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

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#### **Abstract**

Paired  $\delta^{13}C_{carb}$  and  $\delta^{13}C_{org}$  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  $pCO_2$  during the well-known Ireviken (early Wenlock) positive carbon isotope ( $\delta^{13}C_{carb}$ ) excursion. Our investigation provides the first detailed  $\delta^{13}C_{org}$  stratigraphy through this interval and documents a negative excursion in  $\delta^{13}C_{org}$  associated with the positive  $\delta^{13}C_{carb}$  excursion. This is consistent with the notion that the Ireviken positive  $\delta^{13}C_{carb}$  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  $pCO_2$  remains tenuous until it can be shown that the  $\delta^{13}C_{org}$  trends shown herein can be reproduced globally.

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#### 1. Introduction

Variations in atmospheric *p*CO<sub>2</sub> 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<sub>2</sub>-driven global climate models. However, the CO<sub>2</sub>-driven models remain

Positive  $\delta^{13}C_{carb}$  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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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  $pCO_2$  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  $pCO_2$ .

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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  $pCO_2$  proxies). This data can be used as a paleo- $pCO_2$  barometer because the isotopic difference between carbonate and organic matter is dominated by photosynthetic fractionation ( $\varepsilon_p$ ), 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  $\delta^{13}C_{carb}$  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  $\delta^{13}C_{carb}$  excursions (e.g. Joachimski and Buggisch, 1993; Brand et al., 2004). Positive  $\delta^{13}C_{carb}$  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; Munnecke 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  $\delta^{13}C_{carb}$  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 pCO<sub>2</sub> during the onset of the early Sheinwoodian (Ireviken)  $\delta^{13}C_{carb}$  excursion, revealing a complex relationship between atmospheric pCO<sub>2</sub> 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	$\delta^{13}C_{carb}$	Carbon 3pt.	Standard deviation	$\delta^{13}C_{\rm org}$	Organic 3pt.	Standard deviation	$\Delta$	$\Delta$ 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.

<sup>&</sup>lt;sup>a</sup> Base of section is the unconformity making the base of the Wayne (top of the Brassfield).

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