Carbon and nitrogen isotope stratigraphy of the Cambrian SPICE record in the UK

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Link to abstract

Abstract

Carbon isotope fluctuations have been determined globally within the late Cambrian with particular focus on the Steptoean Positive Carbon Isotope Excursion (SPICE) and the negative Hellnmaria-Red Tops Boundary/Top of the Cambrian Excursion (HERB/TOCE). These events correspond to global anoxia/euxinia, increased global weathering of organic rich material and a shift in dissolved inorganic carbon availability. We have extended our knowledge of SPICE and HERB/TOCE in the UK by conducting coupled carbon and nitrogen isotope analysis of cores (Merevale #1, #3) and quarry samples from Warwickshire (Oldbury Quarry). Our organic $\delta^{13}C$ record replicates the changes previously published for SPICE in other global records. The bulk sediment $\delta^{15}N$ record reveals a rapid positive excursion at the start of SPICE followed by a gradual decline through the remaining SPICE interval. We interpret the $\delta^{15}N$ record as reflecting expansion of the oxygen minimum zone into the upper water column and replacing nitrification with denitrification processes. Denitrification is also supported during the SPICE interval from previously published iron-speciation data from the same cores. The negative $\delta^{13}C$ HERB/TOCE record is coupled with a more subtle $\delta^{15}N$ positive excursion. There is a paucity of organic carbon isotope records through this time interval, and hence a lack of global comparability is possible. The shift in $\delta^{13}C$ and $\delta^{15}N$, coupled with changes in redox conditions in Cambrian oceans may also reflect biological shifts between red and green phytoplankton superfamilies making up the upper water column community. Additional research on organic carbon, nitrogen and redox proxies are required to ascertain the link between phytoplankton superfamily dominance, species richness, diversity and/or the onset of the Phytoplankton Revolution and the Great Ordovician Biodiversity Event.

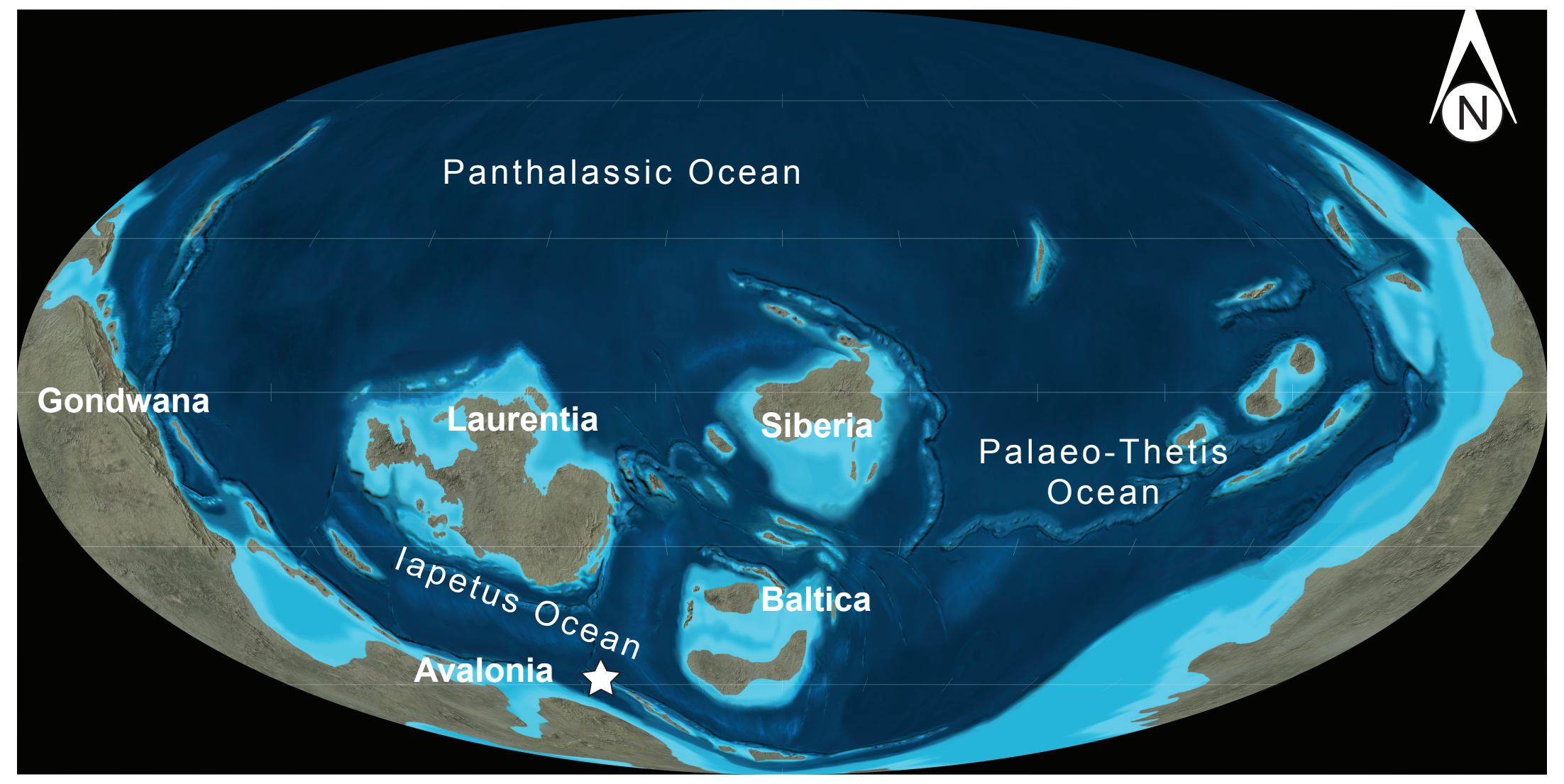
1. Introduction

The Cambrian was a period of mass extinctions and biotic radiations (e.g., Fang et al., 2019; Saltzman et al., 2000; Harper et al., 2019) partnered with oceanic anoxia, euxinia (e.g., LeRoy et al., 2021; Gill et al., 2021) and eustatic sea level fluctuations (e.g., Faggetter et al., 2018). The most effective way to record these environmental changes are through stable isotope curves, with inorganic and organic carbon isotopes being the most important. Within the late Cambrian fluctuations in anoxia and weathering have been determined through global carbon isotope excursions such as the Steptoean Positive Carbon Isotope excursion (SPICE) and the Hellnmaria-Red Tops Boundary/Top of the Cambrian excursion (HERB/TOCE) respectively. From this point, the HERB/TOCE shall be referred to as the HERB. Both of these excursions have been found in marine carbonate and organic carbon reservoirs. Palaeogeographically, the Cambrian consisted of the supercontinent Gondwana with a continents: Laurentia, Baltica and Sibera within the Iapetus and Panthalassic Ocean. The UK (Avalonia) was part of a shallow basin at a high latitude of ~60°S (Fig. 1).

We further extended the previously published stable isotope record by Woods et al. (2011) and previously extended by LeRoy et al. (2021) with a carbon ($\delta^{13}C_{org}$), nitrogen ($\delta^{15}N_{tot}$) and sulphur ($\delta^{34}S_{decarb}$) stable isotope record of cores Merevale Core #1 and #3, and Oldbury Quarry from Warwickshire UK (Fig. 2) to provide a detailed UK record of the late Cambrian excursions mentioned previously. This not only provides a carbon record representing global changes to the carbon cycle but also provides information towards the regional redox changes within the shallow basin of Avalonia. LeRoy et al. (2011) provided an iron speciation record to further provide evidence towards a euxinic marine setting as well as anoxic. The anoxic event indicated by the SPICE has been correlated to an increase in productivity within the upper water column but data suggests this anoxia/euxinia was also within deeper waters. Palaeoceanographically, Warwichshire, UK was situated in a shallow marine, mid-shelf region of Gondwana on the shores of the Iapetus Ocean (Fig. 1). These records will also help in determining how mixed the global ocean was within the late Cambrian.

Figure 1:

Palaeogeographic map of the late Cambrian modified from Blakey (2018). The star indicates the UK locations in this study.



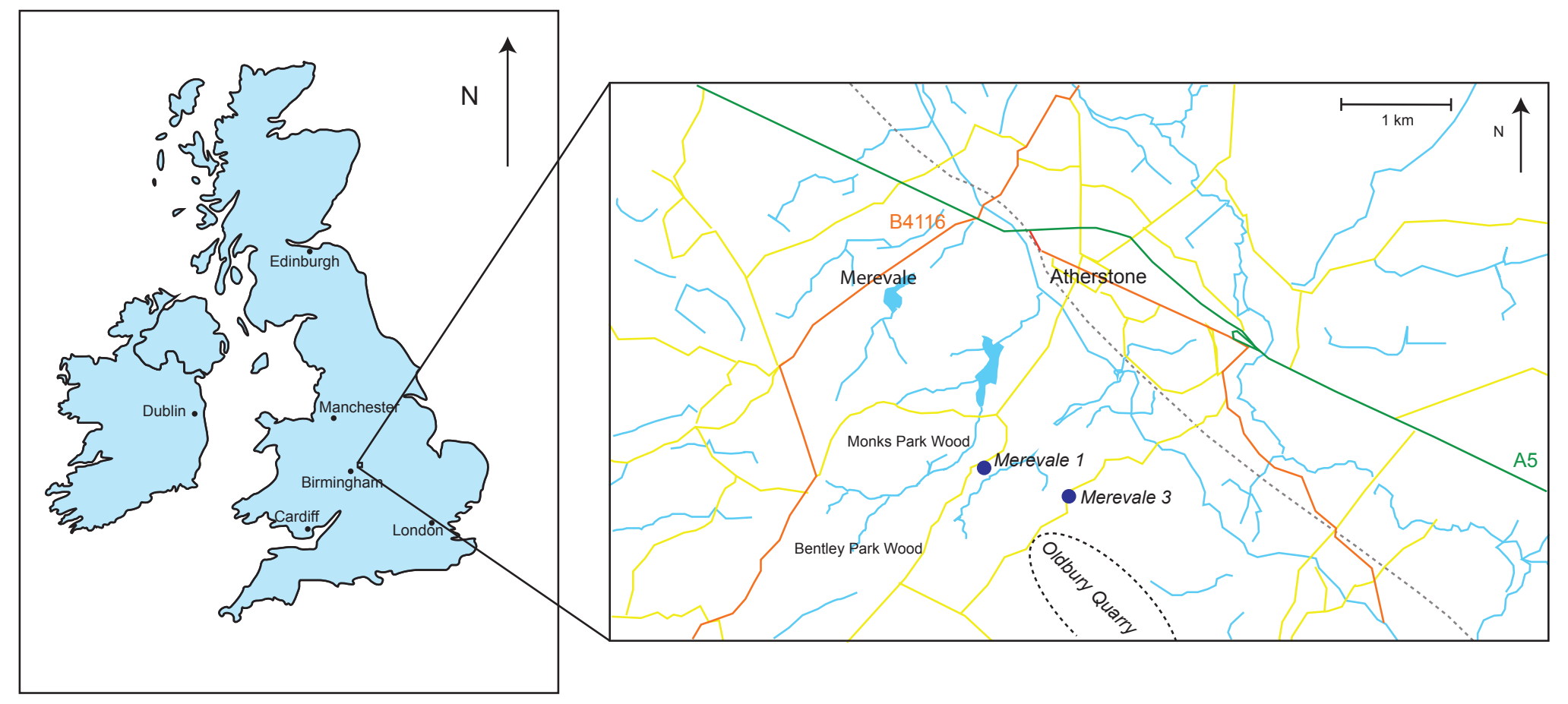


Figure 2:

Map of the UK with reference to known major cities. Inset: Local map with the core locations and Oldbury Quarry that are investigated in this study. Green line indicates the A5, orange line is the B4116 and yellow lines are other minor roads. The dotted grey line is the rail line and blue are water ways.

2. Methods

Samples were taken from cores Merevale Core #1 and #3, and from the Oldbury Quarry stored at the British Geological Survey core repository (Keyworth, Nottingham). The initial cores were taken from Atherstone, approximately 34 km northwest of Birmingham (Fig. 2). Samples were taken every 16 ft where previously sampled by Woods et al. (2011) and were extended into Merevale Core #1 and #3 by 321 ft and 565 ft respectively at approximately a 4 ft resolution. The chipped samples were then ground into a fine powder and split into bulk sediments and sediments to be decalcified. Sediments were decalcified with 3M HCl for approximately 24 hours and then rinsed three times with de-ionised water in a centrifuge before drying in an oven. 23 samples were each taken from Merevale #1 and Merevale #3 for sulphur analyses and all of the quarry samples were analysed. Decalcified sediments were used for carbon and sulphur analyses and bulk sediment was used for nitrogen analysis. Isotope measurements were carried out at the Stable Isotope and Biogeochemistry Laboratory (SIBL) in Durham University where they were weighed into tin capsules and ran on a Costech elemental analyser (ESC4010) coupled to a Thermo Scientific Delta V Advantage isotope ratio mass spectrometer. When measuring for nitrogen isotope ratios, the Costech elemental analyser was fitted with a carbosorb/soda lime trap to remove any acidic gases (e.g., CO_2) from entering the mass spectrometer.

3. Results & Discussion

Rather than describe all the elemental excursions recorded in this late Cambrian sedimentary record (Fig. 3) the general trends are only presented. The total organic carbon (TOC) record through this time interval fluctuates between 0.5 wt % to 2.0 wt %, with moderate enrichments (up to 4.0 wt %) above this in the Drumian to Paibian stages. However, TOC increases well above this in Stage 10, up to almost 7.0 wt %. Total nitrogen (TN) remains relatively stable throughout the entire stratigraphic record between 0.13 wt % and 0.16 wt%, except for two intervals. TN at the base of the record is below 0.13 wt % declining from 500 ft to 800 ft in M3. The CN ratio is, of course, an artefact of these two analyses, and since TOC is much more variable in magnitude than TN, it is the dominant controller on the CN ratio. The CN ratio dominantly ranges between 5 and 30. Organic matter dominated by marine algae ranges up to 10 in marine sediments, whereas values greater that 20 is typical of vascular land plants (i.e., Meyers, 1994). Since the sediments were deposited well before the evolution of vascular land plants, this elevation in CN may represent several separate mechanisms: (1) variation in the Redfield ratio; (2) diagenetic alteration; (3) sediment remineralisation; (4) changes in organic matter composition (terrestrial versus marine algae/bacteria); and/or (5) palaeo-pCO_2 effects.

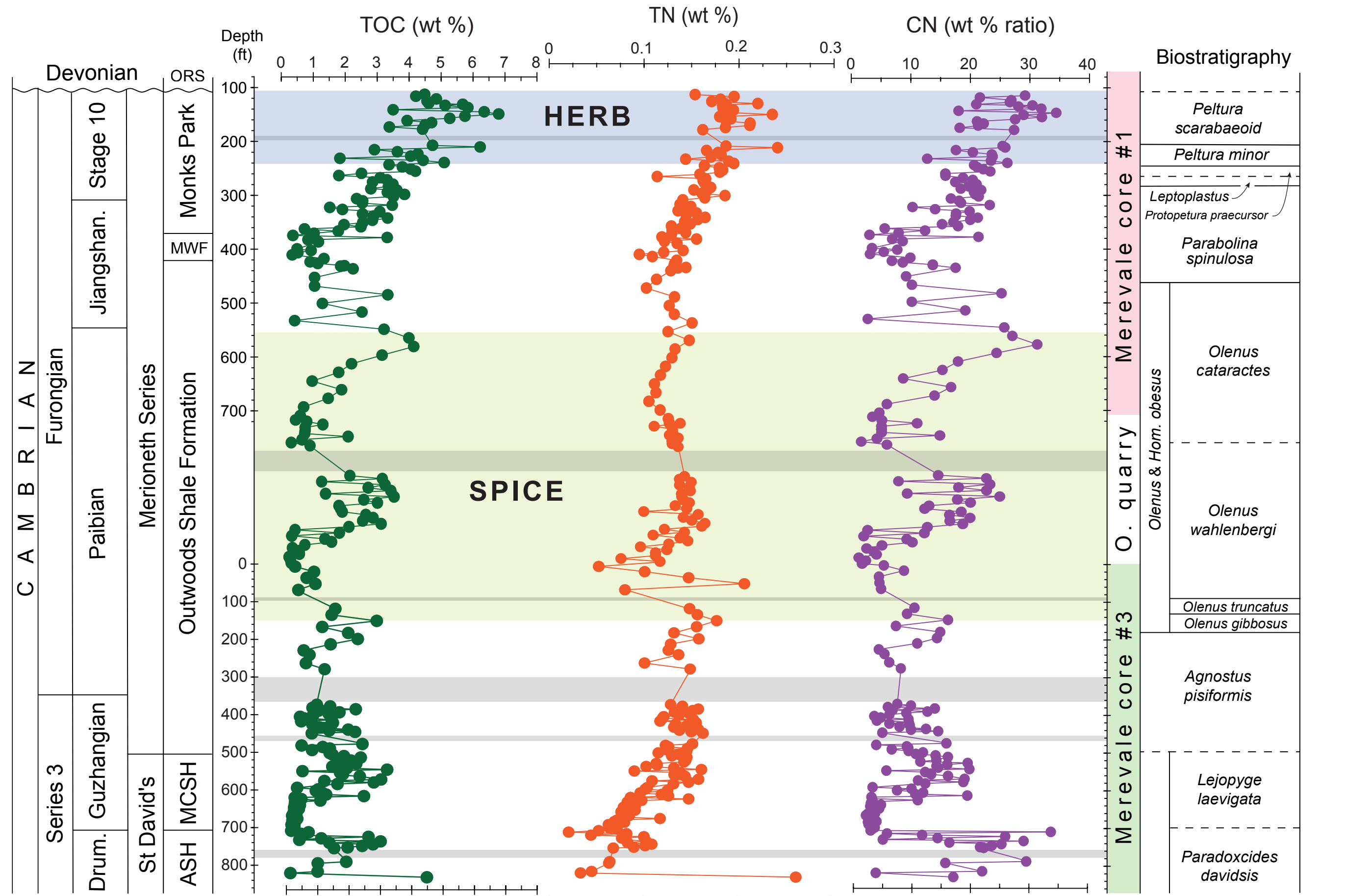
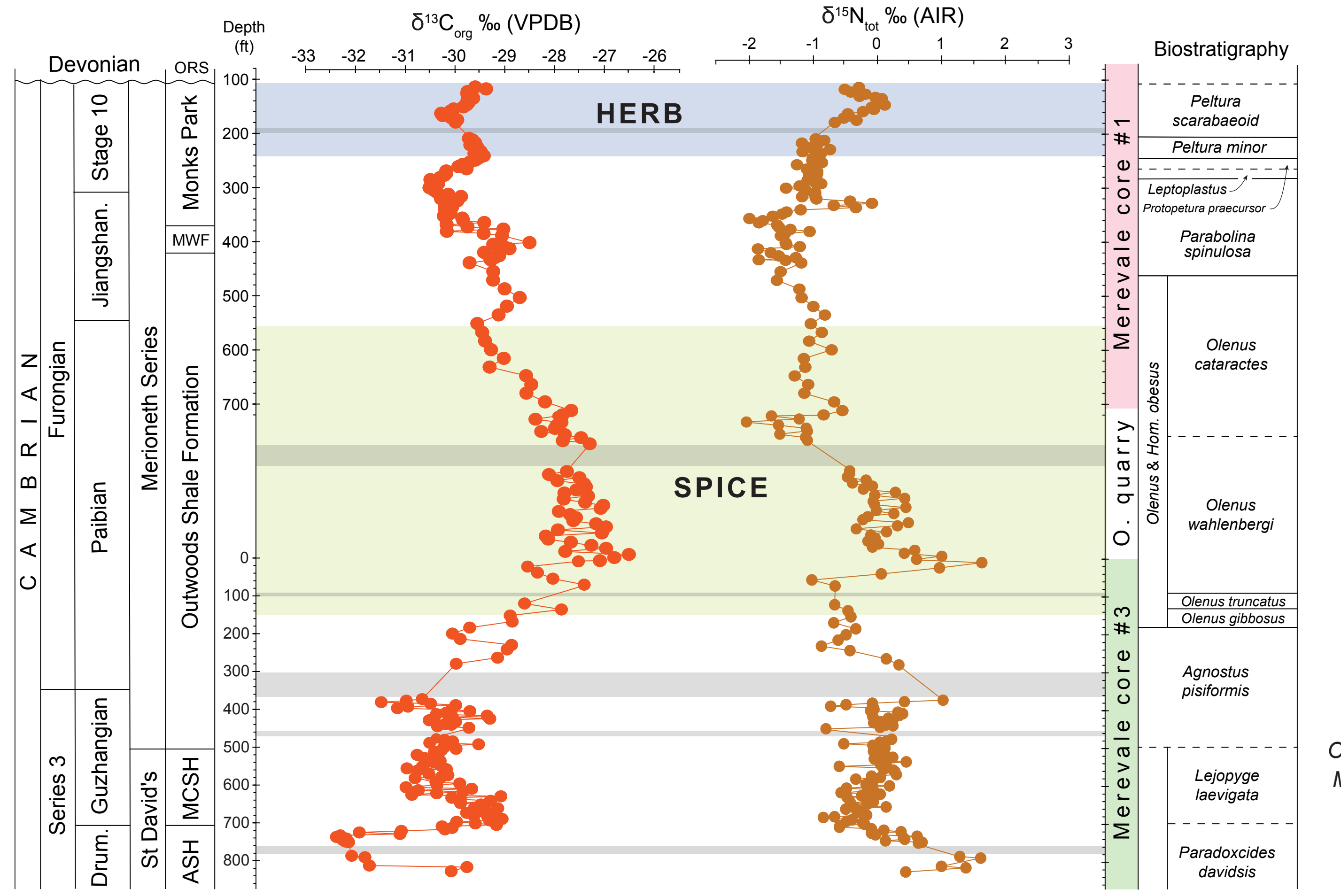


Figure 3:

Stratigraphic, biostratigraphic and geochemical records (TOC, TN and CN) from Merevale #1, #3 and Oldbury Quarry. Grey boxes indicate sills in the stratigraphic interval. Samples affected by the intrusion of the sills have been removed from this figure. Borehole thickness does not equate to stratigraphic thickness as the borehole was not taken perpendicular to dip (see Woods et al., 2011). Zonal ages are from Woods et al. (2011), LeRoy et al. (2021) and Cramer and Jarvis (2020), whereas biostratigraphy is from Taylor and Rushton (1971), Woods et al. (2011) and Geyer (2019).



Although it may be the result of one or many of these mechanisms it is tantalising to suggest that this record of CN may in fact relate to changes in the microbial ecology of phytoplankton in the early Palaeozoic (Arrigo, 2005) and/or the shifting in dominance between eukaryotic phytoplankton superfamilies (green *versus* red) which have different macronutrient stoichiometries – Redfield ratios (Quigg et al., 2003). The $\delta^{13}C_{org}$ curve produced in Woods et al. (2011) and LeRoy et al. (2021) is reproduced in our analyses. Although, there are subtle differences in the absolute $\delta^{13}C_{org}$ values reported in Woods et al. (2011) compared to this study, the shape, and often the magnitude of the $\delta^{13}C_{org}$ curve is very comparable. The $\delta^{13}C_{org}$ produced from this study is illustrated in Figure 4, clearly showing the SPICE record and also the HERB event in the latest Cambrian. The absolute $\delta^{13}C_{org}$ values between LeRoy et al. (2021) and this study are also similar. The Drumian/Guzhangian boundary in Merevale Core #3 records a distinct negative $\delta^{13}C_{org}$ excursion, even after excluding samples affected by the sill. This negative $\delta^{13}C$ excursion is recorded at the Drumian/Guzhangian GSSP and thus, may prove to be a very reliable marker for determining the position of this boundary (Peng et al., 2009). This negative $\delta^{13}C_{org}$ excursion is followed by a significant positive excursion in the lower part of the Mancetter Shale Formation (MCSH; Fig. 4). Following this is the SPICE $\delta^{13}C$ positive excursion. The previous interpretation of SPICE, as given by Woods et al. (2011) and others stands.

Figure 4:

Organic carbon ($\delta^{13}C_{org}$) and bulk nitrogen ($\delta^{15}N_{tot}$) isotope curves generated from Merevale #1, #3 and Oldbury Quarry. See Figure 3 for details of the stratigraphy and biostratigraphy. Samples affected by the intrusion of the sills (grey boxes) have been removed from this figure.

The resultant $\delta^{13}C_{org}$ curve reveals a second positive excursion (~1 ‰) at the start of the Jiangshanian Stage at ~500 ft in Merevale Core #1 identified by Woods et al. (2011) as the 'post-SPICE'. The negative excursion seen during Stage 10 (on the order of ~1‰) in the $\delta^{13}C_{org}$ curve (~160 ft) is interpreted to represent the HERB.

Unlike carbon isotope stratigraphy which reflects global changes in the carbon cycle, nitrogen isotope stratigraphy represents local upper water column changes in the nitrogen cycle. The base of Merevale Core #3 reveals a negative $\delta^{15}N_{tot}$ excursion on the order of 3.5 ‰ starting at the Drumian/Guzhangian boundary (Fig. 4). After the main sill, $\delta^{15}N_{tot}$ values fluctuate between –0.5 ‰ and –1.0 ‰. $\delta^{15}N_{tot}$ values increase rapidly from –1.0 ‰ to +1.5 ‰ in the topmost part of Merevale Core #3, after which the record continues in the Oldbury Quarry. $\delta^{15}N_{tot}$ values are not as elevated (~+1.0 ‰), although Woods et al. (2011) indicates that there is a 5–10 m gap in stratigraphy. The $\delta^{15}N_{tot}$ record for the remainder of the Oldbury Quarry shows a general decline to values near to –2.0 ‰. Merevale Core #1 reveals greater variation in $\delta^{15}N_{tot}$ between –0.8 ‰ and –2.0 ‰ until the uppermost Jiangshanian and the presence of a positive $\delta^{15}N_{tot}$ excursion (from –2.0 ‰ to 0 ‰) that occurs prior to the HERB interval. $\delta^{15}N_{tot}$ values remain relatively constant at ~ –1.0 ‰ until the uppermost part of Stage 10 where there is another positive $\delta^{15}N_{tot}$ excursion on the order of 0.7 ‰ that occurs during the HERB event (Fig. 4, 5).

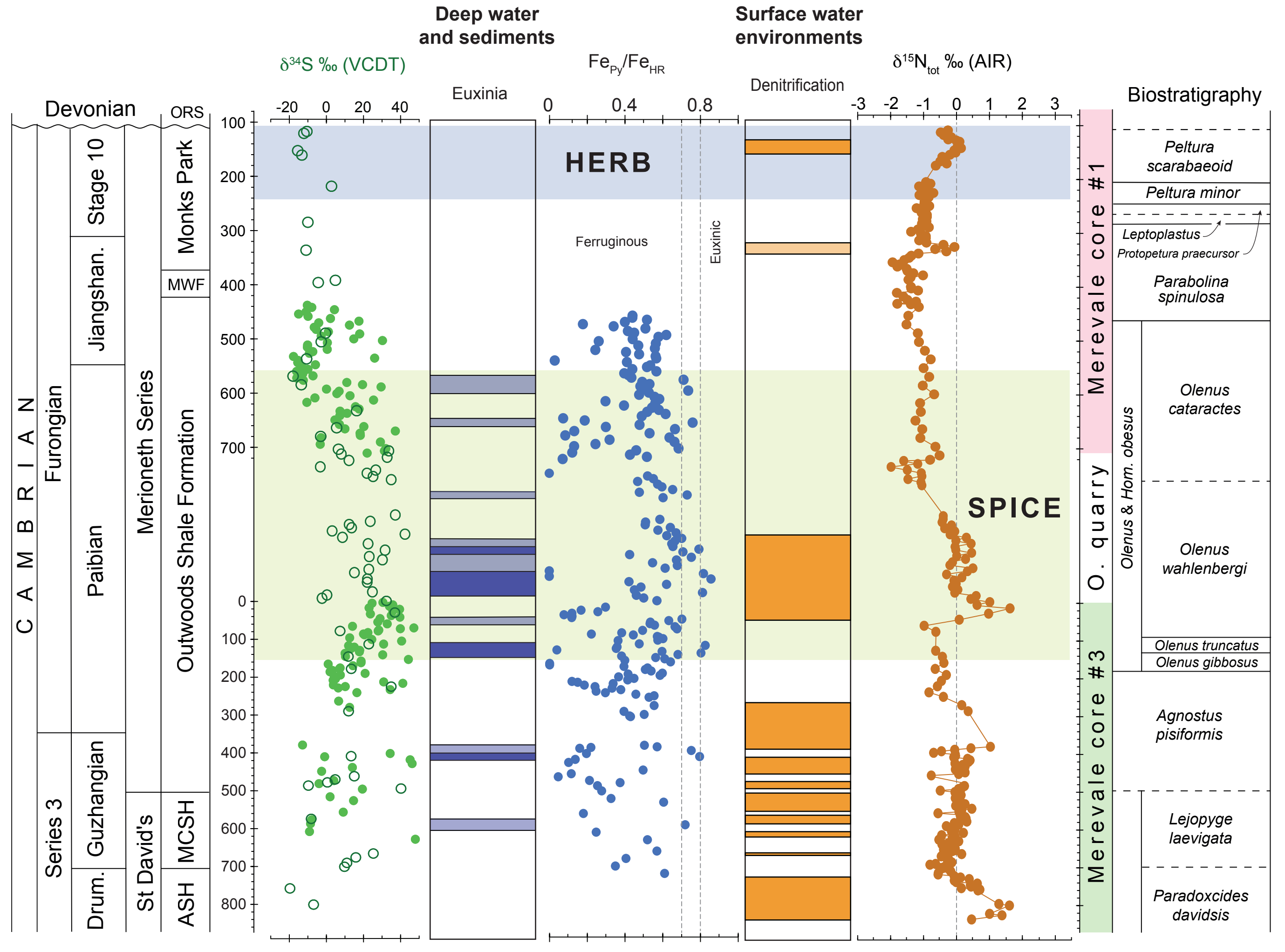


Figure 5:

Environmental changes through the late Cambrian indicated by sulphur ($\delta^{34}S$), Fe_{Py}/Fe_{HR} ratios (LeRoy et al., 2021), and $\delta^{15}N_{tot}$. The darker the colour of the box the stronger the likelihood of the environmental change associated with each column. The $\delta^{34}S$ curve is made of two datasets: open circles (this study); solid circles (LeRoy et al., 2021).

3. Results & Discussion (cont.)

The stratigraphic record of $\delta^{13}C_{org}$ and $\delta^{15}N_{tot}$ clearly reveal positive and negative excursions throughout the late Cambrian time interval investigated in this study. The nitrogen isotope record reveals there are shifts between states of nitrification and denitrification in the upper water column (Fig. 5): these do not correspond to periods of euxinia as indicated by LeRoy et al. (2021), except during the initial stages of the SPICE interval. The stadial in $\delta^{15}N_{tot}$ at the start of the SPICE zone is coupled with the initial rise in $\delta^{13}C_{org}$ values indicating the reduction in oxygen and therefore an increase in the decaying and falling of organic matter through the water column. In turn the oxygen minimum zone (OMZ) reaches a 'tipping point' and expands into the upper water column . The immediate decline within $\delta^{15}N_{tot}$ values indicates rapid denitrification following the productivity bloom that initiated the SPICE which remains fairly steady across 30 m of the Oldbury Quarry. Although our interpretation of denitrification (above 0 ‰) may be incorrect, changes from more negative to less negative (or even positive) $\delta^{15}N_{tot}$ must suggest changes in the nitrogen cycle. As previously mentioned, it is possible that the culmination of changes in surface and deep water environments was a triggering mechanism for major biotic shifts to occur between red and green phytoplankton superfamilies.

The most striking excursion is SPICE. This long duration (>1 Myr) and large $\delta^{13}C_{org}$ positive excursion has been classically interpreted as a result of weathering and increased marine productivity (e.g., Saltzman et al., 2000; Kouchinsky et al., 2008; Rooney et al., 2022). This interpretation is comparable to the "classic" oceanic anoxic event that occurs at the Cenomanian/Turonian boundary (OAE2) in the Cretaceous. The cause behind OAE2 has been attributed to large-scale volcanism (Caribbean large igneous province), causing increased weathering and intensified thermohaline circulation (e.g., Arthur et al., 1987; Kump & Arthur, 1999; Jarvis et al., 2011; du Vivier et al., 2014; Li et al., 2022; Matsumoto et al., 2022). SPICE (at present) is not associated with large-scale volcanism, and thus increased weathering (e.g., Yuan et al., 2022) and delivery of nutrients driving global oceanic productivity must have been triggered by another mechanism (Fig. 6).

Sea-level changes have been proposed as a major driving mechanism behind SPICE (Saltzman et al., 2000; Pulsipher et al., 2021). A SPICE sea-level transgression could drive increased upwelling of deoxygenated nutrient-rich water into the photic zone driving productivity. Transgressions flood previously exposed continental shelves expanding the photic zone area and recycling of previously buried nutrients from shelf sediments into the water column. Differential productivity between continental shelves, continental margins and the open ocean is most likely the driving mechanism behind changes in the depth gradient between $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ during the SPICE interval (e.g., Li et al., 2018; Pulsipher et al., 2021).

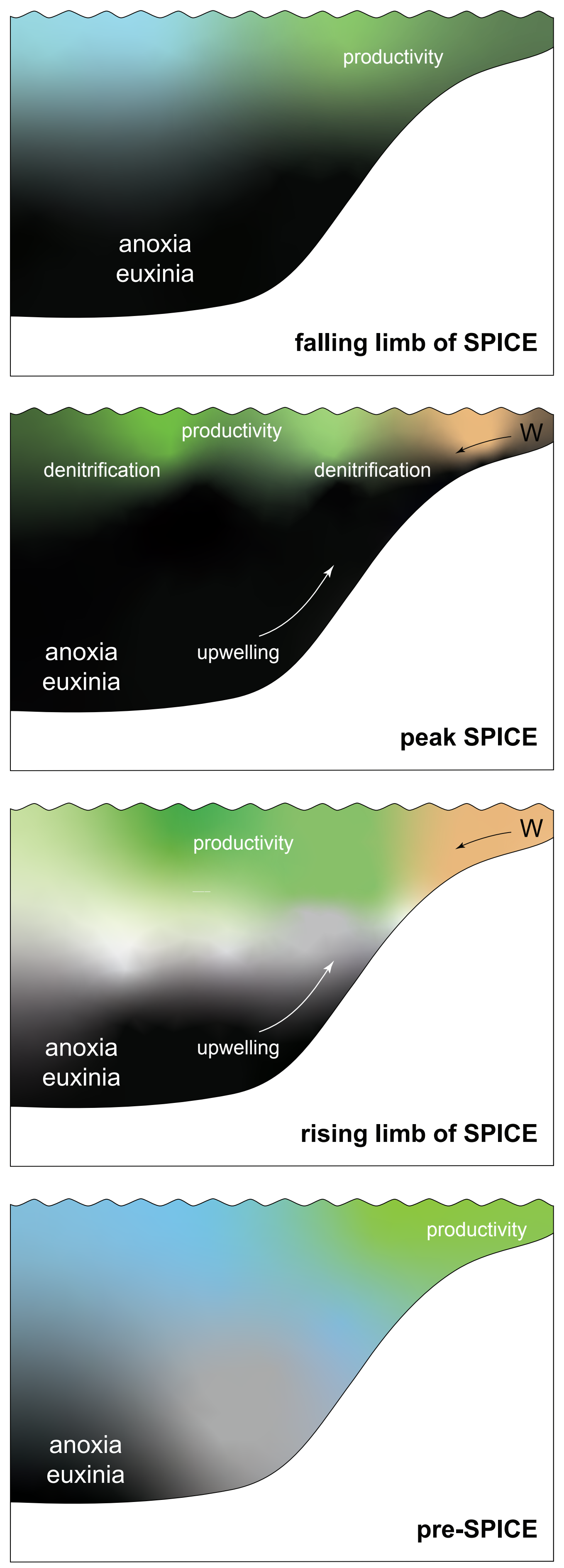


Figure 6:

Proposed water column environmental changes across the SPICE interval based on this study and modelled from Mesozoic oceanic anoxic events (OAEs).

4. Conclusions

The most influential of these changes correlate to the $\delta^{13}C_{org}$ excursions: SPICE and HERB, which suggest a period of anoxia and euxinia during the Paibian and increased weathering of organic rich material altering DIC availability, respectively. Geochemical changes have been found in Avalonia through the analysis of core samples taken from Merevale Cores #1 and #3 and the Oldbury Quarry. Moreover, it is indicated that the redox conditions of the shallow seas of Avalonia were also affected by the SPICE and HERB, suggesting that thermohaline circulation was intense allowing the oceans to remain well mixed. In turn we have suggested that the Cambrian seas experienced widespread anoxia and frequent transgression/regression cycles which greatly altered the geochemistry of the shallow seas. Further investigation should focus on evidence that will increase our understanding of nutrient availability and ocean structure within the Cambrian. This could be achieved through the generation of more organic carbon and nitrogen isotope records globally. We suggest that a tipping point occurred in the late Cambrian through a culmination of environmental changes, such as thermohaline circulation, nutrient supply, productivity, anoxia/euxinia and the nitrogen cycle that sparked the evolution of phytoplankton superfamily dominance. This ultimately shifted the ocean structure and chemistry causing changes to species richness, biodiversity and mass extinctions — e.g., the Phytoplankton Revolution and the Great Ordovician Biodiversity Event.

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