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Sequestration of ^{12}C in the deep ocean during the early Wenlock (Silurian) positive carbon isotope excursion

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Abstract

Marine carbonates from three biostratigraphically well-dated Silurian sections from the mid-continent of North America were analyzed for carbon isotopic ($\delta^{13}\text{C}_{\text{carb}}$) study. The early Wenlock positive carbon isotope excursion (Ireviken Excursion) is recorded in three sections from Tennessee, Iowa, and Ohio, with values of $>+4.5\%$. This global shift in the carbon isotopic ratio of marine waters began during a protracted extinction event (Ireviken Event) that spanned the Llandovery–Wenlock boundary. Although several oceanographic models have been developed to account for the coincident changes in lithology, biology, and carbon isotope stratigraphy during this interval of the Silurian, their proposed causal connections among glaciation, oceanography, primary productivity, and the global carbon cycle remain a matter of debate. This investigation provides carbon isotopic and lithologic evidence that the Ireviken Excursion occurred during a time of relatively oligotrophic conditions, a third order transgressive–regressive cycle, and increased carbonate production throughout the mid-continent of North America. The Ireviken Excursion is recorded in relatively pure carbonate sequences and is immediately preceded by a significant unconformity in each of the measured sections. It is proposed that the Ireviken Excursion was the product of sequestration and burial of ^{12}C in deep water as a result of altered deep ocean circulation.

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Keywords: Ireviken; Carbon isotope; North America; Glaciation; Oceanography

1. Introduction

Historically, the Silurian System has been considered an interval of relative climatic stability within a greenhouse period (Fischer, 1983; Scotese and McKerrow, 1990; Bassett and Edwards, 1991). How-

ever, recent investigations of Silurian carbon isotope stratigraphy suggest a more volatile ocean–atmosphere system. The presence of four major positive carbon isotope ($\delta^{13}\text{C}_{\text{carb}}$) excursions during the Silurian indicates that fundamental changes in the global carbon cycle were more frequent during the Silurian (4 excursions of $>+4\%$ in 30 million years) than any other System of the Phanerozoic (Odin et al., 1986; Harland et al., 1990; Samtleben et al., 1996;

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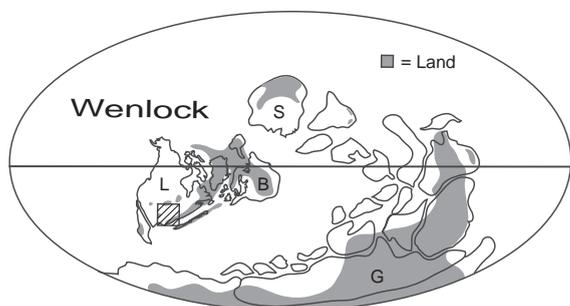


Fig. 1. Wenlock paleogeography (primarily after Woodcock, 2000; Cocks, 2001; Johnson et al., 2001). Grey areas denote land. Capital letters refer to major emergent landmasses: (L) Laurentia; (B) Baltica; (S) Siberia; (G) Gondwana. Diagonally hatched box indicates area shown in Fig. 2.

Bickert et al., 1997; Azmy et al., 1998; Saltzman, 2001, 2002a; Calner et al., 2004).

The positive carbon isotope excursions of the Silurian are all closely associated with major biotic crises and changes in the health of the shallow water carbonate factory (Jeppsson, 1990, 1998; Jeppsson et al., 1995; Quinby-Hunt and Berry, 1991; Berry, 1998; Mikulic and Kluessendorf, 1999; Saltzman, 2001, 2002a; Munnecke et al., 2003; Calner et al., 2004). In an effort to explain the apparent cyclicity of extinction events and lithologic changes in Silurian strata of Gotland, an oceanographic model was developed based on changes in climate (i.e., icehouse–greenhouse transitions) and the hydrologic cycle (Jeppsson, 1990). However, the location and timing of increased organic matter production and burial (^{12}C sequestration) in shelf or deep sea sediments during the Silurian remain a matter of debate (e.g., Wenzel and Joachimski, 1996; Bickert et al., 1997; Azmy et al., 1998).

A unique feature of Silurian $\delta^{13}\text{C}_{\text{carb}}$ excursions is that they generally occurred during periods of widespread carbonate deposition in shelf environments (Azmy et al., 1998; Brunton et al., 1998; Saltzman, 2001). For example, the early Wenlock is characterized by high $\delta^{13}\text{C}_{\text{carb}}$ values and has also been identified as a global episode of prolific reef development by Brunton et al. (1998). This contrasts with other Paleozoic positive carbon isotope excursions such as the Frasnian–Famennian boundary excursion, which shows peak $\delta^{13}\text{C}_{\text{carb}}$ values during periods of organic rich deposition in shelf environments (e.g., Joachimski and Buggisch, 1993). As modeling for $\delta^{13}\text{C}$ excursions shows (Kump and Arthur, 1999), we

expect the positive excursions in the Silurian to be the result of increased organic carbon burial relative to carbonate carbon which would leave the ocean enriched in ^{13}C . However, a high burial fraction of organic carbon in shallow settings is seemingly inconsistent with the widespread reef building episodes that coincide with Silurian $\delta^{13}\text{C}$ excursions, but can be resolved if organic carbon burial is taking place in deeper water away from the shelf.

The Llandovery–Wenlock boundary interval was chosen as the focus of this investigation because it is a particularly well-studied, representative transition between climate states in the Silurian that has provided the basis for many aspects of climatologic and oceanographic models (e.g., Jeppsson, 1990). We have examined three sections that span a wide region of the mid-continent of North America in an effort to extend the geographic coverage of Silurian carbon isotope data between the well studied sections of the Baltic region (e.g., Samtleben et al., 1996; Kaljo et al.,

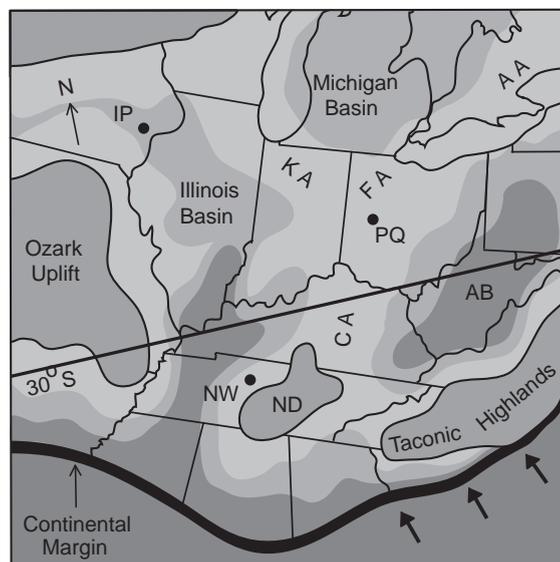


Fig. 2. Paleogeographic and paleobathymetric reconstruction of the mid-continent of North America (compiled mainly from Horvath, 1969; Berry and Boucot, 1970; Shaver, 1996). Darker shaded areas of basins represent deeper water. Relative size and emergence of the Ozark uplift are speculative. Abbreviations: (KA) Kankakee Arch; (FA) Findlay Arch; (AA) Algonquin Arch; (CA) Cincinnati Arch; (AB) Appalachian Basin; (ND) Nashville Dome. Black dots indicate location of the three measured sections: (NW) Newsom Roadcut, Tennessee; (IP) IPSCO core OW-5, Iowa; (PQ) Piqua Quarry, Ohio.

1997, 2003; Munnecke et al., 2003; Calner et al., 2004), western North America (Saltzman, 2001), and eastern Australia (Talent et al., 1993). The vast epicontinental carbonate platforms of the Laurentian craton represent an ideal opportunity to test whether the association between high $\delta^{13}\text{C}_{\text{carb}}$ and increased carbonate production observed elsewhere is a global pattern.

2. Geological setting

The Silurian succession of the mid-continent of Laurentia is represented by epicontinental carbonate and shale successions, located far from the clastic wedges of the Taconic Orogeny that occur on the eastern side of the Appalachian Basin (Berry and Boucot, 1970). The widespread, well-dated, and easily accessible carbonate sequences of the mid-continent of North America are well-suited for detailed investigation of Silurian carbon isotope stratigraphy.

2.1. Paleogeography

Although the position of Gondwana and location of the numerous Asian micro-continents during the Silurian continue to be problematic, there is better agreement over the paleolocation of Baltica and Laurentia (Scotese and McKerrow, 1990; Woodcock, 2000; Cocks, 2001; Johnson et al., 2001; Lees et al., 2002; Fortey and Cocks, 2003). Current paleogeographic reconstructions (Fig. 1) place the northwest corner of Laurentia near the equator, with the mid-continent of North America between 15° and 35° S. latitude (Van der Voo, 1988; Witzke and Scotese, 1990; Woodcock, 2000; Smethurst and McEnroe, 2003). The three sections investigated (Tennessee, Iowa, and Ohio) were most likely within the southern subtropical high-pressure zone during the Wenlock (Parrish, 1982; Parrish et al., 1983; Baarli, 1998). The Silurian sea in the mid-continent U.S.A. was divided into three major basins (Fig. 2): the Appalachian, Illinois, and Michigan basins. The Cincinnati, Algonquin, Findlay, and Kankakee arches were the primary

Nicoll & Rexroad 1969 (Indiana)	Barrick & Klappner 1976 (Oklahoma)	Barrick 1983 (S. Central U.S.)	Kleffner 1995	Jeppsson 1997b Wenlock Standard Conodont Zonation	Oceanic Circulation Regime Jeppsson ('93, '97b)
			-21.30		
	K.	K.	-17.88	<i>O. s. sagitta</i> Zone	Hellvi S. E.
			-17.81	<i>K. o. ortus</i> Zone	Valleviken Event
			-18.66	post <i>K. walliseri</i> inter.	Allekvia P. Episode
	<i>amsdeni</i>	<i>amsdeni</i>	-17.81	uppermost <i>K. wallis.</i> range	Lansa S. Episode
	Zone	Zone	-17.30	<i>K. patula</i> Zone	Boge Event
			-17.73	Middle <i>K. walliseri</i> Zone	Sanda Primo Episode
<i>P. amorpho-</i>			-17.62	Lower <i>K. walliseri</i> Zone	
<i>gnathoides/</i>	<i>K. ranuli-</i>	<i>K. ranuli-</i>	-16.90	<i>O. s. rhenana</i> Zone	Vattenfallet Secundo Episode
<i>Spatho-</i>			-16.32	Upper <i>K. ranuliformis</i> Zone	
<i>gnathodus</i>	<i>formis</i>	<i>formis</i>	-15.85	Lower <i>K. ranuliformis</i> Zone	
<i>ranuliformis</i>			-15.80	Upper <i>P. procerus</i> Zone	
Assemblage	Zone	Zone	-15.70	Lower <i>P. procerus</i> Zone	Ireviken
Zone	? ? ?	<i>P. am.</i>	-15.70	Upper <i>Ps. bicornis</i> Zone	Event
	<i>P. am. Z.</i>	Zone	-15.58	Lower <i>Ps. bicornis</i> Zone	
			-14.48	<i>P. amorphognathoides</i> Zone	Snipklint P. E.

Ireviken Excursion

Fig. 3. Telychian through Homerian standard conodont zonation and correlation with the mid-continent zonations. Length of zones is not intended to represent time. Modified from Jeppsson (1997b) to show duration of the Ireviken Excursion, which is from Calner et al. (2004).

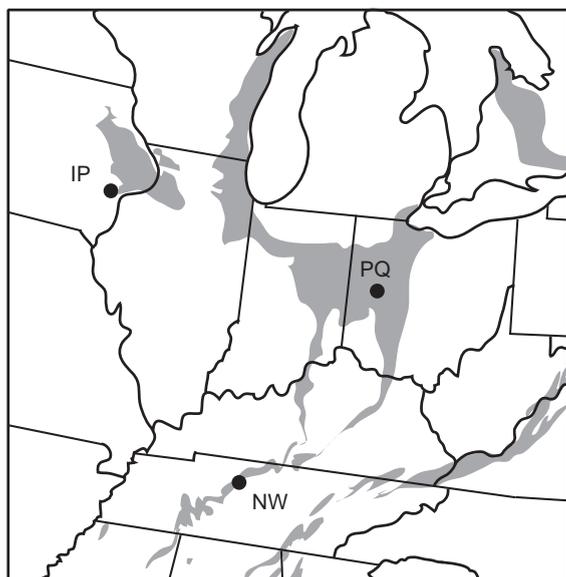


Fig. 4. Silurian outcrop belts in the mid-continent from Berry and Boucot (1970). As in Fig. 2, the black dots indicate location of the three measured sections: (NW) Newsom Roadcut, Tennessee; (IP) IPSCO core OW-5, Iowa; (PQ) Piqua Quarry, Ohio.

restrictions to deep connection between the basins, and often experienced subaerial exposure during Silurian regressions or flexural uplift (Horvath, 1969; Kleffner, 1994, 2000; Etensohn, 1994; Goodman and Brett, 1994; Kluessendorf and Mikulic, 1996; Ross and Ross, 1996; Shaver, 1996; Etensohn and Brett, 1998).

2.2. Biostratigraphy

Carbonate exposures on the Swedish island of Gotland have yielded a late Llandovery to Wenlock (Telychian–Homerian) standard conodont biozonation that is exceptionally high resolution and useful as a reference standard for global correlations (Jeppsson, 1997b). The marine biotic crisis known as the Ireviken Event (Jeppsson, 1983, 1987), which spanned the Llandovery–Wenlock boundary, affected conodonts, graptolites, trilobites, and many other marine organisms (Mabillard and Aldridge, 1985; Chatterton et al., 1990; Jeppsson, 1990, 1997a; Melchin, 1994; Eriksson and Hagenfeldt, 1997; Berry, 1998; Mikulic and Kluessendorf, 1999). *Pterospathodus amorphognathoides*, one of the most cosmopolitan species of Silurian conodonts (Männik and

Table 1

Stable isotope data, Newsom Roadcut, TN

Meter ^a	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Conodont zone	Wayne FM. member
13.12	2.20	-2.34	<i>K. amsdeni</i>	Maddox
12.87	1.35	-4.20	<i>K. amsdeni</i>	Maddox
12.62	1.13	-4.06	<i>K. amsdeni</i>	Maddox
12.37	1.14	-4.62	<i>K. amsdeni</i>	Maddox
12.12	1.15	-4.48	<i>K. amsdeni</i>	Maddox
11.87	1.06	-4.08	<i>K. amsdeni</i>	Maddox
11.62	1.06	-4.36	<i>K. amsdeni</i>	Maddox
11.37	0.91	-4.21	<i>K. amsdeni</i>	Maddox
11.12	0.89	-4.39	<i>K. amsdeni</i>	Maddox
10.87	0.50	-4.28	<i>K. amsdeni</i>	Maddox
10.62	0.81	-4.27	<i>K. amsdeni</i>	Maddox
10.37	0.96	-3.61	<i>K. amsdeni</i>	Maddox
10.12	1.01	-3.75	<i>K. amsdeni</i>	Maddox
9.87	1.03	-3.78	<i>K. amsdeni</i>	Maddox
9.62	0.91	-3.78	<i>K. amsdeni</i>	Maddox
9.37	1.06	-3.87	<i>K. amsdeni</i>	Maddox
9.12	1.12	-3.66	<i>K. amsdeni</i>	Maddox
8.87	0.98	-4.14	<i>K. amsdeni</i>	Maddox
8.62	0.96	-4.02	<i>K. amsdeni</i>	Maddox
8.37	0.92	-4.08	<i>K. amsdeni</i>	Maddox
8.12	0.99	-4.40	<i>K. amsdeni</i> (?)	Maddox
7.87	1.22	-3.84	<i>K. amsdeni</i> (?)	Maddox
7.62	1.08	-3.87	<i>K. amsdeni</i> (?)	Maddox
7.37	1.17	-4.09	<i>K. amsdeni</i> (?)	Maddox
7.12	1.19	-3.74	<i>K. amsdeni</i> (?)	Maddox
6.87	1.20	-4.23	<i>K. amsdeni</i> (?)	Maddox
6.62	1.38	-3.76	<i>K. ranuliformis</i> (?)	Maddox
6.37	1.48	-3.82	<i>K. ranuliformis</i> (?)	Maddox
6.12	1.75	-3.93	<i>K. ranuliformis</i> (?)	Maddox
5.87	1.96	-3.75	<i>K. ranuliformis</i> (?)	Maddox
5.62	2.10	-3.76	<i>K. ranuliformis</i>	Maddox
5.37	2.00	-3.89	<i>K. ranuliformis</i>	Maddox
5.12	2.86	-3.59	<i>K. ranuliformis</i>	Maddox
4.87	2.92	-3.59	<i>K. ranuliformis</i>	Maddox
4.62	2.00	-3.98	<i>K. ranuliformis</i>	Maddox
4.37	3.34	-3.82	<i>K. ranuliformis</i>	Maddox
4.12	3.33	-3.49	<i>K. ranuliformis</i>	Maddox
3.87	2.34	-3.70	<i>K. ranuliformis</i>	Maddox
3.62	3.93	-3.22	<i>K. ranuliformis</i>	Maddox
3.37	3.15	-3.42	<i>K. ranuliformis</i>	Maddox
3.12	3.37	-3.28	<i>K. ranuliformis</i>	Maddox
2.87	3.21	-3.58	<i>K. ranuliformis</i>	Maddox
2.62	2.92	-3.62	<i>K. ranuliformis</i>	Maddox
2.37	2.61	-3.46	<i>K. ranuliformis</i>	Maddox
2.12	3.45	-3.44	<i>K. ranuliformis</i>	Maddox
1.87	3.82	-3.35	<i>K. ranuliformis</i>	Maddox
1.62	3.92	-3.01	<i>K. ranuliformis</i>	Maddox
1.37	3.92	-2.91	<i>K. ranuliformis</i>	Maddox
1.12	3.72	-3.61	<i>K. ranuliformis</i>	Maddox
0.87	3.90	-3.18	<i>K. ranuliformis</i>	Maddox
0.62	3.01	-2.18	<i>K. ranuliformis</i>	Maddox

Table 1 (continued)

Meter ^a	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Conodont zone	Wayne FM. member
0.37	3.58	-3.68	<i>K. ranuliformis</i>	Maddox
0.18	2.23	-3.25	<i>K. ranuliformis</i> (?)	Maddox
0.12	2.51	-3.97	<i>P. amorphognathoides</i>	Maddox
0.1	2.15	-4.05	<i>P. amorphognathoides</i>	Maddox
0.05	2.21	-4.16	<i>P. amorphognathoides</i>	Maddox
0.00	2.40	-3.84	<i>P. amorphognathoides</i>	Maddox

^a Section begins at the unconformity marking the top of the Brassfield Formation (equivalent to base of section for Barrick, 1983).

Aldridge, 1989), is found globally at or near the base of the Ireviken Excursion (Saltzman, 2001; Munnecke et al., 2003; Calner et al., 2004). Although the available conodont biostratigraphy of the mid-continent does not match the resolution of Gotland, sufficient collections have been documented to allow for confident correlation of the two regions (Fig. 3). The Ireviken Excursion began near the top of the *P. amorphognathoides* biozone in North America but can be more precisely defined as coincident with the base of the upper *Pterospathodus procerus* biozone (sensu Jeppsson, 1997b) in Europe (Munnecke et al., 2003). The Ireviken Excursion lasted into the Lower *Kockelella walliseri* biozone in Europe (Calner et al., 2004), which correlates to a position close to the boundary between the *Kockelella ranuliformis* and *Kockelella amsdeni* biozones in the mid-continent.

3. Methods and results

3.1. Methods

Carbonates from three sections in the mid-continent of North America (Fig. 4) were sampled at regular stratigraphic intervals (meterage for each section is shown in Tables 1–3) in order to produce high resolution $\delta^{13}\text{C}$ stratigraphy through the Ireviken Excursion. Silurian micrites have been shown to faithfully preserve the primary carbon isotopic signature when compared with brachiopods from the same formations (compare Munnecke et al., 1997 with Bickert et al., 1997), which are assumed to be the most reliable material for chemostratigraphic investigation (e.g., Mii et al., 1999). The bulk rock data of Kaljo et al. (1997) and fine-grained carbonate data of

Saltzman (2001) also indicate that samples containing admixtures of carbonate cement and select skeletal components are reliable recorders of primary isotopic signatures. Use of fine-grained carbonate for $\delta^{13}\text{C}$ stratigraphy is not limited to the Silurian and its reliability has been demonstrated in the Cambrian (Ripperdan et al., 1992; Saltzman et al., 1998, 2000), Ordovician (Finney et al., 1999; Kump et al., 1999), Devonian (Joachimski and Buggisch, 1993; Wang et al., 1996), and Mississippian (Saltzman, 2002b). Dolomitization has also been shown to have a negligible effect on overall $\delta^{13}\text{C}$ trends (Glumac and Walker, 1998).

Table 2
Stable isotope data, IPSCO core OW-5, IA

Meter ^a	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Conodont zone	Formation
94.7	4.041	-4.360	<i>K. ranuliformis</i> (?)	Gower
96.3	3.441	-4.503	<i>K. ranuliformis</i> (?)	Gower
98.7	4.387	-4.510	<i>K. ranuliformis</i> (?)	Gower
103.6	3.946	-3.916	<i>K. ranuliformis</i> (?)	Gower
110.9	4.525	-4.510	<i>K. ranuliformis</i> (?)	Gower
120.7	4.553	-3.784	<i>K. ranuliformis</i> (?)	Scotch Grove
129.2	4.201	-3.938	<i>K. ranuliformis</i> (?)	Scotch Grove
137.7	4.258	-3.879	<i>P. amorphognathoides</i> (?)	Scotch Grove
138.3	4.280	-3.984	<i>P. amorphognathoides</i> (?)	Scotch Grove
139.2	4.337	-3.991	<i>P. amorphognathoides</i> (?)	Scotch Grove
139.9	4.504	-3.967	<i>P. amorphognathoides</i> (?)	Scotch Grove
141.4	4.193	-4.065	<i>P. amorphognathoides</i> (?)	Scotch Grove
142.6	4.635	-3.924	<i>P. amorphognathoides</i> (?)	Scotch Grove
143.2	3.280	-5.304	<i>P. amorphognathoides</i> (?)	Scotch Grove
144.4	4.078	-4.006	<i>P. amorphognathoides</i> (?)	Scotch Grove
145.3	4.335	-4.170	<i>P. amorphognathoides</i> (?)	Scotch Grove
145.9	4.218	-4.039	<i>P. amorphognathoides</i> (?)	Scotch Grove
147.5	4.458	-4.362	<i>P. amorphognathoides</i> (?)	Scotch Grove
148.1	4.528	-4.313	<i>P. amorphognathoides</i> (?)	Scotch Grove
149.0	4.833	-3.940	<i>P. amorphognathoides</i> (?)	Scotch Grove
149.9	4.423	-4.176	<i>P. amorphognathoides</i> (?)	Scotch Grove
150.5	4.523	-4.379	<i>P. amorphognathoides</i> (?)	Scotch Grove
151.1	2.943	-4.340	<i>P. amorphognathoides</i> (?)	Scotch Grove
152.4	2.544	-4.364	<i>P. amorphognathoides</i> (?)	Scotch Grove
153.0	2.468	-4.368	<i>P. amorphognathoides</i> (?)	Scotch Grove
153.9	2.533	-4.436	<i>P. amorphognathoides</i> (?)	Scotch Grove
155.4	2.451	-4.549	<i>P. amorphognathoides</i> (?)	Scotch Grove
155.7	1.878	-4.145	<i>P. amorphognathoides</i> (?)	Scotch Grove
156.3	1.101	-5.395	<i>P. amorphognathoides</i> (?)	Scotch Grove
156.6	1.812	-4.624	<i>P. amorphognathoides</i> (?)	Scotch Grove
156.9	0.940	-5.425	<i>P. celloni</i> (?)	Hopkinton
157.5	1.130	-5.396	<i>P. celloni</i> (?)	Hopkinton
157.8	0.644	-5.752	<i>P. celloni</i> (?)	Hopkinton
157.8	0.618	-5.647	<i>P. celloni</i> (?)	Hopkinton

^a Meterage shown is number of meters from the top of the core.

Table 3
Stable isotope data, Piqua Quarry, OH

Meter ^a	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Conodont zone	Formation
2.90	2.67	-5.15	Zone undefined	Dayton
2.70	2.63	-6.21	Zone undefined	Dayton
2.50	2.35	-6.52	Zone undefined	Dayton
2.30	2.57	-6.54	Zone undefined	Dayton
2.10	2.77	-6.62	Zone undefined	Dayton
1.90	3.06	-6.27	Zone undefined	Dayton
1.70	3.10	-4.80	Zone undefined	Dayton
1.50	3.11	-4.20	Zone undefined	Dayton
1.30	3.07	-4.40	Zone undefined	Dayton
1.10	3.42	-5.51	Zone undefined	Dayton
0.90	3.06	-6.69	Zone undefined	Dayton
0.70	3.05	-6.19	Zone undefined	Dayton
0.50	2.98	-6.07	Zone undefined	Dayton
0.30	2.80	-5.08	<i>P. amorphognathoides</i>	Dayton
0.10	2.36	-4.74	<i>P. amorphognathoides</i>	Dayton
-0.10	0.91	-5.09	<i>D. kentuckyensis</i>	Brassfield
-0.40	0.90	-5.20	<i>D. kentuckyensis</i>	Brassfield
-0.80	0.98	-5.01	<i>D. kentuckyensis</i>	Brassfield

^a Sampling datum is the base of the Dayton Formation. Meterage represents distance above or below the unconformity between the Brassfield and Dayton Formations.

The $\delta^{18}\text{O}$ record of marine carbonates can be more easily reset by meteoric fluids than the comparatively stable $\delta^{13}\text{C}$ record due to the much smaller amount of carbon in ground water than in the limestone it is permeating. Several authors have demonstrated that diagenesis of marine carbonate does not usually result in resetting of $\delta^{13}\text{C}$ values (Magaritz, 1983; Banner and Hanson, 1990). The samples from all three sections show a trend and variability in the $\delta^{18}\text{O}$ record similar to the signal recorded in brachiopods on Gotland (Samtleben et al., 1996; Bickert et al., 1997), consistent with the view that primary carbon isotopic signals have been preserved.

Analyzed powders were micro-drilled from micritic matrix whenever possible but some samples were too coarse grained to guarantee that no skeletal material was sampled (i.e., crinoids and brachiopods). Volatiles were removed by roasting under vacuum at 380 °C and the samples were reacted with 100% phosphoric acid at 75 °C in an online carbonate preparation line connected to a Finnigan Mat 252 mass spectrometer. The analytical precision based upon duplicate analyses and multiple analyses of NBS19 was $\leq 0.04\text{‰}$. Stable isotope samples were analyzed at the University of Michigan.

3.2. Newsom Roadcut, Tennessee

The biostratigraphically best constrained section included in this investigation is a roadcut west of Nashville, Tennessee. Newsom Roadcut was sampled for conodont biostratigraphy by Barrick (1983). Silurian sections from central Tennessee consist of a nearly complete sequence of Lower–Middle Silurian carbonates, with the only appreciable gap occurring in the late Llandovery. This unconformity, equivalent to the top of the Brassfield Formation throughout the mid-continent (Kleffner, 1994, 2000; Shaver, 1996; Manzo, 2002), is the base of the measured section at Newsom Roadcut (Fig. 5). The uppermost Brassfield at this location consists of open marine wackestones and packstones with nodular chert. The lowermost Maddox Member of the Wayne Formation is a red, calcareous, siltstone with sparse carbonate grains. The lower Maddox is predominantly a packstone to crinoid grainstone lithology. The Maddox becomes a mudstone/wackestone immediately above the Ireviken Excursion before becoming predominantly encrinitic at the top.

The conodont *Pterospirifer amorphognathoides* was recovered from the lowermost Maddox in a sample from the first 12 cm above the unconformity. Another diagnostic conodont, *Ozarkodina sagitta rhenana*, was recovered from a sample between 3.20 m and 3.32 m above the base of the Maddox (Barrick, 1983). The conodont *Kockelella walliseri* was also recorded at this level, which allows a very precise correlation between the well known sections of Gotland and Newsom Roadcut. The co-occurrence of these two conodonts is the basis for identification of the Lower *K. walliseri* conodont subzone (sensu Jeppsson, 1997b). Conodont and stable isotope data are shown in Table 1. Carbon isotope values begin to rise immediately above the base of the Maddox and reach two distinct peaks. The first peak is $+3.92\text{‰}$ at 1.37 m above the base of the Maddox and the second is $+3.93\text{‰}$ at 3.62 m above the base with a low of $+2.61\text{‰}$ between the two peaks at 2.37 m. $\delta^{13}\text{C}$ values returned to a stable baseline of approximately $+1\text{‰}$ by 8.12 m above the base of the Maddox.

3.3. IPSCO Core OW-5, Iowa

Outcrops and cores in eastern Iowa representing the northern portions of the Illinois basin contain a

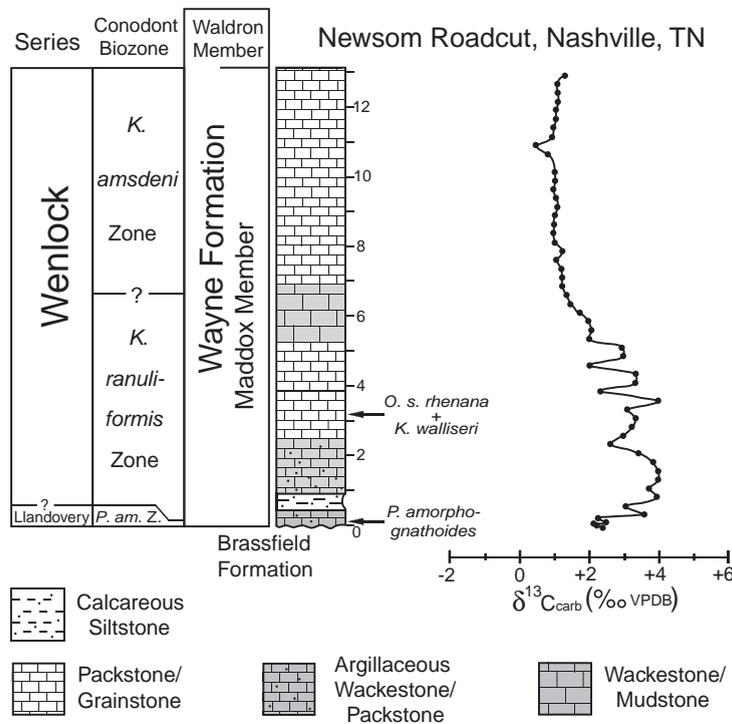


Fig. 5. Carbon isotope data from Newsom Roadcut, Nashville, TN. Conodont biozones from Barrick (1983). Note unconformity at the base of section and the argillaceous interval that marks the onset of the carbon isotope excursion. The unconformity marks both the base of the Maddox Member and the Wayne Formation, but also serves as the baseline from which the carbon isotope sampling was carried out. Numbers to the right of the stratigraphic column represent meters above the sampling datum, in this case, the base of the Wayne Formation.

thick succession of Lower–Middle Silurian carbonates. Biostratigraphy has been primarily based upon brachiopods, and the typically low conodont yields of Silurian dolomites have hindered global correlation of the region’s stratigraphic succession. No conodont biostratigraphy was performed on the core but tentative correlation was accomplished by comparison of the core log (Witzke, unpublished data) with the detailed Iowa stratigraphy presented in Witzke (1981) and Witzke and Bunker (1996).

The sampled section of the IPSCO core includes, in stratigraphic order, the uppermost Hopkinton, Scotch Grove, and Gower Formations (Fig. 6). The uppermost Hopkinton Formation consists of crinoid-moldic dolowackestones and packstones with silicified or moldic stromatoporoids and tabulate corals. The Hopkinton Formation has a sharp upper boundary overlain by the Scotch Grove Formation. The lowermost Scotch Grove includes the John’s Creek Quarry Member, an argillaceous dolomudstone. The silici-

clastic source area for this facies is inferred to be the Transcontinental Arch to the west (Witzke, 1981). The rest of the Scotch Grove Formation in east-central Iowa consists of complex, laterally discontinuous facies. The Welton Member immediately overlies the John’s Creek Quarry (JCQ) Member and consists of finely crystalline, crinoid-rich dolomite. The overlying mixed Welton–Palisades–Kepler Member is a vuggy, porous, crinoidal dolostone. The Gower Formation penetrated by the IPSCO core consists of the LeClaire reef/mound facies.

The conodont *Pterospirifer amorphognathoides* has been recovered from lower and middle Scotch Grove strata (Rexroad and Nicoll, 1971; Witzke, 1981), and the conodont *Ozarkodina sagitta rhenana* has been recovered from the upper Scotch Grove (Witzke, 1981). $\delta^{13}\text{C}$ values are low, $\sim +0.62\text{‰}$, in the upper Hopkinton Formation, and abruptly increase to $+1.81\text{‰}$ in the lowermost Scotch Grove before steadily increasing to a peak of $+4.83\text{‰}$ at 6.62 m

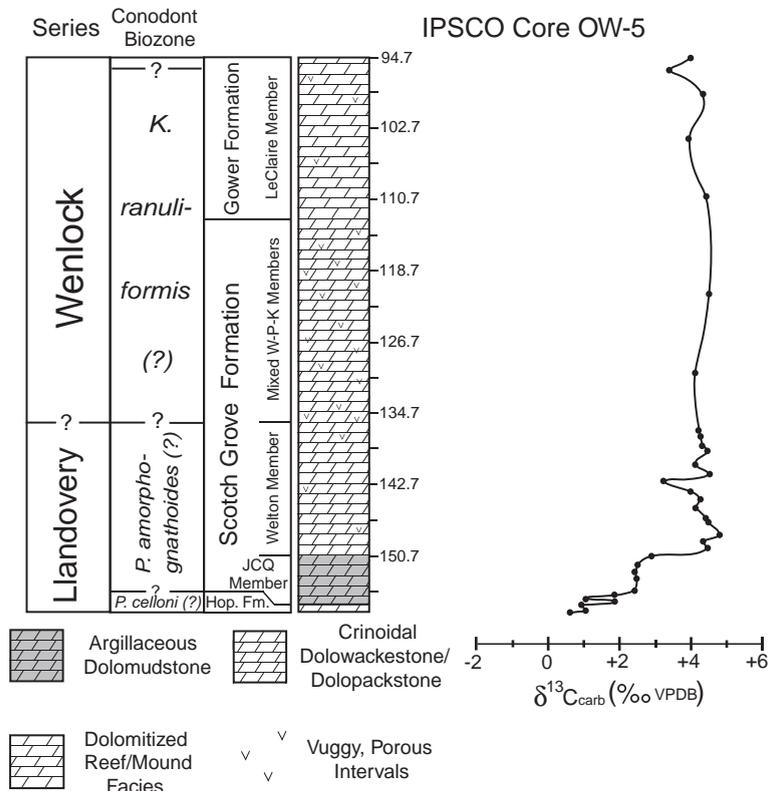


Fig. 6. Carbon isotope data from the IPSCO core OW-5, east-central Iowa. Conodont biozones tentatively placed after (Witzke, 1981; Witzke and Bunker, 1996; Barrick, 1983, 1997; and carbon isotope data presented herein). The question marks in the biostratigraphic column of this figure and Table 2 are used to demonstrate the disagreement between the traditional placement of Iowa stratigraphic units in Silurian time and the isotope data presented herein. In this figure, the Llandoverly–Wenlock boundary is drawn at its traditional placement, in the middle of the Scotch Grove. However, according to the highest resolution correlation available (Mabillard and Aldridge, 1985; Jeppsson, 1997b; Munnecke et al., 2003), the Ireviken Excursion begins just above the Llandoverly–Wenlock boundary Stratotype. Therefore, the proper placement for the L–W boundary should be the base of the Scotch Grove Formation in Iowa. This change has been made to the Iowa stratigraphy in Figs. 8 and 9. Note argillaceous John’s Creek Quarry Member that marks the onset of the carbon isotope excursion. Numbers to the right of the stratigraphic column represent meters down core.

above the base of the Scotch Grove. Values remain heavy throughout the rest of the core with $\delta^{13}\text{C}$ values staying near +4.0‰. The data from the IPSCO OW-5 core are shown in Table 2.

3.4. Piqua Quarry, Ohio

The Piqua Quarry, located in Piqua, Ohio, roughly 25 miles north of Dayton exposes Llandoverly–Wenlock strata. The Dayton Formation, a highly time transgressive unit (Kleffner, 1994), is exposed above the Brassfield Formation in the quarry (Fig. 7). The uppermost Brassfield at Piqua quarry is a dolowackestone to dolograinsstone with green argillaceous

intervals and crinoid debris. Black stained, organic rich rocks of the lowermost Dayton Formation immediately overlie the unconformity at the top of Brassfield. The lowest 4 cm of the Dayton are organic rich, silty dolomudstones to dolowackestones, which continue upsection with decreasing organic staining in the first half meter. The black staining occurs at several stratigraphic intervals of the Dayton Formation in the quarry but not to the degree at the unconformity. The conodont *Pterospathodus amorphognathoides* has been recovered from basal Dayton strata in the Piqua Quarry (Kleffner, unpublished data). Conodont biostratigraphy and carbon isotope data are shown in Table 3.

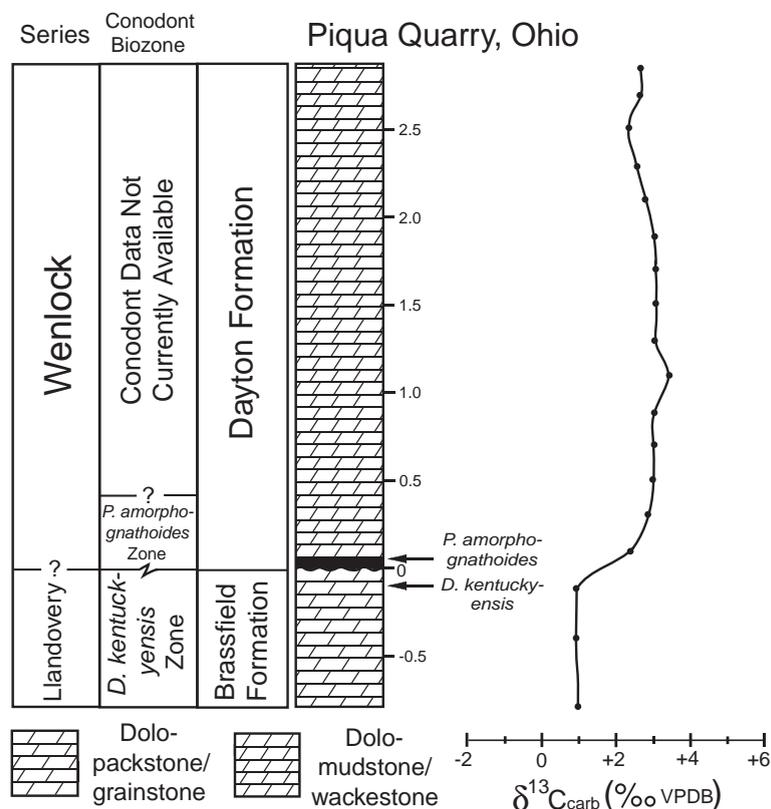


Fig. 7. Carbon isotope data from the Piqua Quarry. Note the significant unconformity at the base of the Dayton Formation. Black coloring denotes organic rich interval at the base of the Dayton. Conodont data from Kleffner, personal communication (2004). Numbers to the right of the stratigraphic column represent meters above or below the sampling datum, in this case, the base of the Dayton Formation.

The $\delta^{13}\text{C}$ signal shifts to heavier values across the Brassfield–Dayton contact (a gap of more than one conodont biozone), with values around $+0.90\text{‰}$ in the uppermost Brassfield increasing to a value of $+2.36\text{‰}$ in the lowest Dayton. Carbon isotope values peak at $+3.42\text{‰}$, 1.10 m above the base of the Dayton. Values remain high $\sim +2.80\text{‰}$ throughout the rest of the exposed Dayton strata.

4. Discussion

The early Wenlockian (Ireviken) $\delta^{13}\text{C}$ Excursion shows a consistent relationship to lithologic changes in the U.S. mid-continent and elsewhere in the world. The $\delta^{13}\text{C}$ shift follows a major unconformity and is subsequently recorded in a coarsening-upward, clean carbonate succession. We first address the timing and

significance of these lithologic correlations for current models of Silurian paleoceanography and carbon cycling. We then propose a new interpretation of the Ireviken Excursion that couples enhanced organic carbon burial in the deep oceans to a change in the site of deep-water formation.

4.1. Timing of Ireviken Excursion and eustatic changes across the mid-continent, U.S.A.

The Llandovery–Wenlock (L–W) boundary throughout much of the mid-continent of North America is missing due to erosion or non-deposition. The significant unconformity marking the top of the Brassfield Formation in both the Newsom Roadcut (NW) and Piqua Quarry (PQ) sections likely spans the Llandovery–Wenlock boundary based on conodont biostratigraphy and the carbon isotope data presented

herein. The $\delta^{13}\text{C}$ shift to heavier values that marks the Ireviken Excursion occurs immediately above this unconformity, consistent with an earliest Wenlock (Sheinwoodian) age for the overlying strata (Mabillard and Aldridge, 1985; Jeppsson, 1997b; Munnecke et al., 2003; Calner et al., 2004). The Hopkinton–Scotch Grove contact in Iowa (IP) is also coincident with a lowstand (T-R cycle four of Witzke and Bunker, 1996) and is immediately followed by the increasing $\delta^{13}\text{C}$ values characteristic of the earliest Wenlock (Fig. 8).

According to the sequence stratigraphic interpretation of Barrick (1997), the L–W boundary was coincident with a lowstand marking the onset of a single Sheinwoodian T-R cycle (Fig. 9). The silty argillaceous interval that marks the onset of transgression in all three studied sections reflects the proximity of a siliciclastic source area that suppressed carbonate production. As clastics and nutrients were stranded farther inshore during transgression, a healthy carbonate factory was established across the mid-continent during the early Sheinwoodian (Witzke, 1981; Barrick, 1983), which records the Ireviken Excursion.

The unconformity near the Llandovery–Wenlock boundary signals a major climatic shift at the end of the Late Ordovician–Early Silurian icehouse period (Frakes et al., 1992). The Ordovician glacial epoch, which may have begun as early as the Caradoc (e.g., Pope and Steffen, 2003) continued into the late Llandovery (Grahn and Caputo, 1992; Caputo, 1998; Diaz-Martinez, 1998). Several authors have suggested that the Ireviken Excursion was the result of an early Wenlock glaciation that enhanced upwelling of nutrient rich deep waters and stimulated primary production (Wenzel and Joachimski, 1996; Kaljo et al., 1997, 2003). However, recent work on South American glaciogenic sediments indicates that glaciation was mostly limited to the Llandovery. For example, in Bolivia, a thin carbonate unit (Sacta Member) immediately overlies the Cancañiri diamictite and contains the conodont *Ozarkodina sagitta rhenana* (Diaz-Martinez, 1997, 1998). This cosmopolitan conodont species occurs exclusively during the Ireviken Excursion in Gotland (Jeppsson, 1997b; personal communication, Jeppsson, 2004) indicating that the glaciation had ended prior to the Ireviken Excursion. This conclusion is consistent with the early

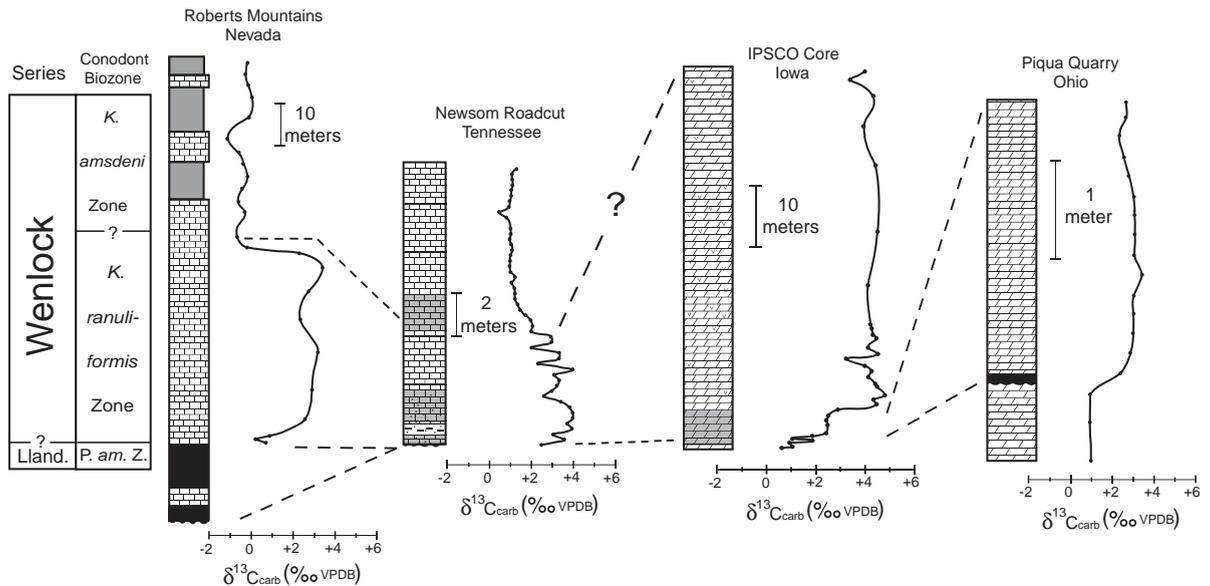


Fig. 8. Correlation of the measured sections using the Roberts Mountains section of Saltzman (2001) for reference. Dashed lines indicate approximately equivalent time slices. The convergence of the two lines coming from the base of the Roberts Mountains data indicates an interval of time not recorded in the other sections. The lowest dashed line represents the unconformity recorded in all three sections. Note that the Piqua Quarry section appears to only have recorded the initial onset of the Ireviken Excursion.

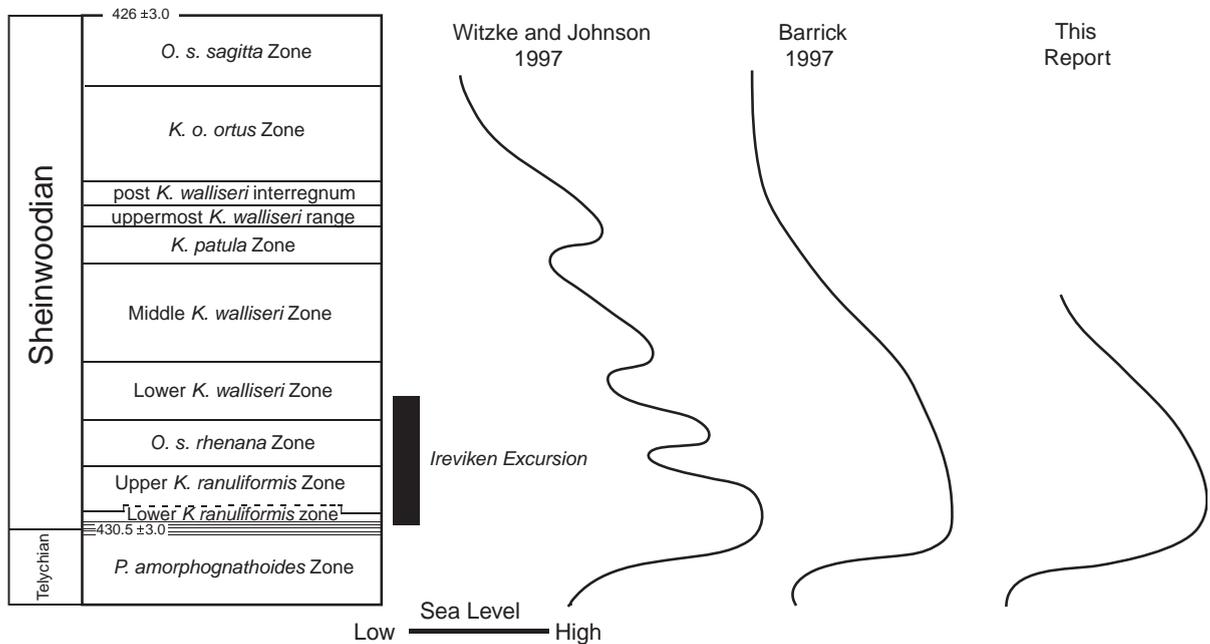


Fig. 9. Eustatic interpretations for the Lower Silurian (from Witzke and Johnson, 1997; Barrick, 1997, and the present investigation). See text for explanation of placement of the Llandovery–Wenlock boundary in Iowa. Standard conodont zonation from Jeppsson (1997b). Radiometric dates originally from Odin et al. (1986).

Wenlock transgression and positive $\delta^{13}\text{C}$ excursion throughout the mid-continent of North America documented in this study.

The timing of glaciation and sea level change with respect to lithologic and $\delta^{13}\text{C}$ shifts is also consistent with Jeppsson's (1990) oceanic states that alternated during the Silurian, referred to as Primo and Secundo (P and S) episodes. Primo (P) episodes often experienced glaciation and correspond with cold high latitudes and humid low latitudes, while climatic optima during Secundo (S) episodes correspond with warmer high latitudes and arid low latitudes. The increased moisture and erosion experienced at low latitudes during P episodes, coupled with vigorous thermohaline circulation, enhances nutrient delivery to the low-latitude shallow shelf. The high nutrient flux at low sea level would inhibit shelf carbonate production by favoring bioeroders over bioproducers (e.g., Hallock, 1988, 2001; Peterhänsel and Pratt, 2001; Mutti and Hallock, 2003; Halfar et al., 2004). In contrast, carbonate production is favored during S episodes because shelf environments are characterized by downwelling as deep water production shifts to these low/mid-latitude regions of high salinity. Fur-

thermore, the increased aridity that the low latitudes experience during S episodes also reduces terrestrial runoff and nutrient availability contributing to an overall expansion of the carbonate platform environment. Despite the evidence of lower rates of net primary production on the shelves during the Ireviken Excursion S episode, $\delta^{13}\text{C}$ values increased, particularly in shelves characterized by anti-estuarine circulation (Bickert et al., 1997). This suggests that oceanographic changes associated with deglaciation and a longer-term shift to greenhouse conditions may have produced a deep ocean that sequestered ^{12}C .

4.2. Organic carbon burial during the Ireviken Excursion

The prolific reef development (Brunton et al., 1998) during the Ireviken Excursion indicates that shallow epicontinental platforms were not the location of organic rich deposition during the early Wenlock. In addition to the mid-continent sections examined here, transitions from argillaceous to relatively pure calcareous sediments at or near the Llandovery–Wenlock boundary are known from sections globally

(Jeppsson, 1987; Jeppsson et al., 1995) and some well-known examples include: Upper and Lower Visby Formations to the Höglint Formation (Gotland, Hede, 1921; Samtleben et al., 1996); Adavere shales to the Jaani marls (Estonia, Kaljo et al., 1997); Hughley shales to the Woolhope and Buildwas Formations (Midland Platform, U.K., Woodcock, 2000); Prices Falls Shale to the Fitzhugh Member of the Clarita Formation (Oklahoma, U.S., Barrick and Klapper, 1976); basal cherts to clean carbonates of the Roberts Mountain Formation (Nevada, U.S., Murphy et al., 1979).

A shelf to basin transect has been reconstructed for several intervals of the Silurian in the Baltic region and shows that intervals of clean limestone deposition on the shelf correlate with organic rich deposits in deeper water sections (Jeppsson and Calner, 2003; Kiipli et al., 2004). This pattern is consistent with halothermal circulation driven by sinking of warm, low latitude waters during climatic optima (S episodes) providing less oxygen to the deep ocean (Arthur et al., 1987; Jeppsson, 1990; Herbert and Sarmiento, 1991). Therefore, it is likely that organic burial during Silurian carbon isotope excursions (S episodes; Bickert et al., 1997) took place in the deep ocean, not on the shallow shelf.

4.3. Anoxia and deep circulation

A latitudinal change in the formation site of deep water during the early Wenlock could quickly promote deep ocean anoxia (Herbert and Sarmiento, 1991). This is because the oxygen content of the deep ocean is related to the oxygen demand of surface waters at the site of deep water formation. The increased efficiency of nutrient use in shallow water at low latitudes versus high latitudes would have a tendency to induce anoxia in the deep ocean via the equation

$$O_{2d} = O_{2s} - 169(PO_{4d} - PO_{4sf}) \quad (1)$$

where O_{2d} and O_{2s} are the oxygen content of deep and shallow water, respectively, 169 represents a Redfield ratio modified to account for the opposing effects of anoxia on carbon and phosphorous burial, PO_{4d} is the total content of phosphate in the ocean at any given time, and PO_{4sf} is the phosphate content of surface waters at the site of deep water formation (modified from Herbert and Sarmiento, 1991).

In the modern ocean, the $\delta^{13}C$ gradient between shallow and deep waters is maintained by a balance between the downward transport of biological material enriched in ^{12}C (the biological pump) with upwelling of nutrients and light carbon (e.g., Hotinski et al., 2004). As more organic matter is buried in the deep ocean, less ^{12}C and less nutrients are returned to low/mid-latitude shallow waters. If organic carbon burial in the anoxic deep oceans is responsible for the one–two million-year long Ireviken Excursion, why does the decrease in nutrient delivery to low-latitude shallow water (and consequent decrease in primary productivity) not counteract the initial increase in $\delta^{13}C_{carb}$?

Two factors have been proposed to resolve this issue. The first is the effect of anoxia on phosphorus burial. Under anoxic conditions, the ratio of carbon to phosphorus being buried (C/P ratio) increases, allowing nutrients to return to the ocean while carbon is removed (e.g., VanCappellen and Ingall, 1996; Lenton

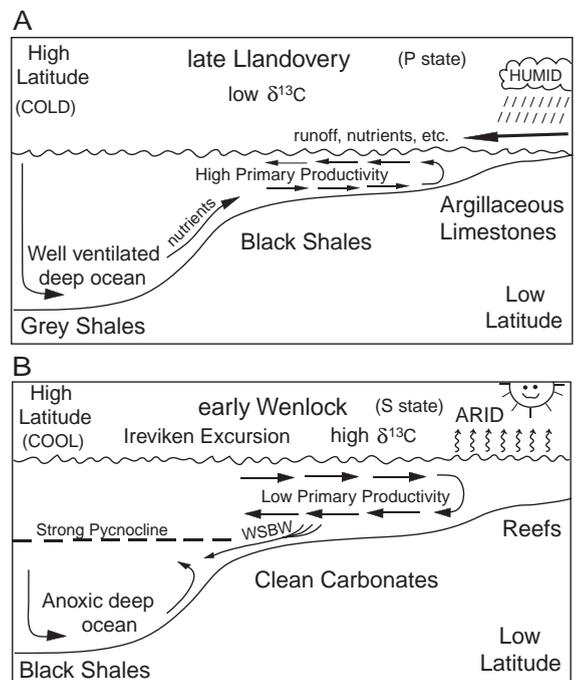


Fig. 10. Paleooceanographic reconstruction for the late Llandovery (A) and the early Wenlock (B). Diagrams modified from Jeppsson (1990) and Bickert et al. (1997). Black shales in panel A are the result of local anoxia from high rates of primary production on the shelf. Black shales in panel B are the result of deep ocean anoxia from a change in the site of deep water formation to low latitudes; warm saline bottom water (WSBW).

and Watson, 2000). However, the evidence from clean carbonate deposition in low-latitude shelf environments is inconsistent with the continued delivery of high phosphorus levels to surface waters that could have sustained high productivity during the Ireviken Excursion. Therefore, we suggest that even though marine primary productivity was considerably reduced at low-latitudes, increased organic carbon preservation in the anoxic deep oceans (e.g., Bralower and Thierstein, 1984) produced the Ireviken Excursion.

Bralower and Thierstein (1984) calculated this “organic carbon preservation factor” during Cretaceous anoxic events as the rate of marine primary production divided by the organic carbon accumulation rate. Their data indicate that organic rich, low-latitude, deep-water, mid-Cretaceous deposits were associated with low primary productivity and low deep water renewal rates. The Ireviken Excursion may represent a similar linkage among low-latitude driven halothermal circulation (warm saline bottom water; Arthur et al., 1987), low primary productivity, and increased organic carbon burial in the anoxic deep oceans (Fig. 10). The reduced nutrient delivery does indeed decrease primary productivity in low-latitude shallow waters, but in the global ocean, the ratio of organic carbon buried to the rate of primary production (organic carbon preservation factor) increases, hence increasing $\delta^{13}\text{C}_{\text{carb}}$.

The increased burial of organic carbon in deep water provides a natural mechanism to end the Ireviken Excursion as well. Since the enhanced burial of organic matter in this instance appears to be related to global warming and a change in the site of deep water formation, the drawdown of CO_2 and thereby global temperatures associated with increased organic carbon burial would eventually act to restore the latitudinal temperature gradient responsible for polar downwelling and thermohaline circulation. Once deep water formation moved back to high-latitudes, deep ocean anoxia would have subsided, ending the enhanced organic carbon burial and the Ireviken Excursion.

5. Conclusions

The high-resolution $\delta^{13}\text{C}_{\text{carb}}$ data presented herein are a useful tool for stratigraphic correlation and provide insight into the nature of the Llandovery–Wenlock interval throughout the mid-continent of

North America. A significant unconformity occurs at or just below the L–W boundary in Ohio and Tennessee, and a hiatus of uncertain length occurred in Iowa at approximately the same time. This eustatic lowstand correlates well with recent interpretations of evidence for early Silurian (latest Llandovery) glaciation in South America. The Ireviken Excursion is recorded in all three sections, and its base is coincident with transgression indicating that the onset of the positive change in $\delta^{13}\text{C}_{\text{carb}}$ was related to deglaciation.

The associated post-glacial increase in global temperatures during an icehouse–greenhouse transition altered ocean circulation and moved the site of deep water formation to low latitudes. This change in oceanography promoted deep water anoxia and decreased nutrient delivery to low-latitude shallow waters allowing a healthy carbonate factory to develop throughout the mid-continent. Although low-latitude primary productivity was reduced, the increased organic carbon preservation factor (a result of deep anoxia) drove the positive $\delta^{13}\text{C}_{\text{carb}}$ excursion. Eventually, the drawdown of global temperatures and CO_2 associated with enhanced organic carbon burial acted to re-establish thermohaline circulation, ending deep ocean anoxia and the Ireviken Excursion.

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