

Early Silurian paired $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ analyses from the Midcontinent of North America: Implications for paleoceanography and paleoclimate

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Abstract

Paired $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ samples from well-preserved marine carbonates of the Wayne Formation in central Tennessee were analyzed to test a previously proposed model of relative changes in atmospheric $p\text{CO}_2$ during the well-known Ireviken (early Wenlock) positive carbon isotope ($\delta^{13}\text{C}_{\text{carb}}$) excursion. Our investigation provides the first detailed $\delta^{13}\text{C}_{\text{org}}$ stratigraphy through this interval and documents a negative excursion in $\delta^{13}\text{C}_{\text{org}}$ associated with the positive $\delta^{13}\text{C}_{\text{carb}}$ excursion. This is consistent with the notion that the Ireviken positive $\delta^{13}\text{C}_{\text{carb}}$ excursion was associated with elevated global temperatures that began during an icehouse–greenhouse transition. Although our data are consistent with predictions made by the Silurian oceanographic model [Jeppsson, L., 1990. An oceanic model for lithological and faunal changes tested on the Silurian record. *J. Geol. Soc. (Lond.)* 147, 663–674], a link to global changes in atmospheric $p\text{CO}_2$ remains tenuous until it can be shown that the $\delta^{13}\text{C}_{\text{org}}$ trends shown herein can be reproduced globally.

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1. Introduction

Variations in atmospheric $p\text{CO}_2$ are commonly taken to be the main driver of climate change on geological timescales (Berner and Kothavala, 2001; Royer et al., 2004), although there is still considerable debate about this fundamental issue. Shaviv and Veizer (2003) have suggested that the cosmic ray flux record correlates more closely with the Phanerozoic paleotemperature estimates of Veizer et al. (2000) than recent CO_2 -driven global climate models. However, the CO_2 -driven models remain

robust when the full spectrum of geologic data is compared to the isotopic proxy data (Royer et al., 2004). Thus, although a multi-proxy approach is necessary to fully evaluate proposed correlations between atmospheric $p\text{CO}_2$ and climate, this investigation examines paired carbon isotope analyses of carbonates and organic matter as a starting point for discussion of high-resolution changes in Silurian atmospheric $p\text{CO}_2$.

Positive $\delta^{13}\text{C}_{\text{carb}}$ excursions in marine carbonates are traditionally interpreted to reflect enhanced burial of organic matter in the global oceans. Furthermore, these events are frequently linked to drawdown of atmospheric carbon dioxide in scenarios of global environmental change (e.g. Vincent and Berger, 1985; Crowley and Berner, 2001). The information that may be used to test

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these hypotheses in lower Paleozoic sediments however, in the form of paired carbon isotope analyses of carbonates and organic matter (Kump and Arthur, 1999), is often lacking (see Royer et al., 2001 for discussion of pre-Quaternary atmospheric $p\text{CO}_2$ proxies). This data can be used as a paleo- $p\text{CO}_2$ barometer because the isotopic difference between carbonate and organic matter is dominated by photosynthetic fractionation (ϵ_p), which many authors have shown is in part dependent on the concentration of dissolved CO_2 in sea water (e.g., Popp et al., 1989; Freeman and Hayes, 1992; Hayes et al., 1999).

The notion that positive $\delta^{13}\text{C}_{\text{carb}}$ excursions are the result of sequestration and burial of organic carbon in shallow epeiric seas has dominated Paleozoic carbon isotope literature. The fact that the overwhelming majority of organic carbon burial in the modern ocean takes place along continental margins (e.g. Berner and Canfield, 1989) has led researchers to apply a similar situation to the Paleozoic, assigning a causal relationship between individual epicontinental black shales and individual positive $\delta^{13}\text{C}_{\text{carb}}$ excursions (e.g. Joachimski and Buggisch, 1993; Brand et al., 2004). Positive $\delta^{13}\text{C}_{\text{carb}}$ excursions during the Silurian, however, show an increase in carbonate production and an expansion of carbonate platforms in epeiric

seas not a coincidence with organic–carbon-rich black shales (Jeppsson, 1990; Bickert et al., 1997; Brunton et al., 1998; Munneke et al., 2003; Cramer and Saltzman, 2005). The oceanographic model first developed by Jeppsson (1990), and later expanded by Cramer and Saltzman (2005), accounts for this discrepancy but still invokes an increase in organic carbon burial as the driver of the positive $\delta^{13}\text{C}_{\text{carb}}$ excursion. Our previous investigations have suggested that the Ireviken Excursion was the result of increased organic carbon burial in an anoxic deep ocean resulting from a change in the site of deep-water formation from high to low latitudes as the global climate warmed during the early Wenlock. Here, we present paired analyses of carbon isotopes in both carbonates and organic matter consistent with increasing atmospheric $p\text{CO}_2$ during the onset of the early Sheinwoodian (Ireviken) $\delta^{13}\text{C}_{\text{carb}}$ excursion, revealing a complex relationship between atmospheric $p\text{CO}_2$ and organic carbon burial during a global environmental perturbation (Table 1).

2. Geologic background

A major faunal crisis known as the Ireviken Event spans the Llandovery–Wenlock boundary (as defined

Table 1
Paired stable carbon isotope data

Meter ^a	$\delta^{13}\text{C}_{\text{carb}}$	Carbon 3pt.	Standard deviation	$\delta^{13}\text{C}_{\text{org}}$	Organic 3pt.	Standard deviation	Δ	Δ 3pt.	% carbon
12.75	2.20			−25.78			27.98		98.72
12.00	1.14	1.47	−0.33	−26.80	−26.49	−0.31	27.94	27.96	96.47
11.50	1.06	1.03	0.03	−26.90	−26.18	−0.72	27.96	27.21	96.21
10.75	0.89	0.97	−0.08	−24.83	−25.65	0.82	25.72	26.62	96.91
10.00	0.96	0.92	0.04	−25.22	−25.78	0.56	26.18	26.71	92.60
9.25	0.91	1.00	−0.08	−27.30	−26.20	−1.10	28.21	27.20	96.49
8.75	1.12	1.00	0.12	−26.07	−26.99	0.92	27.19	27.99	96.42
8.25	0.96	1.02	−0.06	−27.60	−26.30	−1.30	28.56	27.32	96.96
7.75	0.99	1.01	−0.02	−25.22	−26.55	1.33	26.21	27.56	93.70
7.25	1.08	1.09	−0.01	−26.82	−25.95	−0.87	27.90	27.03	97.24
6.75	1.19	1.22	−0.03	−25.80	−26.59	0.79	26.99	27.81	96.57
6.25	1.39	1.44	−0.05	−27.16	−25.47	−1.69	28.55	26.91	98.29
5.75	1.75	1.75	0.00	−23.44	−25.96	2.52	25.19	27.71	97.12
5.25	2.10	2.23	−0.14	−27.29	−25.77	−1.52	29.39	28.00	95.14
4.75	2.86	2.32	0.54	−26.57	−26.39	−0.18	29.43	28.71	98.95
4.25	2.00	2.73	−0.73	−25.31	−26.01	0.70	27.31	28.73	95.28
3.75	3.33	3.09	0.24	−26.14	−26.57	0.43	29.47	29.66	91.46
3.25	3.94	3.55	0.40	−28.27	−27.17	−1.10	32.21	30.71	88.55
2.75	3.37	3.41	−0.04	−27.09	−28.49	1.40	30.46	31.90	97.69
2.25	2.92	3.25	−0.33	−30.11	−28.77	−1.34	33.03	32.02	91.01
1.75	3.45	3.40	0.05	−29.12	−29.26	0.14	32.57	32.66	91.12
1.00	3.84	3.67	0.17	−28.55	−28.69	0.14	32.39	32.37	94.33
0.75	3.73	3.83	−0.10	−28.41	−28.44	0.03	32.14	32.27	81.94
0.50	3.91	3.54	0.37	−28.37	−27.95	−0.42	32.28	31.49	82.80
0.25	2.99	3.49	−0.51	−27.06	−27.81	0.75	30.05	31.30	86.73
0.00	3.58			−28.00			31.58		97.59

Maddox Mbr. Wayne Fm., Newsom Roadcut Nashville, TN.

^a Base of section is the unconformity making the base of the Wayne (top of the Brassfield).

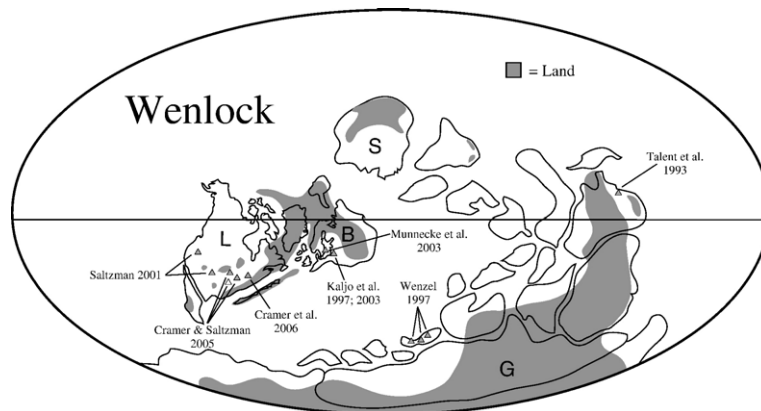


Fig. 1. Wenlock paleogeographic reconstruction after Woodcock (2000); Cocks (2001); and Johnson et al. (2001). Available published literature documenting the Ireviken carbon isotope excursion shown. The white triangle represents the locality investigated herein. The record of this excursion over a wide area indicates that the Ireviken Excursion was a global event. Grey areas denote land. Capital letters refer to major emergent landmasses: L = Laurentia; B = Baltica; S = Siberia; G = Gondwana. (Saltzman, 2001; Cramer and Saltzman, 2005; Cramer et al., 2006; Kaljo et al., 1997, 2003; Wenzel, 1997; Munnecke et al., 2003; Talent et al., 1993).

by the placement of the GSSP at Leasows, United Kingdom) and marks a major climatic turning point during the Silurian (Jeppsson, 1990). A pronounced positive excursion (Ireviken Excursion) in the carbon isotope ratio of marine carbonates began during the Ireviken Event and lasted through much of the early Wenlock (Sheinwoodian) (Munnecke et al., 2003; Cramer and Saltzman, 2005; Eriksson and Calner, 2005). We take the maximum rate of positive change in the $\delta^{13}\text{C}_{\text{carb}}$ isotope record to define the base of the excursion at datum 4 of the Ireviken Extinction Event (Jeppsson, 1987; Munnecke et al., 2003), and have placed the end of the excursion within the Lower *Kockelella walliseri* Zone as shown on Gotland, Sweden (Eriksson and Calner, 2005). Jeppsson (1990) proposed that the Llandovery–Wenlock boundary interval marked a major transition between climate states as Earth moved from a Late Ordovician–Early Silurian icehouse world back to a middle Paleozoic greenhouse and evidence of Early Silurian glaciation in South America and a major coeval eustatic regression in North America indicates that post-glacial transgression coincided with the Ireviken Excursion (Murphy et al., 1979; Grahn and Caputo, 1992; Díaz-Martínez, 1997, 2007; Grahn, 1998; Cramer and Saltzman, 2005, 2007).

The Ireviken $\delta^{13}\text{C}_{\text{carb}}$ excursion has been documented world wide (Fig. 1), but this investigation represents the first high-resolution paired $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ stratigraphy. Our paired analyses of $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ are from the Midcontinent of North America from a section west of Nashville, Tennessee known as Newsom Roadcut (Fig. 2). This section was sampled for

conodont biostratigraphy by Barrick (1983) and $\delta^{13}\text{C}_{\text{carb}}$ stratigraphy by Cramer and Saltzman (2005).

3. Methods and results

3.1. Methods

The Maddox Member of the Wayne Formation was sampled at 25 cm intervals for $\delta^{13}\text{C}_{\text{carb}}$ analysis (Cramer

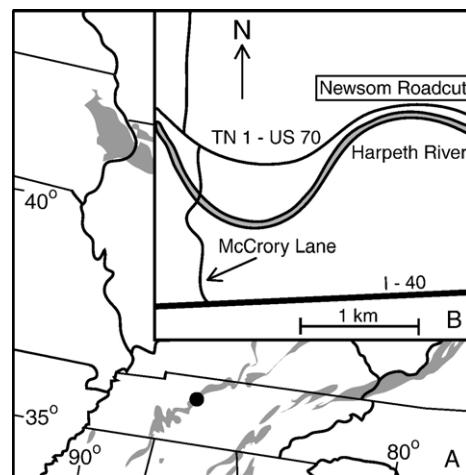


Fig. 2. (A) Silurian outcrop map in the Midcontinent of North America from Berry and Boucot (1970). Black dot left of center on bottom represents the sample locality just west of Nashville, Tennessee. (B) Inset map shows the location of the Newsom Roadcut in relation to major roads in the area. McCrory Lane, the easiest access to the outcrop, is also a well-known sample locality for conodont biostratigraphy (Barrick, 1983).

and Saltzman, 2005) and roughly every other sample was taken for paired $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ analyses for this investigation. Samples were cut and polished to expose fresh surfaces and placed in a sonic bath to remove any loose organic matter. Polished slabs were microdrilled to generate ~ 1.5 g of powder, with a preference for micrite and fine-grained carbonate (Saltzman, 2002). The major advantage of micrite and fine-grained carbonate as the sampling medium is the ability to sample at any resolution in any carbonate section, therefore not being limited to sections or intervals where brachiopods are present. Micritic sampling has been shown to faithfully record the original isotopic signature of Paleozoic marine waters (Saltzman, 2001), and brachiopods and micritic samples from the same outcrops produce nearly identical results (compare Munnecke et al., 1997 with Bickert et al., 1997).

Organic carbon samples were reacted with HCl to remove carbonate and heated at 85 °C to remove remaining water. Samples were cleaned, homogenized, and dried before being loaded into 6mm quartz tubes containing a stoichiometrically excessive amount of organic-free cupric oxide. Samples were degassed under vacuum for a minimum of 1 h, sealed using a gas/oxygen torch, and reacted at 800 °C for 24 h. The resultant CO_2 was cryogenically separated from any water or other non-condensable by-products of the reaction. The purified CO_2 was transferred to a 6 mm Pyrex tube and detached from the extraction line using a gas/oxygen torch. The isotopic composition of the $\delta^{13}\text{C}$ of the CO_2 was determined using a Finnigan MAT Delta S mass spectrometer. Data are reported relative to the VPDB scale, and accuracy and precision of NBS 22 standard were maintained at better than $\pm 0.12\text{‰}$. Isotopic analyses were carried out at the University of Michigan.

3.2. Data analysis

Sedimentary $\delta^{13}\text{C}_{\text{org}}$ of TOC (total organic carbon) trends are controlled by an array of factors. Heterotrophic reworking, changes in the dominant primary producer, varying terrestrial organic carbon input, kinetic isotope effects from varying metabolic pathways, as well as the isotopic composition and concentrations of dissolved CO_2 have all been shown to affect $\delta^{13}\text{C}_{\text{org}}$ (Hinga et al., 1994; Hayes et al., 1999; Kienast et al., 2001). In addition, diagenetic factors such as thermal maturation and migration of hydrocarbons can affect $\delta^{13}\text{C}_{\text{org}}$. A brief discussion of the relative importance of these factors is included below.

Respiratory remineralization of organic matter in the sediment column under oxic conditions can produce an

enrichment ($\leq 1.50\text{‰}$) in $\delta^{13}\text{C}_{\text{org}}$ (Hayes et al., 1989; Gong and Hollander, 1997; Fischer et al., 1998). This isotopic enrichment increases in sediments deposited beneath an anoxic water column (Fischer et al., 1998) where it can reach as high as 3.0‰. The sediments in our section were deposited in a shallow epeiric sea under mostly well-oxygenated conditions.

The influence of terrestrial input of organic carbon on our data is minimized in part by the interval of time we are studying. The Ireviken Excursion, during the Lower Silurian predates the proliferation of land plants during the Devonian (Algeo and Scheckler, 1998) therefore reducing the possible influence of terrestrial organic carbon. However, Stricanne et al. (2006) have demonstrated a quantitative increase in terrestrial spores (specimens per gram of sediment) during the Lau (Late Silurian) positive $\delta^{13}\text{C}_{\text{carb}}$ excursion and although no such data exists for the earlier Ireviken Excursion, we cannot rule out the possibility of some input of organic matter from land. Changes in the dominant species of marine primary producer have also been shown to affect $\delta^{13}\text{C}_{\text{org}}$ analysis of TOC (Pancost et al., 1999). In their late Middle Ordovician example, an abundance of compounds inferred to be from an uncommon organic-walled microfossil *Gloeocapsomorpha prisca* overprinted the global $\delta^{13}\text{C}_{\text{org}}$ signal making $\delta^{13}\text{C}_{\text{org}}$ values heavier.

The conodont alteration index (CAI) of specimens collected by Barrick (1983) is ≤ 1.5 , which indicates that burial temperatures never exceeded 100 °C (cf. Epstein et al., 1977). These temperatures are unlikely to have played a major role in the trends we observe (temperatures approaching those of oil generation are required to significantly alter $\delta^{13}\text{C}_{\text{org}}$; Hayes et al., 1999). Furthermore, thermal maturation due to overburden or regional

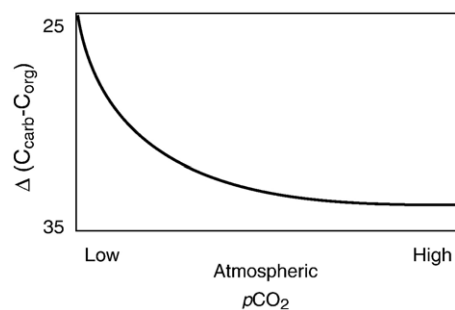


Fig. 3. Generalized curve showing the relationship between Δ (the isotopic difference between $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$) and atmospheric CO_2 levels; modified from Kump and Arthur (1999). The relationship between $p\text{CO}_2$ and Δ is that photosynthesizing organisms can be more selective of their carbon intake in the presence of abundant CO_2 . When CO_2 levels are reduced, photosynthesis must incorporate a greater portion of ^{13}C driving Δ to lower levels.

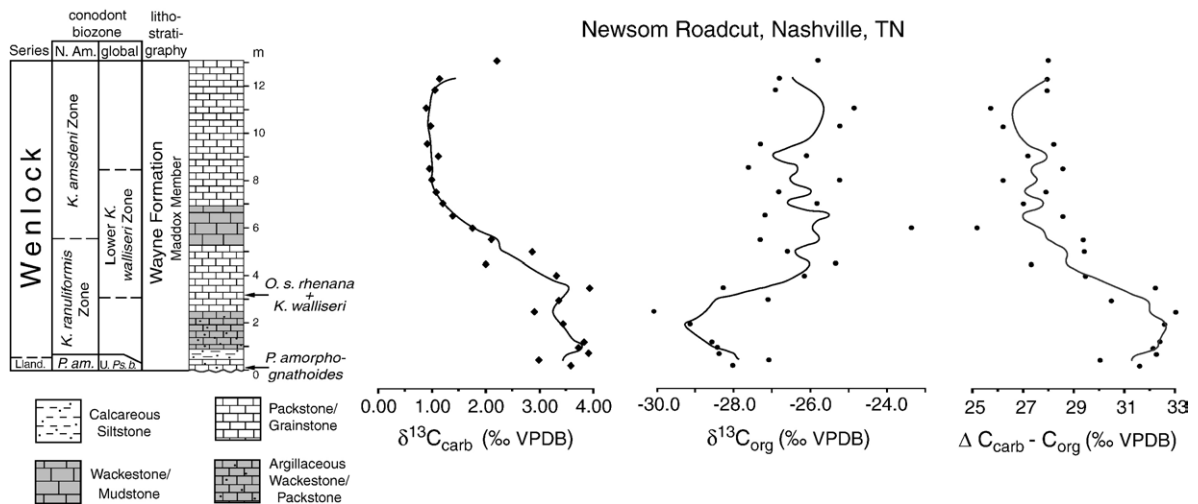


Fig. 4. Carbon isotope data from Newsom Roadcut, Nashville, TN. North American conodont biozones from Barrick (1983). The low conodont yields from this outcrop do not allow a complete correlation with the global standard conodont zones of Jeppsson (1997). For instance, only a single specimen of *O. s. rhenana* has been reported (Barrick, 1983). Therefore, we have only been able to make a limited effort to tie this section directly into the global standard conodont zonation. Numbers to the right of the stratigraphic column represent meters above the sampling datum, in this case, the base of the Wayne Formation. The curves fitted to the data represent a three point floating average. Note that Δ was increasing and remained high during the Ireviken Excursion, as well as the coincidence of a negative excursion in $\delta^{13}\text{C}_{\text{org}}$ with the positive excursion in $\delta^{13}\text{C}_{\text{carb}}$.

tectonism should have affected the entire section equally and therefore is an unlikely cause of any excursion in our data.

Even with these complications, $\delta^{13}\text{C}_{\text{org}}$ analysis of TOC has been shown to faithfully record the original isotopic trend when compared with compound specific $\delta^{13}\text{C}_{\text{org}}$ analysis of short chain *n*-alkanes as well as acyclic isoprenoids pristane, phytane and hopane from identical samples (Joachimski et al., 2002). The baseline values of the different analyses varied by a few per mille but the trends shown were practically identical. For these reasons we do not use our data to calculate empirical values for CO_2 , but instead calculate $\Delta^{13}\text{C}$, which is the isotopic difference between $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$. An inverse square relationship (Fig. 3) exists between $\Delta^{13}\text{C}$ and atmospheric $p\text{CO}_2$ (Kump and Arthur, 1999). As Δ increases, atmospheric $p\text{CO}_2$ increases and therefore, we use changes in Δ as a proxy for changes in atmospheric $p\text{CO}_2$.

3.3. Results

Values of $\delta^{13}\text{C}_{\text{carb}}$ begin near +2.0‰ at the base of the Wayne Formation and quickly increase to nearly +4.0‰ within the first 50 cm, while $\delta^{13}\text{C}_{\text{org}}$ values begin near -28.0‰ and decrease to a minimum of -30.0‰ within the first few meters (Fig. 4). The $\delta^{13}\text{C}_{\text{carb}}$ values record a positive excursion and reach two distinct peaks. The first reaches a high of +3.91‰ at 0.50 m above the

base of the Maddox, and the second peak of +3.94‰ occurs at 3.25 m. Values of $\delta^{13}\text{C}_{\text{org}}$ record a negative excursion with only one peak of -30.1‰ at 2.25 m above the base of the Maddox. The peak in $\delta^{13}\text{C}_{\text{org}}$ values occurs between the $\delta^{13}\text{C}_{\text{carb}}$ peaks. The $\delta^{13}\text{C}_{\text{org}}$ curve returns to baseline before $\delta^{13}\text{C}_{\text{carb}}$. The isotopic difference (Δ) increases during the excursion to a maximum of 33.0‰ at 2.25 m before returning to a baseline near 28.0‰ after the excursion.

4. Discussion

The oceanographic model presented by Jeppsson (1990) and later expanded by Cramer and Saltzman (2005) makes predictions about changes in ocean chemistry and atmospheric $p\text{CO}_2$. It has been suggested (Jeppsson, 1990; Cramer and Saltzman, 2005) that the Ireviken Excursion was the result of increased organic carbon burial rates in the deep oceans that began during a transition from icehouse to greenhouse conditions. Our data indicate that a positive excursion in $\delta^{13}\text{C}_{\text{carb}}$ coincided with a minimum in $\delta^{13}\text{C}_{\text{org}}$ values. Therefore $\Delta^{13}\text{C}$, here used as a proxy for paleo- $p\text{CO}_2$, shows elevated values and high atmospheric $p\text{CO}_2$ during the Ireviken Excursion.

A change in the site of deep-water formation at the end of the Late Ordovician–Early Silurian icehouse state is consistent with the isotopic results. Jeppsson (1990) suggested that the early Wenlock climatic optimum

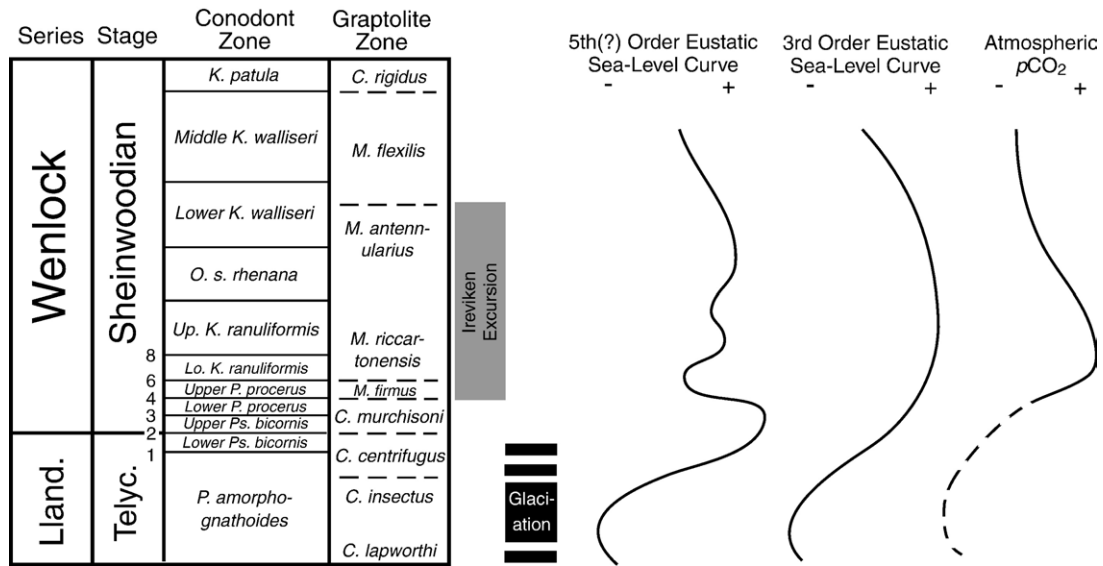


Fig. 5. Correlation of biostratigraphic zonation, the Ireviken Excursion, glaciation, eustacy, and changes in atmospheric carbon dioxide across the Llandovery–Wenlock boundary interval. The base of the diagram is above the base of *P. amorphognathoides* and *C. lapworthi*. Note that the figure is not scaled to time. The biostratigraphic correlation is from Jeppsson (1990), and Calner et al. (2004). Correlation of the excursion and glacio-eustacy is after Cramer and Saltzman (2005) and Cramer and Saltzman (2007). 5th order sea-level curve is from Loydell, 1998. Compare the eustatic curves shown here with Fig. 9 of Cramer and Saltzman (2005).

caused a shift in deep-water formation from high to low latitudes, which led to deep-ocean anoxia and enhanced preservation of organic carbon (Bralower and Thierstein, 1984; Herbert and Sarmiento, 1991; Cramer and Saltzman, 2005). The increased sequestration and burial of ^{12}C (as organic matter) in the deep ocean produced the positive $\delta^{13}\text{C}_{\text{carb}}$ excursion while the elevated atmospheric $p\text{CO}_2$ that produced the climatic optimum was responsible for the negative $\delta^{13}\text{C}_{\text{org}}$ excursion.

During the middle of the Ireviken Excursion $\Delta^{13}\text{C}$ values reach as much as 33.0‰ and may therefore indicate the presence of sulfide oxidizing or other chemoautotrophic bacteria (Hayes et al., 1999). Canfield (1998) and Kump et al. (2005) discuss the possibility of a euxinic deep ocean during times of marine biotic crises and increased organic carbon burial in the deep ocean.

Although strata immediately prior to the onset of the excursion are not recorded in the sampled section, it appears that during the early part of the Ireviken Excursion, atmospheric $p\text{CO}_2$ was increasing despite high organic carbon burial rates (Fig. 5). Only later during the Ireviken Excursion does atmospheric $p\text{CO}_2$ respond to high organic carbon burial rates in the expected manner where increased organic carbon burial tends to force the oceans to compensate by drawing down atmospheric $p\text{CO}_2$ (Kump and Arthur, 1999). Organic carbon burial acts as a buffer for atmospheric $p\text{CO}_2$, limiting the magnitude of fluctuations in global climate.

The oceanographic system appears to respond to the elevated global temperatures during the Ireviken Excursion in the following sequence: 1) deglaciation; 2) change in the site of deep-water formation from high to low latitudes; 3) decreased oxygenation of the deep ocean; 4) increased organic carbon burial rates in the deep ocean producing the positive $\delta^{13}\text{C}_{\text{carb}}$ excursion; 5) drawdown of atmospheric $p\text{CO}_2$ that compensates for increased organic carbon burial 6) decreasing global temperatures; 7) re-establishment of latitudinal thermal gradient and a shift in deep-water formation back to high latitudes, which re-oxygenated the deep ocean and ended the Ireviken Excursion. This oceanographic system may have exerted a restorative control over atmospheric $p\text{CO}_2$ during the early–middle Paleozoic.

The trigger of the Ireviken Excursion and coincident rise in atmospheric $p\text{CO}_2$ that led to deglaciation remains uncertain. Based on high-resolution correlations (Jeppsson, 1997), the Ireviken Excursion lasted roughly two million years. Therefore, the elevated atmospheric $p\text{CO}_2$ was likely related to a perturbation in the long-term carbon cycle. The Salinic Orogeny occurred at roughly the same time along eastern Laurentia (Goodman and Brett, 1994; Cramer et al., 2006) as the late Llandovery (South American) glaciation (Cramer and Saltzman, 2007) and could provide a link via changes in silicate weathering (e.g., Raymo, 1994). The early Wenlock transgression represents one of the highest

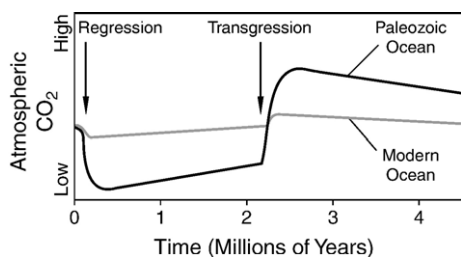


Fig. 6. Consequences of changes in eustatic sea level on atmospheric CO_2 due to the ‘coral reef effect’ (simplified from Ridgwell et al., 2003). Because the deposition of CaCO_3 results in the liberation of CO_2 to the atmosphere, eustatic changes that affect carbonate production and burial will impact atmospheric CO_2 levels. Today (grey line) this effect is small, because the modern ocean preserves carbonate in the deep ocean during sea-level lowstands. In the lower Paleozoic, prior to the proliferation of planktic calcifying organisms (black line), the production and preservation of carbonate in the pelagic environment was considerably reduced. During regression in the Paleozoic, the total area of shallow shelf and epeiric sea settings was reduced, diminishing carbonate production and burial, and slowing the release of CO_2 into the atmosphere. The increased space available for carbonate production and burial during transgression produces a concomitant increase in CO_2 liberation to the atmosphere. This serves as a positive (reinforcing) feedback for global warming or cooling during the Paleozoic.

sea levels in the Silurian and may have reduced silicate weathering enough to induce increased atmospheric $p\text{CO}_2$. Furthermore, increased aridity at low latitudes during the early Wenlock (Bickert et al., 1997) would have reduced weathering and riverine burial of organic carbon, lowering CO_2 consumption (France-Lanord and Derry, 1997). Thus the high silicate weathering (Salinic Orogeny) and high CO_2 consumption (increased moisture) during the late Llandovery was followed by a period of low silicate weathering and CO_2 consumption during the early Wenlock (high sea level, increased aridity) that contributed to increasing atmospheric $p\text{CO}_2$ and deglaciation at the onset of the Ireviken Excursion.

Another contributing factor was the relative lack of planktic calcifiers during the lower Paleozoic. Due to the fact that carbonate production in the lower Paleozoic was limited to shelf and epicontinental sea environments, carbonate production and burial (and consequently atmospheric $p\text{CO}_2$) were highly sensitive to changes in sea level (Ridgwell et al., 2003). In the modern ocean, the reduction in neritic carbonate production and burial during sea-level lowstands is compensated by increased pelagic carbonate preservation, which helps attenuate changes in atmospheric $p\text{CO}_2$ caused by eustatic sea-level change. During the lower Paleozoic however, the ocean–atmosphere system would have been much more

volatile (Fig. 6) due to paucity of pelagic carbonate production and preservation.

5. Conclusions

This investigation highlights the importance of paired $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ analyses to paleoclimatology and paleoceanography. Although meaningful empirical calculations of Paleozoic atmospheric $p\text{CO}_2$ are still out of reach due to the multiplicity of estimated or approximated factors in most data sets, our data (pending verification from other localities) provides considerable insight into the nature of changes to the global carbon cycle through this interval of the Silurian. The data presented herein indicate a complex relationship between organic carbon burial and atmospheric $p\text{CO}_2$, where changes in the fraction of carbonate versus organic carbon being buried (f_{org}) act as a buffer for atmospheric $p\text{CO}_2$ in the long-term carbon cycle. It appears that changes in atmospheric $p\text{CO}_2$ were the driving factor for the Ireviken Excursion, which is represented by both a positive $\delta^{13}\text{C}_{\text{carb}}$ excursion and a negative $\delta^{13}\text{C}_{\text{org}}$ excursion. During the Ireviken Excursion, high atmospheric $p\text{CO}_2$ directly led to the negative $\delta^{13}\text{C}_{\text{org}}$ excursion and was ultimately responsible for the positive $\delta^{13}\text{C}_{\text{carb}}$ excursion by altering deep-ocean circulation and increasing organic carbon burial.

Although the negative excursion in $\delta^{13}\text{C}_{\text{org}}$ during the early Wenlock has been demonstrated from the Newsom Roadcut section alone, work is underway to replicate this result from other sections. We hope this investigation will draw greater attention to the need for high-resolution study of paired $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{13}\text{C}_{\text{carb}}$ during the Paleozoic.

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