A new high-resolution $\delta^{13}C_{carb}$ isotope curve through the lower Wenlock Series of Buttington Quarry, Wales

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Abstract

New high-resolution $\delta^{13}C_{carb}$ isotope data are presented through the lower part of the early Sheinwoodian carbon isotope excursion from a section in Buttington Quarry, Wales. The graptolite biostratigraphy of the section is established, with the base of the measured section within the Cyrtograptus murchisoni Biozone. The first appearance datums of the biozonal indices Monograptus firmus and Monograptus riccartonensis are recorded. The new isotope curve will provide the basis for future studies, particularly on the palynology of the section.

Introduction

The purpose of this paper is to present new high-resolution $\delta^{13}C_{carb}$ isotope data through the lower Sheinwoodian section exposed at Buttington Quarry in eastern mid-Wales. This rock section is the subject of a number of ongoing studies, including detailed palynological (both biostratigraphical and palaeoenvironmental) investigations that it is hoped will advance our understanding of the causes and impacts of the globally recognised early Sheinwoodian positive carbon isotope excursion (see Cramer et al. 2010 for review).

Locality and previous studies

Buttington Quarry (previously known as Buttington Brick Works/Pit, when the Telychian Tarannon Shales Formation was being extracted from here for brick making) lies approximately 4 km northeast of Welshpool, Powys, Wales. The Ordnance Survey grid reference for the quarry is SJ 265100. Locality maps are provided by Loydell & Cave (1993) and Mullins & Loydell (2002); an aerial photo of the quarry as it appeared at the time of the main phase of sample collection is provided as Fig. 1. The quarry exposes a 275m + thick sequence of near vertical lower Silurian strata, younging to the southeast, with a strike of 055°.

Fig. 1. Aerial photo of Buttington Quarry (from Google Earth: Infotera Ltd and Bluesky), showing location of measured section.

The Llandovery strata (Cefn Formation and Tarannon Shales Formation) of the quarry have been logged and described in detail (Cave & Dixon 1993; Loydell & Cave 1993) with separate studies published on Telychian graptolite (Loydell & Cave 1993) and chitinozoan (Mullins & Loydell 2002) biostratigraphy. With the exception of the basal Butterley Mudstone Member (of late Telychian–early Sheinwoodian age), the Trewern Brook Mudstone Formation, the remainder of which is entirely of Sheinwoodian age in the quarry, has been studied thus far in considerably less detail. Cocks & Rickards (1969) recognised three horizons above the Tarannon Shales Formation (referred to by them as the "Purple Shale") and assigned these to probably the Cyrtograptus centrifugus Biozone and confidently the Cyrtograptus murchisoni and Monograptus riccartonensis biozones. Underwood (1995) described interstipe webbing in material of C. murchisoni from Buttington, and Mullins & Loydell (2002) described chitinozoan assemblages from the Margachitina margaritana Biozone from two samples from the lowermost graptolitic shale above the Butterley Member.

Lithologies and methods

The Butterley Member at the base of the Trewern Brook Mudstone Formation is an olive-buff bioturbated silty mudstone, approximately 9m thick. It yields numerous shelly fossils (including some of the trilobites monographed by Curtis & Lane 1997, 1998) and rare graptolites. The remainder of the formation is grey mudstones and shales, the latter being graptolitic, the former usually bioturbated. Numerous bentonites are interbedded with the mudstones and shales.

The sampled interval was the 12.4m of section (at latitude 52.68388°N, longitude 3.08290°W) from the top of the Butterley Member to a break in exposure (Fig. 1). The base of the sampled interval is clearly marked by a rapid transition from the bioturbated mudstones of the Butterley Member to laminated graptolitic shales. Bulk samples were collected, each representing a maximum of 5 cm thickness of strata. Bed surfaces were examined under a microscope and significant graptolites and any other macrofossils retained prior to the remaining material being made available for geochemical and palynological processing and analyses. $\delta^{13}C_{carb}$ isotope analyses were undertaken on every other sample collected (i.e. at 10 cm intervals), starting with the 0–0.05m sample. Rock powders selected from collected samples by hand drill were reacted with 100% phosphoric acid at 70°C using a Gasbench II connected to a ThermoFinnigan Five Plus Mass Spectrometer. All values are reported in per mil relative to Vienna Pee Dee Belemnite by assigning a $\delta^{13}C$ value of + 1.95‰ and a $\delta^{18}O$ value of - 2.20‰ to NBS19. Reproducibility was checked by replicate analysis of laboratory standards and is better than ± 0.07.

Thus far, the focus of the graptolite work has been on establishing the overall biostratigraphy of the section, by detailed examination of all samples within the lower part of the sampled interval to establish the first appearances of biozonal index taxa.

Graptolite and chitinozoan biostratigraphy

The lowest sample includes *C. murchisoni* and this species is common throughout much of the lowest 43 cm sampled. The assemblages accompanying *C. murchisoni* include *Monoclimacis*, *Monograptus* and *Barrandeograptus*, but no *Retiolites* were encountered amongst the many hundreds of graptolites examined. By comparison with the Banwy River section, where *Retiolites* occurs up until the lower part of the *murchisoni* Biozone (Loydell & Cave 1996), this suggests that sampling commenced at Buttington in the middle of the murchisoni Biozone, at a horizon correlating probably with the + 11.75 m level in the Banwy River section (see Mullins & Loydell 2001, text-fig. 1), where a thick bioturbated interval is overlain by graptolitic mudstones. The first *Monograptus firmus* occurs in the 0.90–0.95 m sample, with *M. riccartonensis* appearing in the 2.25–2.30 m sample and continuing through to the top of the sampled section which is thus entirely within the *riccartonensis* Biozone.

Mullins & Loydell (2002) assigned a sample from 0.23 to 0.43 m above the base of the section sampled herein to the upper part of the *M. margaritana* Biozone, based upon the co-occurrence of *M. margaritana* and *Conochitina flamma*. In the Banwy River section, these taxa co-occur in the upper part of the *C. murchisoni* graptolite Biozone. Further study of the Buttington chitinozoans is ongoing.

The new $\delta^{13}C_{carb}$ isotope curve

The new $\delta^{13}C_{carb}$ data are presented in Fig. 2. Initially low values (–0.24‰) rise rapidly to +0.78‰ over 60 cm, fall to +0.30‰ then rise again to +0.92‰ at 1.30–1.35 m. A similar pattern through the upper *murchisoni* to lower *firmus* biozones is shown in the Banwy River $\delta^{13}C_{carb}$ data (Cramer et al. 2010, fig. 4).

Values fall from +0.92‰ to +0.33‰ at 1.60–1.65 m and are then moderately stable for 1.3m (to 2.90–2.95 m) through the middle *firmus* to lowermost *riccartonensis* Biozone. Above this, values generally rise (but with minor fluctuations) to + 1.39‰ at 3.90–3.95 m. Thereafter, fluctuations are rapid and pronounced with a maximum of + 1.86‰ at 4.95–5.00 m and a minimum of +0.45‰ at 5.75–5.80 m. Another rapid rise to + 1.28–1.33‰ (two analyses of the same sample) at 6.05–6.10 m is succeeded by three samples with lowered values between +0.87‰ and 0.96‰, before another rise. This is succeeded by a protracted interval (from 7.05 to 8.25 m) in which values are rather low (+0.54‰ to +0.98‰) after which there is a very rapid increase from +0.60‰ to +1.51‰ over 10 cm with a further rise over the next two samples to +2.09‰ (at 8.50–8.55 m). Fluctuating, but high values characterise the succeeding interval (up to 9.85–9.90 m) with a maximum of +2.41‰ at 9.75–9.80 m. The remainder of the section records a general decline in values (to +1.04‰ at 10.45–10.50 m) followed by generally higher values, peaking at +2.43‰ at 12.25–12.30 m.

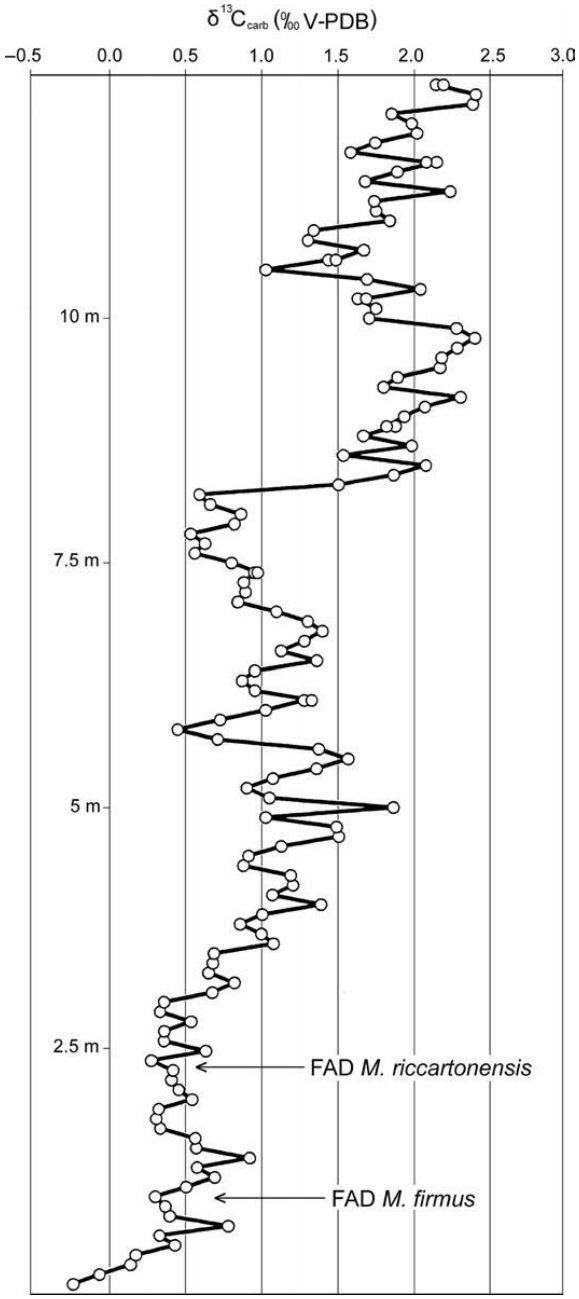

Fig. 2. The new d13Ccarb isotope curve through the measured lower Sheinwoodian section in Buttington Quarry, commencing in the Trewern Brook Mudstone Formation immediately above the top of the Butterley Member. First appearance datums of biozonal index graptolites are shown. Detailed sedimentological description of the section is at a preliminary stage: lithologies are grey mudrocks (shales and mudstones) throughout. For these reasons, no lithological log is provided.

It is clear that the sampled Buttington section does not record the entirety of the early Sheinwoodian positive carbon isotope excursion. Indeed, by comparison with the Banwy River section, from which *Monograptus flexilis* has been recovered from strata within the descending limb of the excursion and *Cyrtograptus rigidus* 20 m stratigraphically below this (the excursion extends in the Banwy River section over a stratigraphical thickness of 70 m), it seems likely that perhaps only approximately the lower half to two-thirds of the excursion is/are present in our data. With this in mind, it is tempting to correlate the interval of generally lower values within the Buttington data (the 7.05–8.25m interval referred to above, but one could perhaps extend this down to 5.65 m) with a similar decline recorded by Cramer

et al. (2010) from the Banwy River section and elsewhere. It may be that future chitinozoan biostratigraphical work can help to confirm this; unfortunately the low diversity of graptolite assemblages through the *riccartonensis* Biozone, and particularly its lower/middle parts, makes subdivision of the biozone and thus high-resolution biostratigraphical correlation using graptolites exceedingly challenging.

What will be interesting to determine from ongoing and future studies will be the response of chitinozoans and acritarchs to the environmental changes presumably responsible for the rapid and major fluctuations in $\delta^{13}C_{carb}$ values recorded in this section.

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