; Carden, 1994, and 1994, personal commun.; Brenchley et al., 1995) and in Llandovery time with glaciations (Fig. 9) is easiest to understand in terms of the preservation of the $\delta^{18}O$ record.

In summary, we consider the $\delta^{18}O$ record based on well-preserved brachiopods shells (low-Mg calcite) to be essentially a primary feature (cf. also Veizer et al., 1997). This has significant consequences regarding the $^{18}O/^{16}O$ composition of ancient seawater.

The brachiopod $\delta^{18}O$ signals reflect mainly the temperature of summer seasons during which the rate of shell precipitation is assumed to be optimal (Clarkson, 1993). If Silurian sea-surface temperatures during warm episodes were about 20 to 30 °C, similar to those of modern environments in summer (Skinner and Porter, 1987), the lowest brachiopod $\delta^{18}O$ values (–4.5‰ to –6.4‰ PDB) would indicate a seawater $\delta^{18}O$ of about –3.5‰ SMOW (Fig. 11). During glacial times, with seawater $\delta^{18}O$ suggested to have been heavier by ~ 1‰ (cf. Guilderson et al., 1994; Crowley, 1994; Railsback, 1990), the heaviest brachiopod signals (–2‰ to –4‰ PDB) would correspond to a temperature range of 14 to 23 °C (Fig. 11), comparable to tropical temperatures of 14 to 28 °C during the latest Quaternary glaciation (Skinner and Porter, 1987). Silurian surface seawater is thus suggested to have had ^{18}O compositions of –2.5‰ to –3.5‰ SMOW.

A persistent problem remaining is how to generate the proposed –3‰ ± 0.5‰ isotope composition for Silurian seawater. Interaction of seawater with basalts in high-temperature hydrothermal systems results in preferential enrichment of ^{18}O in seawater, whereas the low-temperature submarine weathering causes an opposite effect (Muehlenbachs, 1986). The overall Silurian $\delta^{18}O$ gradient of about –1‰/30 m.y. (Fig. 9) could perhaps be accommodated in this way, since the required adjustments to the model in favor of the low-temperature processes would have to be relatively minor. However, the general global warming that followed the Late Ordovician glaciation (e.g., Frakes et al., 1992) is a more plausible scenario, an explanation that is consistent also with the concomitant rise of $^{87}Sr/^{86}Sr$ ratios (Burke et al., 1982; Bertram et al., 1992; Azmy, 1996) due to increased weathering flux from continents.

Regardless of the validity of these scenarios, the model in its present version cannot explain the advocated overall –3‰ ± 0.5‰ ^{18}O depletion of Silurian seawater, because it presumes that the high- and low-temperature fluxes cancel each other (Muehlenbachs, 1986; Gregory, 1991), thus buffering the $\delta^{18}O$ composition of seawater at about the present-day value. This is not the case in the model of Walker and Lohmann (1989), which does permit unidirectional $^{18}O/^{16}O$ evolution of seawater. Tentatively, we suggest that the proposition of equal high- and low-temperature fluxes in depth profiles of ophiolites (and other locales) be reexamined, as indeed may be possible within the scatter of the existing experimental database. If this proves unwarranted, the explanation for the large ^{18}O depletion of Paleozoic samples (and presumably seawater) remains enigmatic.

Carbon Isotopes

The Silurian $\delta^{13}C$ record shows several remarkable shifts, of 3‰ to 8‰ magnitude, during early and late Wenlock and late Ludlow time (Fig. 9). A similar positive $\delta^{13}C$ spike during the latest Ordovician time (Hirnantian) coincides with a glacial interval and sea-level lowstand (Middleton et al., 1991; Brenchley et al., 1995). The Silurian spikes also correlate with sea-level lowstands and with positive $\delta^{18}O$ shifts, i.e., glacial periods. These periods would likely experience vigorous circulation and highly oxygenated deep ocean water (e.g., Railsback, 1990; Wenzel and Joachimsky, 1996). Such conditions are amenable to a high oxidation rate of the sinking organic

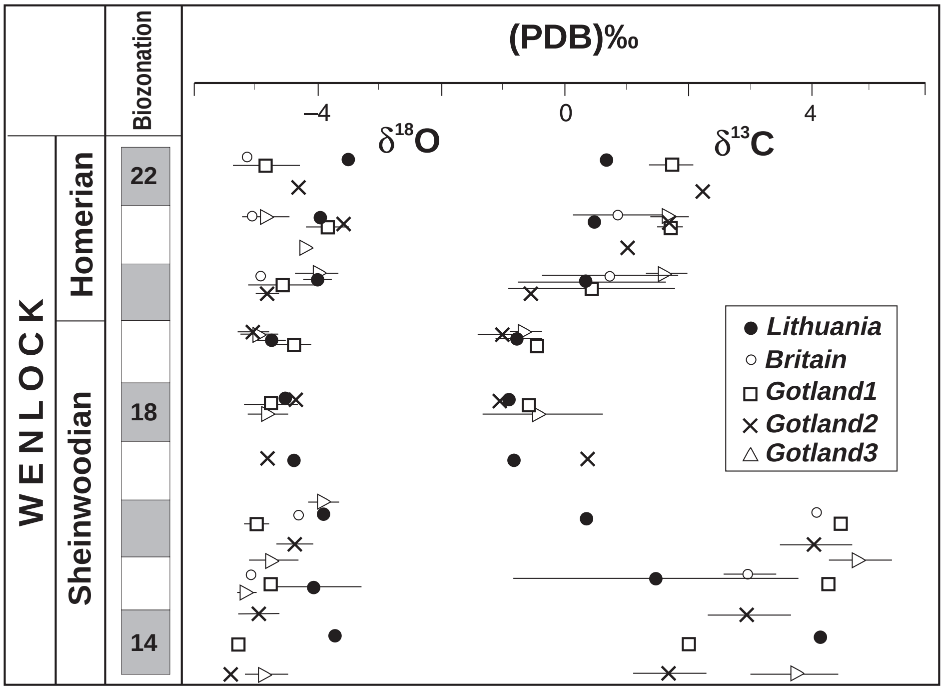

Figure 10. Regional variations in $\delta^{18}O$ and $\delta^{13}C$ for Wenlock brachiopods. Graptolite biozones (14 to 22) as in Figure 2. Symbol and bar represent the mean and ±1 standard deviation for each biozone. Gotland 1 (present data), Gotland 2 (Wenzel and Joachimski, 1996), and Gotland 3 (Samtleben et al., 1996).

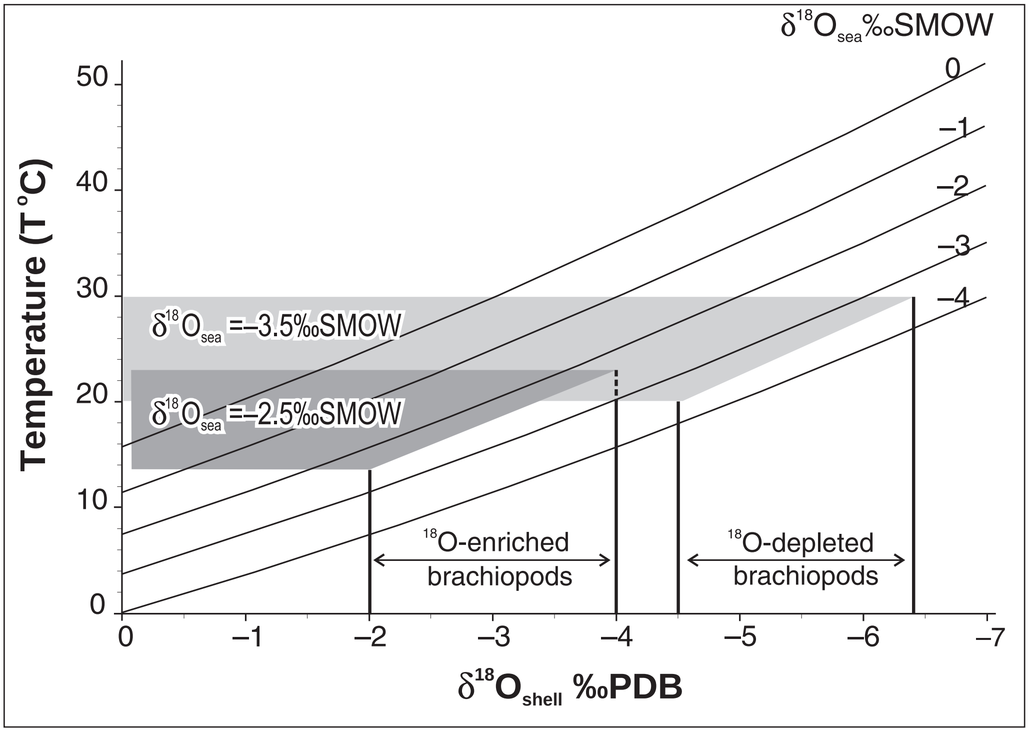

Figure 11. Temperature vs. $\delta^{18}O_{shell}$ for various $\delta^{18}O_{seawater}$ values. The vertical bars indicate the ranges of $\delta^{18}O_{shell}$ for the most enriched and depleted Silurian brachiopods, and shaded areas mark the preferred temperature ranges. SMOW—standard mean ocean water.

matter, a scenario that would return the light carbon to surface waters. The positive $\delta^{13}C$ spikes may have been due therefore to increased productivity rather than enhanced burial of organic matter (cf. Schidlowski and Aharon, 1992). It must be pointed out, however, that the Silurian paleontological record shows no clear evidence of anomalously high primary oceanic productivity, such as the Cenozoic plankton blooms, that could be made accountable for a large-scale $\delta^{13}C$ shift of as much as ~ 8‰, such as the one in the Ludfordian (Fig. 9). We are uncertain whether this large excursion is a local feature of the Gotland basin or a global phenomenon, although the whole-rock data at Braker River in Australia (Andrew et al., 1984a, 1984b) indicate that it may be of greater than local importance. Similarly, the documentation of the Wenlock peaks (Fig. 9) in Britain, Gotland, and Lithuania (Fig. 10) argues for their regional to global significance.

Considering that the most pronounced positive $\delta^{13}C$ (and $\delta^{18}O$) peaks may have persisted for several million years (Fig. 9), it appears likely that any postulated increased productivity would have to be sustained by a geological factor external to oceans, such as continuous increased supply of nutrients. At this stage, however, we are unable to suggest any plausible geological scenario that would explain all the observations considered herein or the fate of the generated organic matter that is not accounted for by the burial in sediments. We therefore prefer to defer the consideration of carbon isotope excursions until a sufficient regional coverage of Silurian strata becomes adequate to the task.

CONCLUSIONS

1. Silurian brachiopods sampled appear to have retained their primary isotope signals without exerting any major vital control on fractionation of O and C isotopes during their incorporation into shells.
2. The δ^{18}O signal for the Silurian Period shows a minor long-term depletion with decreasing age and superimposed short-term oscillations. These short-term oscillations in the Silurian δ^{18}O values show positive peaks that correlate with glacial episodes documented from the Early Silurian rocks of Brazil and Africa. Younger observed isotope shifts, however, are not correlatable with any such events.
3. Assuming low latitude temperatures of 20 to 30 °C during warm episodes, the isotope signals of brachiopods suggest a seawater isotopic composition that varied from –2.5‰ during cold episodes to –3.5‰ (SMOW) during warm episodes.
4. The Silurian brachiopods of the Wenlockian Lithuanian basin exhibited relatively higher δ^{18}O values than their counterparts from other locations, possibly reflecting deeper water conditions of their communities.
5. The δ^{13}C record shows three remarkable positive excursions (early and late Wenlock and late Ludlow) that appear to coincide with sea-level lowstands and likely are of regional to global significance. At present, we are not in a position to propose an unequivocal scenario for their origin.

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