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## High-Resolution carbon isotope stratigraphy of the basal Silurian Stratotype (Dob's Linn, Scotland) and its global correlation

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**Abstract:** Since its designation as the Global Stratotype Section and Point (GSSP) for the base of the Silurian System, the choice of Dob's Linn, Southern Scotland, has received criticism due to the difficulties of relating its well-constrained graptolite biostratigraphy to shallow-water sequences elsewhere. Kerogen samples from across the Ordovician–Silurian boundary interval at Dob's Linn have yielded carbon stable-isotope signatures consistent with those recorded elsewhere, in particular showing a clear positive  $\delta^{13}\text{C}$  excursion in the terminal Ordovician. The architecture of the  $\delta^{13}\text{C}$  curve from Dob's Linn enables very high-resolution stratigraphic subdivision and direct correlation between the deep water Dob's Linn section and time-equivalent carbonate shelf deposits. An integrated stratigraphic scheme using isotope stratigraphy and biostratigraphy of graptolites, conodonts and shelly faunas has been constructed. This direct correlation shows that the shallow water successions, including the former stratotype candidate at Anticosti Island, are generally incomplete, with hiatuses related to the rapid sea-level changes during the Hirnantian stage. This confirms and greatly increases the global utility of Dob's Linn as a boundary stratotype.

**Keywords:**  $^{13}\text{C}$ , Ordovician, Silurian, graptolites, stratigraphy.

The Ordovician–Silurian boundary interval has long been known to represent a period of intense facies and faunal change, and the Hirnantian Stage of the Ashgill Series (latest Ordovician) is recognized as a period of major regression related to a short-lived glacial episode (Brenchley 1988; Brenchley *et al.* 1994). This glacial event is coincident with two major extinction events and the temporary establishment of eurytopic biotas such as the *Hirnantia* fauna (Brenchley 1988). The regressive phase is succeeded by a rapid transgression and radiation of some biotas, and it is within this transgressive episode that the basal Silurian boundary has been placed, marked by a distinct evolutionary burst within the graptolites (Rickards 1988).

Since the Global Stratotype Section and Point (GSSP) for the base of the Silurian System was chosen by the IUGS in May 1985 as the base of the *acuminatus* Zone at Dob's Linn in southern Scotland (Cocks & Rickards 1988), there have been several criticisms of this choice (e.g. Barnes 1988; Berry 1987; Lespérance *et al.* 1987) based largely on the dominantly graptolitic nature of the section and the difficulty in correlating it with other sections which contain a predominantly shelly fauna. The utility of the Dob's Linn section as the stratotype for the base of the Silurian would be significantly up-graded if boundary sections worldwide could be correlated independently of faunal content and depositional environment. Patterns of change in the ratio of stable isotopes of carbon ( $^{13}\text{C}/^{12}\text{C}$ ) preserved in both contemporary marine organic matter ( $\delta^{13}\text{C}_{\text{org}}$ ) and biogenic carbonate ( $\delta^{13}\text{C}_{\text{carb}}$ ) offer a potential method for worldwide correlation providing that factors controlling carbon isotope signals are synchronous and of a global scale. Because dissolved inorganic carbon in sea water is in isotopic equilibrium with the dissolved  $\text{CO}_2$  utilized by primary marine producers, any significant change in the global marine carbon cycle should be reflected in time-equivalent changes in the carbon isotopic composition of both  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_{\text{carb}}$ . Although the relationship between the

carbon isotope record preserved in organic matter and biogenic carbonate is far from simple (Hayes *et al.* 1989 and references therein), positive correlations between  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_{\text{carb}}$  (e.g. Knoll *et al.* 1986; Hayes *et al.* 1989) suggest that patterns of isotopic change, and in particular the architecture of individual isotopic excursions, may be used for chemostratigraphic correlation on both intra-basinal and inter-basinal scales (e.g. Gale *et al.* 1993; Magaritz *et al.* 1983; Mitchell 1995).

The general pattern of carbon isotope change for shelf carbonates across the Ordovician–Silurian boundary is well established on the basis of the analysis of whole-rock limestones and well-preserved brachiopods (Brenchley *et al.* 1994, 1995), and positive carbon isotope excursions reported from the boundary intervals are considered to reflect global-scale environmental change associated with the end-Ordovician glaciation (Brenchley *et al.* 1994). Despite the large differences in composition between carbon fixed in marine organic matter and carbon incorporated into biogenic carbonate ( $\Delta^{13}\text{C}_{\text{carb-org}}$  is about  $-28\%$ , Knoll *et al.* 1986; Hayes *et al.* 1989), the global nature of the  $\delta^{13}\text{C}_{\text{carb}}$  record across the Ordovician–Silurian boundary provides an opportunity to investigate correlations between  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{org}}$ , and to tie boundary section biostratigraphies preserved in both shallow- and deep-water sequences.

To date, the only attempt to document changing patterns of carbon isotope ratios preserved in organic matter in graptolite-bearing, Ordovician–Silurian rocks has been made using samples from Yichang, China (Xu *et al.* in Wang *et al.* 1993a). Nevertheless, the relationships between graptolite biostratigraphy, and hence position relative to the Ordovician–Silurian boundary, and the carbon isotope excursions remains uncertain. The possibility of a faunally independent means of correlation, using stable isotopes, between different facies and faunal realms offers a range of possibilities including: (a) the correlation of graptolite and conodont biozones and shelly 'faunas'

and the ability to detect diachroneity of biostratigraphic units; (b) the detection of hiatus horizons in formations where these are not readily evident from sedimentological criteria; (c) the correlation of physical, chemical and biological events across the boundary interval; (d) the sub-biozonal correlation of Ordovician–Silurian boundary sections.

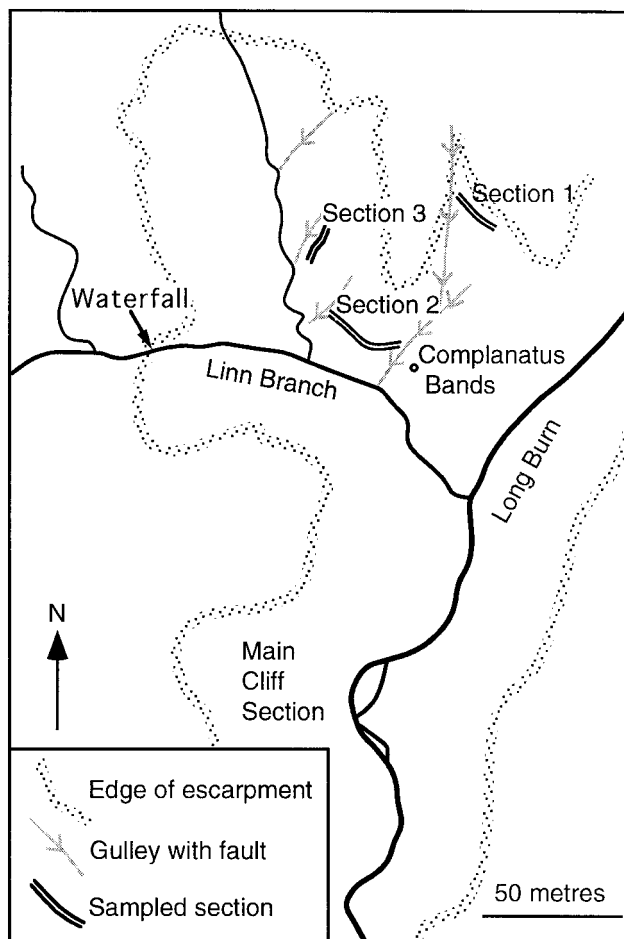
### Geological setting

The sections at Dob's Linn expose a small, tectonically complex inlier within the Central Belt of the Southern Uplands terrane. Sediments preserved in these sections represent a period of deep marine deposition associated with an accretionary prism system (see Kemp & Kelling 1990, for a review of depositional models). Deposits comprise a succession of Upper Ordovician to lower Silurian cherts, shales and mudstones of the Moffat Shale Group overlain by greywackes of the lower Silurian Gala Group. The exposed Moffat Shale Group consists of four formations: Glenkiln Shale, Lower Hartfell Shale, Upper Hartfell Shale (all Ordovician) and Birkhill Shale (largely Silurian); a total thickness of about 75 m. Sedimentation of the mudstones was slow, but appears to have been largely continuous. A sedimentation rate (after compaction) of between 2 and 4 m Ma<sup>-1</sup> has been estimated (Leggett 1980). The Glenkiln, Lower Hartfell and Birkhill shales consist largely of black shales, whilst the Upper Hartfell Shale is dominated by bioturbated pale mudstones with occasional black shale partings (Complanatus, Anceps and Extraordinarius bands). The base of the Silurian is taken as the base of the *Parakidograptus acuminatus* Zone (Cocks & Rickards 1988) which, at the stratotype section, is within graptolitic black shale facies 1.6 m above the base of the Birkhill Shale.

Despite the long history of studies on graptolite biostratigraphy at Dob's Linn since the work of Lapworth (1878), many of the zones are poorly defined (see Rickards (1995) for a review of Silurian graptolite biozonation). For this reason, the zones used here are defined on a range of criteria, and are not always coincident with the first occurrence of the zonal taxon. The base of the *linearis* Zone, for example, is marked by the appearance of *Climacograptus tubuliferus* (following Zalasiewicz *et al.* 1995). The *vesiculosus* and *gregarius* zones are based on acme occurrences. The *extraordinarius* Zone of Williams (1988) is not defined by any appearances (R. B. Rickards pers. comm. 1996), only the continued presence of *Normalograptus extraordinarius* after the extinction of most 'Ordovician' taxa (the dicranograptid–diplograptid–orthograptid–retiolitid [DDOR] fauna of Chen & Zhang 1995). Although this zone is possibly best considered an interregnum, *sensu* Jaeger (1959), it is retained here as a 'normal' graptolite zone for consistency. The *persculptus* Zone is used here in the sense of Williams (1986, 1988), with the base indicated by the first appearance of post-extinction graptolite taxa 10 cm above the base of the Birkhill Shale. *Normalograptus persculptus* is absent in this section (Zalasiewicz & Tunnicliff 1994; Storch & Loydell in press), and the synonymy of *N. persculptus* with '*Glyptograptus bohemicus*, which has been used as the zonal index for the underlying zone (Storch & Loydell in press) suggests that the *persculptus* Zone as used here is unlikely to equate directly with the *persculptus* Zone in other areas.

### Sampling methods

Samples for isotopic and geochemical analysis were collected from the Linn Branch section of Dob's Linn (Fig. 1, see Clarkson & Taylor



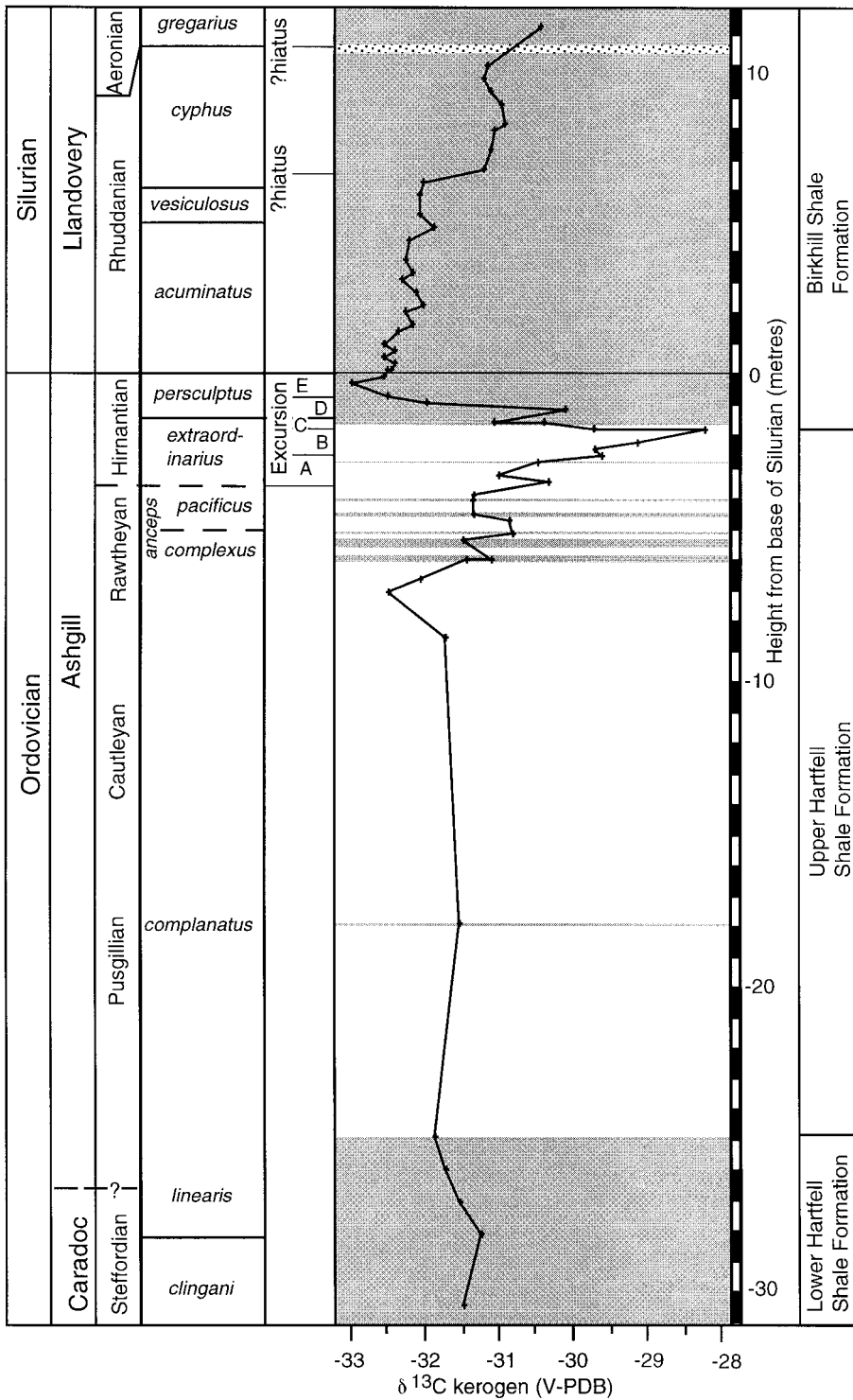
**Fig. 1.** Map showing the positions of the sampled sections at Dob's Linn [National Grid Reference NT 197 158]. Section 1 is within the Lower Hartfell Shales (described in Williams 1982). Section 2 is the stratotype section within the Upper Hartfell Shales and Birkhill Shales (largely described in Williams 1988). Section 3 is within the Birkhill Shales. Material from the Complanatus Bands was sampled along a sheep track to the South East of Section 2. Partly redrawn from Clarkson & Taylor (1993).

1993 for locality map). Levels within the Lower Hartfell, Upper Hartfell and Birkhill formations were sampled, spanning a range of ages from late Caradoc (Ordovician) to early Aeronian (Silurian); particular attention was paid to the Ordovician–Silurian boundary interval (*anceps* to *acuminatus* zones) (Fig. 2). As the section is repeatedly faulted there is no continuous succession through this interval, and samples were collected from a composite section along the northern side of the Linn Branch exposure. Correlation across a fault which cuts the Birkhill Shale low in the *cyphus* Zone was made *via* a distinctive suite of bentonites.

The Upper Hartfell Shale is, for the most part, too poor in organic matter for reliable isotopic analysis, and samples were collected only from the thin black shale bands and relatively organic-rich massive mudstones near the top of the formation. Samples were cleaned of any surface contamination, washed in distilled water, and hand-crushed in a ceramic mortar.

### Stable isotope analysis

Samples for carbon isotope analysis were solvent extracted to remove bituminous material using a soxhlet reflux system with a mixture (90:10) of dichloromethane and methanol and then pretreated to



**Fig. 2.**  $\delta^{13}\text{C}_{\text{kerogen}}$  isotope curve across the Ordovician-Silurian boundary at Dob's Linn, showing its relationship to chronostratigraphy, graptolite biostratigraphy and local lithostratigraphy. Grey shading indicates units or beds of predominantly black shale; lack of shading indicates predominantly organic-poor bioturbated mudstones, and stipple indicates a prominent siltstone.

eliminate any carbonate minerals by reacting 1–2 g of powdered material with 50 ml of 6N HCl for 24 hours at 55°C. Residues were washed and centrifuged several times with (HCl) acidified distilled water to remove all acid-soluble components. Traces of acid were then removed by repeated washing with distilled water. A small number of samples, containing low concentrations of organic matter, were further treated with 50 ml of 40% HF and 10 ml of 6N HCl for 24 hours in order to concentrate the kerogens. HF treated samples were also repeatedly washed with (HCl) acidified water and distilled water to remove acid-soluble components. All samples were subsequently freeze-dried prior to isotopic analysis.

Carbon dioxide for carbon isotope ratio measurement was prepared by combusting kerogens with Cu(II)O and silver wire (to remove  $\text{SO}_2$ ) in quartz tubes at 850°C for 2 hours. The resultant  $\text{CO}_2$  was separated cryogenically and carbon isotope ratios were measured on an automated VG SIRA 12 mass spectrometer. All data were corrected for  $^{17}\text{O}$  effects following Craig (1957). Carbon isotope data are reported (Table 1) in conventional delta ( $\delta$ ) notation in 'parts per mil' (‰) relative to V-PDB (Coplen 1995). Accuracy and reproducibility ( $\sigma_{n-1}$ ) of isotopic analyses were determined by replicate analysis of NBS 22, IAEA-CH-6 (sucrose) and JMG (Liverpool internal graphite standard). The mean values obtained for NBS 22 (–29.80‰) and

**Table 1.**  $\delta^{13}\text{C}_{\text{kerogen}}$  H/C (atomic) and N/C (atomic) data for the Ordovician–Silurian boundary section at Dob's Linn

Depth (metres relative to O/S boundary)	$\delta^{13}\text{C}_{\text{kerogen}}$ (‰ V-PDB)	H/C (atomic)	N/C (atomic)
+11.55	– 30.41		
+10.30	– 31.11		
+9.90	– 31.15		
+9.40	– 31.08		
+8.90	– 30.94		
+8.40	– 30.87		
+8.10	– 31.05		
+7.40	– 31.07		
+6.80	– 31.18		
+6.40	– 32.00		
+5.90	– 32.05		
+5.40	– 32.05		
+4.90	– 31.87		
+4.50	– 32.20		
+3.90	– 32.25		
+3.40	– 32.14		
+9.15	– 32.29		
+2.75	– 32.07	0.427	0.009
+2.40	– 32.01		
+2.20	– 32.23		
+1.80	– 32.13		
+1.40	– 32.33		
+1.15	– 32.54		
+0.90	– 32.39		
+0.55	– 32.50		
+0.40	– 32.38		
+0.27	– 32.42	0.265	0.012
+0.10	– 32.45	0.363	0.012
– 0.05	– 32.53	0.258	0.011
– 0.20	– 32.97		
– 0.60	– 32.48	0.272	0.010
– 0.75	– 32.45		
– 0.90	– 31.92		
– 1.10	– 30.06		
– 1.51	– 31.01	0.311	0.009
– 1.60	– 30.35	0.325	0.008
– 1.60	– 30.35	0.297	0.010
– 1.70	– 29.66	0.398	0.012
– 1.72	– 28.20		
– 2.20	– 29.09		
– 2.36	– 29.66	0.389	0.011
– 2.66	– 29.60		
– 2.86	– 30.47	0.285	0.012
– 3.16	– 30.96	0.351	0.008
– 3.43	– 30.29		
– 3.78	– 31.33		
– 4.00	– 31.31	0.315	0.014
– 4.40	– 31.33		
– 4.60	– 30.85		
– 5.05	– 30.78	0.326	0.014
– 5.25	– 31.47	0.268	0.010
– 5.90	– 31.07		
– 6.05	– 31.42	0.283	0.012
– 6.70	– 32.04		
– 7.10	– 32.49		
– 8.45	– 31.71		
– 18.00	– 31.53	0.255	0.018
– 25.00	– 31.84		
– 26.00	– 31.69	0.285	0.012
– 27.00	– 31.49	0.258	0.013
– 28.20	– 31.23	0.298	0.014
– 30.50	– 31.48	0.282	0.014

IAEA-CH-6 (– 10.40‰) were identical, within experimental error, to those reported by Gonfiantini *et al.* (1995), while long-term reproducibility ( $\sigma_{n-1}$ ) of NBS 22, IAEA-CH-6 and JMG (analysed with each batch of unknowns) was found to be better than 0.06‰.

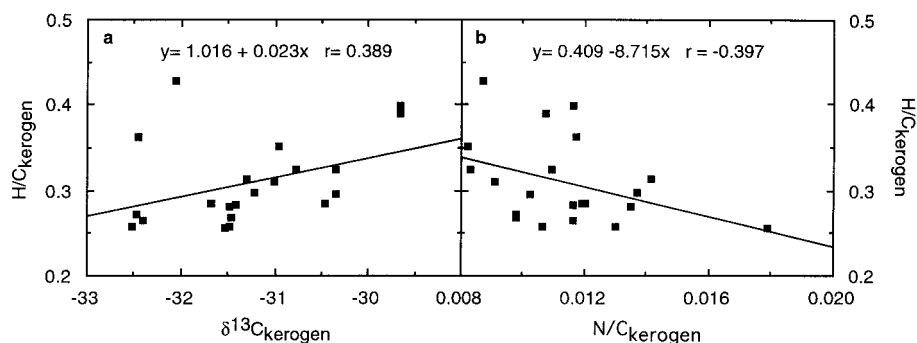
### Carbon–hydrogen–nitrogen analysis

Although the carbon isotope ratios preserved in organic matter are relatively unaffected by thermal maturation at diagenetic temperatures, exposure of organic carbon to higher (metamorphic) temperature regimes may result in the progressive modification of depositional isotopic compositions to more positive  $\delta^{13}\text{C}$  values with increasing temperature (McKirdy & Powell 1974; Hayes *et al.* 1983). In order to assess the possible effects of thermal maturation on the  $\delta^{13}\text{C}$  of kerogens (Hayes *et al.* 1983), a representative suite of samples was analysed to determine H/C and N/C (atomic) ratios. Selected samples were dissolved in HCl and HF, as described above, to remove carbonate and hydrous aluminosilicate minerals, washed free of acid-soluble residues with hot (*c.* 80°C) 6N HCl and deionised water, and subsequently freeze dried. The prepared kerogens were analysed for C–H–N using a Carlo-Erba Elemental Analyser. All samples were analysed in duplicate and the data reported as atomic H/C and N/C (Table 1).

### Preservation of the environmental signal

Two important factors, contamination by mobile hydrocarbons and thermal alteration, may affect the preservation of the primary carbon isotopic composition of organic matter. Although effects of contaminating hydrocarbons can be readily eliminated by analysing the immobile kerogen component of samples as opposed to total organic carbon (including bituminous fractions), the potential effects of thermal alteration need to be assessed on the basis of organic maturity indicators (see Hayes *et al.* 1983). Previous investigations of the relationship between thermal maturation, as indicated by decreasing H/C and N/C ratios, and  $\delta^{13}\text{C}$  of kerogens (McKirdy & Powell 1974; Hayes *et al.* 1983; Strauss *et al.* 1992*a, b*) have shown that isotopic alteration of organic matter can occur as mobile hydrocarbons (petroleum, methane) and carbon dioxide are progressively released under the effects of increasing diagenetic/metamorphic temperatures. Kinetic isotope fractionation effects associated with the maturation of organic compounds commonly lead to the gradual loss of  $^{12}\text{C}$  from organic matter, and result in a progressive increase in the  $\delta^{13}\text{C}$  of the residual kerogens with increasing thermal maturity (McKirdy & Powell 1974; Hayes *et al.* 1983). Although changes in the  $\delta^{13}\text{C}$  of kerogen appear to occur progressively with decreasing H/C, correlations between  $\delta^{13}\text{C}$  and H/C (Hayes *et al.* 1983) show that significant modifications in isotopic composition tend to be restricted to kerogens with H/C ratios of less than 0.2–0.3 (Hayes *et al.* 1983; Strauss *et al.* 1992*a*), while Strauss *et al.* (1992*b*) have shown that strong positive correlations between H/C and N/C are to be expected from isotopically altered kerogens.

The average H/C ratio of Dob's Linn kerogens is 0.31 (range 0.26–0.43) and all samples have H/C ratios which are close to the inferred cut-off between isotopically altered and unaltered organic matter. However, if the carbon isotope ratios of kerogen samples have been affected by thermal maturation then a negative co-variant relationship between H/C and  $\delta^{13}\text{C}$  would be expected (Hayes *et al.* 1983; Strauss *et al.* 1992*b*). Figure 3a shows that H/C and  $\delta^{13}\text{C}$  in Dob's Linn kerogens are characterized by a very weak positive correlation. This suggests that thermal maturation has either not significantly affected the isotopic composition of the kerogens, or that all



**Fig. 3.** Bivariate plots showing the relationships between: (a) carbon isotopic composition and H/C ratio, and (b) H/C and N/C ratios for kerogen samples from Dob's Linn. Despite the high thermal maturity as indicated by the low H/C, there are no significant correlations between these variables.

kerogens have been modified to the same relative extent such that differences in the present carbon isotope ratios of the kerogens are internally consistent with original variations present in the organic matter. The preservation of an unmodified isotopic signal in Dob's Linn kerogens is supported by the relationship between H/C and N/C (Fig. 3b) which shows a weak negative correlation, as opposed to the strong positive correlation predicted for isotopically altered organic matter (Strauss *et al.* 1992b). Despite the undoubted high degree of thermal maturity of the organic component preserved at Dob's Linn (cf. Pearce *et al.* 1991), we conclude that the  $\delta^{13}\text{C}$  of kerogen samples was only minimally affected by thermal maturation processes.

### Nature of the $\delta^{13}\text{C}$ signal

Kerogen  $\delta^{13}\text{C}$  signatures from most of the Ordovician part of the section (*clingani* to *anceps* zones) are relatively constant at between  $-31$  and  $-32\%$  V-PDB (Fig. 2). Two samples from just below the Anceps Bands give a  $\delta^{13}\text{C}$  value that is slightly more negative than from within adjacent rocks. It is unclear whether this represents a primary signal, as the organic carbon content of these samples is very low (under 0.1%). Above this there is a progressive but rapid positive  $\delta^{13}\text{C}$  shift of about 4‰. This reaches a peak within the top 0.2 m of the Upper Hartfell Formation, some distance above the *Normalograptus extraordinarius*-bearing horizon. Immediately below the base of the Birkhill Shale there is a sudden but progressive negative  $\delta^{13}\text{C}$  shift. The  $\delta^{13}\text{C}$  becomes more negative throughout much of the *persculptus* Zone, falling to  $-33\%$  V-PDB, 0.2 metres before the faunal change indicating the base of the Silurian.

Throughout the succeeding *acuminatus* to *vesiculosus* zones there is a gradual rise in  $\delta^{13}\text{C}$  of about 1‰. There is a sudden positive  $\delta^{13}\text{C}$  excursion near the base of the *cyphus* Zone, followed by an interval with a relatively constant isotopic value of about  $-31\%$  V-PDB, then a second sharp positive shift at the base of the *triangulatus* Zone. These sudden positive shifts within the Llandovery both coincide with distinct facies changes. The *cyphus* Zone shift separates two periods of gradually rising  $\delta^{13}\text{C}$  values which show a similar gradient and coincides with a change from blocky, bentonite-poor shales (the '*acuminatus* Flags' of Lapworth 1878) to fissile, bentonite-rich facies (Toghill 1968). The basal Aeronian shift coincides with a 0.3 metre hard siltstone and a sudden faunal change. It is likely that, in both cases, the sudden change in  $\delta^{13}\text{C}$  values coincides with a hiatus.

By using a combination of the architecture of the  $\delta^{13}\text{C}$  isotope shift and palaeontological markers, it is possible to erect five informal subdivisions of the Hirnantian (units A-E, Fig. 2). The top of the Upper Hartfell Formation above the

last appearance of a *pacificus* Subzone fauna, and basal 0.1 m of the Birkhill Shale, approximates to the *extraordinarius* Zone or Lower Hirnantian. This may be divided into a lower unit (A) with a climbing  $\delta^{13}\text{C}$  signature and a band yielding *Normalograptus extraordinarius*, a middle unit (B) with a uniformly high  $\delta^{13}\text{C}$  signature and a fauna entirely of the long-ranging taxa *Normalograptus normalis* and *N. angustus* (recorded in Berry 1987), and an upper unit (C) with a rapidly falling  $\delta^{13}\text{C}$  signature but the same fauna. The upper part of the Hirnantian is within the black shales of the *persculptus* Zone. This too may be subdivided. The lower unit (D) contains the post-extinction form *Glyptograptus venustus* cf. *venustus* and a  $\delta^{13}\text{C}$  signature falling rapidly to its pre-excursion levels. This is overlain by an upper unit (E) bearing *Normalograptus parvulus* and a  $\delta^{13}\text{C}$  signature continuing to fall to a low point near the top of the Zone.

### Stratigraphic significance and correlation

Hirnantian  $\delta^{13}\text{C}$  excursions are known from a number of localities worldwide: Anticosti Island, Canada (Orth *et al.* 1986; Long 1993; Brenchley *et al.* 1994, 1995), the Selwyn Basin, Canada (Wang *et al.* 1993b), Yichang, China (Xu *et al.* in Wang *et al.* 1993a), Sweden (Marshall & Middleton 1990), Argentina (Marshall *et al.* in press) and the Baltic States (Brenchley *et al.* 1994, 1995, 1997; Marshall *et al.* in press). Some of these studies have involved analyses of carbonate whole rock samples (e.g. Orth *et al.* 1986; Long 1993; Wang *et al.* 1993b), which are highly prone to diagenetic alteration, whilst analysis of calcitic bioclasts monitored for diagenetic alteration has been less extensive (e.g. Marshall & Middleton 1990; Brenchley *et al.* 1994, 1995; Marshall *et al.* in press and references therein).

Despite the recognition of Hirnantian  $\delta^{13}\text{C}$  excursions on a global scale, it is only at Dob's Linn that a progressive increase and decrease of  $\delta^{13}\text{C}$  values has been recognised. This, combined with (albeit incomplete) faunal evidence, suggests that only Dob's Linn shows a continuous sedimentary record across the Hirnantian. It is therefore possible to correlate the Dob's Linn section with recorded  $\delta^{13}\text{C}$  excursions in other localities, using a combination of the architecture of the isotope excursion and faunal evidence.

Although the Hirnantian  $\delta^{13}\text{C}$  excursion is a global event, its magnitude is rather variable despite the consistent architecture. The magnitude of the original rise in  $\delta^{13}\text{C}$  varies from 2‰ for whole rock carbonate (Orth *et al.* 1986) and 4‰ for bioclasts (Brenchley *et al.* 1994) at Anticosti Island to about 6‰ (Brenchley *et al.* 1994) for whole rock carbonate in Estonia. This variation in magnitude of carbon isotope excursions, whilst retaining the excursion architecture, has been

recognized elsewhere in the stratigraphic record (Beauchamp *et al.* 1987; Jenkyns *et al.* 1994). These differences are probably due to local variations in basin-scale carbon cycling.

### Anticosti Island

A thick sequence of fossiliferous carbonates spanning the Caradoc to the Wenlock is exposed at Anticosti Island, Quebec. The Ordovician–Silurian boundary of Lespérance (1985) has been correlated with a major faunal change at the top of the Ellis Bay Formation (Member 7 of Petryk 1979; Laframboise Member of Long & Copper 1987). This member has a basal coral–oncolite packstone (the oncolite platform bed of Long & Copper 1987) overlain by coral–stromatoporoid bioherms and inter-reef wackestones. The member is overlain by variable marls and packstones of the Becscie Formation. The Ordovician–Silurian boundary stratotype was proposed for these sections at a level 0.4 metres above the oncolite platform bed with the first appearance of conodonts of ‘Silurian’ affinities of the *nathani* Zone (McCracken & Barnes 1981; Barnes 1988). These ‘Silurian’ conodonts coexist with established ‘Ordovician’ taxa (such as *Amorphognathus*) until the latter’s extinction at the base of the Becscie Formation.

Several studies of both brachiopod bioclasts (Brenchley *et al.* 1994, 1995) and whole rock carbonate (Orth *et al.* 1986; Long 1993) have shown that the  $\delta^{13}\text{C}_{\text{carbonate}}$  in pre-Laframboise member units is relatively constant at about +1 to +2‰ PDB.  $\delta^{13}\text{C}$  of bioclasts within the oncolite platform bed is uniformly high (about +3.5‰ PDB) (Brenchley *et al.* 1994, 1995), although whole rock samples are more variable (Orth *et al.* 1986); this is probably as a result of reworking or early diagenetic phases within this lithology. The rest of the member has uniformly high  $\delta^{13}\text{C}$ . All samples from the Becscie Formation have low  $\delta^{13}\text{C}$  (0 to +2‰ PDB) with no sign of a transitional zone. By comparing the isotopic curves of oxygen and carbon from Anticosti Island to those from the Baltic region, Carden (1995) noted that the late Ordovician excursion at Anticosti Island occupies a thinner lithostratigraphic interval and was of a smaller magnitude. This was taken to indicate that the Hirnantian Stage was incomplete or condensed.

The bulk carbonate  $\delta^{13}\text{C}$  signature of Anticosti Island is similar in general form to the organic carbon curve of Dob’s Linn (Fig. 4), and as such allows correlation of the isotopic events. The relatively stable pre-Laframboise  $\delta^{13}\text{C}$  levels correlate with the pre-excursion part of the Dob’s Linn section, and as such can be interpreted as representing levels up to the *pacificus* Subzone. This is supported by occurrence of rare pre-Hirnantian graptolites (Riva 1988). The interval of rising values of  $\delta^{13}\text{C}$ , corresponding to the levels around the *Extraordinarius* Band at Dob’s Linn, does not appear to be directly represented on Anticosti Island. It is possible, however, that the oncolite platform bed represents a condensed and reworked equivalent of this interval (G. Carden pers. comm. 1996). The uniformly high  $\delta^{13}\text{C}$  of the succeeding part of the Laframboise Member suggests that it represents the upper part of the *extraordinarius* Zone at Dob’s Linn.

The few data available from the basal Becscie Formation indicate that there is no evidence for a period of progressive  $\delta^{13}\text{C}$  fall and, by correlation with Dob’s Linn, this suggests that the top of the *extraordinarius* Zone and the entire *persculptus* Zone is absent. Faunal graphic correlation has suggested that a hiatus is present at the top of the Laframboise Member (Armstrong 1995), whilst sedimentological analysis shows a possible omission surface (Carden 1995).

### Selwyn Basin

The Selwyn Basin, northwest Canada, records a shelf to basin transition over the Ordovician–Silurian boundary interval. Although largely within carbonate facies, a mixed shelly and graptolitic fauna has been recorded, and the sedimentary geochemistry has been extensively studied (Wang *et al.* 1993b). The sections are generally moderately expanded, but the Hirnantian is very thin, with only 1.3 m separating *pacificus* Subzone and Silurian graptolite faunas. Whole rock analysis shows that the  $\delta^{13}\text{C}_{\text{carbonate}}$  within the boundary interval rises from a background of 0 to +1‰ PDB by about 2‰ over a 20 cm interval above the last occurrence of *Dicellograptus*, before falling suddenly by about 3‰. This is followed by a rise to a second slight high over the next 40 cm before stabilising at about 0 to +1‰ PDB.

By analogy with Dob’s Linn (Fig. 4), the initial increase in  $\delta^{13}\text{C}$  equates with the lower part of the *extraordinarius* Zone, possibly up to about the point of the *Extraordinarius* Band itself. The bulk of the rest of the Hirnantian appears to be absent, the remainder of the boundary interval recording the post-recovery rise within the extreme top of the *persculptus* Zone. The base of the Silurian is well marked by the replacement of *persculptus* Zone by *acuminatus* Zone graptolites.

### Other sections

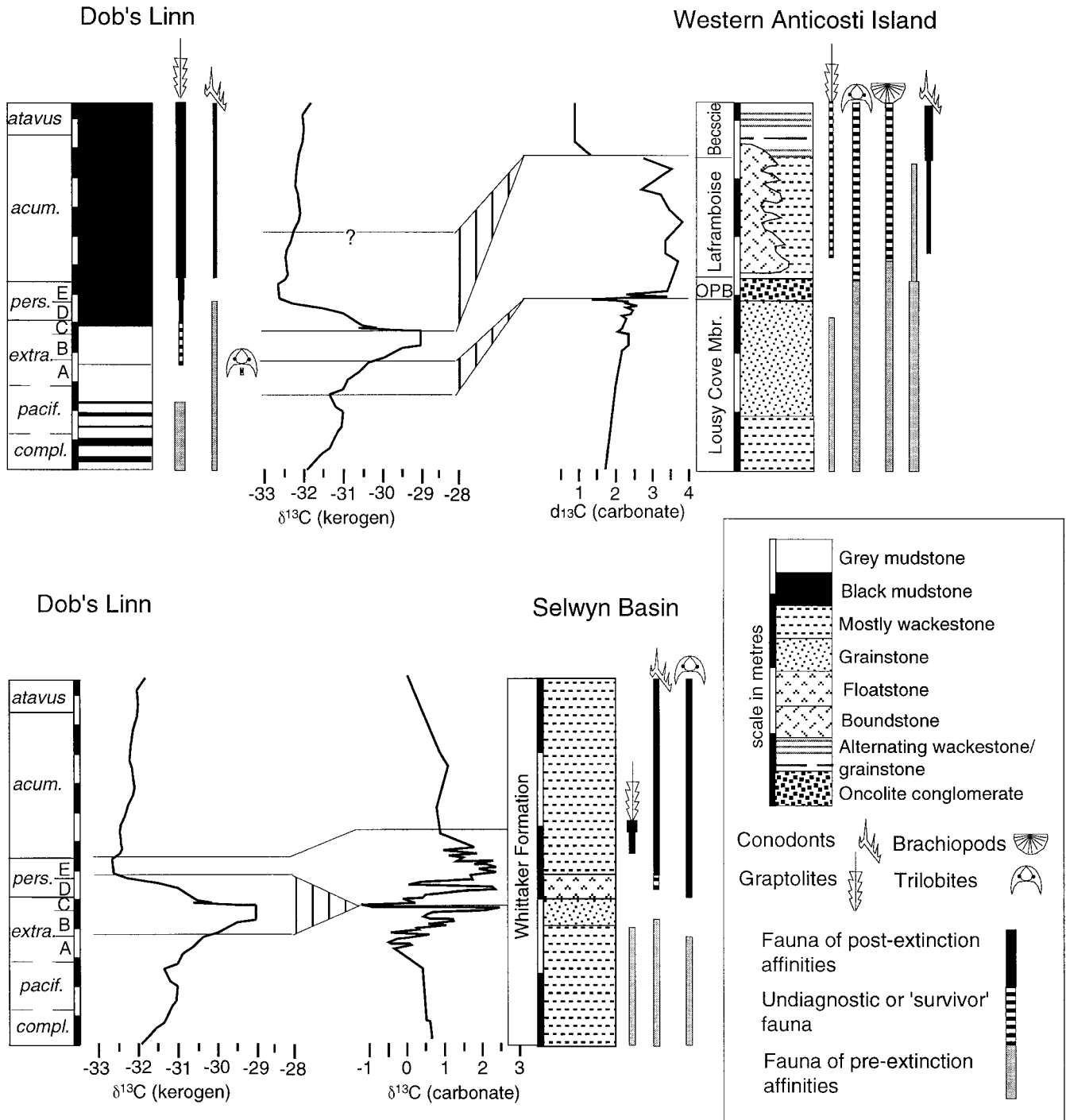
Although only the Anticosti Island and Selwyn Basin sections have well constrained isotopic and palaeontological data, there are other sections with which comparisons can be made. In China,  $\delta^{13}\text{C}_{\text{kerogen}}$  data are recorded from two sections at Yichang, Hubei Province (Xu *et al.* in Wang *et al.* 1993a). Unfortunately, both sections are very condensed, have undocumented thermal maturity, and the precise relationships between the isotope record, biostratigraphy and lithological units are not recorded. There is a general positive  $\delta^{13}\text{C}$  excursion within the Hirnantian of both sections, with the Wangjiawan section also showing the rapid fall in  $\delta^{13}\text{C}$  in the lower *persculptus* Zone. Otherwise, there is little architecture of use for correlation.

The initial part of the Hirnantian  $\delta^{13}\text{C}$  excursion is recorded within carbonate mud mounds at Boda, Sweden (Marshall & Middleton 1990). Bioclasts within the bulk of the mounds have a  $\delta^{13}\text{C}$  signature of +1 to +2‰ PDB. Within the *Hindella* coquinas capping the buildups, there is a  $\delta^{13}\text{C}$  rise of 4 to 5‰ before the exposures are erosively cut out. In this case, the  $\delta^{13}\text{C}$  shift can be seen to equate to the incoming of a new brachiopod fauna, allowing correlation of this with the start of the *extraordinarius* Zone.

Composite  $\delta^{13}\text{C}$  curves also exist for bioclasts (Brenchley *et al.* 1995) and kerogen (Marshall *et al.* in press) from borehole material from the Baltic States. These again show raised  $\delta^{13}\text{C}$  within the regressive phase, which correlates with the *extraordinarius* Zone of Dob’s Linn. However, the data are a composite from a number of cores and as such it is not possible to determine a detailed architecture.

### Biostratigraphic correlation

Several attempts have been made to correlate graptolitic sequences with shelly sequences across the Ordovician–Silurian boundary interval, generally by means of biostratigraphic graphic correlation (Armstrong 1995), or rare co-occurrences of taxa (e.g. Melchin *et al.* 1991). However, these studies have



**Fig. 4.** Ordovician–Silurian boundary interval at Dob's Linn compared to that at Anticosti Island and the Selwyn Basin, showing the inferred correlations using isotopic and palaeontological events. The Dob's Linn  $\delta^{13}\text{C}_{\text{kerogen}}$  curve is shown as a three point moving average for clarity. Hatch pattern on correlation lines indicates periods of probable hiatus. The bulk of the Anticosti Island  $\delta^{13}\text{C}_{\text{carbonate}}$  curve is modified from Orth *et al.* (1986), with the raised area corresponding to the interreef Laframboise Member and the basal Oncolite Platform Bed. The data for the overlying Becscie Formation are taken from Brenchley *et al.* (1994). The Selwyn Basin  $\delta^{13}\text{C}_{\text{carbonate}}$  curve is modified from Wang *et al.* (1993*b*). Note that the isotope curve for Dob's Linn is  $\delta^{13}\text{C}_{\text{kerogen}}$ , whilst that for the other localities is  $\delta^{13}\text{C}$  bulk carbonate.

relied on a very limited number of tie lines, and are at best rather simplistic. Cross correlation using isotopic excursions provides an independent means of constructing a composite biostratigraphic zonal scheme (Fig. 5).

Faunas from the interval at Dob's Linn immediately preceding the  $\delta^{13}\text{C}$  excursion reveal a diverse, pre-extinction Ordo-

vician biota. This interval yields diverse *pacificus* Subzone graptolites, diverse *ordovicicus* Zone conodonts, and a shelly fauna of Rawtheyan affinities. The start of the  $\delta^{13}\text{C}$  rise coincides approximately with the extinction of the DDOR graptolite faunas of Chen & Zhang (1995), with graptolites either absent or represented by the extremely impoverished



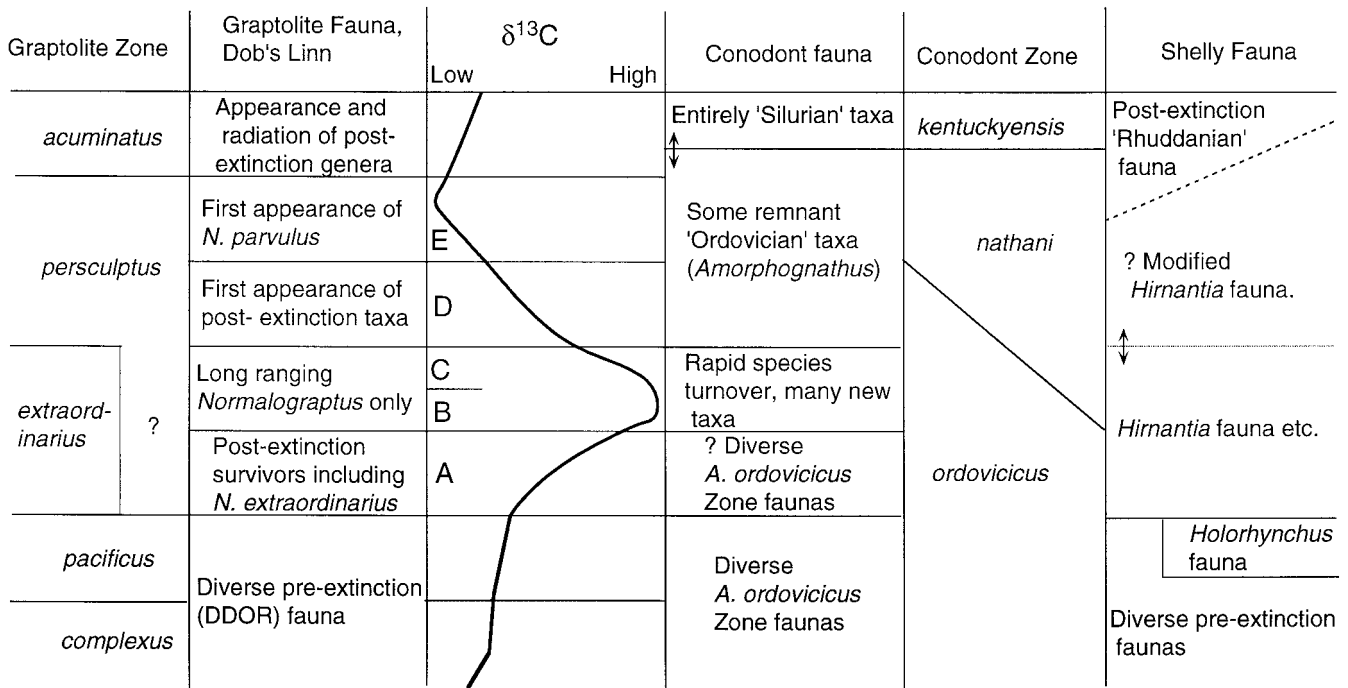


Fig. 5. Composite stratigraphic framework for the Ordovician–Silurian boundary interval, comparing  $\delta^{13}\text{C}$  stratigraphy, graptolite and conodont biozonal schemes and graptolite, conodont and brachiopod–trilobite faunal events. Note that the recent synonymy of *N. persculptus* and '*G. bohemicus*' (Storch & Loydell in press) may result in the expansion of the *persculptus* Zone to include most of the Hirnantian in some areas.

*extraordinarius* Zone fauna once the  $\delta^{13}\text{C}$  excursion is underway.

Although a true *Hirnantia* fauna is not recorded from any of the sections with a good continuous isotope record, there is indirect evidence that it is established by the level of the Extraordinarius Band at Dob's Linn. Analyses of *Hirnantia* and co-occurring brachiopods from Argentina and the Oslo region, Norway reveal a raised  $\delta^{13}\text{C}$  signature (Brenchley *et al.* 1997; Marshall *et al.* in press), whilst in Sweden, the *Hindella* coquinas showing high  $\delta^{13}\text{C}$  values probably also represent a reduced *Hirnantia* fauna. At Dob's Linn, the trilobite *Dalmanitina* (*Songxites*) sp. is known from immediately below the Extraordinarius Band (Lespérance 1988) and has strong affinities with well known Hirnantian taxa. The oncolite platform bed at Anticosti Island, which may also represent this level, contains a fauna in which both shelly elements and conodonts are of 'normal Ordovician' type (Barnes 1988). The survival at Anticosti Island of a typically pre-extinction conodont and, to a lesser extent, shelly fauna into a period with raised  $\delta^{13}\text{C}$  levels suggests that the initial stages of the Hirnantian extinction may have been later within low latitude carbonate shelves. The base of the true *Hirnantia* fauna may, at least in part, be diachronous (Rong 1984; Mu 1988), although in a number of these sections which exhibit evidence of diachroneity, it is uncertain whether hiatuses and downcutting, so widespread at this level, may be present.

Faunas from within the highstand of the  $\delta^{13}\text{C}$  excursion in the Anticosti Island sections include brachiopods, trilobites and other shelly faunas of long-ranging, non-diagnostic taxa (Barnes 1988). These are probably the low latitude equivalent of the *Hirnantia* fauna. Conodonts, however, show a progressive but rapid taxonomic turnover. The first taxa of 'post extinction' affinities appear near the top of the oncolite platform bed, associated with a loss of a number of 'Ordovician' forms. Throughout the Laframboise Member this piecemeal

replacement continues with some characteristically 'Ordovician' forms (such as *Amorphognathus*) surviving to the end of the member. The *nathani* conodont Zone on Anticosti Island is defined by this coexistence of old and new taxa (Barnes 1988; Melchin *et al.* 1991), and correlates with the upper part of the *extraordinarius* Zone at Dob's Linn. Elsewhere the base of the *nathani* Zone is rather later. Within Arctic Canada (Melchin *et al.* 1991), faunas from interbedded shales and carbonates show that the base of the *nathani* Zone occurs within the *persculptus* Zone. As the *persculptus* Zone both in Arctic Canada and at Dob's Linn coincides with a transgression-related facies change, a globally recognisable event (Brenchley 1988), it is probable that it is the conodont fauna which is diachronous, and not the graptolite one.

Graptolites recorded from the extreme top of the Upper Hartfell Shales, above the Extraordinarius Band at Dob's Linn, are abundant but of low diversity (Berry 1987) and lack *N. extraordinarius*. It is unclear whether this is simply a local event, or whether *N. extraordinarius* became extinct before the first appearance of a *persculptus* Zone (*sensu* Williams 1986) fauna. Certainly there are graptolite-bearing intervals in China (Li *et al.* 1984 in Berry 1987) and Kazakhstan (Apollonov *et al.* 1988) between occurrences of *N. extraordinarius* and *persculptus* Zone indices where only long-ranging *Normalograptus* are present.

The nature of shelly faunas within the upper *extraordinarius* and *persculptus* zones are poorly known, especially as this interval appears to be absent on Anticosti Island. A *Hirnantia* fauna has been reported from the *persculptus* Zone of the Mirny Creek section, northern Russia (Koren' *et al.* 1988), and in several sections in Kazakhstan (Apollonov *et al.* 1988). A rather modified *Hirnantia* fauna is known from the English Lake District associated with ?*N. parvulus* (Ashgill Quarry; C.J.U. personal observation) and with *Akidograptus ascensus* (Yewdale Beck, D. Harper & S. H. Williams pers. comm. 1996), indicating its survival into the upper *persculptus* and

*acuminatus* zones. *Hirnantia* faunas are also well known from the strongly transgressive upper part of the Hirnantian in the Bohemian Massif (Storch 1990).

Conodonts are known from the *persculptus* Zone from several localities including Dob's Linn (Barnes & Williams 1988), Yukon (Lenz & McCracken 1988), Nevada (Finney *et al.* 1995) and Arctic Canada (Melchin *et al.* 1991). These generally consist of a low-diversity fauna containing some characteristically 'Ordovician' taxa, including *Amorphognathus*. In Arctic Canada, conodonts are well known into the *acuminatus* Zone, and here it is not until some way into this zone that there is a replacement of these survivor taxa of conodonts by indicators of the succeeding *kentuckyensis* Zone (Melchin *et al.* 1991). As there is no sign of 'Ordovician' conodonts within the lower Becsie Formation on Anticosti Island, it suggests that the hiatus at the top of the Laframboise Member extends up into the *acuminatus* Zone.

The exact timing of the replacement of the *Hirnantia* fauna by the shelly faunas of the Rhuddanian is at present uncertain and may be diachronous. The *Hirnantia* fauna does extend, in a modified form, into the *acuminatus* Zone in northern England. Elsewhere, evidence suggests the replacement of the *Hirnantia* fauna was close to the Ordovician–Silurian boundary. In the Mirny Creek section, northern Russia, the base of the *acuminatus* Zone is roughly synchronous with the change from a *Hirnantia* fauna to beds with a *Skenidioides*–*Acernaspis* fauna (Koren' *et al.* 1988). Rhuddanian shelly faunas are also well known from the *acuminatus* Zone elsewhere, including within the Llandoverly type area (Cocks *et al.* 1984).

## Conclusions

Despite its high degree of thermal maturity, the mudstones of the basal Silurian Stratotype section at Dob's Linn contain kerogen which is sufficiently unaltered to retain carbon isotope ratios consistent with primary depositional values. The results of this investigation reveal a pattern of  $\delta^{13}\text{C}_{\text{kerogen}}$  which is not only consistent with that recorded from elsewhere, but also of higher resolution across critical intervals. For the first time, this has allowed close correlation between the  $\delta^{13}\text{C}$  isotope curve and well constrained graptolite biostratigraphy. The  $\delta^{13}\text{C}$  signature shows a pattern of relatively constant values through much of the Ashgill, with a rapid rise during the early *extraordinarius* Zone and a fall during the *persculptus* Zone to a level below that obtained prior to the excursion. This is followed by a gradual rise through the Rhuddanian, with sudden jumps within the *cyphus* Zone and at the base of the Aeronian.

Correlation of isotopic events allows the Dob's Linn succession to be compared directly to other sections, including those on carbonate platforms which have few if any fossils in common with it. This direct comparison has revealed that the bulk of basal Silurian boundary sections are incomplete, with hiatuses within either the lower or upper parts of the Hirnantian which are probably related to periods of rapid sea level change. Direct correlation also allows for the development of a combined high resolution stratigraphic framework, including carbon isotope stratigraphy and multi-group biostratigraphy. This reinforces the global significance of Dob's Linn as not only the basal Silurian Stratotype, but also as retaining the best constrained stratigraphy across the upper Ashgill to Rhuddanian interval.

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