

A weathering hypothesis for glaciation at high atmospheric $p\text{CO}_2$ during the Late Ordovician

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Abstract

New paired carbonate and organic-carbon isotope analyses from Nevada, USA, together with a consideration of the effects of mountain-building and ice-sheet coverage of the continents on atmospheric $p\text{CO}_2$, lead to a new hypothesis for the cause of the Late Ordovician glaciation. We suggest that the Taconic orogeny, which commenced in the late-middle Ordovician, caused a long-term decline in atmospheric $p\text{CO}_2$ through increased weatherability of silicate rocks. Ice-sheet growth was triggered when $p\text{CO}_2$ decreased to a threshold of $\sim 10\times$ present atmospheric level and proceeded by positive ice-albedo feedback. In the midst of glaciation, atmospheric $p\text{CO}_2$ began to rise as continental silicate weathering rates declined in response to coverage of weathering terrains by ice sheets. At first, this enhanced greenhouse effect was overcompensated for by ice-albedo effects. Ultimately, however, atmospheric $p\text{CO}_2$ reached a level which overwhelmed the cooling effects of ice albedo, and the glaciation ended. The isotope results can be interpreted to indicate that atmospheric $p\text{CO}_2$ rose during the glaciation, consistent with other proxy information, although alternative interpretations are possible. The large, positive carbonate isotope excursion observed in Late Ordovician rocks around the world is explained as the expected response to increased carbonate-platform weathering during glacioeustatic sea-level lowstand, rather than as a response to increased organic-carbon burial. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The glaciation of the Gondwana supercontinent 440 million years ago (e.g., Hambrey, 1985) has proven paradoxical (Crowley and Baum, 1991, 1995; Kasting, 1992). Carbon isotopic proxies in goethites

(Yapp and Poths, 1992) and carbon-cycle modeling results (Berner, 1994) indicate that atmospheric $p\text{CO}_2$ was as high as $10\text{--}16\times$ PAL (Present Atmospheric Level) at the time of glaciation. The resultant strong greenhouse effect would seem to be inconsistent with glaciation. However, a positive carbon isotopic excursion of as much as 5–7‰ has been identified in Hirnantian (latest Ordovician) limestones at a number of sites around the world (Marshall and Middleton, 1990; Middleton et al., 1991; Long, 1993; Brenchley et al., 1994; Qing and Veizer, 1994;

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Kump et al., 1995; Marshall et al., 1997). The excursion appears to be coincident (within the resolution of the data) with a 2–3‰ positive oxygen isotopic excursion, interpreted to represent the development of a large, continental ice sheet (Brenchley et al., 1994). Moreover, an organic-carbon isotopic excursion of similar to somewhat smaller magnitude than the inorganic-carbon excursion has been noted in Hirnantian shales (Marshall et al., 1997; Wang et al., 1997; Underwood et al., 1997; cf. Goodfellow et al., 1992). If the isotopic data bracket the interval of glaciation, the glaciation was intense, but short-lived, being confined to the early Hirnantian (latest stage of the Ordovician) and thus probably lasting no more than 500 k.y. to 1 m.y. (Brenchley et al., 1994).

Brenchley et al. (1994, 1995) proposed that the Hirnantian carbon isotope excursion represented a large increase in marine productivity and burial of organic carbon, initiated by an invigoration of the thermohaline circulation of the ocean. According to their model, the burial of organic carbon caused a large removal of carbon from the ocean–atmosphere system, promoting a drawdown in atmospheric $p\text{CO}_2$, and a climatic cooling leading to glaciation. They suggested that the return to a ‘greenhouse’ state was driven by a reduction in nutrient levels and productivity in the ocean. A facies analysis of the Dob’s Lin, Scotland, boundary stratotype by Armstrong and Coe (1997) was interpreted in terms of a similar mechanism of intensified thermohaline circulation, glaciation, and rapid deglaciation with the resumption of more sluggish deep-water circulation.

Although we have championed the Brenchley et al. model in the past (Kump et al., 1995), a new consideration of the likely effects of orogeny, glaciation, and sea-level fall on the global carbon cycle leads to an alternative explanation of the cause of the carbon isotope excursion and a new interpretation of the $p\text{CO}_2$ history of the Late Ordovician. We suggest that the positive carbon isotopic excursion was a consequence of an increase in limestone weathering rates during the glacioeustatic sea-level fall that exposed the expansive Ordovician carbonate platforms, rather than an organic-carbon burial event. The initiation and termination of the glaciation, on the other hand, were linked to changes in atmospheric $p\text{CO}_2$ driven by oscillations in the global rate of silicate weathering. These oscillations

were the consequence of two competing factors: mountain-building, which tended to promote silicate weathering (CO_2 consumption) throughout the Late Ordovician and Silurian, and ice-sheet coverage of silicate terrains, which tended to diminish silicate weathering (and CO_2 consumption) at the height of Hirnantian glaciation. According to this *weathering hypothesis*, atmospheric $p\text{CO}_2$ fell prior to and during the initial phases of ice-sheet growth, but then rose during glacial maximum times because of reduced weathering. Eventually, the greenhouse effect of CO_2 overcame the cooling albedo effect of glacial ice, and the glaciation ended.

Here we present both new isotopic data from an Upper Ordovician section from Nevada, USA, and numerical modeling results to provide a framework for interpreting the data. The isotopic results illustrate the clearest signal yet obtained of the marine carbon isotopic excursion, and the first paired analyses of both inorganic and organic carbon for this time interval. These data are consistent with the weathering hypothesis, but further tests are clearly needed.

2. The Late Ordovician isotope record

2.1. The Copenhagen Canyon section

To establish a high-resolution carbon isotopic record for the Hirnantian, we analyzed the isotopic composition of samples of marine carbonates (micrite) and associated organic matter from a thick, well-studied section in Copenhagen Canyon, Nevada, USA, that contains the Ordovician–Silurian boundary (Fig. 1A; Mullens and Poole, 1972; Dunham, 1977; Murphy et al., 1979; Dunham and Olson, 1980; Hurst and Sheehan, 1985; Hurst et al., 1985; Carpenter et al., 1986; Murphy, 1989; Sheehan, 1989; Sheehan and Boucot, 1991; Finney et al., 1995; Harris and Sheehan, 1996). The section is located distally on a westward-dipping carbonate ramp leading from a shallow carbonate platform on the east to a deep basin on the west (Carpenter et al., 1986). Changing lithofacies from 30 to 78 m up from the base of our measured section (Fig. 1A) suggest a shallowing of depositional environments. At 35 m, thinly bedded carbonate mudstones grade

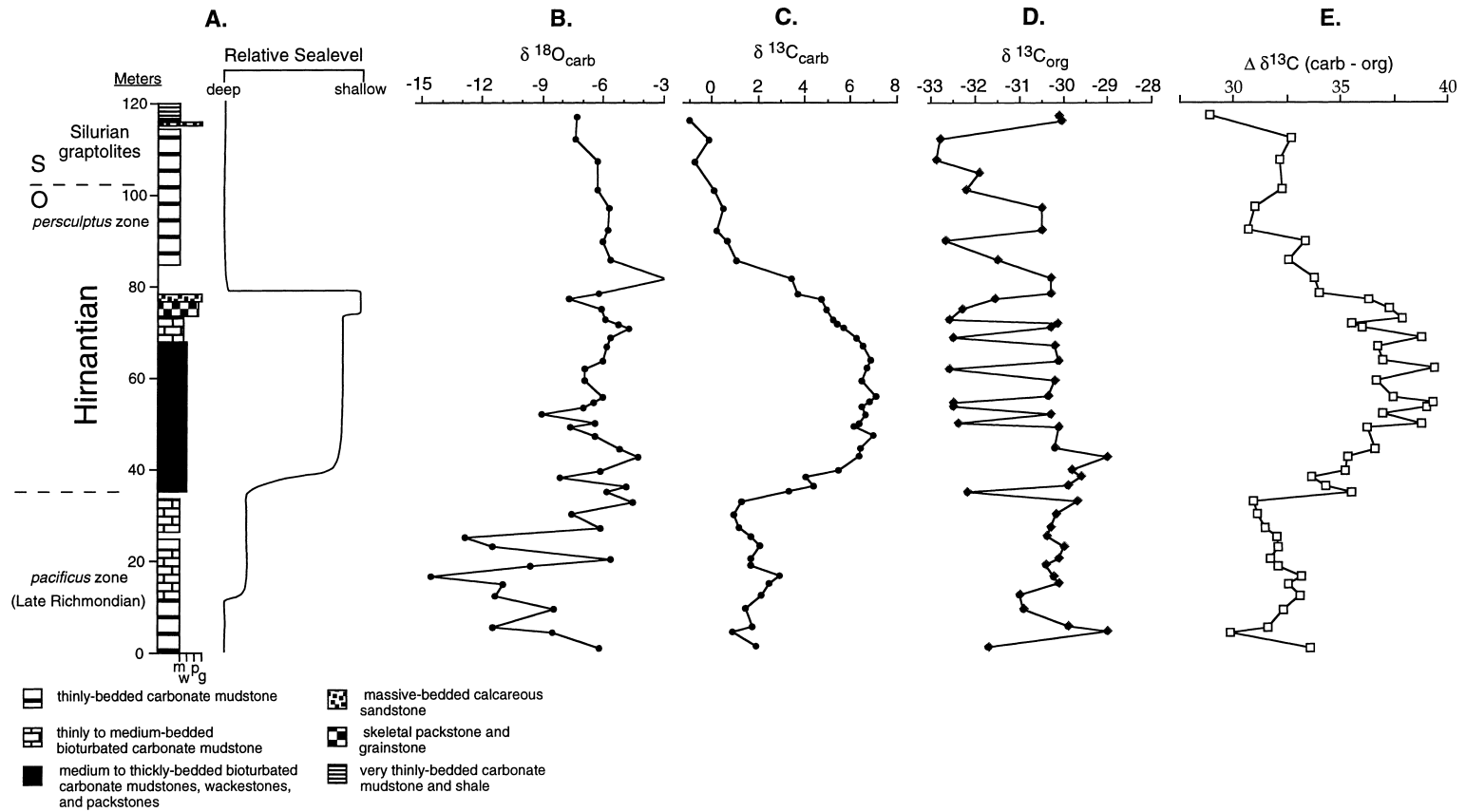


Fig. 1. Stratigraphic and stable isotopic data from Copenhagen Canyon, Nevada. (A) Stratigraphic section within the Hanson Creek Formation (COP M-I; Dunham and Olson, 1980) in Copenhagen Canyon, Nevada (*m* = mudstone; *w* = wackestone; *p* = packstone; *g* = grainstone/sandstone). (B) Whole-rock $\delta^{18}\text{O}_{\text{carb}}$ of limestone samples; results expressed as per mil relative to PDB (VPDB). (C) Whole-rock $\delta^{13}\text{C}_{\text{carb}}$ of inorganic carbon from limestones samples, expressed as per mil relative to PDB (VPDB). (D) $\delta^{13}\text{C}_{\text{org}}$ of organic matter from limestones, after complete removal of carbonate. (E) The isotopic difference between the $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$, of individual samples, expressed as $\Delta^{13}\text{C}$ in per mil units.

Table 1
Copenhagen Canyon section data

Depth (m)	Other	$\delta^{13}\text{C}$ (‰, VPDB)	$\delta^{18}\text{O}$ (‰, VPDB)	% CaCO_3	% TOC	$\delta^{13}\text{C}_{\text{org}}$ (‰, VPDB)	Replicate $\delta^{13}\text{C}_{\text{org}}$
0.1		1.89	−6.19	89.36	0.73	−31.74	
4.2		0.88	−8.53			−29.03	
5.4		1.73	−11.54	47.38	0.56	−29.89	
9.3		1.43	−8.48	93.62	0.56	−30.88	
12.2		2.12	−11.41			−30.95	
14.8		2.47	−10.98			−30.07	
16.4		2.93	−14.58	98.64	0.70	−30.24	
18.8		1.67	−9.66			−30.40	
20.2		1.65	−5.61	99.46	0.30	−30.12	
22.9		2.08	−11.51	98.14	0.26	−30.04	−29.89
25.0		1.68	−12.89			−30.38	
27.0		1.19	−6.16	99.83	0.32	−30.29	
29.9		0.96	−7.60	99.01	0.22	−30.18	−30.33
32.7	A	1.25	−4.56	86.08	0.67	−29.68	−29.45
34.8		3.32	−5.83			−32.19	
36.1	C	4.41	−4.89	94.64	0.77	−29.85	
38.1	A	4.07	−8.15	90.71	0.37	−29.62	
38.1	B					−31.97	
39.5	A	5.45	−6.15	96.00	0.26	−29.76	
42.5		6.37	−4.26	95.44	0.59	−28.98	−28.76
44.3		6.41	−5.16			−30.17	
47.1		7.02	−6.41				
49.0		6.14	−7.65	99.86	0.00	−30.06	
49.8		6.39	−6.39	97.27	0.42	−32.42	−32.29
51.8		6.68	−9.08			−30.30	
53.4		6.49	−6.99	96.72	0.47	−32.48	−32.25
54.4		6.81	−6.48	99.72	0.14	−32.46	
55.6		7.10	−6.00	93.34	0.95	−30.34	
59.2		6.49	−6.92	99.10	0.15	−30.19	
61.8		6.74	−6.91	99.17	0.44	−32.62	
63.5		6.87	−6.04	101.53	0.02	−30.05	−30.10
66.7		6.53	−5.81	100.48	0.56	−30.16	
68.6		6.29	−5.63	98.54	0.54	−32.51	
70.7		5.71	−4.71	100.55	0.62	−30.34	
71.5		5.39	−5.27			−30.15	
72.6		5.24	−5.90	98.42	0.53	−32.58	
74.8		4.98	−6.11	99.96	0.68	−32.27	
77.0		4.72	−7.70			−31.57	
78.2	B	3.73	−6.21	101.14	0.15	−30.26	
81.5		3.45	−2.91	98.70	0.60	−30.29	
85.6		1.05	−5.67	100.63	0.25	−31.50	
89.7		0.65	−6.05			−32.71	
92.1	B	0.21	−5.76			−30.49	−30.60
92.8	B					−30.60	
97.0	A	0.49	−5.68	101.83	0.23	−30.50	
100.9		0.08	−6.29	100.78	0.36	−32.20	
104.6						−31.91	
107.3		−0.77	−6.31			−32.85	−32.85
112.0	B	−0.13	−7.38			−32.77	−32.62
116.0						−30.06	
117.0		−1.16	−7.31			−30.06	

into medium to thickly bedded bioturbated skeletal wackestones and packstones. At 78 m skeletal packstones and grainstones are overlain by calcareous sandstones with planar or low-angle cross-lamination. Abrupt deepening above this level is marked by a return to thinly bedded carbonate mudstones. The shallowing and abrupt deepening has been attributed to eustatic fluctuations in sea level due to the growth and demise of an Ordovician (Hirnantian) ice sheet (Mullens and Poole, 1972; Murphy et al., 1979; Dunham and Olson, 1980; Hurst and Sheehan, 1985; Hurst et al., 1985; Berry, 1986; Carpenter et al., 1986; Murphy, 1989; Finney et al., 1995). The lower 20 m of section has yielded a late Richmondian age fauna (conodont Zone 12 and graptolite Zone 15; *pacificus* zone) (Finney et al., 1995). The interval between 35 and 78 m lacks a biostratigraphically diagnostic fauna, but this interval in adjacent areas (Mountain Boy Range) contains Zone 13 conodonts (Ross et al., 1979). Just above the sandstone at 78 m the carbonate mudstones (Martin Ridge beds) have yielded graptolites characteristic of the *persculptus* zone. Graptolites characteristic of Zone 18 (early Llandovery) occur at the top of the Martin Ridge beds at approximately 115 m (Finney et al., 1995). Thus the Ordovician–Silurian boundary must occur within the Martin Ridge beds.

2.2. Analytical methods

2.2.1. Sample screening

Samples were collected from outcrop and cut on a diamond saw to reveal a smooth, unweathered face. Only micrites were analyzed in our study because megascopic calcareous organisms were rare in our samples. Fortunately, this section escaped the pervasive secondary dolomitization that occurred at other nearby sections (Dunham and Olson, 1980). Micritic carbonate was recovered from cut surfaces by micro-drilling. Care was taken to avoid veins and vug-filling cements. Total carbon (TC) was determined on most samples by combustion using a Coulometrics Coulometer System 140. Organic carbon (OC) was determined on subsamples that were acidified with 2 N HCl (Engleman et al., 1985). Precision of the coulometric technique is better than 2% for both TC and OC. Inorganic carbon (IC) was determined by difference between TC and OC. Percent carbonate,

as CaCO_3 , was calculated by dividing percent IC by 0.12, the fraction of carbon in CaCO_3 .

2.2.2. Stable isotope analysis

Micrite samples were ground to a uniform powder and reacted in a common acid bath ('Fairbanks device') at 90°C on-line and introduced into a Finnigan MAT 252 isotope-ratio mass spectrometer. Isotopic ratios were corrected for ^{17}O contribution (Craig, 1957) and are reported in per mil (‰) relative to the VPDB standard. Fractionation factors used to calculate the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of carbonate are 0.98793 and 1.0052, respectively. Precision is better than 0.10‰ for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values and was monitored through multiple analyses of NBS-19 and other powdered calcite standards.

Powdered samples for carbon-isotope determinations on organic carbon were oven dried at 40°C and reacted with an excess of 0.5 N HCl for 24 h to dissolve carbonate minerals. The washed and filtered residue from each sample was combusted in sealed, evacuated quartz tubes containing reduced silver and cupric oxide in a furnace at 1000°C for 1 h. The resulting CO_2 was dehydrated and purified in a high-vacuum, glass gas-transfer system. All isotope ratios for CO_2 were determined using a dual inlet Finnigan MAT 252 isotope-ratio mass spectrometer. Results are reported in the standard per mil (‰) δ -notation relative to the VPDB standard:

$$\delta^{13}\text{C} = [(R_{\text{sample}}/R_{\text{VPDB}}) - 1] \times 10^3$$

where R is the ratio ($^{13}\text{C}:^{12}\text{C}$). Analytical precision of these analyses is $\pm 0.2\text{‰}$.

Analytical results are presented in Table 1 and in Fig. 1.

2.3. Results

2.3.1. Oxygen isotopes

There does not appear to be any distinguishable temporal trend in oxygen isotopic composition of the micrites ($\delta^{18}\text{O}_{\text{carb}}$; Fig. 1B). The $\delta^{18}\text{O}_{\text{carb}}$ of micrites is more susceptible to diagenetic overprinting than are the brachiopods available for analysis elsewhere (Brenchley et al., 1994), so this result is not surprising. It is most likely that the oxygen isotope composition of the lower part of the sequence (below the carbon isotope excursion) has been altered to more

negative values, whereas the oxygen isotopic values of Hirnantian limestones at Copenhagen Canyon are within the range reported for brachiopods and marine cements for that interval by other workers (–3 to –8‰ PDB; e.g., Veizer et al., 1997). Nonetheless, we are hesitant to interpret these oxygen isotopic values in terms of primary processes.

2.3.2. Inorganic-carbon isotopes

On the other hand, the excursion in $\delta^{13}\text{C}_{\text{carb}}$ is well defined (Fig. 1C), beginning about 30 m above the base of the section, where sedimentological and faunal indicators suggest shallowing (Fig. 1A), and extending vertically over 50 m. The overall positive excursion in $\delta^{13}\text{C}_{\text{carb}}$ is between 6 and 7‰. After the positive excursion, $\delta^{13}\text{C}_{\text{carb}}$ falls to a value somewhat more less positive than the pre-excursion value (~ 0 ‰). By comparison to Brenchley et al. (1994), we assume that the $\delta^{13}\text{C}_{\text{carb}}$ excursion marks the interval of Hirnantian glaciation.

2.3.3. Organic-carbon isotopes

The $\delta^{13}\text{C}_{\text{org}}$ (Fig. 1D) record is much more variable. We do not observe an excursion that parallels the excursion in $\delta^{13}\text{C}_{\text{carb}}$, although there is an overall positive shift of around 3‰ that precedes the excursion in the carbonates. $\delta^{13}\text{C}_{\text{org}}$ then rises irregularly from –32‰ at the base of the section to –29‰ at 42 m. This part of the record has virtually the same range of isotopic values as that in the Underwood et al. (1997) paper (from –31.5 to –28‰; actually only one point more positive than –29‰). Thereafter, $\delta^{13}\text{C}_{\text{org}}$ decreases and fluctuates back and forth between –30‰ and –33‰. Although the other studies do not exhibit the variability in $\delta^{13}\text{C}_{\text{org}}$ we see here, we suggest that the very condensed sequences studied by previous workers do not allow them to resolve the true variability or trends for that time period. They could easily be missing some parts of the record, in particular the fluctuating part we observe here, even though the biostratigraphy suggests that all zones are present.

2.3.4. Carbonate–organic-carbon isotopic differences

One reason to simultaneously measure both $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{13}\text{C}_{\text{carb}}$ is to determine their difference ($\Delta^{13}\text{C}$), which may serve as an atmospheric $p\text{CO}_2$

proxy (see below). Because we have determined the $\Delta^{13}\text{C}$ record by difference, it is subject to the same variability observed in $\delta^{13}\text{C}_{\text{org}}$. Nevertheless, a fairly clear pattern emerges. $\Delta^{13}\text{C}$ decreases (in absolute magnitude) irregularly in the lower part of the section (Fig. 1E) as $\delta^{13}\text{C}_{\text{org}}$ undergoes a 2–3‰ trend toward more ^{13}C -enriched values. Then, as $\delta^{13}\text{C}_{\text{carb}}$ increases to its Hirnantian maximum, so too does $\Delta^{13}\text{C}$. Finally, as $\delta^{13}\text{C}_{\text{carb}}$ falls at the end of the excursion, $\Delta^{13}\text{C}$ returns to its lower pre-excursion value.

3. Discussion

3.1. Adequacy of sampling and state of preservation of the isotopic signals

The same stratigraphic intervals in other studies where either $\delta^{13}\text{C}_{\text{carb}}$ or $\delta^{13}\text{C}_{\text{org}}$ have been determined are highly condensed with thicknesses ranging from 0.3 to 4 m (Brenchley et al., 1994; Wang et al., 1997; Underwood et al., 1997). This alone indicates that, barring other problems, the Copenhagen Canyon section provides the best opportunity to observe the detailed and, presumably, complete behavior of carbon isotope covariation through the Hirnantian. Our analyses of micritic carbonate, for example, provide a continuous record of the excursion, whereas the carbon isotope records derived from previous studies of ‘least altered’ brachiopods and marine cements provide only a range of values for any given stratigraphic level (e.g., see Marshall and Middleton, 1990; Brenchley et al., 1994).

In carbonate-rich and relatively organic-carbon poor sequences, such as the Upper Ordovician strata exposed in Copenhagen Canyon where most samples were at least 80% carbonate (Table 1), the system is usually rock-dominated with respect to carbon, and diagenesis does not substantially alter the $\delta^{13}\text{C}_{\text{carb}}$ values of obvious unrecrystallized micrites (Scholle and Arthur, 1980; Banner and Hanson, 1990; Marshall, 1992). Accordingly, $\delta^{13}\text{C}_{\text{carb}}$ has been shown to produce reliable isotopic signatures that can be correlated worldwide (Knoll et al., 1986; Arthur et al., 1988; Ripperdan, 1994; Kaufman and Knoll, 1995). Oxygen isotopes, on the other hand, reflect diagenesis in a largely water-dominated system dur-

ing diagenesis, and, therefore, are not usually as amenable to interpretation as primary signals. Study of carbonate peels suggests that the micrites have not been extensively recrystallized, except, perhaps, in some zones low in the sampled section.

3.2. Oxygen isotope data

In general, we consider the micrite $\delta^{18}\text{O}$ values suspect because of likely diagenetic overprints. One cannot observe major systematic $\delta^{18}\text{O}$ variations in the micrite data that might reflect glacial–interglacial fluctuations during the Hirnantian, at least none that systematically correspond to the $\delta^{13}\text{C}_{\text{org}}$ variations. Overall, the Hirnantian part of the record is characterized by heavier $\delta^{18}\text{O}$ than units above and below, as might be expected for a glacial interval. However, because of the likelihood of alteration of the oxygen isotopic signal, particularly in the lower part of the sequence, we are not certain of this interpretation. It is likely that our sampling interval actually aliased the signal of any high-amplitude, high-frequency variations, and sampling and analysis should be carried out at a higher resolution.

3.3. Fluctuations in $\delta^{13}\text{C}_{\text{org}}$

We are puzzled by the fluctuations in the organic-carbon isotopic values, and can only offer the following suggestions for their origin.

(1) They may result from high-frequency atmospheric $p\text{CO}_2$ fluctuations, or higher-order glacio-eustatic sea-level fluctuations leading to periodic reworking of older organic matter of a distinctive carbon isotopic composition into the sediment. Little direct evidence exists for multiple advances and retreats of the Hirnantian ice sheets, although five discrete conodont extinctions have been identified, and have been suggested to reflect events related to multiple ice-sheet fluctuations in response to orbital variations in insolation (Armstrong, 1995).

(2) There is a possibility that this may represent some analytical problem or a diagenetic overprint. In an attempt to document the fidelity of this record, we analyzed for the weight fraction of total carbonate-C and organic C (orgC) in our sample set (Fig. 2A). With one exception, all orgC concentrations are between 0.1 and 1.0%, and there is no systematic rela-

tionship between $\delta^{13}\text{C}_{\text{org}}$ and wt% orgC as might be expected if differential alteration of organic matter in lean versus relatively orgC-rich intervals caused the carbon isotopic variation. There was ample orgC for all isotopic analyses and the carbon isotope ratio of samples analyzed is not a function of the inlet pressure at full bellows closure (Fig. 2B), as one might expect if low yields caused analytical problems. Replicate analyses were completed for eight samples, and all were within $\pm 0.2\text{‰}$.

The Copenhagen Canyon sequence where we sampled is classified as thermally mature, based on a conodont alteration index (CAI) of about 3 (Epstein et al., 1977; Harris et al., 1980). This suggests that the organic matter experienced alteration at temperatures of over 100°C during burial. Overall, this thermal alteration might shift the bulk $\delta^{13}\text{C}_{\text{org}}$ values of all organic C (assuming same general type and preservation) by up to 1–2‰ higher (see review by Dean et al., 1986; cf. Hayes et al., 1982; Lewan, 1983; Clayton, 1991). However, thermal maturation would not be likely to cause the trends or variability seen in our data unless by local intrusions, or if the original organic matter type was highly variable, or if there were migrated hydrocarbons (bitumen) present in some but not all samples. None of the explanations appear to be reasonable for our data set. The organic matter is constrained to have been largely of marine origin, because there were no documented, established terrestrial organic matter sources in the Late Ordovician. That does not preclude different marine sources (phytoplankton vs. shallow-water algal sources vs. bacterial contributions), but, because of the high degree of thermal alteration, neither pyrolysis nor biomarker work will shed any further light on this problem. As for the possibility of contamination by bitumen, a survey of samples by optical microscopy indicates that none is present (A. Davis, pers. commun., 1997).

Our $\delta^{13}\text{C}_{\text{org}}$ values are largely consistent with analyses from other sections reported elsewhere. The organic matter in Hirnantian shales at Dob's Lin, Scotland (Underwood et al., 1997) has $\delta^{13}\text{C}_{\text{org}}$ values (–28 to –33‰) which overlap ours completely. More isotopically enriched $\delta^{13}\text{C}_{\text{org}}$ values (and a larger overall excursion of up to 7‰) are reported for Hirnantian shales from Yichang, China (Wang et al., 1997), but these data are from a highly condensed section (only

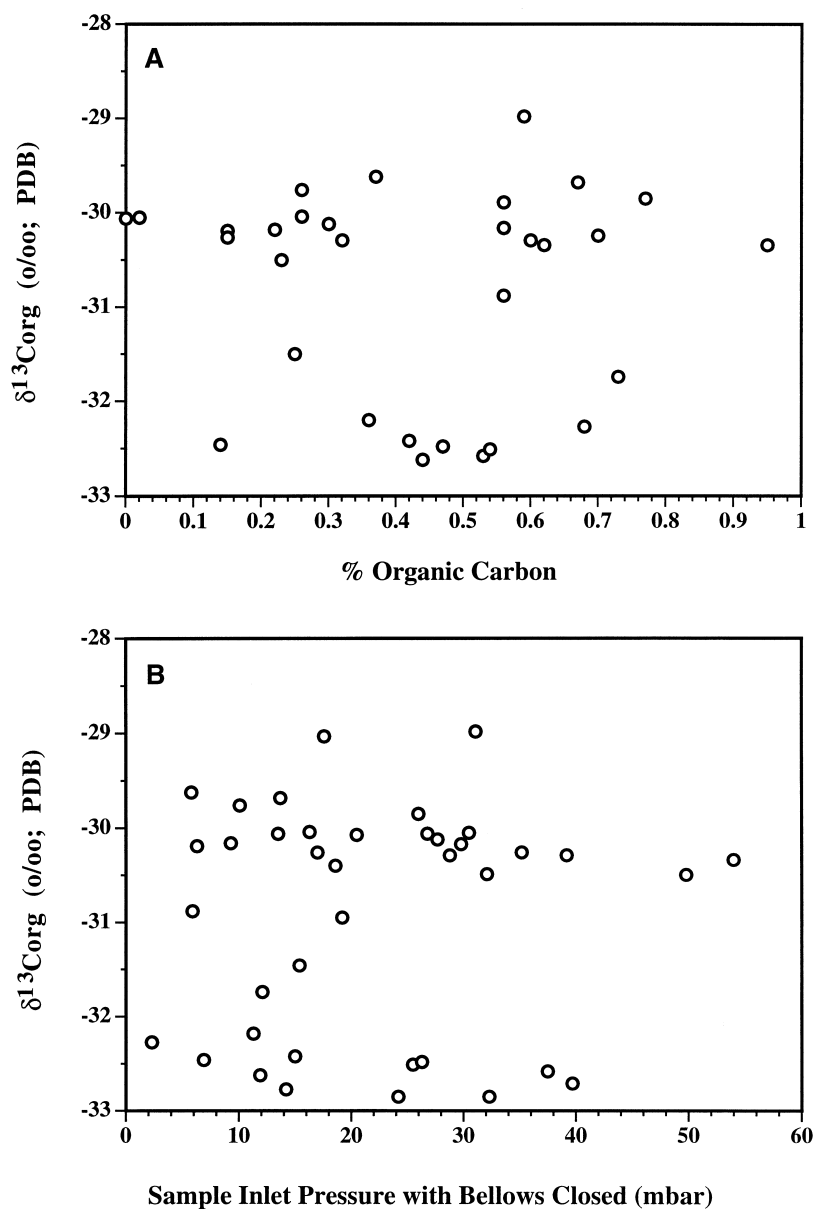


Fig. 2. (A) Relationship between $\delta^{13}\text{C}_{\text{org}}$ and the total organic-carbon content of the samples. (B) Relationship between $\delta^{13}\text{C}_{\text{org}}$ and the inlet pressure at full bellows closure, which is a measure of sample yield during mass spectrometry.

40 cm thick for the Hirnantian interval) that may have recorded unusual oceanographic conditions.

Our results are unique in that they are paired to $\delta^{13}\text{C}_{\text{carb}}$ values, and indicate that a positive shift in $\delta^{13}\text{C}_{\text{org}}$ may have preceded the $\delta^{13}\text{C}_{\text{carb}}$ excursion. Other paired analyses from the late-middle

Ordovician demonstrate even more convincingly that excursions in carbonates need not be contemporaneous with those in organic matter (Patzkowsky et al., 1997). Clearly one should not attempt precise correlation between limestone and shale sequences based on carbon isotopic excursions of the two com-

ponents without first demonstrating elsewhere that the $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ co-vary precisely.

3.4. *Paleo- CO_2 proxy*

The isotopic difference between contemporaneous carbonate and organic matter deposited from the ocean ($\Delta^{13}\text{C}$) has been proposed as a proxy for paleoatmospheric $p\text{CO}_2$ (e.g., Arthur et al., 1985; Popp et al., 1989). This difference arises from the isotopic discrimination that accompanies photosynthesis, and it decreases as aqueous CO_2 concentrations decrease (e.g., Arthur et al., 1985; Popp et al., 1989; Freeman and Hayes, 1992; Rau et al., 1992; Bidigare et al., 1997). Thus, $\delta^{13}\text{C}$ has been used as an atmospheric $p\text{CO}_2$ proxy. To estimate absolute values of $p\text{CO}_2$, however, changes in $\Delta^{13}\text{C}$ must be calibrated with laboratory or field studies of photosynthetic fractionation by modern, aquatic organisms, and these may not be good analogues of ancient photoautotrophs. Moreover, it has not been demonstrated that photosynthetic isotope discrimination would be CO_2 -dependent at such high concentrations. The photosynthetic isotope effect also appears to depend on growth rate (e.g., Bidigare et al., 1997), and diagenesis can alter $\Delta^{13}\text{C}$ (see above). Finally, one must presume equilibration with the atmosphere at a specified temperature to infer absolute values of atmospheric $p\text{CO}_2$ from $\Delta^{13}\text{C}$. Thus, the proxy is best used as a rough indicator of relative changes in atmospheric $p\text{CO}_2$, especially for such ancient times as we explore here.

Accordingly, and with caveats emphasized, we offer the following interpretation of the CO_2 history of the Hirnantian glaciation. The isotopic data indicate that although atmospheric $p\text{CO}_2$ may have fallen prior to the glaciation, it rose during the glaciation. This result is inconsistent with the productivity hypothesis (Brenchley et al., 1994), but is consistent with our weathering hypothesis, which we discuss further below. Then, after the peak of the $\delta^{13}\text{C}_{\text{carb}}$ excursion, and the end of the glaciation, atmospheric $p\text{CO}_2$ fell.

3.5. *Late Ordovician weathering*

Our new hypothesis arises from the unusual characteristics of the Late Ordovician weathering envi-

ronment. The Cambrian and Ordovician represent an interval of abundant and widespread marine limestone deposition on vast low-latitude continental shelves (Opdyke and Wilkinson, 1988; Fig. 3). In the late-middle Ordovician, although sea level remained relatively high and carbonate deposition continued, mountain-building began in the Appalachians and Caledonides (Richter et al., 1992; van Staal, 1994). This shift in global tectonic regime toward collision and orogeny is also reflected in the Ordovician/Silurian Sr isotopic record of marine limestones. The Sr isotope trend reversed in the Late Ordovician, trending toward increasingly more radiogenic values through the Silurian (Burke et al., 1982), presumably as more radiogenic rocks became exposed and weathered in the Appalachians and Caledonides. In analogy to the presumed consequences of Cenozoic Himalayan orogeny (e.g., Raymo and Ruddiman, 1992; Kump and Arthur, 1997), atmospheric $p\text{CO}_2$ likely fell as chemical erosion rates in orogenic regions were accelerated by enhanced relief, increasing the overall ‘weatherability’ of the continents (Kump and Arthur, 1997; and references therein).

3.6. *Climate sensitivity*

Our previous investigation of Late Ordovician climate sensitivity to atmospheric $p\text{CO}_2$ variations using the GENESIS climate model (Gibbs et al., 1997) revealed that a critical $p\text{CO}_2$ threshold ($\sim 10\text{--}12\times \text{PAL}$) may have been reached in the early Hirnantian, below which the reduced radiative effects from lowered atmospheric $p\text{CO}_2$ allowed the initiation and rapid growth of continental ice sheets, accelerated by positive ice-albedo feedback. As the ice sheets grew, and sea level fell, the extensive area of low-latitude carbonate platforms became exposed (Fig. 3), and two other positive feedbacks came into play: planetary albedo likely increased because of the high reflectivity of the exposed limestone relative to seawater (Gildner and Cisne, 1987) and chemical erosion rates likely increased in response to increased limestone exposure (Gibbs and Kump, 1994). We argue that the latter change was recorded in the $\delta^{13}\text{C}$ of the oceans, and therefore in the isotopic composition of limestones deposited from the ocean. However, as the ice sheets expanded,

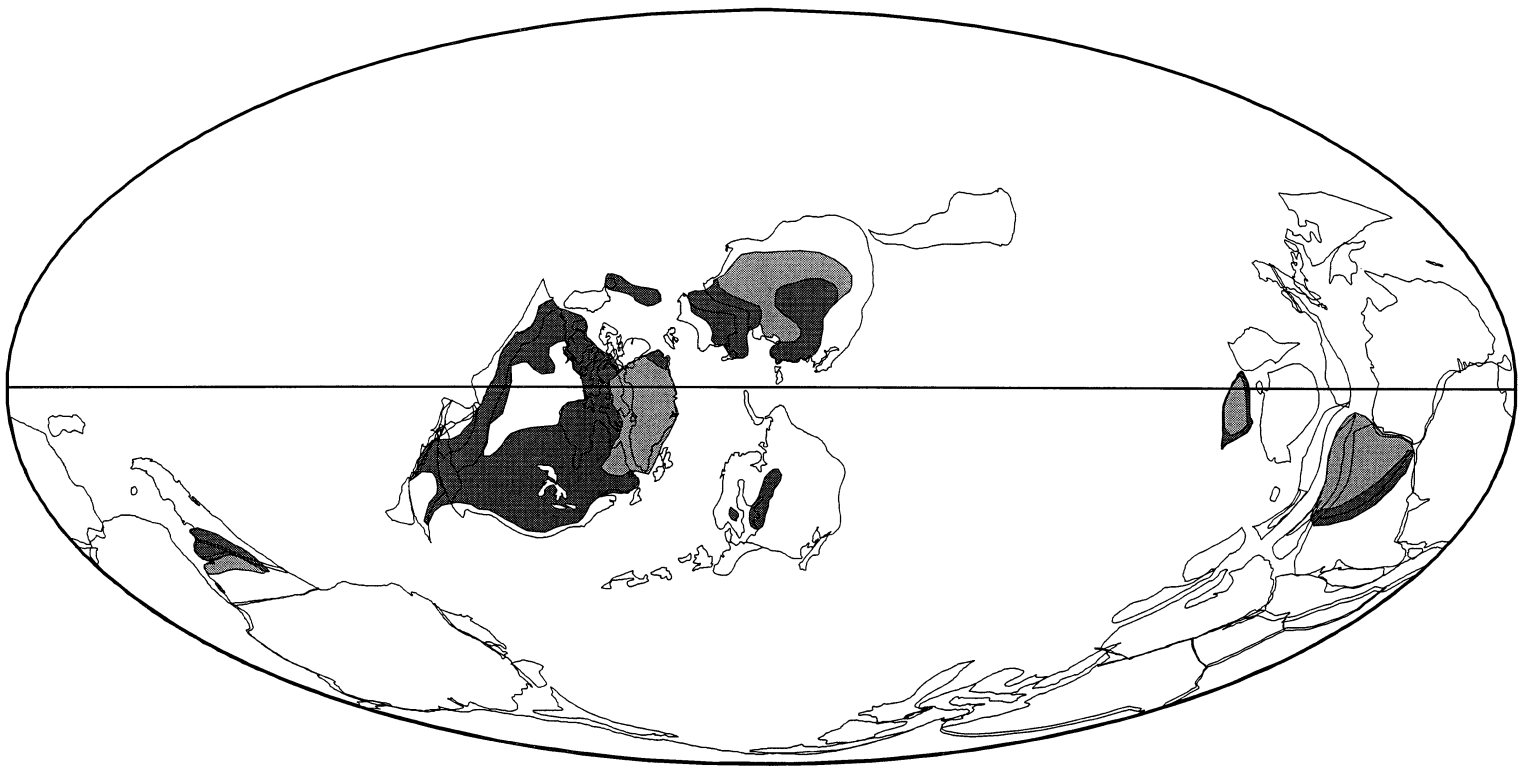


Fig. 3. Hirnantian paleogeography (after Scotese, 1994) showing carbonate platforms that would have been exposed by a glacioeustatic drawdown of sea level. Heavy shading: after Brenchley (1989); light shading: area of maximum extent of carbonate platforms according to C.R. Scotese, pers. commun.

areas of silicate rock exposure (preferentially located on glaciated continents, because the low-latitude regions were limestone covered in the Hirnantian) diminished, overwhelming the effects of increased weatherability due to orogeny, and reducing the long-term sink for atmospheric CO_2 below the level of the inputs from volcanism and metamorphism (Berner, 1994). Atmospheric $p\text{CO}_2$ thus rose, reversing the long-term downward trend caused by orogeny, and climbing to a level that may have exceeded the maximum for ice-sheet stability. The radiative effects of enhanced atmospheric $p\text{CO}_2$ then overcame the ice-albedo feedback, and the ice sheets melted. As they did, silicate terrains became re-exposed, and weathering rates increased. In response, atmospheric $p\text{CO}_2$ fell to the pre-glaciation level.

3.7. Comparison to the productivity hypothesis

To contrast the implications of this scenario for the isotopic composition of the Hirnantian ocean to those of the productivity hypothesis (Brenchley et al., 1994), the steady-state mass-balance equation for carbon isotopes in the ocean (e.g., Kump, 1991) can be rearranged to yield f_{org} , the fraction of the total carbon burial in sediments occurring as organic carbon:

$$f_{\text{org}} = \frac{\delta^{13}\text{C}_{\text{carb}} - \delta^{13}\text{C}_{\text{riv}}}{\Delta^{13}\text{C}} \quad (1)$$

Here $\delta^{13}\text{C}_{\text{carb}}$ is the isotopic composition of marine carbonates, which is typically assumed to represent the isotopic composition of the ocean, because the isotopic fractionation between seawater inorganic carbon and calcite/aragonite is small. $\delta^{13}\text{C}_{\text{riv}}$ is the carbon isotopic composition of the riverine input of carbon to the oceans, which represents most of the carbon delivered to the ocean–atmosphere system (other smaller sources include volcanoes and metamorphic releases).

The productivity hypothesis would require a ~50–75% increase in f_{org} to explain a 6‰ increase in $\delta^{13}\text{C}_{\text{carb}}$ (using typical values for the other variables). In contrast, a riverine isotopic excursion of +6‰ could drive the $\delta^{13}\text{C}_{\text{carb}}$ excursion with no change f_{org} . If we assume the original riverine value was –7‰, representing contributions from kerogen weathering (28% at –25‰) and limestone weathering (72% at 0‰), a +6‰ excursion would require

limestone weathering to increase to 96% of the total flux. However, if we allow for a 7‰ excursion in $\Delta^{13}\text{C}$ to represent the response to increasing atmospheric $p\text{CO}_2$ (based on our isotopic analyses; see below), $\delta^{13}\text{C}_{\text{riv}}$ would only have to increase by about 4‰ to explain the observed shift in $\delta^{13}\text{C}_{\text{carb}}$ (Table 1). Such a change requires an increase in the carbonate weathering contribution to the total carbon weathering flux, f_{wcarb} , from 72% to 88%, entirely consistent with the exposure of Ordovician and older limestones as sea level fell. At the termination of the glaciation, and as sea level rose, $\delta^{13}\text{C}_{\text{riv}}$ presumably returned to its pre-excursion value.

3.8. Numerical modeling

Are the required magnitude and duration of atmospheric $p\text{CO}_2$ changes in the Late Ordovician reasonable in terms of the response to these changes in the weathering environment? Quantitative evaluation of changes in atmospheric $p\text{CO}_2$ requires a more sophisticated treatment of the carbon cycle than that required for interpreting the isotopic signal (as in Table 2). A preliminary analysis has been made, using the ocean–atmosphere–lithosphere carbon-cycle model of Walker and Kasting (1992). We ran the model using present-day parameters for ocean volumes and exchange rates, recognizing that although these were undoubtedly quite different in the past, on the long time scales we are interested in, details of basin–basin partitioning within the ocean are of little importance to the global trend. An elevated atmospheric $p\text{CO}_2$ baseline for the early Paleozoic was achieved by increasing the volcanic and metamorphic outgassing rate by a factor of 2.2 (consistent with the GEOCARB modeling of Berner, 1994). We forced a change in atmospheric $p\text{CO}_2$ by instantaneously increasing continental weatherability

Table 2
Isotopic scenarios for the Late Ordovician

Interval	$\delta^{13}\text{C}_{\text{carb}}$ (observed) (‰)	$\Delta^{13}\text{C}$ (observed) (‰)	$\delta^{13}\text{C}_{\text{riv}}$ (proposed) (‰)	f_{wcarb}	f_{org}
Pre-excursion	1	31	–7	0.72	0.26
Excursion	7	38	–2.9	0.88	0.26
Post-excursion	0	30	–7	0.72	0.23

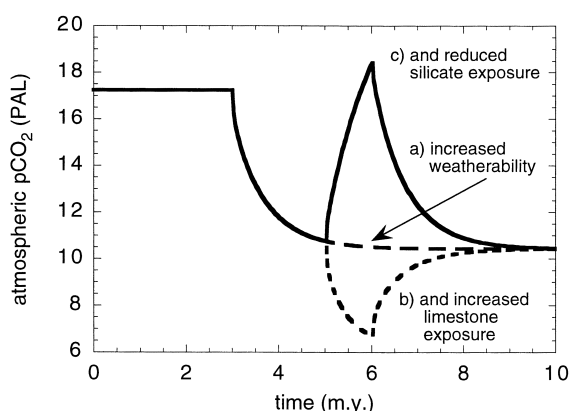


Fig. 4. Results from carbon-cycle modeling experiments, using the model of Walker and Kasting (1992), as presented by Mellinger (1992). Line *a*. Effect of instantaneously increasing continental weatherability by 10% at 3 m.y. Line *b*. Same conditions that generated line (*a*), except relative exposure area of limestones increased by 22% for the period from 5 to 6 m.y. Line *c*. Same conditions that generated line (*b*), except relative exposure area of silicate terrains reduced by 50% from 5 to 6 m.y. All other model parameters, including oceanic water-mass exchange rates, were fixed at modern-day values, except volcanic outgassing, which was elevated to 2.2 times today's value to yield an elevated baseline atmospheric $p\text{CO}_2$ for the early Paleozoic (consistent with Berner, 1994).

by 10%, similar to the number used by Kump and Arthur (1997) to simulate the effects of Cenozoic orogeny and uplift. This change alone (Fig. 4, line *a*) caused a reduction in atmospheric $p\text{CO}_2$ from the steady-state value of $\sim 17 \times \text{PAL}$ before the perturbation to a new steady state of around $10 \times \text{PAL}$ within ~ 1 m.y. The actual drawdown could well have been more protracted, extending throughout the Late Ordovician. We then specified, in addition, a 22% increase in f_{wcarb} , the area available for carbonate weathering relative to the arbitrary pre-excursion area, for the interval from 5 to 6 m.y. This increase in limestone exposure is consistent with the carbon isotopic constraints provided by Table 2. The effect of adding limestone exposure (Fig. 4, line *b*) was that $p\text{CO}_2$ fell abruptly, from $10 \times \text{PAL}$ before exposure to $\sim 7 \times \text{PAL}$, over a period of a few hundred thousand years. However, upon relaxation of the perturbation, atmospheric $p\text{CO}_2$ returned to the value set by the long-term increase in weatherability.

To evaluate the possibility that the $p\text{CO}_2$ drawdown associated with carbonate weathering was offset by

the reduction in silicate weathering rates, the preferential coverage of silicate terrains by ice sheets was simulated by reducing f_{wsil} , the area of silicate exposure relative to the arbitrary pre-excursion area. We applied a 50% reduction in silicate exposure area simultaneously with the 22% increase in carbonate exposure (i.e., from 5 to 6 m.y.), based on visual inspection of the paleogeographic map (Fig. 3). The result was an *increase* in atmospheric $p\text{CO}_2$ (Fig. 4, line *c*); the effect of reducing the CO_2 sink associated with silicate weathering more than compensated for the transient effect of increased limestone weathering. With alkalinity adjustment, atmospheric $p\text{CO}_2$ soared to a transient peak of $\sim 18 \times \text{PAL}$. Thus, we find that reasonable changes in areal exposure of carbonate and silicate terrains yield atmospheric $p\text{CO}_2$ variations that, according to GCM studies (Gibbs et al., 1997), would bring the climate system in and out of glaciation.

4. Conclusion

The interplay among tectonism, carbonate and silicate weathering, and eustasy provides a mechanism for fast initiation and demise of Hirnantian ice sheets. The weathering hypothesis is intuitive, and the carbon isotopic data are supportive of it. The organic-carbon isotope data, however, are problematic. They may represent a global signal of oscillations in atmospheric $p\text{CO}_2$, but they also may reflect a local oscillation in organic-matter source or diagenesis. The organic matter at Dob's Lin (Underwood et al., 1997) and in China (Wang et al., 1997) display positive carbon isotope excursions during the Hirnantian, but the timing relative to the carbonate-carbon isotope excursion is unclear, and the magnitude of the excursion is not larger than that in carbonates from other sites (as one would expect had the excursion been associated with a drop in atmospheric $p\text{CO}_2$). Thus, there is no evidence for a $p\text{CO}_2$ reduction during the ice age. However, further study of the Nevada sections and at other locales is clearly needed.

If the weathering hypothesis is correct, another paradox arises: the geological evidence for extensive continental ice sheets is restricted to the Hirnantian (Paris et al., 1995), but the forcing factor for low atmospheric $p\text{CO}_2$ (orogeny) presumably continued through the Silurian (Richter et al., 1992). Why

did not the greenhouse effect of atmospheric CO₂ decline again to critically low values, initiating other glaciations?

Perhaps it did. Recently acquired isotopic data (Wenzel and Joachimski, 1996; Azmy et al., 1998) indicate that positive excursions in carbon and oxygen isotopic compositions occurred during sea-level lowstands in the Llandoveryan, Wenlockian, and Ludlovian Epochs of the Silurian. Opting not to invoke glaciation in the absence of supporting geological data, Wenzel and Joachimski (1996) provided alternative explanations for the oxygen isotopic excursions, involving changes in ocean stratification and circulation. However, Azmy et al. (1998) entertained glaciation as a probable causal mechanism for the Llandoveryan and Early Wenlockian events, but were hesitant to conclude that glaciation was the cause of the Ludlovian event because of lack of any documented glacial deposits. Given the great similarity between these excursions and the Hirnantian one, we feel compelled to conclude differently, that there were at least three episodes of glaciation in the Silurian. Glacial geological indicators have been recognized from the Llandovery/earliest Wenlockian in Amazonia (Grahn and Caputo, 1992), and others may one day be discovered from later in the Silurian.

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