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Reconstructing the environmental conditions around the Silurian Ireviken Event using the carbon isotope composition of bulk and palynomorph organic matter

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[1] The carbon isotope composition ($\delta^{13}\text{C}$) of bulk organic matter and two palynomorph groups (scolecodonts and chitinozoans) from the Llandovery-Wenlock strata of Gotland (E Sweden) are compared to gain knowledge about carbon cycling in the Silurian (sub)tropical shelf environment. The $\delta^{13}\text{C}$ values of the palynomorphs are mostly lower than the $\delta^{13}\text{C}$ values of the bulk organic matter, and the $\delta^{13}\text{C}$ values of the benthic scolecodonts are lower than those of the planktonic chitinozoans. While the difference between bulk and palynomorph $\delta^{13}\text{C}$ may be in part a function of trophic state, the lower values of the scolecodonts relative to those of chitinozoans, which are assumed to live in the well-mixed water column, might imply

an infaunal mode of life for the polychaetes that carried the scolecodonts. Lower $\delta^{13}\text{C}$ for the scolecodonts in the middle of the section may represent variations in primary marine productivity (supported by acritarch abundance data), oxidation of organic matter in the bottom waters, or genera effects. In general, however, trends between the three data sets are parallel, indicating similarities in the low frequency, environmentally forced controls. The $\delta^{13}\text{C}$ data show a decreasing trend from the base of the section, up to a horizon well below the base of the Upper Visby Formation. At this level, and therefore probably several 10 kyr before the $\delta^{13}\text{C}$ increase in the carbonates, the $\delta^{13}\text{C}$ organic values increase by $\sim 1\%$. This perhaps is an expression of a changed composition of the bulk organic matter associated with the extinction events prior to the Llandovery-Wenlock boundary.

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1. Introduction

[2] Based on records of the carbon isotope composition of marine carbonates ($\delta^{13}\text{C}_{\text{carb}}$), the Late Ordovician and the Silurian represent one of the most dynamic intervals in the Phanerozoic. It is characterized by several global, short-lived, positive $\delta^{13}\text{C}_{\text{carb}}$ excursions with amplitudes exceeding $+5\%$, and maxima of over $+10\%$ [Munnecke *et al.*, 2003, 2010; Bergström *et al.*, 2009; Cramer *et al.*, 2011]. New radiometric ages constrain the duration of some of these excursions to notably less than 1 Myr [Cramer *et al.*, 2012]. The positive excursions are considered to be records of rapid and large-scale changes in the ancient Earth's global carbon cycle, oceanography, and climate system; however, currently there is no consensus interpretation that integrates cause-and-effect scenarios with the totality of the stratigraphic data [Jeppsson *et al.*, 1995; Bickert *et al.*, 1997; Cramer and Saltzman, 2005, 2007a; Noble *et al.*, 2012]. Bulk organic matter associated with the carbonates often has a carbon isotope composition ($\delta^{13}\text{C}_{\text{org}}$) that is covariant with that of $\delta^{13}\text{C}_{\text{carb}}$ [e.g., Cramer and Saltzman, 2007b; Young *et al.*, 2008; Noble *et al.*, 2012]. However, the interpretation of $\delta^{13}\text{C}_{\text{org}}$ can be complex because of the various factors that influence the values, including varying sources of organic matter (e.g., bacteria, phytoplankton, zooplankton), varying production rates of the organic material, growth rates and geometry of phytoplankton cells, and the potential presence of carbon concentrating mechanisms, properties of the ambient sea water (temperature,

pH, $p\text{CO}_2$, light, nutrients), preservation and diagenesis, the inorganic C pool, and the analytical (e.g., acid digestion) method [e.g., Hinga *et al.*, 1994; Popp *et al.*, 1997, 1998; Laws *et al.*, 2002; Brodie *et al.*, 2011a, 2011b; Könitzer *et al.*, 2012]. Despite these difficulties, Early Paleozoic global $\delta^{13}\text{C}_{\text{org}}$ events are widely interpreted in terms of global climate variation. Here we focus on the variety of sources that could constitute the bulk organic carbon that is measured for $\delta^{13}\text{C}_{\text{org}}$ in rocks of Llandovery-Wenlock age. Lécuyer and Paris [1997] tested the contributions of several palynomorph types to the $\delta^{13}\text{C}$ composition of Paleozoic organic matter. They indicated variations of up to 4% among marine palynomorphs (in a range of Silurian-Devonian marine sediment samples), and up to 2.5% within a single sediment sample. Where there is evidence for a significant contribution of terrestrial derived organic matter, they showed a greater range in $\delta^{13}\text{C}_{\text{org}}$. Other studies have also shown the potential for isotope bias caused by the presence of noncontemporaneous carbon (i.e., reworked geological carbon) and of allochthonous components (e.g., land and fresh water derived plant remains in marine deposits), and the origin of amorphous organic matter is still debated [Paris *et al.*, 2008]. It is clear that it is important to know about the composition of the different organic components that contribute to the “bulk organic matter” of marine sediments that form sedimentary rocks if $\delta^{13}\text{C}_{\text{org}}$ is to be used to make inferences about environmental change. Other studies have realized the potential flaw in the bulk organic carbon approach.



For example, isotope variation of up to 4‰ in the Late Ordovician Guttenberg Carbon Isotope Excursion (GICE) from Iowa was interpreted in terms of wide-spread environmental change and perturbations of the carbon cycle, linked to organic carbon burial and $p\text{CO}_2$ (ascribed to the GICE in other areas), as well as a partial local shift from normal-marine to *Gloeocapsomorpha prisca*-dominated organic matter [Pancost *et al.*, 1999]. The GICE excursion in Iowa exhibited values more than 4‰ more positive than in other places in the U.S. (e.g., Pennsylvania), and the authors (also see recommendations by Popp *et al.* [1997]) suggested that one way to decipher local from global effects on $\delta^{13}\text{C}$ is by compound-specific (i.e., molecules or groups of molecules) or component-specific (i.e., in our case, on isolated specimens of a particular organic-walled fossil group) isotope analyses.

[3] A component-specific study was undertaken by Snelling *et al.* [2011]. They analyzed $\delta^{13}\text{C}$ of graptolite (Ordovician-Silurian macro-zooplankton) periderm in comparison to $\delta^{13}\text{C}_{\text{org}}$ of the enclosing whole rock, and noted that the difference between both signals is inconsistent over the Ordovician-Silurian, but also that the $\delta^{13}\text{C}$ of the Aeronian (Early Silurian) graptolites from Wales and Scotland are “in general” more positive than the values of whole rock samples. This was also described by LaPorte *et al.* [2009] in the U.S., where they suggested that graptolites occupied a higher trophic level than algae, which were assumed to make up the bulk of the organic matter in the samples. Lo Duca and Pratt [2002] noted that algae taxa co-occurring with the graptolites were 1–2‰ more negative than associated graptolites. Other interpretations for this offset between selected fossil and bulk rock $\delta^{13}\text{C}_{\text{org}}$ data include differences in time represented by the graptolite periderm and by the whole rock sample (the latter integrating a much longer time period), and selective diagenetic modification between the different organic matter types. Snelling *et al.* [2011], based on their Aeronian data set, concluded that for chemostratigraphic purposes whole rock $\delta^{13}\text{C}$ will likely produce more reproducible results than graptolite $\delta^{13}\text{C}$, because of the small scale inhomogeneities in the graptolite signals. However, for those sections prone to nonmarine input, or time intervals of greater riverine discharge, they suggest that graptolite carbon may be a better proxy for marine bulk organic matter, despite heterogeneities.

[4] Here we present $\delta^{13}\text{C}_{\text{org}}$ data from the Llandovery-Wenlock boundary interval in Gotland and $\delta^{13}\text{C}$ data

from handpicked, organic-walled microfossils, chitinozoans (egg cases of marine zooplankton) and scolecodonts (jaws of benthic polychaete annelids). Chitinozoans, and likely their parent-animals, were part of the epizooplankton, lived in the shallow “mixed layer” of the Ordovician-Silurian oceans, and thus occupied a habitat comparable to that of the graptolites [Vandenbroucke *et al.*, 2009, 2010a, 2010b]. Chitinozoan animals are now widely accepted as metazoans (i.e., nonautotrophes), based on solid morphological analyses of chitinozoan clusters [Paris and Nölvak, 1999]. Chitinozoan animals and graptolites have been hypothesized to occupy a higher trophic level than primary producers such as acritarchs, mainly based on inferred modern analogues for acritarchs and parallel biodiversity trends between these groups [Servais *et al.*, 2008]. Scolecodont-bearing worms, in contrast, are known to have been benthic animals living close to the water-sediment interface [Eriksson *et al.*, 2004]. They are (at least) secondary consumers, based on their advanced feeding/predatory apparatus. The aim is to better understand the contribution of the various fossil groups to the bulk organic signal, and hence the variation within the isotope signals.

2. Geological Setting and Sampling

[5] The Silurian strata, which outcrop on the island of Gotland, are the erosional remains of a low-latitude carbonate platform along the margins of the Baltic Basin. The platform rocks show little diagenetic alteration or tectonic disturbance. Witness to this excellent state of preservation are: (1) the very low Conodont Alteration Index [Jeppsson, 1983], (2) the exceptional preservation of a variety of calcareous microfossils and nanofossils such as “calcispheres” [Munnecke *et al.*, 2000; Munnecke and Servais, 2008], and (3) the abundance of excellently preserved organic-walled microfossils (“palynomorphs”) such as full relief chitinozoans, almost unique in the world [Laufeld, 1974; Munnecke and Servais, 1996]. On the Correia [1967] scale they represent stage N1, suggesting they have never been heated above 100°C [Laufeld, 1974]. Snelling *et al.* [2011] detected no significant difference between $\delta^{13}\text{C}$ of organic graptolite periderm from low- and high-anchizone-grade localities, which suggests that any low-grade metamorphism suffered by the Gotland succession would have had negligible influence on $\delta^{13}\text{C}$.

[6] The waters on the Gotland shelf were well-mixed, and the depositional depth for our samples was not deeper than a few tens of meters. This is based on $\delta^{18}\text{O}$ values from brachiopods from shallow platform environments that are systematically only about 0.5 to 1‰ lower than values from coeval deeper shelf environments [Samtleben *et al.*, 1996], indicating ~ 2 to 4°C higher water temperatures. However, no difference was observed with respect to the $\delta^{13}\text{C}_{\text{carb}}$ values. In addition, fossil, photosynthetic, encrusting algae are recovered from the Lower and Upper Visby formations, which also yield the data of this study [Nitecki and Spjeldnaes, 1993; Calner *et al.*, 2004]. Moreover, the lithological and faunal changes from the Lower to the Upper Visby formations near the top of the section through into the overlying Högklint Formation (not sampled), reflect a continuous development of a gradually shallower depositional depth. The reconstructed sea level for this interval is controversial; whereas Calner *et al.* [2004] and Cramer and Saltzman [2005] suggest sea-level rise and highstand (based on sequence stratigraphic arguments, and the development of keep-up reefs in the Högklint Fm), Brand *et al.* [2006] and Lehnert *et al.* [2010] proposed a sea-level drop and (glacial) low stand based on oxygen isotope data. Understanding the depositional environment has its importance. These well-mixed, shallow waters a priori prohibit the use of a declining $\delta^{13}\text{C}$ gradient through the water column [Kroopnick *et al.*, 1972] to explain any $\delta^{13}\text{C}$ differences between fossils of organisms living at different water depths. Such mechanisms would have required a much deeper environment than that of the Silurian Gotland platform.

[7] A 15.5 m long trench in the Luskint 1 section on Gotland was cleaned and sampled with an average resolution of 10 cm (Figure 1). The section spans the regularly alternating limestone and marls of the Lower Visby Formation (marls dominating) and the more irregularly alternating limestones and marls of the Upper Visby Formation (limestones dominating). The *Phaulactis* layer (a ~ 20 cm thick layer with abundant large rugose corals) marks the boundary between the Lower and Upper Visby formations [Samtleben *et al.*, 1996], and distinctive bentonite beds allowed us to position the samples in the stratigraphic succession [Jeppsson *et al.*, 2005]. The sampled Luskint 1 section incorporates most of the famous Ireviken Event (Figures 1 and 2). The extinction event affected many groups of organisms, but perhaps most impacted were the conodonts, with over 80% of species loss and as many as eight

discrete conodont extinction datums recognized [Jeppsson, 1987; Jeppsson *et al.*, 2005]. The first four of these precede the Ireviken oxygen and carbon (carbonate) isotope excursion by a few meters in the rock record [Munnecke *et al.*, 2003], representing a time interval of several tens of kiloyears [Cramer *et al.*, 2010, 2012].

3. Methods

[8] Samples for bulk organic matter analysis were cleaned mechanically. The weathered crust was removed by a saw; the remaining part was powdered with an agate ball mill. Two grams of each powder were reacted with 40 mL of 10% HCl to remove CaCO_3 . The residue was treated with distilled water to wash out remaining chloride ions, dried at 25°C , and pestled again to achieve a homogenous powder.

[9] A series of rock subsamples, 50 to 200 g each, were selected for extraction of organic-walled palynomorphs at the Institute of Geology of the Tallinn University of Technology (Estonia), using standard palynological techniques. This involved mechanical cleaning of the rock surface, crushing of the rock samples into pieces of $\sim 1\text{ cm}^3$, followed by acid digestion using 10% HCl at room temperature ($\sim 25^\circ\text{C}$) until all carbonates were dissolved (usually, this is followed by an HF treatment, although this was not necessary in this case, due to the virtual absence of silicates in the samples). The organic residue is washed with distilled water until neutral, and sieved at $45\ \mu\text{m}$. For each of these samples, a few tens to a hundred specimens of scolecodonts (depending on size) were handpicked from the organic residue (fraction $> 45\ \mu\text{m}$) using glass micropipettes, washed repeatedly in distilled water, and dried. The bulk of the specimens represented the families Paulinitidae, Polychaetaspidae and Mochtyellidae. Jawed polychaete faunas across the Llandovery-Wenlock boundary in Gotland are discussed in detail by Eriksson [2006]. The same organic residue was then handpicked for chitinozoans at the University of Ghent (Belgium). These are smaller (typically around $100\text{--}200\ \mu\text{m}$, 10^{-3} to 10^{-4} mg, 60 wt % carbon), thus 1000 to 1500 specimens per sample were isolated using glass micropipettes and washed, thereby avoiding contamination by other organic matter in the residues. The chitinozoan faunas predominantly contain a number of different species of the genera *Conochitina*, *Ancyrochitina*, and *Angochitina*, in various relative concentrations.

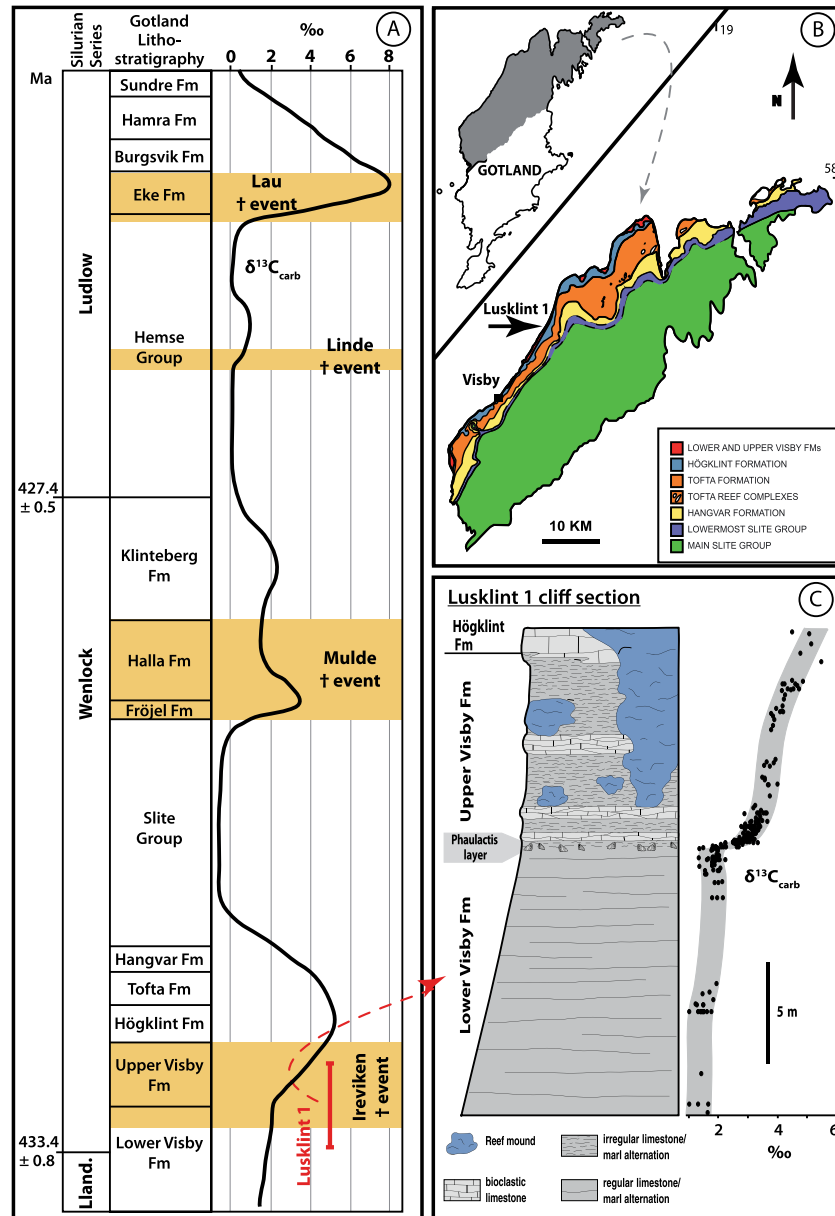


Figure 1. (A) Gotland chrono- and lithostratigraphy, and generalized $\delta^{13}\text{C}_{\text{carb}}$ curve, after *Calner et al.* [2005] and *Cramer et al.* [2011]. Numerical ages from *Cohen et al.* [2012]. (B) Geological map of the northern part of the Island of Gotland, after *Calner et al.* [2005], including the location of the Lusklint 1 section. (C) Sketch profile of the Lusklint cliff, detailed lithostratigraphy and compilation of Gotland brachiopod $\delta^{13}\text{C}_{\text{carb}}$ data, after *Munnecke et al.* [2003].

A detailed appraisal of the chitinozoan assemblages within the Upper and Lower Visby formations can be found in *Laufeld* [1974]. The isotope measurements were carried out in the same way as for the bulk organic material (see above).

[10] The acid processing for both groups of palynomorphs (chitinozoans and scolecodonts) was undertaken in Tallinn to avoid the possibility of inter-laboratory variation [*Brodie et al.*, 2011a, 2011b]. Such effects, however, can a priori not be excluded

when comparing the results from bulk organic matter (acid treatment in Erlangen) with those from the palynomorphs. For the transfer of liquid residue between Tallinn and Ghent, a few drops of formaldehyde were added to the residue to exclude the potential risk of the growth of, and contamination by, modern organisms. We confirmed that the formaldehyde did not have an influence on the $\delta^{13}\text{C}$ measurements of the palynomorphs, by processing an additional sample in Ghent (L2-26c, from the

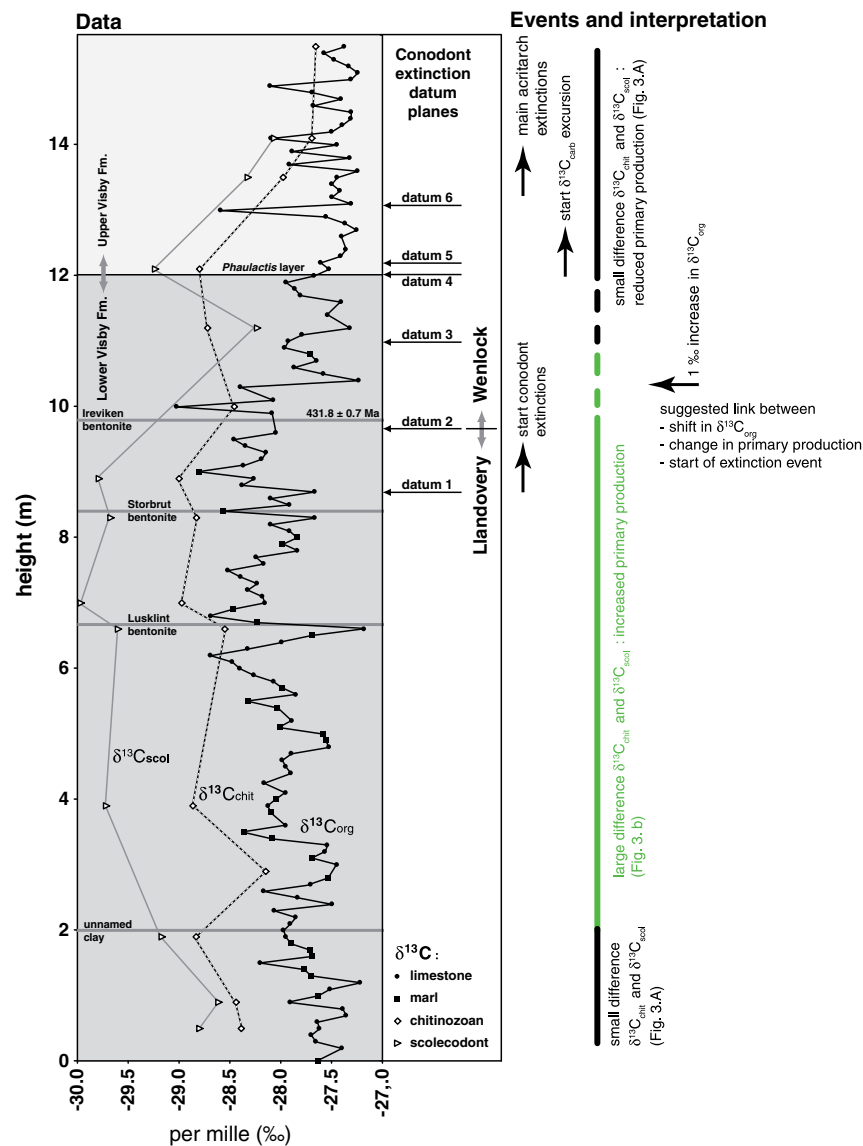


Figure 2. $\delta^{13}\text{C}_{\text{org}}$ from bulk organic matter (“whole rock”), separated according to the lithology of the sample (“limestones” versus “marls”) alongside $\delta^{13}\text{C}$ results from the isolated palynomorph groups “chitinozoans” and “scolecodonts” in the Lusklint 1 section. Other events are from the literature: onset of $\delta^{13}\text{C}_{\text{carb}}$ excursion [Munnecke et al., 2003; Cramer et al., 2010], start of conodont extinction [Jeppsson, 1987; Munnecke et al., 2003], main extinction of acritarch species [Gelsthorpe, 2004]. The bentonite beds are reference levels in the section and allow precise dating [e.g., Cramer et al., 2012, for the Ireviken bentonite].

nearby Lickershamn section), once without adding formaldehyde, and a second time with added formaldehyde: the difference in $\delta^{13}\text{C}$ between these two tests only was of 0.15‰, i.e., much lower than significant offsets discussed in the results section (L2-26c without formaldehyde: 0.08 mg of chitinozoans: -26.68% ; L2-26c with formaldehyde: 0.05 mg of chitinozoans: -26.83%).

[11] Isotope analysis of the organic materials (decalcified rocks, chitinozoans, and scolecodonts)

were performed with an elemental analyzer (Carlo-Erba1110) interfaced with a ThermoFinnigan Delta Plus mass spectrometer in the isotope laboratory at GeoCenter Erlangen (Germany). All carbon isotope values are reported relative to the Vienna-PDB standard. Accuracy and reproducibility of the analyses were checked by replicate analyses of an international standard (USGS 40). Reproducibility was better than $\pm 0.08\%$ (1σ). In addition, replicate analyses of four $\delta^{13}\text{C}_{\text{org}}$ samples were performed (Table 1), indicating reproducibility

Table 1. Replicate Analyses of Bulk Organic Matter

Date	Identifier	Weight [mg]	Ampl. 44 mV	$\delta^{13}\text{C}$ ‰ Vienna-PDB
19 August 2008	Lu 44	13.76	4745	-27.91
19 August 2008	Lu 44	13.66	5559	-27.93
6 August 2008	Lu 46	1.83	581	-28.04
6 August 2008	Lu 46	10.43	3119	-27.94
6 August 2008	Lu 121	0.55	177	-27.53
6 August 2008	Lu 121	7.97	2124	-27.86
15 August 2008	Lu 155	9.97	2003	-27.41
18 August 2008	Lu 155	10.22	5394	-27.36

better than 0.1‰ for samples under similar conditions (LU 44, 155), and better than 0.33‰ for samples of highly different weights (LU 46, 121). Variation below 0.3‰ will not be discussed here.

4. Results

[12] The $\delta^{13}\text{C}$ data are presented in Figure 2 and Table 2. The $\delta^{13}\text{C}$ from whole rock (bulk) organic matter ($\delta^{13}\text{C}_{\text{org}}$) are separated according to their original sample lithology, “limestone” or “marl” [cf. *Munnecke and Samtleben*, 1996]. No systematic difference is observed in $\delta^{13}\text{C}_{\text{org}}$ data between the limestones and the marls (Figure 2). The $\delta^{13}\text{C}$ from chitinozoans and scolecodonts are abbreviated to $\delta^{13}\text{C}_{\text{chit}}$ and $\delta^{13}\text{C}_{\text{scol}}$, respectively.

[13] The $\delta^{13}\text{C}_{\text{org}}$ data show a decreasing trend from the base of the trench section up to a height of ~10 m (from ~-27.6‰ to -28.3‰). At ~10.5 m, i.e., ~2 m below the *Phaulactis* layer, $\delta^{13}\text{C}_{\text{org}}$ increases abruptly by ~1‰. Above 10.5 m $\delta^{13}\text{C}_{\text{org}}$ are relatively constant at about -27.5‰. The data therefore do show increasing $\delta^{13}\text{C}_{\text{org}}$ during the Ireviken Event, but deviate in detail from the $\delta^{13}\text{C}_{\text{carb}}$ excursion (Figure 1) as published by *Munnecke et al.* [2003] and *Cramer et al.* [2010]. The increase in $\delta^{13}\text{C}_{\text{org}}$ starts earlier (about 2 m lower), and does not display a continuous increase; rather, it represents a marked and abrupt 1‰ rise (or “step”) in the curve. In addition to the section-wide tendencies, the $\delta^{13}\text{C}_{\text{org}}$ displays more rapid variations, that at times is of important amplitude: for instance, there is a sudden and short-lived ~1.5‰ increase of $\delta^{13}\text{C}_{\text{org}}$ just below the Lusklint Bentonite (Figure 2).

[14] There is an apparent systematic difference in $\delta^{13}\text{C}_{\text{org}}$, $\delta^{13}\text{C}_{\text{chit}}$, and $\delta^{13}\text{C}_{\text{scol}}$, with the fossil data being generally lower. Chitinozoans are ~0.5 to 1.5‰ lower than $\delta^{13}\text{C}_{\text{org}}$, and $\delta^{13}\text{C}_{\text{scol}}$ are ~0.5 to 1‰ lower than $\delta^{13}\text{C}_{\text{chit}}$, with an average difference of 0.6‰ (single exception in sample LU 121 at +11.2 m). The difference in $\delta^{13}\text{C}$ between

chitinozoans and scolecodonts is not constant, however, and differs between samples. Nevertheless, there seems to be a trend in these data: in the lower section (between 0 m and +3 m) the difference is significantly less than average (well below 0.5‰), in the middle section (+3 m to ~+10 m) it rises higher than average (between 0.8 and 1‰), and in the upper section roughly from the *Phaulactis* layer upward (+10–12 m and above), it drops again below average values (< 0.5‰).

5. Discussion

[15] Chitinozoan egg-cases, frequently found in Ordovician to Devonian strata, have a different preservation potential than their weak-bodied parent organisms, currently unknown from the fossil record [*Paris and Nölvak*, 1999]. This is probably due to differences in organic compounds between the egg-cases and organisms, which might imply a certain degree of isotope fractionation. However, because this has not yet been quantified in the Paleozoic, we will treat $\delta^{13}\text{C}$ of chitinozoan egg-cases as identical, or very close to that of the chitinozoan parent animals. Similarly, fossilizing scolecodonts must have had a significantly different original organic composition than their soft-bodied polychaete hosts, which are extremely rare in the fossil record [*Eriksson et al.*, 2004], entailing a fractionation that we cannot quantify here.

[16] The $\delta^{13}\text{C}_{\text{chit}}$ data are consistently higher (by 0.5 to 1.5‰) than $\delta^{13}\text{C}_{\text{scol}}$. This is in contrast to what might be expected from their hypothetical position in the Silurian food chain sketched in the introduction, assuming that “you are what you eat plus a few per mil” applies [*DeNiro and Epstein*, 1976, 1978], and that chitinozoans did not biologically fractionate carbon isotopes in a particularly unusual way. Instead, $\delta^{13}\text{C}$ signatures of the scolecodonts, lighter than those of both the whole rock and chitinozoans, may in part be a function of their habitat,

Table 2. $\delta^{13}\text{C}$ From the Luskint Section

Sample	Height in Section (m)	$\delta^{13}\text{C}_{\text{org}}$ Marl	$\delta^{13}\text{C}_{\text{org}}$ Limestone	Scolecodont Weight (mg)	$\delta^{13}\text{C}_{\text{scol}}$	Chitinozoan Weight (mg)	$\delta^{13}\text{C}_{\text{chit}}$	Difference Between $\delta^{13}\text{C}$ of Palynomorphs
Lu 1	0.00	-27.63						
Lu 3	0.20		-27.40					
Lu 4	0.30		-27.66					
Lu 5	0.40		-27.71					
Lu 6	0.50		-27.62	0.03	-28.80	0.05	-28.39	0.41
Lu 7	0.60		-27.65					
Lu 8	0.70		-27.36					
Lu 9	0.80		-27.39					
Lu 10	0.90		-27.91	0.05	-28.61	0.04	-28.44	0.17
Lu 11	1.00	-27.63						
Lu 12	1.10		-27.52					
Lu 13	1.20		-27.22					
Lu 14	1.30	-27.70						
Lu 15	1.40	-27.77						
Lu 16	1.50		-28.21					
Lu 17	1.60	-27.69						
Lu 18	1.70	-27.71						
Lu 19	1.80	-27.91						
Lu 20	1.90		-27.95	0.03	-29.17	0.04	-28.84	0.33
Lu 21	2.00		-27.98					
Lu 22	2.10		-27.91					
Lu 23	2.20		-27.86					
Lu 24	2.30		-28.07					
Lu 25	2.40		-27.50					
Lu 26	2.50		-27.84					
Lu 27	2.60		-28.17					
Lu 28	2.70		-27.71					
Lu 29	2.80	-27.54						
Lu 30	2.90			0.05	no signal	0.03	-28.15	
Lu 31	3.00		-27.45					
Lu 32	3.10	-27.70						
Lu 33	3.20		-27.57					
Lu 34	3.30		-27.55					
Lu 35	3.40	-28.09						
Lu 36	3.50	-28.37						
Lu 37	3.60		-27.96					
Lu 39	3.80	-28.10						
Lu 40	3.90		-28.13	0.04	-29.72	0.05	-28.87	0.85
Lu 41	4.00	-28.05						
Lu 42	4.10		-27.96					
Lu 43	4.25		-28.17					
Lu 44	4.40		-27.91					
Lu 45	4.50		-27.96					
Lu 46	4.60		-27.99					
Lu 47	4.70		-27.90					
Lu 48	4.80		-27.53					
Lu 49	4.90	-27.55						
Lu 50	5.00	-27.59						
Lu 51	5.10	-28.01						
Lu 52	5.20		-27.90					
Lu 53	5.30							
Lu 54	5.40	-28.04						
Lu 55	5.50	-28.32						
Lu 56	5.60		-27.86					
Lu 57	5.70	-27.99						
Lu 58	5.80		-28.08					
Lu 59	5.90		-28.27					
Lu 60	6.00		-28.41					
Lu 61	6.10		-28.48					
Lu 62	6.20		-28.70					

Table 2. (continued)

Sample	Height in Section (m)	$\delta^{13}\text{C}_{\text{org}}$ Marl	$\delta^{13}\text{C}_{\text{org}}$ Limestone	Scolecodont Weight (mg)	$\delta^{13}\text{C}_{\text{scol}}$	Chitinozoan Weight (mg)	$\delta^{13}\text{C}_{\text{chit}}$	Difference Between $\delta^{13}\text{C}$ of Palynomorphs
Lu 63	6.30		-28.33					
Lu 64	6.40		-28.00					
Lu 65	6.50	-27.70						
Lu 66	6.60		-27.19	0.03	-29.60	0.07	-28.55	1.05
Lu 68	6.70	-28.24						
Lu 69	6.80		-28.69					
Lu 70	6.90	-28.47						
Lu 71	7.00		-28.16	0.04	-29.97	0.05	-28.98	0.99
Lu 72	7.10		-28.19					
Lu 73	7.20		-28.33					
Lu 74	7.30		-28.24					
Lu 75	7.40		-28.40					
Lu 76	7.50		-28.52					
Lu 77	7.60		-28.17					
Lu 78	7.70		-28.25					
Lu 79	7.80		-27.84					
Lu 80	7.90	-27.99						
Lu 81	8.00	-27.85						
Lu 82	8.10		-27.92					
Lu 83	8.20		-28.10					
Lu 84	8.30		-27.67	0.04	-29.67	0.05	-28.83	0.84
Lu 85	8.40	-28.57						
Lu 86	8.50		-27.92					
Lu 87	8.60		-28.10					
Lu 88	8.70		-27.67					
Lu 89	8.80		-28.39					
Lu 90	8.90		-28.27	0.02	-29.79	0.02	-29.00	0.78
Lu 91	9.00	-28.81						
Lu 92	9.10		-28.37					
Lu 93	9.20		-28.19					
Lu 94	9.30		-28.15					
Lu 95	9.40		-28.35					
Lu 96	9.50		-28.47					
Lu 97	9.60		-28.05					
Lu 99	9.90		-28.09					
Lu 100	10.00		-29.03	0.11	no signal	0.05	-28.46	
Lu 101	10.10		-28.08					
Lu 103	10.30		-28.40					
Lu 104	10.40		-27.24					
Lu 105	10.50		-27.58					
Lu 106	10.60		-27.87					
Lu 107	10.70		-27.65					
Lu 108	10.80	-27.72						
Lu 109	10.90		-27.97					
Lu 110	11.00		-27.93					
Lu 111	11.10		-27.80					
Lu 112	11.20		-27.33	0.05	-28.23	0.06	-28.72	0.49
Lu 113	11.30							
Lu 114	11.40		-27.54					
Lu 115	11.50							
Lu 116	11.60		-27.41					
Lu 117	11.70		-27.81					
Lu 118	11.80		-27.87					
Lu 119	11.90		-27.95					
Lu 120	12.00		-27.68					
Lu 121	12.10		-27.53	0.05	-29.24	0.07	-28.80	0.43
Lu 122	12.20		-27.61					
Lu 123	12.30		-27.42					
Lu 124	12.40		-27.37					
Lu 125	12.50		-25.45					

Table 2. (continued)

Sample	Height in Section (m)	$\delta^{13}\text{C}_{\text{org}}$ Marl	$\delta^{13}\text{C}_{\text{org}}$ Limestone	Scolecodont Weight (mg)	$\delta^{13}\text{C}_{\text{scol}}$	Chitinozoan Weight (mg)	$\delta^{13}\text{C}_{\text{chit}}$	Difference Between $\delta^{13}\text{C}$ of Palynomorphs
Lu 126	12.60		-27.41					
Lu 127	12.70		-27.26					
Lu 128	12.80		-27.37					
Lu 129	12.90		-27.56					
Lu 130	13.00		-28.60					
Lu 131	13.10		-27.31					
Lu 132	13.20		-27.50					
Lu 133	13.30		-27.42					
Lu 134	13.40		-27.50					
Lu 135	13.50		-27.45	0.02	-28.32	0.06	-27.98	0.34
Lu 136	13.60		-27.25					
Lu 137	13.70		-27.92					
Lu 138	13.80		-27.33					
Lu 139	13.90		-27.89					
Lu 140	14.00		-27.45					
Lu 141	14.10		-28.10	0.05	-28.06	0.05	-27.70	0.37
Lu 142	14.20		-27.50					
Lu 143	14.30		-27.40					
Lu 144	14.40		-27.32					
Lu 145	14.50		-27.31					
Lu 146	14.60		-27.69					
Lu 147	14.70		-27.41					
Lu 148	14.80		-27.70					
Lu 149	14.90		-28.11					
Lu 150	15.00		-27.31					
Lu 151	15.10		-27.25					
Lu 152	15.20		-27.34					
Lu 153	15.30		-27.48					
Lu 154	15.40		-27.58					
Lu 155	15.50		-27.38	0.10	no signal	0.04	-27.66	
							Average:	0.59

on or within the sea bed of the Silurian Gotland shelf. We suggest that (part of) these jaw-bearing polychaetes were burrowing in the sea bottom, consuming ^{12}C -enriched organic matter, or in contact with bacterially respired CO_2 , explaining the light $\delta^{13}\text{C}_{\text{scol}}$ values of their fossilized jaws. Alternatively, the dissolved carbon flux on the seafloor may be derived from organic-bearing sediments depending on the redox state at the sediment-water interface.

[17] $\delta^{13}\text{C}_{\text{chit}}$ and $\delta^{13}\text{C}_{\text{scol}}$ contribute to, but are both lower than $\delta^{13}\text{C}_{\text{org}}$, so an isotopically heavier component must also exist in the system. An important group of palynomorphs, the acritarchs, have not been analyzed, because of their very small size. Nevertheless, acritarch census from the (~8 Myr younger) Lau Event on Gotland shows that acritarchs and other primary producers make up the bulk of the number of fossilized palynomorphs specimens in the pre-event interval, with up to several thousand specimens per gram of sediment [Stricanne et al., 2006]. However, we hypothesize that acritarchs, believed to be primary producers

[Servais et al., 2008], produced lighter rather than heavier $\delta^{13}\text{C}$ values relative to the other organic fossil components (Figure 3A). Still, other Early Paleozoic “consumers” with a $\delta^{13}\text{C}$ lower than “producers” have been reported before: graptolites and scolecodonts from the Prague Basin are isotopically lighter than leiosphere-phytoplankton from the same samples [Lécuyer and Paris, 1997]. Another potential, and perhaps more likely source of heavier C isotopes, is present in the organic fraction residues; a relatively important weight-percentage fraction of the organic carbon can consist of nonpalynomorph, amorphous organic matter, of unknown origin.

[18] There is an intriguing increase in the difference between $\delta^{13}\text{C}_{\text{chit}}$ and $\delta^{13}\text{C}_{\text{scol}}$ (~0.8–1‰) in the middle part of the Lusklint trench, roughly between +3 and +10 m, which seems to result from the lower values of the scolecodonts (while chitinozoan values remain relatively more constant). So far, we have discussed the offset between chitinozoan and scolecodont $\delta^{13}\text{C}$ as function of different biological

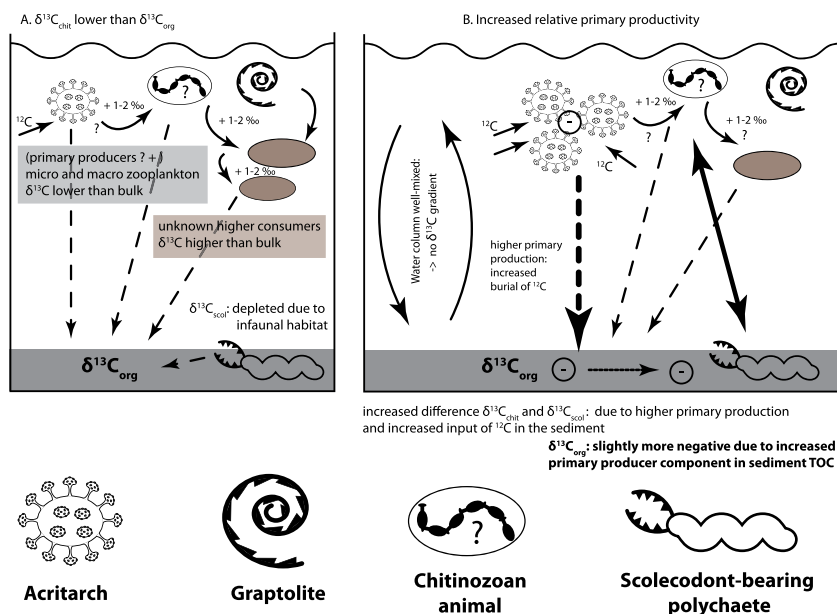


Figure 3. (A) An explanation of the data as a “classic” Silurian food chain. This scenario predicts that $\delta^{13}\text{C}$ of acritarchs (primary producers), if analysed, would at least be 1 to 2‰ lower than those of chitinozoans (low-level consumers?), based on *DeNiro and Epstein* [1976, 1978]. The consequence of such a hypothesis is that an important part of the unidentified (amorph) organic matter has to have a consistently much more positive $\delta^{13}\text{C}$ than the bulk organic material (e.g., of metazoan origin from higher trophic levels). When this material is buried together with the isotopically much lighter components (acritarchs, chitinozoans, scolecodonts) it produces the bulk organic signal (Figure 2). The relatively light scolecodont $\delta^{13}\text{C}$ values can at least be partly explained if they had an infaunal benthic mode of life. (B) The increasing offset between chitinozoans and scolecodonts in this scenario is largely caused by the lower values of the scolecodonts (which is consistent with the raw data), in turn caused by an increased input of microphytoplankton to the sediment during periods of increased primary productivity. When this period of high productivity ended, potentially linked to the start of the Ireviken extinction event, the offset between chitinozoans and scolecodonts reduced, and the $\delta^{13}\text{C}_{\text{org}}$ shifted positively by about 1‰.

fractionations within the fossil groups, their different organic compound composition and subsequent preservation, and their different habitat. Faunal turnovers within the scolecodont group could provide an explanation for the observed pattern. Their diversity curves at generic level for the Visby beds [*Eriksson* 2006, Figure 3, page 93] do display important changes in the genus composition of the scolecodont fauna, but, in detail, these do not exactly reflect the pattern we observe. In addition to biological factors, we are therefore looking for a changing external factor that will mainly (or only) influence the environment in which the scolecodont-bearing polychaetes lived, i.e., the sediments in the sea bottom.

[19] $\delta^{13}\text{C}$ fluctuations can also be driven by variations in primary productivity in these shelf waters, not affecting individual chitinozoans (assuming they do not start consuming more acritarchs simply because they are available). Instead, the increased input of microphytoplankton to the sediment could

affect the carbon pool and eventually the diet of the polychaetes (Figure 3B). A consecutive drop in primary productivity would then explain the reduced difference of $\delta^{13}\text{C}$ between chitinozoans and scolecodonts at $\sim +10$ m in the section.

[20] Fossil acritarch census data (number of specimens per gram of rock) do not provide direct information on primary productivity, but can be used as a proxy for productivity in combination with other data. Such census data are available from a segment of the Lusklint 1 section (Figure 4), as part of a study on the extinction and origination pattern of acritarchs through the Lusklint 1 section [*Gelsthorpe*, 2004]. In general, the high acritarch counts in the lower part of the *Gelsthorpe* [2004] section (between $\sim +7.5$ and 10.5 m in Figure 2) confirm our interpretation of the isotope data in terms of increased productivity, and low acritarch counts above the Ireviken bentonite (between $\sim +10.5$ and 15 m in Figure 2) are in accordance with our suggested decrease in primary productivity. Only the low acritarch counts in the first

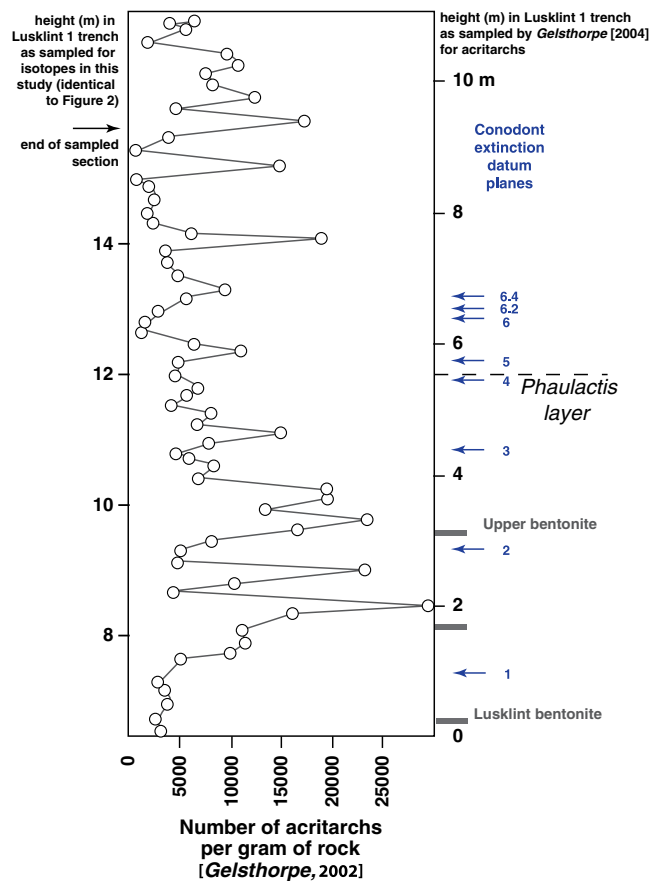


Figure 4. Acritarch census data, previously only available in a (partly unpublished) Ph.D. thesis, are reproduced here [Gelsthorpe, 2002]. For details on sampling, see Gelsthorpe [2004]; for details on methodology, see Gelsthorpe [2002]. Unfortunately, the trench section sampled by Gelsthorpe [2002, 2004] does not fully overlap with the one sampled in this paper. The original measured section (including the position and nomenclature of marker beds used) of Gelsthorpe [2002] is given on the far right of the figure, for completeness, and for easy comparison with the acritarch turnover data [Gelsthorpe, 2004]. This correlates well with the measured section used to collect the isotope samples, although there are some unavoidable, small differences. The latter measurements are given on the far left of the figure (and match those of Figure 2). All measured heights in the column given in the text, refer to the section measured for isotope samples (far left of this figure, or Figure 2). The Lusklint bentonite has been used as reference level for correlation between both stratigraphic frameworks.

sampled meter of the Gelsthorpe [2004] log (between ~ +6.5 and 7.5 m in Figure 2) are difficult to explain.

[21] In terms of diversity, acritarchs did not suffer much during the Ireviken Event, where overall the number of originations was higher than the number of extinctions. Acritarch species that went extinct, essentially did so above datum 6 of the conodont extinction event, i.e., well above the positive shift in our $\delta^{13}\text{C}_{\text{org}}$ data (just above datum 2). Acritarch originations occur throughout the section [Gelsthorpe, 2004]. The $\delta^{13}\text{C}_{\text{org}}$ shift thus seems to be unrelated to acritarch turnover events at species level.

[22] The interpreted productivity changes would also have implications for the amount and preservation of primary producers in relation to other organic components making up the whole rock

carbon (Figure 3), and thus for $\delta^{13}\text{C}_{\text{org}}$. Our data do not allow us to discriminate whether this mechanism has triggered the shift to lower $\delta^{13}\text{C}_{\text{org}}$ values through the Lower Visby Formation, or only provided positive feedback for a trend that already started below the sampled section (unexposed on Gotland). In addition, there is a striking correlation between the interpreted productivity drop based on the $\delta^{13}\text{C}_{\text{chit}}-\delta^{13}\text{C}_{\text{scol}}$ comparison, the stepped 1‰ increase in $\delta^{13}\text{C}_{\text{org}}$ at 10.5 m, and the drop in number of acritarchs per gram of sediment [Gelsthorpe, 2004]. Moreover, a drop in primary productivity, evidenced by decreasing relative and absolute acritarch/sphaeromorph/prasinophyte abundances, has been reported at the onset of the Lau event on Gotland, one of the main other “events” in the Silurian [Stricanne et al., 2006], and has been

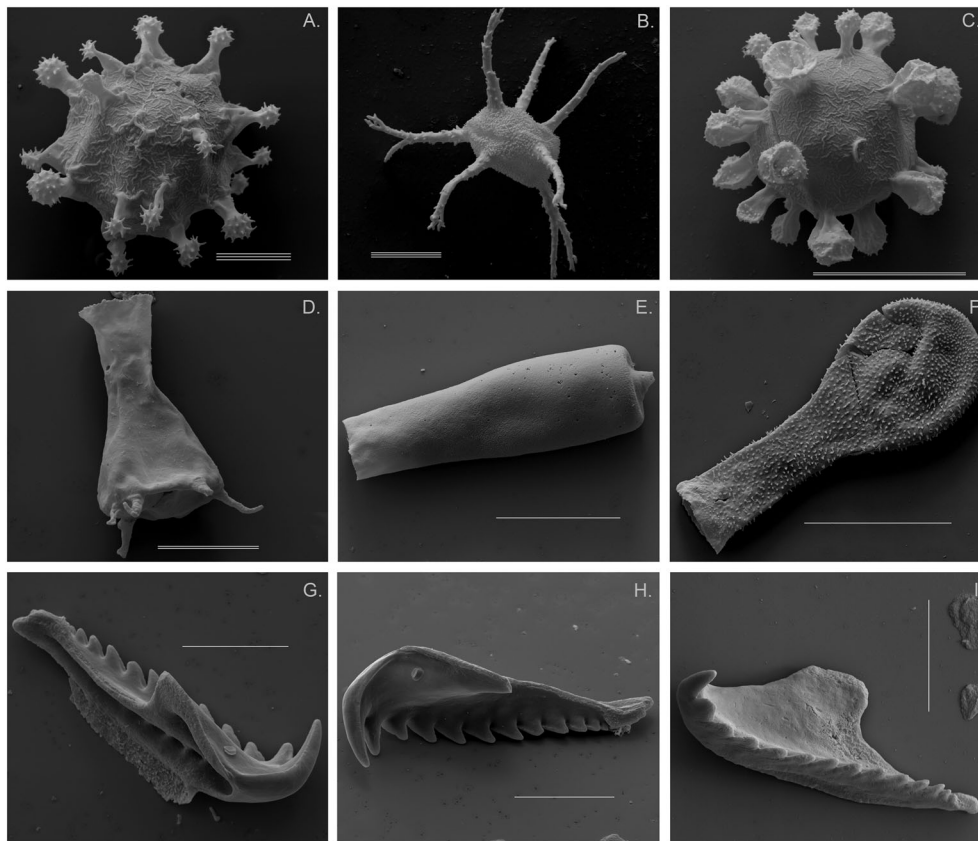


Figure 5. Palynomorphs discussed in the text. All specimens are from sample Lu100. Acritarchs: (A) *Visbysphaera* sp., (B) *Diexallophasis remota*, and (C) *Visbysphaera* sp. Chitinozoans: (D) *Ancyrochitina* sp., (E) *Conochitina visbyensis*, and (F) *Angochitina longicollis*. Scolecodonts: (G–I) *Oeononites* spp. Single-scale bar: 100 μm ; double-scale bar: 50 μm ; triple-scale bar: 20 μm .

suggested as a potential general trigger for the Llandovery-Wenlock $\delta^{13}\text{C}_{\text{carb}}$ excursions [Cramer and Saltzman, 2007a]. This included the $\delta^{13}\text{C}_{\text{carb}}$ excursion at the Ireviken Event, although here we note a stratigraphic offset of a couple of meters between the $\delta^{13}\text{C}_{\text{org}}$ event / suggested drop in biodiversity (between datum 2 and 3) and the onset of the $\delta^{13}\text{C}_{\text{carb}}$ excursion (at the *Phaulactis* layer, i.e., at datum 4).

[23] Changes in the offset between $\delta^{13}\text{C}_{\text{chit}}$ and $\delta^{13}\text{C}_{\text{scol}}$, and a 1‰ shift in the $\delta^{13}\text{C}_{\text{org}}$ at the very beginning of the Ireviken extinction event, suggest a link between the extinction of certain groups or species and the way carbon is distributed in this biotope and its sediments. Overall trends in $\delta^{13}\text{C}_{\text{chit}}$ and $\delta^{13}\text{C}_{\text{scol}}$ follow those in $\delta^{13}\text{C}_{\text{org}}$. The necessity of using isolated palynomorphs (Figure 5), a time-consuming and expensive protocol, as compared to bulk organic matter (or “whole rock”) seems low if the objective of the study is to observe general trends in $\delta^{13}\text{C}_{\text{org}}$ signatures. However, this conclusion should not be generalized for other

sections, especially not those more prone to reworking of fossils and sediments.

[24] Sudden, short-lived variation is even more difficult to explain, and may mainly represent changing local conditions. The Storbrut and Ireviken bentonites seem to be associated with a rapid change from more positive values before the events, to more negative values afterwards, and there might be a causal link between the bentonites and $\delta^{13}\text{C}_{\text{org}}$ anomalies. However, a plausible mechanism has not yet been defined. Similarly, some of the extinction events seem to be preceded by minima in $\delta^{13}\text{C}_{\text{org}}$ (e.g., datums 1, 3, 4/5, and 6); however, since these minima mostly are well within the overall short-term variability of the $\delta^{13}\text{C}_{\text{org}}$ record, their significance, if any, remains speculative.

6. Conclusions

1. In the Luskint section (Llandovery-Wenlock of E. Sweden) $\delta^{13}\text{C}_{\text{org}}$ is consistently higher than $\delta^{13}\text{C}_{\text{chit}}$ and $\delta^{13}\text{C}_{\text{scol}}$.

2. There is a rising trend in the difference in $\delta^{13}\text{C}_{\text{chit}}$ and $\delta^{13}\text{C}_{\text{scol}}$ through the lower part of the section, decreasing again at the start of the Ireviken Event, below the *Phaulactis* layer.
3. The difference between $\delta^{13}\text{C}_{\text{chit}}$ and $\delta^{13}\text{C}_{\text{scol}}$ could, to a certain degree, reflect biological fractionation or biochemical “vital” effects, but can also, at least partly, be explained by their respective epiplanktonic and (infaunal?) benthic mode of life, the latter group perhaps taking up more bacterially respired CO_2 from within the sediment.
4. This $\delta^{13}\text{C}$ difference between the fossil groups is not constant, but displays a trend through the section. Therefore, it must be amplified by environmental change; here we suggest that increased contrast might be due to increased primary productivity, dropping back to background just before, or at the start of, the Ireviken Event. This is largely confirmed by the available acritarch abundance data. This increased productivity may also have triggered or enhanced the declining $\delta^{13}\text{C}_{\text{org}}$ trend through the Lower Visby Formation, while the return to normal or reduced production could have influenced the 1‰ $\delta^{13}\text{C}_{\text{org}}$ abrupt “step” or excursion, a few meters below the onset of the “Ireviken Event” $\delta^{13}\text{C}_{\text{carb}}$ excursion. The changes in the carbon cycle, expressed through the combined $\delta^{13}\text{C}$ data at the very beginning of the Ireviken extinction event suggest a relatively close tie between the both perturbations, although the exact cause-and-effect relations remain unclear.
5. All three components measured for $\delta^{13}\text{C}$ show similar curves suggesting that the carbon isotope variations seen in the Gotland section are to a large degree influenced by carbon cycle fluctuations beyond the Baltic shelf environment, and therefore at least regional rather than local process related.

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References

- Bergström, S. M., X. Chen, J. C. Gutiérrez-Marco, and A. Dronov (2009), The new chronostratigraphic classification of the Ordovician System and its relations to major regional series and stages and to $\delta^{13}\text{C}$ chemostratigraphy, *Lethaia*, *42*, 97–107.
- Bickert, T., J. Pätzold, C. Samtleben, and A. Munnecke (1997), Paleoenvironmental changes in the Silurian indicated by stable isotopes in brachiopod shells from Gotland, Sweden, *Geochim. Cosmochim. Acta*, *61*, 2717–2730.
- Brand, U., K. Azmy, and J. Veizer (2006), Evaluation of the Salinic I tectonic, Cancañiri glacial and Ireviken biotic events: Biochemostratigraphy of the Lower Silurian succession in the Niagara Gorge area, Canada and U.S.A., *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *241*, 192–213.
- Brodie, C. R., M. J. Leng, J. S. L. Casford, C. P. Kendrick, J. M. Lloyd, Z. Yongqiang, and M. I. Bird (2011a), Evidence for bias in C and N concentrations and $\delta^{13}\text{C}$ composition of terrestrial and aquatic organic materials due to pre-analysis acid preparation methods, *Chem. Geol.*, *282*, 67–83, doi:10.1016/j.chemgeo.2011.01.007.
- Brodie, C. R., J. S. L. Casford, J. M. Lloyd, M. J. Leng, T. H. E. Heaton, C. P. Kendrick, and Z. Yongqiang (2011b), Evidence for bias in C/N, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of bulk organic matter, and on environmental interpretation, from a lake sedimentary sequence by pre-analysis acid treatment methods, *Quat. Sci. Rev.*, *30*, 3076–3087, doi:10.1016/j.quascirev.2011.07.003.
- Calner, M., L. Jeppsson, and A. Munnecke (2004), The Silurian of Gotland - Part I: Review of the stratigraphic framework, event stratigraphy, and stable carbon and oxygen isotope development, *Erlanger geologische Abhandlungen – Sonderband*, *5*, 113–131.
- Calner, M., L. Jeppsson, and M. E. Eriksson (2005), The Baltic basin and the Silurian strata of Gotland, Sweden, *SGU Rapport och Meddelanden*, *121*, 6–14.
- Cohen, K. M., S. Finney, and P. L. Gibbard (2012), International Chronostratigraphic chart. Chart reproduced for the 2012 Brisbane 34th International Geological Congress. International Commission on Stratigraphy.
- Correia, M. (1967), Relations possibles entre l'état de conservation des éléments figurés de la matière organique (microfossiles palynoplantologiques) et l'existence de gisements d'hydrocarbures, *Revue de l'Institut Français du Pétrole*, *22*(9), 1285–1306.
- Cramer, B. D., and M. R. Saltzman (2005), Sequestration of ^{12}C in the deep ocean during the early Wenlock (Silurian) positive carbon isotope excursion, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *219*, 333–349.
- Cramer, B. D., and M. R. Saltzman (2007a), Fluctuations in epicontinental sea carbonate production during Silurian positive carbon isotope excursions: A review of proposed paleoceanographic models, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *245*, 37–45.
- Cramer, B. D., and M. R. Saltzman (2007b), Early Silurian paired $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ analyses from the Midcontinent



- of North America: Implications for paleoceanography and paleoclimate, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **256**, 195–203
- Cramer, B. D., D. K. Loydell, C. Samtleben, A. Munnecke, D. Kaljo, P. Männik, T. Martma, L. Jeppsson, M. A. Kleffner, J. E. Barrick, C. A. Johnson, P. Emsbo, M. M. Joachimski, T. Bickert, and M. R. Saltzman (2010), Testing the limits of Paleozoic chronostratigraphic correlation via high-resolution (<500,000 yrs) integrated conodont, graptolite, and carbon isotope ($\delta^{13}\text{C}_{\text{carb}}$) biochemostratigraphy across the Llandovery-Wenlock boundary: Is a unified Phanerozoic timescale achievable?, *Geol. Soc. Am. Bull.*, **122**, 1700–1716, doi:10.1130/B26602.1
- Cramer, B. D., C. E. Brett, M. J. Melchin, P. Männik, M. A. Kleffner, P. I. McLaughlin, D. K. Loydell, A. Munnecke, L. Jeppsson, C. Corradini, F. R. Brunton, and M. R. Saltzman (2011), Revised correlation of Silurian Provincial Series of North America with global and regional chronostratigraphic units and $\delta^{13}\text{C}_{\text{carb}}$ chemostratigraphy, *Lethaia*, **44**, 185–202.
- Cramer, B. D., D. J. Condon, U. Söderlund, C. Marshall, G. J. Worton, A. T. Thomas, M. Calner, D. C. Ray, V. Perrier, I. Boomer, P. J. Patchett, and L. Jeppsson (2012), U-Pb (zircon) age constraints on the timing and duration of Wenlock (Silurian) paleocommunity collapse and recovery during the ‘Big Crisis’, *Geol. Soc. Am. Bull.*, **124** (11/12), 1841–1857, doi:10.1130/B30642.1
- DeNiro, M. J., and S. Epstein (1976), You are what you eat (plus a few ‰): the carbon isotope cycle in food chains, *Geol. Soc. Am. Abstr. Progr.*, **8**, 834–835.
- DeNiro, M. J., and S. Epstein (1978), Influence of diet on the distribution of carbon isotopes in animals, *Geochim. Cosmochim. Acta*, **42**, 495–506.
- Eriksson, M. E., C. F. Bergman, and L. Jeppsson (2004), Silurian scolecodonts, *Rev. Palaeobot. Palynol.*, **131**, 269–300.
- Eriksson, M. E. (2006), The Silurian Ireviken Event and vagile benthic faunal turnovers (Polychaeta; Eunicida) on Gotland, Sweden, *GFF*, **128**(2), 91–95.
- Gelsthorpe, D. N. (2002), Microplankton changes through the Early Silurian Ireviken extinction Event on Gotland, Sweden, PhD thesis, University of Leicester, Leicester, UK.
- Gelsthorpe, D. N. (2004), Microplankton changes through the early Silurian Ireviken extinction event on Gotland, Sweden, *Rev. Palaeobot. Palynol.*, **130**, 89–103.
- Hinga, K. R., M. A. Arthur, M. E. Q. Pilson, and D. Whitaker (1994), Carbon isotope fractionation by marine phytoplankton in culture: the effects of CO_2 concentration, pH, temperature, and species, *Global Biogeochem. Cycles*, **8**, 91–102.
- Jeppsson, L. (1983), Silurian conodont faunas from Gotland, *Fossils and Strata*, **15**, 121–144.
- Jeppsson, L. (1987), Lithological and conodont distributional evidence for episodes of anomalous oceanic conditions during the Silurian, in *Palaeobiology of Conodonts*, edited by R. J. Aldridge, pp. 129–145, Ellis Horwood Ltd., Chichester.
- Jeppsson, L., R. J. Aldridge and K. J. Dorning (1995), Wenlock (Silurian) oceanic episodes and events, *J. Geol. Soc. (London)*, **152**, 487–498.
- Jeppsson, L., M. Calner, and M. Eriksson (2005), Locality descriptions, in *The dynamic Silurian Earth, Subcommittee on Silurian Stratigraphy Field Meeting 2005 – Field Guide and Abstracts, SGU Rapport och Meddelanden 121*, edited by M. E. Eriksson and M. Calner, pp. 22–56.
- Könitzer, S. F., M. J. Leng, S. J. Davies, and M. H. Stephenson (2012), An assessment of geochemical preparation methods prior to organic carbon concentration and carbon isotope ratio analyses of fine-grained sedimentary rocks, *Geochem. Geophys. Geosyst.*, **13**, Q0AI02, doi:10.1029/2012GC004094.
- Kroopnick, P., R. F. Weiss, and H. Craig (1972), Total CO_2 , ^{13}C and dissolved oxygen $-^{18}\text{O}$ At Geosecs II in the North Atlantic, *Earth Planet. Sci. Lett.*, **16**, 103–110.
- LaPorte, D. F., C. Holmden, W. P. Patterson, J. D. Loxton, M. J. Melchin, C. E. Mitchell, S. C. Finney, and H. D. Sheets (2009), Local and global perspectives on carbon and nitrogen cycling during the Hirnantian glaciation, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **276**(1–4), 182–195.
- Laufeld, S. (1974), Silurian Chitinozoa from Gotland, *Fossils and Strata*, **5**, 1–130.
- Laws, E. A., B. N. Popp, N. Cassar, and J. Tanimoto (2002), ^{13}C discrimination patterns in oceanic phytoplankton: likely influence of CO_2 concentrating mechanisms, and implications for palaeoreconstructions, *Funct. Plant Biol.*, **29**, 323–333.
- Lécuyer, C., and F. Paris (1997), Variability in the $\delta^{13}\text{C}$ of lower Palaeozoic palynomorphs: implications for the interpretation of ancient marine sediments, *Chem. Geol.*, **138**, (3–4), 161–170.
- Lehnert, O., P. Männik, M. M. Joachimski, M. Calner, and J. Fryda (2010), Palaeoclimate perturbations before the Sheinwoodian glaciation: A trigger for extinctions during the ‘Ireviken Event’, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **296**, 320–331.
- Lo Duca, S. T., and L. M. Pratt (2002), Stable carbon-isotope compositions of compression fossils from lower Paleozoic Konservat-Lagerstätten, *Palaaios*, **17**(3), 287–291.
- Munnecke, A., and C. Samtleben (1996), The formation of micritic limestones and the development of limestone-marl alternations in the Silurian of Gotland, Sweden, *Facies*, **34**, 159–176.
- Munnecke, A., and T. Servais (1996), Scanning electron microscopy of polished, slightly etched rock surfaces: a method to observe palynomorphs in situ, *Palynology*, **20**, 163–176.
- Munnecke, A., and T. Servais (2008), Palaeozoic calcareous plankton: evidence from the Silurian of Gotland, *Lethaia*, **41**, 185–194.
- Munnecke, A., T. Servais, and D. Vachard (2000), A new family of calcareous microfossils from the Silurian of Gotland, Sweden, *Palaeontology*, **43**, 1153–1172.
- Munnecke, A., C. Samtleben, and T. Bickert (2003), The Ireviken Event in the lower Silurian of Gotland, Sweden – relation to similar Palaeozoic and Proterozoic events, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **195**, 99–124.
- Munnecke, A., M. Calner, D. A. T. Harper, and T. Servais (2010), Ordovician and Silurian sea-water chemistry, sea level, and climate: a synopsis, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **296**(3–4), 389–413.
- Nitecki, M. H., and N. Spjeldnaes (1993), Silurian noncalcareous algae from Gotland, in *Studies on Fossil Benthic Algae*, Bollettino della Società Paleontologica Italiana, Spec. vol. 1, edited by F. Barattolo and P. De Castro, pp. 345–351.
- Noble, P. J., A. C. Lenz, C. Holmden, M. Masiak, M. K. Zimmermann, S. R. Poulson, and A. Kozłowska, (2012) Isotope geochemistry and plankton response to the Ireviken (earliest Wenlock) and *Cyrtograptus lundgreni* extinction events, Cape Phillips Formation, Arctic Canada, in *Earth and Life*, edited by J. Talent, pp. 631–652, Springer, Berlin.
- Pancost, R. D., K. H. Freeman, and M. E. Patzkowsky, (1999), Organic-matter source variation and the expression of a late Middle Ordovician carbon-isotope excursion, *Geology*, **27**, 1015–1018.



- Paris, F., and J. Nölvak (1999), Biological interpretation and paleobiodiversity of a cryptic fossil group: The “chitinozoan-animal”, *Geobios*, *32*, 315–324.
- Paris, F., B. Videt, J.-F. Ghienne, P. Tang, and S. De La Puente (2008), Factors susceptible to alter the original $\delta^{13}\text{C}_{\text{org}}$ signal in Early Palaeozoic marine sediments, paper presented at the Palaeozoic Climates International Congress, Closing Meeting of the International Geoscience Programme (IGCP) n° 503 ‘Ordovician Palaeogeography and Palaeoclimate’, Lille, August 23-31, 2008, France, Abstract: 74.
- Popp, B. N., P. Parekh, B. Tilbrook, R. R. Bidigare, and E. A. Laws (1997), Organic carbon $\delta^{13}\text{C}$ variations in sedimentary rocks as chemostratigraphic and paleoenvironmental tools, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *132*, 119–132.
- Popp, B. N., E. A. Laws, R. R. Bidigare, J. E. Dore, K. L. Hanson, and S. G. Wakeham (1998), Effect of phytoplankton cell geometry on carbon isotopic fractionation, *Geochim. Cosmochim. Acta*, *62*, 69–77.
- Samtleben, C., A. Munnecke, T. Bickert, and J. Pätzold (1996), The Silurian of Gotland (Sweden): Facies interpretation based on stable isotopes in brachiopod shells, *Geologische Rundschau*, *85*, 278–292.
- Servais, T., O. Lehnert, J. Li, G. L. Mullins, A. Munnecke, A. Nützel, and M. Vecoli (2008), The Ordovician Biodiversification: revolution in the oceanic trophic chain, *Lethaia*, *41*, 99–109.
- Snelling A. M., M. J. Leng, J. A. Zalasiewicz, C. C. Kendrick, and A. A. Page (2011), Carbon isotope composition of graptolite periderm and whole-rock from the Aeronian (Silurian, Llandovery) in Wales and Scotland and its use in chemostratigraphy, *Proc. Geol. Assoc.*, *122*, 82–91.
- Stricanne, L., A. Munnecke, and J. Pross (2006), Assessing mechanisms of environmental change: Palynological signals across the late Ludlow (Silurian) positive isotope excursion ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) on Gotland, Sweden, *Palaeogeogr. Palaeoclimatol. Palaeoecol.* *230*, 1–31.
- Vandenbroucke, T. R. A., H. A. Armstrong, M. Williams, F. Paris, K. Sabbe, J. A. Zalasiewicz, J. Nölvak, and J. Verniers (2010a), Epipelagic chitinozoan biotopes map a steep latitudinal temperature gradient for earliest Late Ordovician seas: implications for a cooling Late Ordovician climate, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *294*, 202–219, doi:10.1016/j.palaeo.2009.11.026.
- Vandenbroucke, T. R. A., H. A. Armstrong, M. Williams, F. Paris, K. Sabbe, J. A. Zalasiewicz, J. Nölvak, J. Verniers, and T. Servais (2010b), Polar front shift and atmospheric CO_2 during the glacial maximum of the Early Paleozoic Icehouse, *Proc. Natl. Acad. Sci. U.S.A.*, *107* (no. 34), 14983–14986.
- Vandenbroucke, T. R. A., H. A. Armstrong, M. Williams, J. A. Zalasiewicz, and K. Sabbe (2009), Ground-truthing Late Ordovician climate models using the paleobiogeography of graptolites, *Palaeoceanography*, *24*, PA4202, doi:10.1029/2008PA001720
- Young, S.A., M. R. Saltzman, S. M. Bergström, S. A. Leslie, and X. Chen (2008), Paired $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ records of Upper Ordovician (Sandbian–Katian) carbonates in North America and China: implications for paleoceanographic change, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *270*, 166–178.