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David K. Loydell, Ross R. Large

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Biotic, geochemical and environmental changes through the early Sheinwoodian (Wenlock, Silurian) carbon isotope excursion (ESCIE), Buttington Quarry, Wales

David K. Loydell^{a,*}, Ross R. Large^b

^aSchool of Earth and Environmental Sciences, University of Portsmouth, Burnaby Road, Portsmouth PO1 3QL, UK

^bCODES, ARC Centre of Excellence in Ore Deposits, University of Tasmania, 7001, Tasmania

ABSTRACT

Palaeontological, sedimentological and geochemical data (particularly from LA-ICPMS analyses of pyrite) from a 12.4 m section through the lower Sheinwoodian Trewern Brook Mudstone Formation of Buttington Quarry, Wales are combined to reveal the environmental changes taking place during the early Wenlock Epoch of the Silurian, during the early part of the ESCIE (early Sheinwoodian carbon isotope excursion). The uppermost *Cyrtograptus purchisoni* through to lower *Monograptus riccartonensis* biozones show increased nutrient levels, peaks in palynomorph and graptolite abundance. At this time graptolite diversity globally was declining dramatically, possibly associated with metal (particularly zinc) concentrations attaining toxic levels and probably with the base of the euphotic zone being higher in the water column (resulting from blooms of phytoplankton) causing those graptolites that specialized in feeding on phytoplankton that were outcompeted in this diminished volume of illuminated surface waters to decline in numbers and eventually become extinct. Correlation of the graptolite and conodont biozonations enables the levels of the main stratigraphically higher Ireviken Event Datum Points to be proposed for the Buttington section and this in turn allows events recognised elsewhere (intervals of malformed palynomorphs and re-organization of polychaete faunas, together with an oceanic anoxic event) to be correlated with the lower part of the studied Buttington section. The commencement of the OAE, identified on Gotland at Ireviken Event Datum Point 4, appears to correlate rather well with a rapid transition, marking the top of the Butterley Mudstone Member at Buttington, from heavily bioturbated mudstones to laminated graptolitic mudstones. Surprisingly, the most rapid change in $\delta^{13}\text{C}_{\text{carb}}$ values within the Buttington section (from 0.6 ‰ at 8.19–8.25 m to 2.09 ‰ at 8.50–8.55 m) is not associated with any major faunal, palynological abundance or geochemical changes – these are all coincident with the initial rise in $\delta^{13}\text{C}_{\text{carb}}$ values, up to about the 5 m level in the Buttington section. Another unexplained feature of the graptolite record is a sudden change from *Monograptus*-dominated to *Pristiograptus*-dominated assemblages about half way through the studied section.

* Corresponding author. +44 2392842698

E-mail addresses: david.loydell@port.ac.uk (David K. Loydell), ross.large@utas.edu.au

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1. Introduction

The early Sheinwoodian (early Wenlock, Silurian) was a time of profound environmental and biotic change. An interval of globally high sea levels in the early *Cyrtograptus purchisoni* Zone (Loydell, 1998, 2007) was succeeded by glaciation (Lehnert et al., 2010) and associated drop in sea-level (Loydell, 1998, 2007), culminating in the *Monograptus riccartonensis* Zone (see Fig. 1 for graptolite zonation). The onset of the early Sheinwoodian carbon isotope excursion (ESCIE), a pronounced positive excursion in both the $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ records (Cramer et al., 2010a), is coincident with the fall in sea-level (Loydell, 2007). Significant conodont extinctions (the early phases of the Ireviken Event, including those marked by the greatest declines in global conodont diversity; Loydell 2007; Lehnert et al., 2010) largely preceded the rise in $\delta^{13}\text{C}_{\text{carb}}$ values, whereas a major graptolite extinction (e.g. species diversity reduced from 21 to four species in Bohemian sections; Štorch, 1995; see also Koren', 1987; Melchin et al., 1998; Cooper et al., 2014) took place as $\delta^{13}\text{C}$ values rose through the late *Cyrtograptus purchisoni* Zone to early *Monograptus riccartonensis* Zone (Loydell, 2007). This dramatic decline in graptolite diversity, considered by Cooper et al. (2014) to be the most significant in the Silurian and to be more pronounced even than the Hirnantian graptolite extinction, was accompanied by a major restructuring of polychaete faunas (Tonarová et al., 2014). It has also been proposed (Emsbo et al., 2010) that there was an oceanic anoxic event (OAE) coincident with the later phases of the Ireviken Event. Figure 17 shows these events in relation to the section studied herein.

In order to try to understand more fully the environmental changes taking place through this interval we combine here a detailed study of the graptolites through the lower Sheinwoodian of Buttington Quarry, Wales with sedimentological observations, palynomorph abundance data and trace element (TE) analyses of pyrite. Laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS) has recently been recognised to offer insights into oceanic and atmospheric chemistry (e.g. Large et al., 2014, 2015, 2017), enabling interpretations of, for example, nutrient levels and atmospheric pO_2 . Study of the Buttington section enables such interpretations to be compared and integrated with palaeontological and sedimentological data at a much higher stratigraphical resolution than previously attempted.

2. The ESCIE and $\delta^{18}O$ excursions

2.1. The early Sheinwoodian carbon isotope excursion (ESCIE)

The early Sheinwoodian carbon isotope excursion (ESCIE) is a major positive excursion recognised in both the carbonate and organic carbon records (Cramer et al., 2010a; Fig. 2) of the lower Wenlock Series (Silurian). The term ESCIE is used here in preference to “Ireviken excursion” to avoid confusing the carbon isotope excursion with the Ireviken Event, a series of conodont extinctions (named after the locality on Gotland where they were first recognised; Jeppsson, 1987), the most significant of which precede the ESCIE. Lehnert et al. (2010, fig. 4) showed global conodont diversity through the Ireviken Event: diversity declined from 59 species below Ireviken Event Datum 1 to 24 species above Datum 2 (over a stratigraphical thickness of c. 1 m on Gotland; Vandenbroucke et al., 2013, fig. 2), with the rise in $\delta^{13}C_{carb}$ not commencing on Gotland until Datum 4 (Munnecke et al., 2003). $\delta^{13}C_{org}$ values on Gotland rise at a lower stratigraphical horizon, between Datum 2 and Datum 3 (Vandenbroucke et al., 2013), but still above the two main conodont extinction levels.

Cramer et al. (2010a) and Lehnert et al. (2010) provide detailed reviews of the ESCIE. Since then the ESCIE has been recognised for the first time in the Barrandian area by Frýda et al. (2015) and there have been studies integrating geochemical, sedimentological and fossil data through this interval in Poland (e.g. Racki et al., 2012; Smolarek et al., 2017; Sullivan et al., 2018).

In sections with good graptolite biostratigraphical control (e.g. the East Baltic cores studied by Kaljo and Martma, 2006 – see also Loydell and Frýda, 2007, fig. 4; and also the Aizpute-41 section, Latvia; Cramer et al., 2010a) a marked positive shift in $\delta^{13}C_{carb}$ values, marking the onset of the ESCIE, can be dated to the late *murchisoni* Zone (Fig. 2). Peak $\delta^{13}C_{carb}$ values occur either within the *riccartonensis* Biozone or slightly higher. In the Banwy River section, Wales, which was sampled at

moderately high stratigraphical resolution, an interval of more negative values has been identified within the lower *riccartonensis* Biozone and this was used by Cramer et al. (2010a, fig. 9) for chemostratigraphical correlation with sections on Gotland and in New York lacking good graptolite biostratigraphical control. The ESCIE ends consistently in the mid Sheinwoodian, with *Monograptus flexilis* commonly found in strata at this level (e.g. Loydell and Frýda, 2007; Fig. 2).

In the conodont record there is less consistency with regard to the onset of the ESCIE in relation to the datum points of the Ireviken Event, perhaps reflecting an environmental control on conodont distribution or perhaps the difficulty in recognising biostratigraphical levels which are based upon the absence/disappearance of taxa when sample size is limited (as is inevitably the case with core material). On Gotland, the positive shift in $\delta^{13}\text{C}_{\text{carb}}$ coincides with Datum 4 of the Ireviken Event (Munnecke et al., 2003; Cramer et al., 2010a) equating to the base of the Upper *Pterospathodus procerus* conodont Biozone (Jeppsson, 1997) a level correlated with the uppermost *murchisoni* Biozone by Männik (2007). Nestor et al. (2002) and Munnecke et al. (2003) recorded a hiatus at Datum 4 on Gotland and this may account for the abrupt increase here in $\delta^{13}\text{C}_{\text{carb}}$ values. Munnecke et al. (2003) had only very limited $\delta^{13}\text{C}_{\text{carb}}$ data from below Datum 3 of the Ireviken Event down to about 1 m below Datum 1; this gap was filled by additional sampling and analyses by Cramer et al. (2010a) which provided no evidence for an earlier commencement of the ESCIE. Cramer et al. (2010a) summarized $\delta^{13}\text{C}_{\text{carb}}$ and conodont biostratigraphical data for other sections, noting for example that in the Viki core, Estonia the onset of the ESCIE is at Datum 2, in the Ohesaare core, Estonia it is between Datum 3 and Datum 6, in the Ruhnu core, Estonia it is below Datum 3 and in the Aizpute-41 core, Latvia also below Datum 3.

Although there is a wealth of published $\delta^{13}\text{C}_{\text{carb}}$ data for the Sheinwoodian (Cramer et al., 2010a and references therein), only a few studies presenting $\delta^{13}\text{C}_{\text{org}}$ data have been published. Loydell and Frýda (2007) presented a $\delta^{13}\text{C}_{\text{org}}$ curve for the Banwy River section, Wales (Fig. 2). This shows a pronounced positive excursion in the upper *murchisoni* Biozone. This is succeeded by a negative excursion in the *firmus* Biozone after which there is a protracted interval of more positive values through to the upper Sheinwoodian where the excursion ends (in beds yielding *Monograptus flexilis*). The $\delta^{13}\text{C}_{\text{org}}$ curve for the Luskint 1 section, Gotland (Vandenbroucke et al., 2013) is more complex than the $\delta^{13}\text{C}_{\text{carb}}$ curve of Munnecke et al. (2003). Although there is a small positive shift in values across Datum 4 of the Ireviken Event, the more pronounced (c. 1 ‰) positive shift in $\delta^{13}\text{C}_{\text{org}}$ is between 1.6 m and 1.7 m below Datum 4 and lies between Ireviken Event Datum 2 and Datum 3. Integrated biostratigraphical studies of sections in Estonia and Latvia (Loydell et al., 1998, 2003) place this level within the *murchisoni* Biozone, with Männik (2007) suggesting that it would be at a high level within this graptolite biozone. Most recently, Sullivan et al. (2018) presented $\delta^{13}\text{C}_{\text{org}}$ data

from graptolitic borehole sections in Poland within which the ESCIE is well developed with peak values in the *riccartonensis* Biozone.

2.2. $\delta^{18}\text{O}$ data and interpreted temperature changes through the late Telychian and Sheinwoodian

$\delta^{18}\text{O}$ data from conodonts from the Viki core, Estonia show a positive excursion (Fig. 3), named the Sheinwoodian Oxygen Isotope Excursion (SOIE) by Lehnert et al. (2010), indicating a substantial drop in sea-water temperature (of up to 4° C) in the Baltoscandian Basin. This commenced in the Lower *Kockelella ranuliformis* conodont Biozone which, based on correlation with the Aizpute-41 core (Loydell et al. 2003), would be near the base of the *riccartonensis* graptolite Biozone. The onset of the ESCIE significantly precedes that of the SOIE in the Viki core and, based on correlation of the conodont biozones in the latter core with the graptolite biozonation, it precedes the SOIE's onset elsewhere also.

Trotter et al. (2016) undertook a more extensive study of $\delta^{18}\text{O}_{\text{phos}}$ data from conodonts from four palaeocontinents, leading to recognition of “a multi-step cooling process” commencing in the mid *lapworthi* graptolite Zone (late Telychian, Llandovery) and peaking in the mid Sheinwoodian. Overall temperature decrease was interpreted to have been up to 9°C. The cooling trend was stated to be punctuated by two short-lived rapid warming phases, one in the late *Pterospathodus amorphognathoides amorphognathoides* Zone (and thus below the level of the studied Buttington section), and the second dated to the late *Pt. pennatus procerus* conodont Zone. Note that, according to Trotter et al.'s (2016) Table S1, their samples did not include any conodonts from the Upper *Pt. p. procerus* Biozone (although three samples from core #863 are assigned to this zone on their fig. 2); Peep Männik (pers. comm.) has indicated that there is an error in this table and that sample C95-311 from core #863, on Saaremaa is from the uppermost *Pt. p. procerus* Biozone (equivalent to the lowermost *riccartonensis* graptolite Biozone; Männik, 2007) with the underlying sample (C95-306) from the uppermost *Pt. am. amorphognathoides* Biozone and overlying sample (C95-313) from the *Kockelella ranuliformis* Biozone. It is important to note also that Trotter et al. did not analyse any samples from the *Pseudooneotodus bicornis* Superzone or from the *Pt. p. procerus* Superzone (except for the one mentioned above from the uppermost part) which are equivalent to almost the entirety of the *murchisoni* and *firmus* graptolite biozones (Männik, 2007, fig. 1) and thus including the interval of high sea-level (and presumably warm climate) identified by Loydell (1998, 2007). Trotter et al.'s (2016) $\delta^{18}\text{O}_{\text{phos}}$ data and interpreted temperature changes are consistent with the sea-level changes recognised through the late Telychian–early Sheinwoodian by Loydell (1998,

2007), with cooling in the mid *lapworthi* Zone and again in the *riccartonensis* Zone both at times of falling/low sea-level.

3. Locality information and previous work on Buttington Quarry

Buttington Quarry (Ordnance Survey grid reference SJ 265 100) is a well-known location near Welshpool, in Powys, Wales. The section studied (Fig. 4) is that sampled by Loydell et al. (2014) through strata immediately overlying the Butterley Mudstone Formation, an 8.75 m thick buff-coloured calcareous silty mudstone which forms the lowermost part of the Trewern Brook Mudstone Formation. The Butterley Mudstone Member overlies the Tarannon Shales Formation, predominantly alternating purple and green shales of Telychian age (Loydell and Cave, 1993), which the quarry was established to exploit for brick-making. The lowest Silurian unit in the quarry is the Cefn Formation (interbedded tempestite sandstones and mudstones), which unconformably overlies Upper Ordovician shales.

The combination of good exposure and vertical bedding of a thick sequence (175+ m) of Telychian–Sheinwoodian strata at Buttington has attracted research on various aspects of the section, although much still remains to be done, particularly on the higher Sheinwoodian strata. A useful summary overview of the locality is provided in a field guide (Cave and Dixon, 1993). Cocks and Rickards (1969) referred to three horizons in the lowermost “Wenlock Shale” (= Trewern Brook Mudstones Formation), recording questionable *Cyrtograptus centrifugus* from the lowest, *C. murchisoni* from the middle one and abundant *Monograptus riccardonensis* from the highest. Loydell and Cave (1993) examined the Telychian of the section, focusing on the graptolite biostratigraphy and recognising the *Oktavites spiralis* Biozone for the first time in the British Isles. Underwood (1995) described remarkable specimens of *Cyrtograptus murchisoni* from Buttington showing interstipe webbing. Nothing comparable has appeared in our collections. Thorogood et al. (1998) provided geochemical analyses of some of the numerous bentonites within the Buttington sequence. Mullins and Loydell (2002) described chitinozoans from the Telychian to lower Sheinwoodian, integrating the chitinozoan and graptolite biozonations for the section. Buttington was one of the localities examined as part of the Transhemisphere Telychian Project, with a log of the section and lists of Telychian graptolites from horizons equivalent to beds A–C of Loydell and Cave (1993) provided by Aldridge et al. (2002) and illustrations of some of the graptolites by Rickards and Chen (2002). Loydell et al. (2014) presented high resolution $\delta^{13}\text{C}_{\text{carb}}$ data for the same lower Sheinwoodian section that forms the subject of the present paper. Analyses were undertaken every 10 cm through the section with $\delta^{13}\text{C}_{\text{carb}}$ values in the middle–upper *riccartonensis* Biozone

approximately 3 ‰ more positive than in the upper *murchisoni* Biozone. Llewellyn (2015) undertook a palynological study of the section, focusing on the chitinozoans throughout the section, but including also abundance data for the different palynomorph groups through the lower 8.6 m, i.e. through the main positive shifts in $\delta^{13}\text{C}_{\text{carb}}$ values. Steeman et al. (2016) discussed the Homerian–Gorstian chitinozoan record through the upper part of the Trewen Brook Formation (and overlying formations) of the Long Mountain, in sections 0.5–1.25 km east of Buttington Quarry.

4. Time and proportion of ESCIE represented by the studied Buttington section

Some constraints in terms of overall duration of the ESCIE are provided by radiometric dates derived from zircons from bentonites from the Wenlock of Gotland (Cramer et al., 2012). The Ireviken bentonite lies within the Upper *Pseudooneotodus bicornis* conodont Biozone, between datum 2 and datum 3 of the Ireviken extinction event. This bentonite has been dated as $431.83 \pm 0.23/0.67$ Ma. The $\delta^{13}\text{C}_{\text{carb}}$ ESCIE commences at Datum 4 (Munnecke et al., 2003), 2.45 m above the Ireviken Bentonite. Cramer et al. (2012) also derived a radiometric date ($428.45 \pm 0.35/0.73$ Ma) from the Grötlingbo bentonite, which lies close to the base of the middle Homerian (upper Wenlock) *Gothograptus nassa* Biozone. The duration of the ESCIE as a whole must therefore be significantly less than 3 Myr, particularly when one considers that the lower Homerian *Cyrtograptus lundgreni* Zone, based on stratal thickness (20 m in graptolitic shale facies in the Barrandian area, Czech Republic, compared with, for example, an average here of 2–2.5 m for the *riccartonensis* Biozone), “probably corresponds with a rather long interval if compared with other graptolite zones” (Štorch, 1994a). Biostratigraphically the studied Buttington section is confined to the upper *murchisoni*, *firmus* and *riccartonensis* biozones; the section does not reach the *Cyrtograptus rigidus* Biozone. The top 0.25 m of the studied section yielded only one graptolite species, *Pristiograptus dubius*, suggesting that these strata may belong to the *dubius* Interzone (Fig. 1), an interval of very low diversity graptolite assemblages lacking biostratigraphically short-ranging taxa which has been recognised in Wales (Zalasiewicz et al., 2009) and Bohemia (Štorch, 1994a). Biostratigraphical considerations and comparison of the Buttington isotope curve with that from the Banwy River section (Cramer et al., 2010a) suggests that the Buttington $\delta^{13}\text{C}_{\text{carb}}$ record represents approximately the lower half of the ESCIE. Cramer et al. (2011, fig. 3) and Melchin et al. (2012, fig. 21.1) portrayed the earlier Sheinwoodian graptolite zones (*murchisoni* to *riccartonensis* zones) as being of much shorter duration than the *rigidus/belophorus* Zone. Melchin et al. (2012) referred to Sadler et al. (2009) as providing the methodology (CONOP = constrained optimization) for estimating relative durations of stages and zones. Based on this, Sadler et al. (2009, fig. 10) show the combined

murchisoni to *riccartonensis* zones as comprising about 29% of the duration of the Sheinwoodian. It would seem reasonable therefore to interpret the time represented by the studied Buttington section to be around 0.5 Myr. On this basis, each 5 cm thick sample represents on average 2000 years and thus 10 mm would represent on average c. 400 years. This seems inconsistent with Dimberline and Woodcock's (1987) and Dimberline et al.'s (1990) suggestion that the sub-mm lamination within Welsh Basin hemipelagites was annual and is more in accordance with each silt/mud-organic couplet representing a single depositional event (from a turbulent flow), as suggested by Kemp (1991).

There is no lithological or biostratigraphical evidence for any significant stratigraphical breaks in the section, including at levels where there are sudden changes in $\delta^{13}\text{C}_{\text{carb}}$ values, e.g. between 8.19–8.25 m (+0.60 ‰) to 8.30–8.35 m (+1.51 ‰). The absence of nodules also suggests that there were not any intervals of non-deposition of sufficient duration to enable nodule growth (Raiswell, 1987).

5. Methods

Bulk samples for both palaeontological and geochemical studies, each representing a 5 cm interval, were collected from the Trewern Brook Mudstone Formation, from the top of the Butterley Mudstone Member through a stratigraphical thickness of 12.4 m to the highest exposed strata in this part of the quarry (Figs 4, 5A). The section studied is that of Loydell et al. (2014). Overall sample size varied depending upon fossil abundance, perceived palaeontological importance of the horizon collected and ease of collection. Some horizons could be extracted as large slabs, but the majority fractured into small pieces (a few centimetres in size; see upper part of Fig. 6) and large blocks required embedding in resin or plaster to retain their integrity. Several horizons were re-sampled in an attempt to constrain graptolite biozonal boundaries (based upon FADs of index taxa) as accurately as possible.

Logging of the section in the field was combined with subsequent examination of samples cut perpendicular to bedding in order to reveal lithologies, sedimentary structures and bioturbation index (BI; Taylor and Goldring, 1993). Approximately 250 cut samples were examined. Much more detail was visible on these cut slabs than could be seen on weathered surfaces in the field and on uncut hand specimens. Lithological specimens for photography were polished using 600 grade black silicon carbide mixed with water on a glass plate. Many photographs were taken with specimens immersed in alcohol to enhance contrast. The thicker bentonites shown on the log (Fig. 7) were

identified and collected in the field and proved to be useful marker beds; thinner (in many cases sub-mm) bentonites were discovered when breaking up the bulk samples to reveal the fossil content.

All of the collected rock samples were examined under a light microscope. The graptolites were identified to species level. Other macrofossils (together with ostracods and other non-organic walled microfossils) remain to be studied in detail, but their occurrence and abundance within individual samples were recorded (Fig. 11). Samples for the palynological work of Llewellyn (2015) were processed using the standard HCl-HF-HCl technique.

Trace element analysis of sedimentary pyrite was performed using laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS). Between 8.6 m and 10.55 m analyses were made of samples taken at more closely spaced intervals (0.2–0.35 m) than at other levels in the section. This was because of the rapid and pronounced positive shift in $\delta^{13}\text{C}_{\text{carb}}$ values in the lower part of this interval (Fig. 7). All analyses were conducted at the ARC Centre of Excellence in Ore Deposits, University of Tasmania. Instrumentation used comprised a 213 nm solid-state laser microprobe (UP213, NewWave Research) coupled to an Agilent 7500a quadrupole mass-spectrometer, and a 193 nm solid-state laser microprobe (UP193ss, NewWave Research) coupled to an Agilent 7700s quadrupole mass-spectrometer. Laser microprobes are equipped with custom-made constant-geometry ablation cells. The following analytical parameters and conditions were used: laser beam diameter of 8–40 micrometres, depending on the size of pyrite grains; laser beam fluence $\sim 3.5 \text{ J/cm}^2$ at the sample for UP213 and $\sim 2 \text{ J/cm}^2$ for UP193ss; laser pulse rate 5 Hz; ablation occurred in the atmosphere of pure He flowing at a rate of 0.8 l/min; immediately past the ablation point within the cell, He carrier gas was mixed with Ar (0.85 l/min) for improved efficiency of aerosol transport; both ICP-MS instruments were optimized to maximize sensitivity on mid- to high-mass isotopes (in the range 80–240 amu). Further details of the LA-ICPMS method can be found in Large et al. (2014).

The porous nature of syngenetic and diagenetic pyrite resulted in a variable amount of silicate matrix being ablated together with pyrite. Quantification of the mixed pyrite/matrix signal was achieved by analysing all major elements in the mix and normalizing the total of the analysis to 100% (g/g). The composition of the silicate matrix was determined in each sample by analysing several spots around the diagenetic pyrite. With the composition of the silicate matrix known, the compositions of diagenetic pyrite were derived from the analysis of the mix using a standard mass-balance approach. Concentrations of all major silicate elements, except Fe (i.e., Al, Mg, K, Na, Si, Ti) were used to estimate the proportion of matrix in each analysis by a least squares method. All analyses with the amount of silicate matrix over 50%, or analyses where the least squares method for estimating the amount of matrix gave large errors, were excluded from the data set. Pyrite data

that showed large inclusions of other sulphides were also excluded from the dataset when Zn and Pb > 10,000 ppm, Cu > 30,000 ppm, As > 10 wt% or $0.5 < \text{Fe/S} < 1.2$. Analyses of recrystallized and chemically modified parts of pyrite grains that had lost most of their TE, were also removed from the dataset using the Co content, as Co is tightly held in the pyrite structure and only released after significant recrystallization (Large et al., 2017).

6. Sedimentology

The transition from the uppermost Butterley Mudstone Member into the overlying beds of the Trewern Brook Mudstone Formation takes place over a few centimetres (Fig. 6). The beige, highly bioturbated silty mudstones of the former give way to conspicuously laminated grey shales, mudstones and siltstones with common graptolites many of which are preserved in three dimensions in pyrite (Fig. 9H, 12A,E). The remainder of the section is dominated by medium to dark grey mudrocks (Figs 8, 9) often weathering to a beige colour. The superficially monotonous sequence is punctuated by numerous (38) bentonites (Figs 5B, 7), with the thickest of these at 5.09 m (25 mm), 8.16 m (20–30 mm), 8.72 m (30 mm) and 11.32 m (30 mm). A few fine sandstones, mostly 1–3 mm thick, with the thickest (at 3.30 m) being 7 mm thick, occur predominantly in the lower 4 m of the section (Figs 7, 9F). These are interpreted here as very distal tempestites. Pavements and thin beds of comminuted shell debris are common throughout the section and are assumed to have a similar origin. Four layers extremely rich in crinoid ossicles (effectively thin beds of crinoidal limestone) occur, at 0.45 m, 0.65 m, 0.78 m and 0.86 m, high in the *murchisoni* Biozone and thus from a similar stratigraphical level to that from which Loydell and Cave (1996) recorded a similar crinoidal layer in the Banwy River section, c. 19 km to the west of Buttington.

Where not destroyed/disrupted by bioturbation, the strata can be seen to be laminated (e.g. Figs 6, 8A,B, 9H), appearing similar to the laminated hemipelagites described by Dimberline et al. (1990) from the Wenlock and Ludlow of the Welsh Basin and by Kemp (1991) who reviewed this distinctive mid Silurian facies around the margins of Iapetus. Dimberline et al. (1990) interpreted the alternating darker and lighter laminae as representing (possibly annual) plankton blooms and increased discharges of silt respectively. Kemp (1991), however, considered that “it is more likely that the carbonaceous lamination observed in the hemipelagite originates from the compaction of discontinuous films of organic material which were deposited in intimate association with clay and fine silt from a low concentration turbulent suspension”. Smolarek et al. (2017) illustrated laminated hemipelagic strata from the Sheinwoodian of Poland very similar in appearance to beds from Buttington, but considered the organic material to represent benthic microbial mats and biofilms

and the lighter coloured laminae to result from “periodic deposition from diluted low-density bottom currents” or deposition from “dust clouds of Aeolian origin”. Whilst some of the laterally more continuous organic-rich laminae in the Buttington sequence may have a microbial mat origin (e.g. Fig. 9B), most of the organic-rich material appears as tiny flakes (tens to hundreds of micrometres long) which are concentrated in the darker laminae (Fig. 8B). Thus deposition from plankton blooms or from the later depositional stages of a distal tempestite are considered to represent the most likely origin for the majority of the Buttington organic material.

The pelleted appearance of some laminae, remarked upon by Dimberline et al. (1990) in basinal hemipelagites from Wales, is visible also in many Buttington samples (Fig. 8B). Dimberline et al. (1990) considered the pellets/aggregate structures to be faecal in origin whereas Khan and Kelling (1991) ascribed to them a physico-chemical origin via flocculation. Kemp (1991), however, concluded that they represent the burrows of a low-oxygen meiofauna of polychaetes and nematodes. The fact that they are uniformly oval in cross section (rather than forming elongated burrows) argues against Kemp’s proposal. Similar structures in Sheinwoodian hemipelagites from Poland are referred to by Smolarek et al. (2017) as “mudstone micro-clasts” and interpreted (following Schieber et al., 2010) as having been eroded and then transported from a partially consolidated mudstone substrate. However, neither the Buttington samples nor those from Poland appear to resemble closely the lenticular shale fabric illustrated by Schieber et al. (2010).

A 15-mm-thick cross-laminated bed in the 10.45–10.50 m sample (Fig. 10) provides evidence for mud deposition under energetic conditions (O’Brien, 1996; Schieber and Southard, 2009; Schieber and Yawar, 2009) as do the many horizons with aligned graptolites (Fig. 7) and rare “graptolite comets” (e.g. Fig. 5D).

7. Environment of deposition – observational data

7.1. Bottom water and sediment oxygen levels

Evidence for bottom water and shallow sediment oxygen levels can be derived by the extent of bioturbation (measured via the bioturbation index: BI; Taylor and Goldring, 1993), from the presence of shelly benthos (assuming that this is not allochthonous) and from fossil preservation (especially three dimensional pyrite internal moulds).

Lack of bioturbation (BI = 0) would provide good evidence for anoxia or other unfavourable environmental conditions for infaunal benthic organisms. However, of the 248 lithological samples examined only four had a bioturbation index of 0, indicating that there was at least some oxygen

within the sea floor sediments for the vast majority of the time represented by the section. The BI fluctuates throughout the section, mostly between 1 and 4, with some intervals characterized by predominantly higher or lower values (Fig. 11). Protracted intervals of zero or low bioturbation (taken as two or more consecutive samples with a BI of 0 or 1) occur between 3.20 m and 4.60 m, 8.19 m and 8.40 m and 9.90 m and 11.20 m (Fig. 7). Low BI values (BI = 1 or 2, but no two consecutive samples with BI of 1) are also present in the lowest 0.7 m of the section (Fig. 11). Detailed study of the trace fossil taxa present has not been undertaken, but prominent in many samples are *Teichichnus* (e.g. Fig. 8C, D), a genus recently reviewed by Knaust (2018), and *Chondrites* (e.g. Fig. 9C). Knaust (2018) noted that *Teichichnus* may indicate dysoxic conditions and this would certainly seem to be the case where it occurs in intervals of fairly low BI (e.g. Fig. 8C).

Shelly benthos (predominantly brachiopods, bivalves, trilobites, pelmatozoans and ostracods) are present in the majority of samples through the section (Fig. 11). The only interval of more than a single isolated sample (these are at 1.35–1.40 m, 1.70–1.75 m, 2.80–2.85 m, 3.80–3.85 m and 8.19–8.25 m) to lack any benthic organisms is between 10.00 m and 11.15 m within which 15 (out of 23) samples lack any benthic fossils and in samples where they are present they are rare. This interval is also characterized by low BI (0–2; Fig. 11). However, between 2.95 m and 4.7 m, the other long interval of low BI (0–2, mostly 1), brachiopods were present in almost every sample (Fig. 11), pelmatozoans sporadically, but trilobites in only one sample (at 3.70–3.75 m) and, above 3.15 m, ostracods only in three samples (and in two of these as single specimens). The combination of BI data and presence/absence of shelly benthos suggests that both bottom water and sediment oxygen levels were very low through the 10.00–11.15 m interval and that sediment oxygen levels were low through 2.95–4.70 m, but bottom waters were sufficiently oxygenated at this time to support brachiopods and pelmatozoans, although the occurrence of the latter is much reduced by comparison with the more highly bioturbated beds above and below (Fig. 11).

Loydell et al. (2009a, 2013) used the presence of three-dimensional pyrite internal moulds of graptolites to identify intervals of bottom water oxygenation in sediments deposited under otherwise anoxic conditions (in which pyrite was rapidly precipitated as tiny disseminated crystals and graptolites were preserved simply as flattened periderm). Similar preservational observations have been made on the Buttington graptolites (and also gastropods, either the initial whorls or complete microgastropods) and are shown in Figure 7. In general, intervals interpreted as anoxic/dysoxic based upon their low BI (of 0, 1 or 2) are characterized by flattened graptolites; three dimensional pyrite internal moulds are present through more heavily bioturbated/highly oxygenated intervals where the graptolite rhabdosomes and early whorls of gastropods provided local anoxic microenvironments in which pyrite precipitated, whilst the surrounding sediment retained some

oxygen content. Finely disseminated pyrite can be seen in intervals with little or no bioturbation (e.g. Fig. 8B).

Based on the evidence above, it is interpreted that bottom waters and sediments close to the sediment/water interface (SWI) were not anoxic for any protracted interval during deposition of the sediments in the studied Buttington section. An interval of dysoxic/hypoxic conditions, extending above the SWI occurred during deposition of the 10.00–11.15 m interval, with only a limited infauna of low oxygen tolerant soft-bodied benthos (perhaps nematodes and annelids). The implication from the presence of brachiopods in the stratigraphically lower interval of low BI (3.40–4.60 m) is that there was sufficient oxygen above the SWI to support limited shelly benthos (but not trilobites), but at this time oxygen levels within the sediment were too low for shelly meiofauna (ostracods) to survive.

Emsbo et al. (2010) referred to an oceanic anoxic event (OAE) commencing at Ireviken Event Datum Point (IEDP) 4 on Gotland and extending through to the end of the Ireviken Event (IEDP 8). The impacts of this event have been identified also in the Appalachian Basin, USA (McLaughlin et al., 2012). As noted above, there is a hiatus at IEDP 4 on Gotland, so the OAE may have commenced somewhat earlier than shown in the preserved rock record. Correlating from Baltic sections to Buttington (and thus assuming no diachronism of conodont biozonal boundaries (however caution is required as such diachronism has been demonstrated higher in the Wenlock Series; Cramer et al., 2010b)), IEDP 4 correlates with a level high in the *murchisoni* graptolite biozone, very close to the base of the *firmus* Biozone (Männik, 2007; Fig. 3). In the Buttington section, the most obvious change in facies is at the top of the Butterley Mudstone Member, where there is a rapid transition from heavily bioturbated to laminated graptolitic mudstones (Fig. 6). With the level of this facies change only 0.43 m below the LAD of *Cyrtograptus murchisoni*, it is very tempting to interpret this level as marking the base of this OAE (Fig. 17). It is interesting also that in the Sommerodde-1 core, Bornholm the base of Unit G4, marked by a change from medium grey to dark grey mudstones, occurs at a comparable biostratigraphical level (Loydell et al., 2017).

7.2. Substrate

The terminology used here is that of Taylor et al. (2003). This aspect of the palaeoenvironment is one for which there are no geochemical proxies, so interpretations must be based on observational data alone. The presence of trace fossils throughout most of the section suggests that the seafloor was not a soupy substrate. However, the common occurrence of

orthocones at a high angle to bedding (e.g. Fig. 5D) indicates that these were able to penetrate the top layers of sediment upon reaching the SWI and thus for much of the time the seafloor appears to have been a softground. Conditions were modified, however, when comminuted shelly debris was introduced (interpreted as distal tempestites) and temporarily a harder substrate was available. Strophomenid brachiopods, but few other macrofossils, occur on several of these shell debris layers, suggesting that they were able to take advantage of this change in substrate. Rare firmgrounds, perhaps generated by erosion of the top layers of sediment to reveal more compacted sediment beneath, can be identified by the presence of open burrow systems (small *Thalassinoides*?, e.g. at 7.10–7.15 m and 7.15–7.20 m) filled with sediment from the overlying layer.

7.3 Hydrodynamic conditions

Although it is tempting to consider a sequence dominated by fine-grained sediment as representing exclusively low energy conditions, recent studies (e.g. Schieber and Southard, 2009) have challenged that assumption. Evidence for times of higher energy conditions at Buttington include (1) a single instance of cross lamination (at 10.45–10.50 m; Fig. 10), (2) the several thin layers of fine sandstone (e.g. Fig. 9F; all are shown on Fig. 7) and very numerous layers of comminuted shelly debris representing storm deposition and (3), at several levels, mostly in the middle and uppermost parts of the section (Fig. 7), the presence of aligned graptolites, in rare cases wrapped around an orthocone which was protruding from the sea floor, producing a ‘graptolite comet’ (Fig. 5D). Overall, it is envisaged that the Buttington section represents predominantly a low energy environment, but with occasional (and at times frequent) short-lived higher energy events generating the various features described above.

8. Graptolite record through the ESCIE at Buttington

Graptolite assemblages at Buttington are dominated by a small number of species, some of which (e.g. *Monograptus priodon*, *Pristiograptus dubius*) are stratigraphically long-ranging, whilst others fortunately are the index species for the lower Sheinwoodian graptolite biozones and are present in abundance. Occurrences are shown in Figure 7. Some of the species recorded occur as only one or two specimens (out of the many thousands examined overall) at only one or a small number of horizons. Graptolites from the section are illustrated in Figures 12–14. Figured specimens are housed in the British Geological Survey, Keyworth.

Biogeographically, the Buttington assemblages are typical for Avalonia and very similar also to those recorded from Baltica (e.g. Loydell et al., 1998, 2003) and peri-Gondwanan Europe (e.g. Štorch 1994a, 1994b), although *Cyrtograptus bohemicus* is more common in the *murchisoni* Biozone in Bohemia than *C. murchisoni*. *Monograptus riccartonensis* is known also from North Africa (Štorch and Massa, 2003). Very different graptolite assemblages characterize the equatorial realm, with neither *M. firmus* nor *M. riccartonensis* recorded from Arctic Canada where a *Monograptus instrenuus-Cyrtograptus kolobus* Biozone was erected for strata above the LAD of *C. murchisoni* (Lenz and Melchin, 1991; Lenz et al., 2012). No *Cyrtograptus* species have been recorded from the *riccartonensis* Biozone of Avalonia, Baltica or peri-Gondwanan Europe; following the graptolite extinction coincident with the onset of the ESCIE, the genus was present only at low latitudes until the late Sheinwoodian.

Lower Sheinwoodian graptolite assemblages do not fit existing models of graptolite distribution with regard to water depth or proximity to shoreline. The early ESCIE interval at Buttington (and elsewhere) is unusual in that the stratigraphically useful species (in particular *Monograptus firmus* and *M. riccartonensis*) within the low diversity assemblages appear not to be environmentally restricted in their occurrence. Štorch (1998) had noted that “precise stratigraphical assignment” of the low diversity assemblages typical of his nearest shore graptolite “sub-fauna (a)” is generally difficult, because they are dominated by long-ranging taxa. Overall, the Buttington graptolite assemblages seem transitional between Štorch’s (1998) sub-faunas (a) and (b), the latter being characterized by enrichment by age-diagnostic species including some cyrtograptids. Both Berry and Boucot (1972) and Chen (1990; see also Boucot and Chen, 2009) show *Cyrtograptus* to be restricted to the deepest offshore shelf environments and to be associated with diverse graptolite assemblages. The distribution pattern of *Cyrtograptus murchisoni* at least does not fit this model and indeed appears rather complex. The species is abundant in the lowest part of the studied Buttington section, but in the Banwy River section, which represents a deeper water, outermost shelf locality, the species is much less common, with assemblages dominated by *Monoclimacis* (Loydell and Cave, 1996). Further west, within the turbiditic Welsh Basin *Cyrtograptus murchisoni* is again common (Wood, 1906; pers. obs.).

As there have been numerous studies of *murchisoni* to *firmus* Biozone graptolite biostratigraphy in recent years (e.g. Štorch, 1994b; Loydell and Cave, 1996; Loydell et al., 2003), more detailed discussion of the biostratigraphy below is limited to the comparatively much less studied *Monograptus riccartonensis* Biozone.

The lowest 0.43 m of the section can be assigned to the upper part of the *murchisoni* Biozone. Above this, to 0.90 m (base of *firmus* Biozone) there are no biozonally definitive taxa. Throughout this transitional interval from the uppermost *murchisoni* to lower *firmus* Biozone *Monograptus priodon* is particularly common, as it is also at a comparable stratigraphical level in the Banwy River section (Loydell and Cave, 1996). The *Monograptus firmus* Biozone is only 1.35 m thick (compared with 7+ m in the Banwy River section; Loydell and Cave, 1996), with the FAD of *M. riccartonensis* at 2.25 m. The highest *M. riccartonensis* recorded was in the 12.15–12.20 m sample. Above this (to the top of the section at 12.40 m) graptolites are very rare to uncommon, with only *P. dubius* encountered.

The lowermost part of the *riccartonensis* Biozone yields at Buttington, as it does elsewhere (e.g. Bohemia – Štorch, 1994a; Latvia – Loydell et al., 2003; Bornholm – Loydell et al., 2017) rare occurrences of taxa generally more characteristic of the underlying *murchisoni* and *firmus* biozones, most notably *Cyrtograptus bohemicus* (in the 2.90–2.95 m sample). There are no records anywhere of *C. bohemicus* from above the lower *riccartonensis* Biozone and thus records such as that from unit c of the Upper Visby Formation of Gotland (Loydell and Jeppsson, 2006), approximately 3 m above Datum 6 of the Ireviken Event, are particularly important stratigraphically.

The range of *Monograptus firmus* extends up to just below half way through the *riccartonensis* Biozone. The relative abundance of the two closely related taxa (*M. firmus* and *M. riccartonensis*) fluctuates through the lower *riccartonensis* Biozone (Fig. 7), but at most horizons one or other or both are common. *Monograptus sedberghensis*, first described from the upper *riccartonensis* Biozone of the Howgill Fells, England by Rickards (1965) and subsequently recorded only once, from Estonia (Loydell et al., 1998), appears about one-fifth of the way through the biozone, initially generally rarely and sporadically, but more commonly towards the middle part of the biozone.

A remarkable and abrupt change in assemblage composition occurs at 6.8 m. Below this level, the *riccartonensis* Biozone graptolite assemblages are dominated by *Monograptus* (Fig. 7). Above this level *Monograptus* is largely absent for several metres and *Pristiograptus dubius* is overall the most frequently encountered graptolite until *Monograptus* is consistently present again, above 11 m.

Mediograptus antennularius (Fig. 12G,N) appears high within the Buttington section (in the 9.75–9.80 m sample). In some places (e.g. the English Lake District, Rickards, 1969; Lithuania, Paškevičius, 1979; Southern Uplands of Scotland, White et al., 1992) an *antennularius* Biozone is recognised above the *riccartonensis* Biozone (Fig. 3), with the ranges of the two index species

overlapping. In other papers (e.g. Zalasiewicz et al., 2009), a separate *antennularius* Biozone is not used, with the species shown as appearing in the middle of the *riccartonensis* Biozone. The species is undoubtedly very useful biostratigraphically, consistently appearing in the middle Sheinwoodian significantly above the FAD of *Monograptus riccartertonensis*.

Two species have FADs in the Buttington section at a lower stratigraphical level than previously recorded. *Monoclimacis flumendosae* (Fig. 12B,I) has in the past been only questionably recorded from the upper part of the *riccartonensis* Biozone with the lowest unequivocal specimens recorded from the overlying *dubius* Interzone (Zalasiewicz et al., 2009). In the Buttington section it appears in the middle of the *riccartonensis* Biozone (Fig. 7). Lenz et al. (2012) use the FAD of *Mcl. flumendosae* in Arctic Canada to mark the base of a *flumendosae* Biozone. As Lenz et al. (2012) noted, this is one of very few mid Sheinwoodian species that has an apparently global distribution. *Monograptus flemingii* (Fig. 13M) similarly has a previously recorded FAD of *dubius* Interzone in Britain (Zalasiewicz et al., 2009) or the succeeding *Monograptus belophorus* Biozone in Bohemia (Štorch, 1994a). It has its lowest occurrence in the Buttington section quite low in the *riccartonensis* Biozone (Fig. 7).

Monoclimacis vikensis (Fig. 12J), originally described from Norway where it was associated with a biostratigraphically undiagnostic graptolite assemblage (Bassett and Rickards, 1971), has been identified only questionably from Wales previously (Loydell and Cave, 1996). In the Buttington section uncommon but well preserved specimens occur mostly in the *murchisoni* Biozone, but with rare specimens present also in the *firmus* and *riccartonensis* biozones.

8.1. Notes on graptolite species

Within the *riccartonensis* Biozone two genera dominate most of the assemblages: *Monograptus* and *Pristiograptus*. In the absence of the proximal end, assignment of a specimen to one of the three closely related *Monograptus* species, *M. firmus*, *M. riccartertonensis* and *M. sedgberghensis*, is not possible. When the proximal end is preserved, *M. firmus* (Fig. 13E,J) can be seen to have a straight rhabdosome, *M. riccartertonensis* (Figs 13A,C,D,G,L, 14A,B) is dorsally curved proximally and *M. sedgberghensis* (Fig. 13B,F,K) is ventrally curved proximally. A feature of *M. riccartertonensis* not recorded previously is that in the middle part of its stratigraphical range the sicula in many specimens becomes considerably widened aperturally (Fig. 14A,B), creating a resemblance to the distinctive, trumpet-shaped sicula of the Homeric *Colonograptus deubeli* (Koren' and Suyarkova, 1994). *Monograptus instrenuus* (Fig. 13I), first described from Arctic Canada by Lenz and

Melchin (1991), where it is a biozonal index species for the middle Sheinwoodian, is narrower than *M. riccartonensis*, but otherwise appears similar. Chemically isolated material was described by Lenz et al. (2012). It is the only species from the otherwise biogeographically distinct Arctic Canadian graptolite fauna to have been recorded from Avalonia (herein, and questionably by Zalasiewicz and Williams, 1999 from the Builth area).

The most common *Pristiograptus* species present, *P. dubius* (Fig. 12D,F,L), can be seen to have the thickened apertural lip (Fig. 12L), typical of mid Sheinwoodian specimens, but lacks the additional cortical thickenings recorded from higher stratigraphical levels (Radzevičius, 2003). The only other *Pristiograptus* present, *P. latus* (Fig. 12K), has a broader rhabdosome than *P. dubius*.

8.2. Changes in graptolite diversity globally and in the Buttington section

Commencing in the upper *Cyrtograptus purchisoni* Biozone, the early stages of the ESCIE (through to the lower *Monograptus riccartonensis* Biozone) are characterized by a dramatic decline in graptolite diversity and disparity such that graptolite assemblages above the lowermost *riccartonensis* Biozone are paucispecific and usually dominated by the biozonal index species (and/or morphologically very similar taxa) and/or the extraordinarily long ranging *Pristiograptus dubius* (the *dubius* species group ranges from the *Monograptus firmus* Biozone to the Přídolí; Urbanek et al., 2012). Štorch (1995) referred to this diversity decline as the “*murchisoni* Event” stating that it “nearly brought the Silurian graptolites to extinction” and noting that species diversity in the Barrandian (Bohemia) dropped from 21 species to four by the *dubius* Interzone. Some early Sheinwoodian taxa clearly survived into the earliest *riccartonensis* Zone, with records of *Barrandeograptus pulchellus*, *Cyrtograptus bohemicus*, *C. purchisoni* and *Euroclimacis deflexa* from Bohemia and/or Bornholm (Štorch, 1994b; Loydell et al., 2017). This suggests that the final phase of the extinction event occurred early in the *riccartonensis* Zone. *Cyrtograptus* is unknown from higher levels in the *riccartonensis* Biozone or from higher in the Sheinwoodian of Avalonia, Baltica and peri-Gondwanan Europe until the upper Sheinwoodian *Cyrtograptus rigidus* Biozone. Rare specimens of endemic *Cyrtograptus* species have been recorded from the *Monograptus instrenuus*-*Cyrtograptus kolobus* Biozone of Arctic Canada (e.g. Lenz et al., 2012) which correlates with the *riccartonensis* Biozone of Britain, suggesting that low latitude taxa fared better during the extinction event than those from mid to high latitudes.

The decline in graptolite diversity so apparent from other areas (e.g. Bohemia: Štorch, 1995; Latvia: Loydell et al., 2003; see also global synthesis of Cooper et al., 2014) is not so obviously

manifested in the Buttington section. This is due largely to the environmental setting of the area during the Sheinwoodian which restricted overall graptolite diversity at Buttington despite it being higher elsewhere. *Euroclimacis* and *Mediograptus* are particularly rare in the *murchisoni* and *firmus* biozones at Buttington, with only one specimen of *Mediograptus* (Fig. 12M) encountered. This contrasts with the presence of numerous species recorded in abundance from equivalent stratigraphical levels elsewhere (e.g. Štorch, 1994b).

9. Palynomorph abundance

Palynomorph abundance data for the lower 8.6 m of the section were provided by Llewellyn (2015, table in appendix 12). These data are plotted in Figure 15 (note that the data in figure 7.2 in Llewellyn, 2015 are plotted incorrectly). An abundance peak in all groups except chitinozoans occurs at 0.2 m, for all groups except prasinophytes at 1.0 m, in all groups at 2.0 m and for non-sphaeromorph acritarchs at 3.5 m. The highest sphaeromorph and chitinozoan abundances both occur at 4.0 m, a level at which non-sphaeromorph acritarch and prasinophyte abundances are also significantly above their median values. Non-sphaeromorph acritarch and prasinophyte abundances show a small peak at 5.15 m and chitinozoans at 5.35 m, above which all groups are in relatively low abundance through to the last sample examined at 8.6 m.

It is interesting that all of the main abundance peaks fall within the lower part of the Buttington section (the last being in chitinozoans at 5.35 m) during the interval when graptolite diversity was declining and through the period during which there is a positive shift in $\delta^{13}\text{C}_{\text{carb}}$ values of 2‰. Surprisingly, there is little change in the (low) palynomorph abundance through the most rapid positive shift in $\delta^{13}\text{C}_{\text{carb}}$, from 0.6 ‰ at 8.19–8.25 m to 2.09 ‰ at 8.50–8.55 m.

10. Pyrite geochemistry: results and interpretations

Recent research (Large et al., 2014, 2015, 2017; Gregory et al., 2015, 2017) has demonstrated the value of laser-ablation inductively coupled mass spectrometry (LA-ICPMS) analysis of trace elements in pyrite in marine shales to estimate first order trace element trends in past oceans. The technique is based on the premise that marine pyrite that develops in the water column or the top few centimetres of organic-bearing muds will absorb certain trace elements in proportion to their concentration in seawater (Huertz-Diaz and Morse, 1992; Large et al., 2014; 2017; Gregory et al., 2015). The marine pyrite LA-ICPMS technique is more sensitive to low-level changes in trace

element concentrations than bulk rock geochemical techniques, and enables both increasing and decreasing trends in ocean chemistry to be investigated (Gregory et al., 2017).

10.1. Nutrients

Marine pyrite incorporates many micro-nutrient trace elements (TE) during growth; including Ni, Cu, Zn, Se, Mo and Cd. An additive index of these nutrient elements measured by LA-ICPMS in pyrite has been proposed as a proxy for seawater nutrient concentrations (Large et al., 2015). Trends in this nutrient proxy have been shown to replicate trends in the biolimiting nutrient phosphorus (Large et al., 2017).

Based upon the nutrient TE proxy, it can be seen that nutrient levels at Buttington were generally somewhat above mean Phanerozoic values throughout the early Sheinwoodian (Fig. 15), perhaps a reflection of the ongoing collision of Avalonia with Laurentia, causing uplift and a ready influx of freshly weathered sediment, combined also with frequent volcanism and the deposition of ash. The mean nutrient TE proxy value has been determined from the extensive marine pyrite database of Large et al. (2015, 2017). This proxy is based on pyrite TE in black shales in continental margin settings similar to the Trewern Brook Mudstone Formation. Two peaks in nutrient abundance occur between 1.80 m and 4.45 m, with high values throughout this interval (upper *firmus* to lower *riccartonensis* biozones). Interestingly, the most abundant palynomorphs in the Buttington residues, the sphaeromorphs, show peaks in abundance at the 2 m and 4 m levels, with high values (above 400 per gramme) in all four samples from 3.40 m to 4.30 m and again at 4.80 m (Fig. 15). Non-sphaeromorph acritarchs are also abundant at these levels (Fig. 15). The increased abundance of these two groups suggests enhanced phytoplankton productivity at this time. Increased zooplankton abundance around the 4 m level is reflected in a peak in chitinozoan (egg cases of an unknown invertebrate) abundance at 4 m (Fig. 15) and by numerous samples with very abundant graptolites between 4.00 m and 4.65 m (Fig. 7; see also field photo, Fig. 5C). This increase in primary productivity and subsequent carbon burial presumably contributed to the rising $\delta^{13}\text{C}_{\text{carb}}$ values through this interval.

Throughout the interval with the peaks in nutrient values graptolite diversity was declining rapidly (Štorch, 1995, fig. 3) and assemblages at Buttington become dominated by the two robust *Monograptus* species, *M. firmus* and *M. riccartertonensis* (Fig. 7).

10.2. Zinc at Buttington: nutrient or toxic?

Although zinc is a biolimiting nutrient trace element and known as a growth promoter in phytoplankton (Sunda, 2012), it is present at such high levels in pyrite in some intervals of the Buttington section (Fig. 11), that it is worth considering whether it may have been toxic to some life forms. Zinc generally averages around 380 ppm in Phanerozoic marine pyrite, which corresponds to seawater values of 100 to 500 ng/kg (Sunda, 2010; Large et al., 2014, 2015). However, in the 1.8 to 4.5 m interval of the section, Zn is above 1000 ppm and reaches a value in pyrite of 7437 ppm at 4.4 m, about 20 times the Phanerozoic average, with very high values also (5832 ppm and 5868 ppm respectively) in the 2.4 m and 4.0 m samples. It is possible that the high Zn levels may relate to submarine hydrothermal activity; however, other elements normally associated with hydrothermal activity (e.g., Mn, Ag, As, Tl; Mukherjee and Large, 2017) show no particular enrichment above background values.

The interval of high zinc values extends from the *firmus* Biozone into the lower *riccartonensis* Biozone and thus coincides with the final stages of the global decline in graptolite diversity. It is tempting therefore to suggest that zinc toxicity may have played a role in this diversity decline. Munnecke et al. (2012) and Vandenbroucke et al. (2015) recorded malformed (teratological) palynomorphs from levels (correlated from Gotland) overlapping with the interval of high Zn in Buttington (Fig. 17); they attributed these malformations to increased concentrations of metallic toxins. Llewellyn (2015) did not note any increase in palynomorph malformations in the Buttington section; however, this may have been in part down to preservation significantly less good than that of palynomorphs from Gotland.

The sinking of phytoplankton blooms in areas of high bioproductivity is the key agent in redistributing nutrient elements between sea water in the euphotic zone and the underlying sediments, especially under anoxic or euxinic conditions (Sokol et al., 2017). The ability of phytoplankton cells to take up nutrient metals in quantities far exceeding those needed to support growth and metabolism helps the phytoplankton take advantage of pulsed nutrient inputs (Sunda, 2012), and also will result in enhanced metal flux to bottom sediments upon post-bloom sinking of phytoplankton cells. The effects of the resultant high bottom water and sediment zinc levels on benthos are difficult to disentangle from those resulting from fluctuations in bottom water and interstitial oxygen levels. Based upon bioturbation index values, oxygen levels within the sediment were reasonably high at the time of deposition of the lowest samples with high Zn concentrations in pyrite (Fig. 11) and then declined into the protracted interval of low BI (0 or 1) from 3.4 m to 4.6 m in the lower *riccartonensis* Biozone. Zinc accumulation in sediments today can pose a hazard to sediment-dwelling organisms such as polychaetes and ostracods although other organisms have been found to be attracted to Zn-contaminated sediments (Watzin and Roscigno, 1997). Various

shelly benthic fossil groups are represented throughout the high Zn interval of the Buttington section (Fig. 11) implying that although individual taxa may have been affected by zinc toxicity, many were not. The increase in abundance of benthic organisms after the high Zn interval (Fig. 11) coincides also with a marked increase in BI (used as a proxy for sediment oxygen levels).

10.3. Atmospheric pO_2

Redox sensitive trace elements in marine pyrite, including Se, Mo, Sb, U, V and Co have been used as proxies for oxygen levels in the past atmosphere-ocean system (Anbar et al., 2006; Scott et al., 2008; Gill et al., 2009; Sahoo et al., 2012; Partin et al., 2013; Reinhard et al., 2013; Large et al., 2014, 2015; Mukherjee and Large, 2016; Gregory et al., 2017). Applied to the Buttington section, the Se/Co ratios in pyrite suggest overall moderate to low atmospheric pO_2 conditions during the early Sheinwoodian (Fig. 16) with very low atmospheric oxygen levels indicated in the lowest sample analysed which is at a level correlated with the commencement of the Sheinwoodian OAE identified by Emsbo et al. (2010).

It is interesting that in the part of the section for which there is palynomorph abundance data, the peaks in atmospheric pO_2 coincide with the intervals of highest palynomorph abundance (Fig. 15). Burial of organic carbon is one of the main causes of increased atmospheric pO_2 (Berner, 1987). For example, major increases in pO_2 in the Devonian–Carboniferous have been attributed to increased carbon burial resulting from the rise of larger plants (Catling and Zahnle, 2002; Berner et al., 2003). It may be that similar, but obviously less pronounced increases in atmospheric pO_2 were achieved earlier in the Palaeozoic by increased burial of largely marine derived organic carbon.

11. Proposed scenario

The Buttington section has provided a wealth of sedimentological, palaeontological and geochemical data through the lower Sheinwoodian. Key observations and interpretations from the section are shown on Figure 17 where they are correlated with major events identified from other sections or globally.

The lower part of the Buttington section (0–5 m; upper *murchisoni* through to lower *riccartonensis* biozones) was deposited during a period of major global decline in graptolite diversity; this part of the section records significant changes in pyrite geochemistry indicating much increased nutrient levels; there are pronounced increases in palynomorph abundance (Figs 15, 17) and an

overall positive shift in $\delta^{13}\text{C}_{\text{carb}}$ values of about 2 ‰. The following is an attempt to integrate all of these observations and data, together with previously published work elsewhere on the lower Sheinwoodian.

The fundamental trigger for all of the changes seen through lower Sheinwoodian sections appears to have been climatic cooling and the expansion of Gondwanan ice caps as reflected in the global sea level curve (Loydell, 1998, 2007; Loydell et al., 2009) and, as cooling intensified, in the oxygen isotope record (Lehnert et al., 2010; Fig. 3). A fall in sea level would have exposed a larger land area to subaerial weathering and the locking up of water in ice caps would have increased atmospheric dust levels, especially given the less extensive vegetational cover by comparison with later in the Phanerozoic. These caused increased nutrient inputs to the oceans, as reflected in the nutrient proxy (Fig. 15) and zinc concentrations (Fig. 11). Zinc may have reached levels toxic to some marine organisms and may have contributed to the dramatic decline in graptolite diversity. An increase in biolimiting nutrient levels would have resulted in higher phytoplankton abundance (reflected in increased palynomorph yields; Fig. 15) and increased zooplankton abundance reflecting greater availability of their food source (both chitinozoans and graptolites have their highest abundance during this interval; Figs 7, 15, 17). The sinking of phytoplankton blooms and graptolite rhabdosomes to the sea floor would have resulted in increased carbon burial contributing to a positive shift in $\delta^{13}\text{C}_{\text{carb}}$ values and an increase in atmospheric $p\text{O}_2$. Decay of the sinking plankton at the sea floor would use up oxygen within the water column (through respiration by aerobic bacteria) and within the sediment, resulting in the OAE recorded at this time (Emsbo et al., 2010). It is very likely also that the increased abundance of phytoplankton would have decreased water transparency and thus the depth to the base of the euphotic zone, thus increasing competition between phytoplankton species and potentially contributing to declines in those zooplankton species (including graptolites) that specialized in feeding upon less competitively successful phytoplankton species.

12. Conclusions

High resolution sampling (every 5 cm for 12.4 m) of the lower Sheinwoodian (upper *Cyrtograptus purchisoni* to *Monograptus riccartonensis* biozones) of Buttington Quarry, Wales has provided a huge number of samples for an integrated study (palaeontology, sedimentology, bioturbation intensity, pyrite geochemistry, palynology) of biotic and environmental changes through the lower half of the Early Sheinwoodian Carbon Isotope Excursion (ESCIE). It is within the lower 5 m of the section that graptolites and palynomorphs rise to their greatest abundance and the

pyrite nutrient proxy indicates the highest biolimiting nutrient levels. Globally within this interval graptolites experienced a major extinction. It is interpreted that this was in large part an indirect effect of the increased nutrient levels causing phytoplankton blooms and a reduced depth to the base of the euphotic zone increasing competition within it. It is possible also that toxic levels of zinc contributed to the diversity decline. Correlation with the conodont biozonation for the Sheinwoodian shows that the biotic and geochemical changes seen in the Buttington section were occurring during an Oceanic Anoxic Event, initially recognised on Gotland and manifested also in deeper water strata on Bornholm. Surprisingly, the most rapid and pronounced positive shift in $\delta^{13}\text{C}_{\text{carb}}$ values, about two-thirds up the studied section, is not associated with any dramatic palaeontological, sedimentological or geochemical changes. It is difficult to suggest a cause for the abrupt change in graptolite assemblages seen within the section: several metres of *Monograptus*-dominated strata are succeeded by beds in which *Pristiograptus* predominates and then, near the top of the section, there is a reversion to *Monograptus*-dominated assemblages. Much interesting work remains to be done on the benthos (shelly and trace fossils) of the studied section and upon other sections within Buttington Quarry.

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Fig. 1. Graptolite biozonation for the uppermost Telychian (Llandovery) to lower Homerian (Wenlock) of Wales (modified from Zalasiewicz et al., 2009). The biozones were undoubtedly of different durations (see e.g. Melchin et al. 2012, fig. 21.11 for one interpretation) – more radiometric dates are needed through this interval. Abbreviation: HOM. – HOMERIAN; LL. – Llandovery; TEL. – TELYCHIAN.

Fig. 2. The early Sheinwoodian carbon isotope excursion (ESCIE) developed in the $\delta^{13}\text{C}_{\text{carb}}$ record of core sections from the Baltic States and the $\delta^{13}\text{C}_{\text{org}}$ record of the Banwy River section, Wales (modified from Loydell and Frýda, 2007 in which *antennularius* was assigned to *Streptograptus*). Note that *Cyrtograptus rigidus* occurs at the same stratigraphical level as *Mediograptus antennularius* in the Banwy River section. Abbreviations in Banwy River column: BZ – Biozone; c – *centrifugus*; f – *firmus*; m – *murchisoni*; r – *riccartonensis*.

Fig. 3. Oxygen isotope data from Estonia showing the SOIE (Sheinwoodian oxygen isotope excursion) and its relationship to the conodont biozonation. This is correlated with the graptolite biozonation for the lower Sheinwoodian of Baltica (figure modified from Lehnert et al., 2010). Numbers (4, 6, 8) refer to datum points of the Ireviken Event.

Fig. 4. Location of Buttington in Wales and aerial photograph of Buttington Quarry showing the location of the studied section (latitude and longitude are 52.683954, -3.082877) and the lithostratigraphy of the vertical strata exposed in the quarry (beds young to the south-east).

Fig. 5. Buttington Quarry field photographs. A. Bob Loveridge and Anthony Butcher bulk sampling the studied section. B. Slipping of strata along bentonites along track to the north-east of the

measured section; first author for scale. C. Mass accumulation of graptolites within the lower *riccartonensis* Biozone. Note also the *Berwynia* immediately to the left of the hammer (hammer length 0.3 m). D. Vertically embedded orthocone within lower *riccartonensis* Biozone strata around which is a “graptolite comet” indicating flow from top left to bottom right

Fig. 6. Transition through the top of the heavily bioturbated Butterley Member through to the laminated lowermost part of the section through the Trewern Brook Formation studied herein. This level is interpreted to correlate with the beginning of the oceanic anoxic event (OAE) recognised to commence on Gotland at Ireviken Event Datum Point 4 by Emsbo et al. (2010). Note that it has not proved possible to collect an unbroken sample through this interval – the two pieces of rock are shown in their correct relative positions. The top of the Butterley Member is marked by the base of the first continuous black shale lamina very close to the top of the lower sample.

Fig. 7. Log of studied section through the mudstones of the Trewern Brook Mudstone Formation, Buttington Quarry (see Fig. 4 for location of log site). The 0 point is the top of the Butterley Mudstone Member (Fig. 6). Stratigraphical ranges and abundance of graptolites (thinnest bar = single specimen; thickest = very abundant) are shown, together with horizons displaying current alignment of graptolites. The bases of the *firmus* and *riccartonensis* graptolite biozones are based upon the first appearances of the eponymous taxa. Levels preserving three dimensional pyrite internal moulds of graptolites and gastropods are shown as are those levels with a bioturbation index of 0 or 1. All are plotted adjacent to the $\delta^{13}\text{C}_{\text{carb}}$ curve of Loydell et al. (2014).

Fig. 8. Cut and polished lithological samples of Trewern Brook Formation, Buttington Quarry. A, B. 10.35–10.40 m; laminated sample from the interval of zero to low BI high within the section; close-

up (B) shows pelleted fabric, organic material preserved as tiny flakes, and disseminated pyrite. C, D. 0.65–0.70 m; sample with low BI (=2) with the most obvious trace fossil being *Teichichnus* (close-up of latter in D). E. 1.30–1.35 m; more extensively bioturbated sample (BI=3); pyrite fills or lines some burrows. F. 2.20–2.25 m; one of the most heavily bioturbated intervals (BI=4), although bedding is still recognisable.

Fig. 9. Cut and polished lithological samples of Trewern Brook Formation, Buttington Quarry. A. 6.70–6.75 m; heavily bioturbated interval (BI=4). B. 9.50–9.55 m; includes a continuous organic layer, possibly a former microbial mat. C. 5.05–5.10 m; well-developed *Chondrites*. D. 6.10–6.15 m. E. 0.75–0.80 m. F. 1.40–1.45 m; heavily bioturbated interval (BI=4), although bedding, including a fine sandstone layer, is still recognisable. G. 8.80–8.95 m. H. 0.05–0.10 m; laminated with graptolite three dimensionally preserved, infilled with early diagenetic pyrite.

Fig. 10. Cross laminated mudstone in the 10.45–10.50 m sample.

Fig. 11. Buttington section with $\delta^{13}\text{C}_{\text{carb}}$ curve of Loydell et al. (2014), zinc concentration in pyrite, bioturbation index (recorded from each 5 cm sample through the 12.4 m section) with pale green shading indicating the two long intervals of zero or very low BI, and occurrences of the more common benthic fossil groups (narrow bar = rare; widest bar = very common). Dotted purple line marks average Zn content (380 ppm) in Phanerozoic marine pyrite (calculated from Large et al., 2017).

Fig. 12. Graptolites from the Sheinwoodian of Buttington Quarry. A, H. *Monoclimacis vomerina* (Nicholson): A. BGS DKL 4019, 0–0.05 m, *murchisoni* Biozone; H. BGS DKL 4020, 6.15–6.2 m, *riccartonensis* Biozone. B, I. *Monoclimacis flumendosae* (Gortani): B. BGS DKL 4021, 6.05–6.1 m; I.

BGS DKL 4022, 8.3–8.35 m; both *riccartonensis* Biozone. C. *Monoclimacis deflexa* (Bouček), BGS DKL 4023, 2.4–2.45 m, *riccartonensis* Biozone. D, F, L. *Pristiograptus dubius* (Suess): D. BGS DKL 4024, 3.15–3.2 m; F. BGS DKL 4025, 4.26–4.31 m; L. BGS DKL 4026, 3.0–3.05 m; all *riccartonensis* Biozone. E, *Cyrtograptus murchisoni* Carruthers, BGS DKL 4027, 0.05–0.1 m, *murchisoni* Biozone. G, N. *Mediograptus antennularius* (Meneghini): G. BGS DKL 4028, 9.75–9.8 m; N. BGS DKL 4029, 10.5–10.55 m; both *riccartonensis* Biozone. J. *Monoclimacis vikensis* Bassett and Rickards, BGS DKL 4030, 10.75 m, *riccartonensis* Biozone. K. *Pristiograptus latus* (Bouček), BGS DKL 4031, 5.35–5.4 m, *riccartonensis* Biozone. M. *Mediograptus flexuosus* (Tullberg), BGS DKL 4032, 2.0–2.05 m, *firmus* Biozone. Scale bar represents 1 mm.

Fig. 13. Graptolites from the *Monograptus rickcartonensis* Biozone (Sheinwoodian) of Buttington Quarry. A, C, D, G, L. *Monograptus rickcartonensis* Lapworth: A. BGS DKL 4033, 11.7–11.75 m; C. BGS DKL 4034, 5.3–5.35 m; D. BGS DKL 4035, 5.85–5.9 m; G. BGS DKL 4036, 5.35–5.4 m; L. BGS DKL 4037, 5.85–5.9 m. B, F, K. *Monograptus sedberghensis* Rickards: B. BGS DKL 4038, 5.45–5.5 m; F. BGS DKL 4039, 6.05–6.1 m; K. BGS DKL 4040, 6.05–6.1 m. E, J. *Monograptus firmus* Bouček: E. BGS DKL 4041, 2.45–2.5 m; J. BGS DKL 4042, 6.4–6.45 m. H. *Monograptus priodon* (Bronn), BGS DKL 4043, 2.7–2.75 m. I. *Monograptus instrenuus* Lenz and Melchin, BGS DKL 4044, 3.15–3.2 m. M. *Monograptus flemingii* (Salter), BGS DKL 4045, 6.1–6.15 m. Scale bar represents 1 mm.

Fig. 14. Proximal ends of *Monograptus rickcartonensis* Lapworth from Buttington Quarry showing flaring of the sicular aperture. A. BGS DKL 4046, 5.35–5.4 m; B. BGS DKL 4047, 5.4–5.45 m. Scale bar represents 1 mm.

Fig. 15. Palynomorph abundance (per gramme of rock processed, from data in Llewellyn, 2015, appendix 12), plotted against $\delta^{13}\text{C}_{\text{carb}}$ curve of Loydell et al. (2014) and nutrient proxy. Dotted purple lines mark mean Phanerozoic nutrient values (based upon the nutrient trace element (TE) proxy of Large et al. 2015, 2017) and for the most abundant palynomorph groups highlight those levels with high abundance. Palynomorph abundance (per gramme) can be very significantly affected by the extent of preservation of amorphous organic matter (AOM; e.g. see Loydell et al., 2013). Llewellyn (2015) noted that AOM abundance did not fluctuate significantly throughout the samples.

Fig. 16. Atmospheric $p\text{O}_2$ proxy based on Se/Co ratios in marine pyrite from the Buttington section, compared with the nutrient proxy (Fig. 15) and $\delta^{13}\text{C}_{\text{carb}}$ curve of Loydell et al. (2014) for the section. The Phanerozoic mean O_2 level is determined from mean Se/Co ratio in marine pyrite (Large et al., 2015, 2017).

Fig. 17. Diagram summarizing for the Buttington section: $\delta^{13}\text{C}_{\text{carb}}$ record, graptolite biozones and important occurrences and changes within graptolite assemblages, indicators of bottom water and sediment oxygen levels (3D pyrite preservation; and zero to very low bioturbation index: BI = 0 or 1), levels of peak palynomorph abundance, and intervals where the environmental pyrite geochemical proxy indicates high nutrient levels. Global events are shown to the right of the black dotted line: the Sheinwoodian oxygen isotope excursion (SOIE) of Lehnert et al. (2010), the Silurian OAE identified by Emsbo et al. (2010; see also McLaughlin et al., 2012) based upon geochemical analyses of rocks and fossils from Gotland, the interval of malformed palynomorphs identified by Munnecke et al. (2012), a diagrammatic representation of graptolite diversity, the interval of main changes in polychaete assemblages (from Tonarová et al., 2014) and interpreted levels of Ireviken Event Datum Points

(correlation based upon Männik, 2007 and correlation with Gotland $\delta^{13}\text{C}_{\text{carb}}$ curve of Cramer et al., 2010a).

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Highlights

- Early Wenlock (Silurian) graptolite extinction at time of positive carbon isotope excursion
- Pyrite geochemistry provides a nutrient proxy indicating high nutrient abundance during decline in graptolite diversity
- High zinc concentrations may have contributed to graptolite extinctions
- Major lithological change to laminated shales correlated with beginning of Oceanic Anoxic Event

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Series	Stage	Biozone
WENLOCK	HOM.	<i>Cyrtograptus lundgreni</i>
	SHEINWOODIAN	<i>Cyrtograptus rigidus</i>
		<i>Pristiograptus dubius</i>
		<i>Monograptus riccartonensis</i>
		<i>Monograptus firmus</i>
		<i>Cyrtograptus murchisoni</i>
LL.	TEL.	<i>Cyrtograptus centrifugus</i>

Figure 1

Figure 2

Figure 3

Cefn Formation
Tarannon Shales Formation
Trewern Brook Mudstones Formation
(Butterley Mudstone Member at base)
Measured section

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

Figure 15

Figure 16

Figure 17