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Effect of a Jurassic Oceanic Anoxic Event on belemnite ecology and evolution

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The Toarcian Oceanic Anoxic Event (T-OAE, ~183 million years ago) is possibly the most extreme episode of widespread ocean oxygen deficiency in the Phanerozoic, coinciding with rapid atmospheric pCO_2 increase and significant loss of biodiversity in marine faunas. The event is a unique past tipping-point in the Earth system, where rapid and massive release of isotopically light carbon led to a major perturbation in the global carbon cycle as recorded in organic and inorganic C-isotope records.
Modern marine ecosystems are projected to experience major loss in biodiversity in response to enhanced ocean anoxia driven by anthropogenic release of greenhouse gases. Potential consequences of this anthropogenic forcing can be approximated by studying analog environmental perturbations in the past such as the T-OAE. Here, we present the first organic carbon isotope record derived from the organic matrix in the calcite rostra of early Toarcian belemnites. We combine both organic and calcite carbon isotope analyses of individual specimens of these marine predators to obtain a refined reconstruction of the early Toarcian global exogenic carbon cycle perturbation and belemnite palaeoecology. The novel carbon isotope data combined with new measurements of oxygen isotope values from the same specimens, allow for a more robust interpretation of the interplay between the global carbon-cycle perturbation, environmental change and biotic response during the T-OAE. We infer that belemnites adapted to environmental change by shifting their habitat from cold bottom waters to warm surface waters in response to expanded sea-floor anoxia.

Keywords:
ocean anoxia / Jurassic / marine mollusks changed habitat

Author contributions
Field sampling was conducted by SPH, CK, MR, NT and CVU. Sample preparation and chemical analyses were done by CVU. Drafting of the text and figures was done by CVU, NT, MR, SPH and CK.

Climatic and environmental change driven by anthropogenic greenhouse gases is predicted to severely compromise modern-day marine ecosystems through ocean anoxia and possibly ocean acidification[1,2]. Expanded and intensified oxygen minimum zones, accompanied by deposition of organic-rich sediments, have occurred multiple times in the past and are termed Oceanic Anoxic Events[3]. The Early Jurassic Toarcian Oceanic Anoxic Event (T-OAE) is among the best-studied of OAEs and represents an interval of global warming[3], high continental weathering intensity[3,4] and increased atmospheric pCO_2[5]. This event is associated with an enhanced turnover of taxa, enhanced sedimentary organic matter accumulation, and perturbations in the geochemical cycles of essential elements such as carbon, nitrogen, and sulfur, and redox-sensitive elements such as molybdenum[3]. Cyclostratigraphic studies of the Toarcian sedimentary record suggest a short (< 1 Myr) duration for the event and point to recurring, orbitally paced, pulses of rapid environmental change[6, 7, 8, 9]. The exogenic carbon cycle was globally perturbed as evidenced by a large negative carbon isotope excursion (CIE), which is expressed in marine and terrestrial organic and inorganic carbon in the northern and southern hemispheres[5, 10, 11]. Various potential triggers for the T-OAE have been identified. The event coincided with the extensive volcanic activity of the Karoo-Ferrar large igneous province[6, 7, 8]. Changes in the global carbon cycle through the T-OAE have been hypothesized to be forced by rapid and massive venting of isotopically depleted carbon through the production of thermogenic methane from sill-intruded organic-rich substrates[5] and biogenic methane from ocean-floor clathrates[7, 10].
Constraining the causes and magnitude of the observed changes in the carbon cycle relies on analytical results from the sedimentary record. Major obstacles for these reconstructions arise, because the commonly analyzed bulk samples always represent mixtures of different phases, which may also have been affected by post-depositional alteration. Samples of macrofossil calcite may occur only sparsely, are isotopically more heterogenous than bulk materials, and signals can be complicated by habitat and vital effects. Macrofossil calcite can, however, be assessed for its preservation state and carry significant information about environmental change and the faunal response to it. For the Jurassic and Cretaceous, the bullet-shaped fossilized remains (calcite rostra) of belemnites, extinct marine predatory cephalopods, are one of the prime sources for marine palaeoenvironmental reconstruction. The globally observed early Toarcian negative CIE, which is well known from bulk organic and carbonate carbon isotope records is either small or absent in the calcite of the rostra[12, 13]. This missing expression of the negative CIE in belemnite calcite has led some researchers to question that the T-OAE has been a climatic event of global extent[12, 13].
Isotopic investigations of belemnites have so far only focused on the inorganic matrix of the rostra[12, 13, 14]. The isotopic composition of the organic matrix, which is embedded in the calcite of the rostrum, has previously not been studied, even though its presence has been known for several decades[15, 16]. The or-

Significance Statement

The Toarcian-Ocean Anoxic Event (T-OAE, ~183 million years ago) is marked by one of the largest carbon cycle perturbations in Earth history, rapid climate change, widespread ocean oxygen deficiency, and strong changes in marine ecosystems. The temporal link between increasing atmospheric pCO2, changes in ocean oxygen availability, and marine biotic response during this event are still poorly understood.
Here, we use novel isotopic analyses of calcite and organic matter from belemnites, marine predators of that time, to address their response to bottom water anoxia during the OAE. We infer that some belemnites taxa showed resilience to a strong reduction in ocean oxygen availability and occupied ecological niches in the Cleveland Basin (UK), enabling a strong evolutionary diversification after the event.

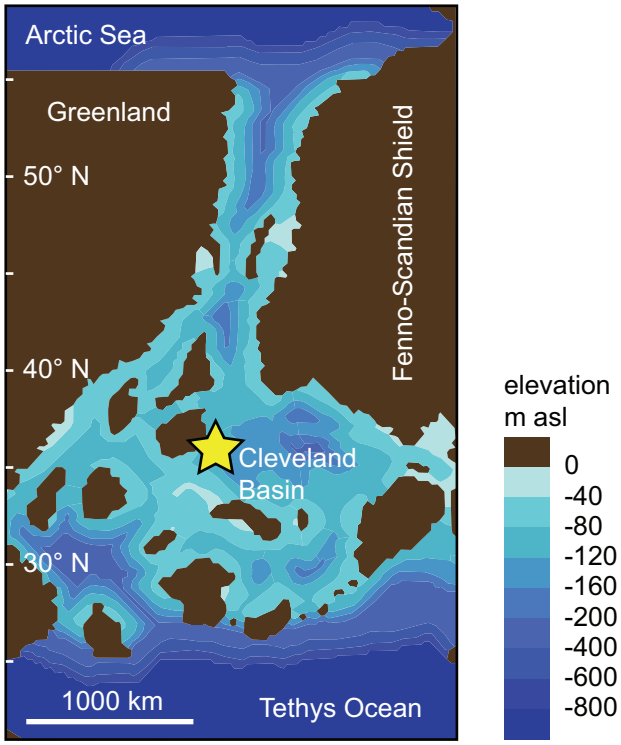

Figure 1: Paleogeography of the Laurasian Seaway (or Viking Corridor), modified from ref. 17. Sampling location is marked by a yellow star.

ganic matter in belemnite rostra can provide complementary information about the animal's habitat and mode of life. In this study we fill this gap by the analysis of the co-genetic organic and inorganic carbon of individual belemnite rostra. The rostra are derived from the Cleveland Basin (Yorkshire, UK), a sub-basin of the epicontinental Laurasian Seaway with water depths of ~100 m during the early Toarcian[17] (Fig. 1). Using our newly generated organic carbon isotope data in combination with isotopic data from the calcite of individual rostra, we reassess the paleoenvironmental significance of the isotopic composition of rostral calcite. We suggest a solution to the apparent paradox of the missing negative CIE in the calcite of the rostra by incorporating the ecological and evolutionary response of belemnites to bottom water anoxia into the interpretation of the isotope data.

Results

Combined analytical results from organic shell matrix and carbonate of well-preserved belemnites from the sedimentary successions of the Cleveland Basin are presented (see chapter Materials and Methods and Supporting Information for methodology and preservation criteria, and Supporting Information Tables S1-S3 for results). The C-isotope record of belemnite calcite ($\delta^{13}C_{bel\text{-}carb}$) through the tenuicostatum ammonite biozone is derived from the genus *Passaloteuthis* and shows an average value of +2.3 ± 1.4 ‰ (2 sd, n = 94). The *Passaloteuthis* record of the top semicelatum subzone lacks the clear representation of a strong negative carbon isotope shift (CIE) observed in coeval bulk organic carbon[12, 13] (Fig. 2). The following *falciferum* zone is characterized by the disappearance of *Passaloteuthis* and the appearance of *Acrocoelites* in the Cleveland Basin (Fig. 2). Within the lower *exaratum* subzone, a distinct negative CIE is observed in the belemnite calcite (Fig. 2). Minimum values of 0.3 ‰ are recorded in the stratigraphic interval where the negative carbon-isotope excursion in bulk organic carbon ($\delta^{13}C_{bulk\text{-}org}$) is at its peak (specimen Haws_NT_3). Isotopically light oxygen-isotope values ($\delta^{18}O_{bel\text{-}carb}$) in the rostra of *Acrocoelites* are associated with this CIE (Fig. 2). This oxygen-isotope spike coincides with widespread anoxia during the event, as evidenced e.g. by positive molybdenum-isotope values, enhanced redox-sensitive trace-element concentrations, increased total organic

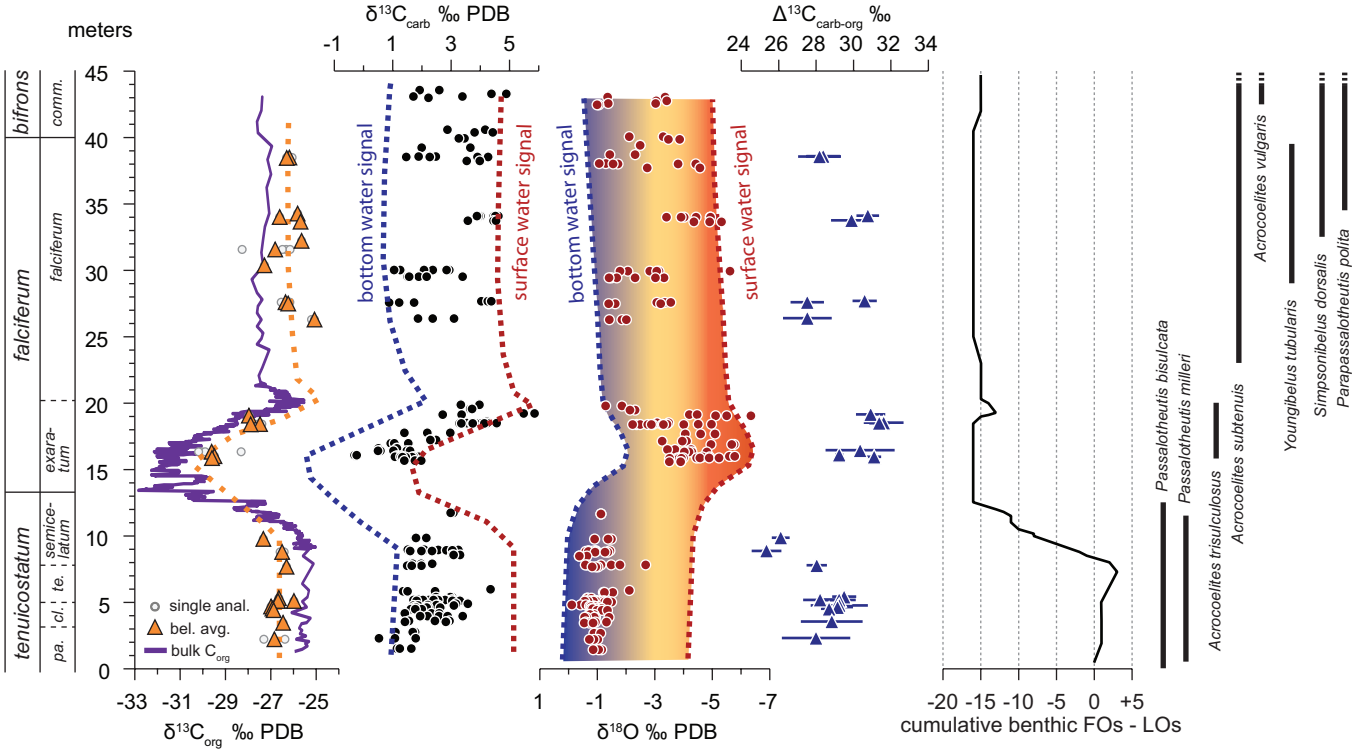

Figure 2: Chemostratigraphy of the early Toarcian. Bulk organic carbon data are from refs. 4, 7, 27. $\delta^{13}C_{bel\text{-}carb}$ and $\delta^{18}O_{bel\text{-}carb}$ are bounded by curves tentatively showing the signatures of belemnite calcite formed in surface water and bottom water in the Cleveland Basin. $\Delta^{13}C$ values are computed as the isotopic difference between average $\delta^{13}C_{bel\text{-}carb}$ and $\delta^{13}C_{bel\text{-}org}$ values of individual rostra. The cumulated number of first occurrences (FOs) and last occurrences (LOs) of benthic species throughout the section starting with zero at the 0 m level are computed from species ranges of bivalves, brachiopods, crinoids, gastropods and serpulids published in ref. 20. Belemnite species ranges are taken from refs. 19 and 20. Ammonite zones in chronological order: Dactylioceras tenuicostatum, Harpoceras falciferum, Hildoceras bifrons; Ammonite subzones in chronological order: Protogrammoceras paltum, Dactylioceras clevelandicum, Dactylioceras tenuicostatum, Dactylioceras semicelatum, Cleviceras exaratum, Harpoceras falciferum, Dactylioceras commune.

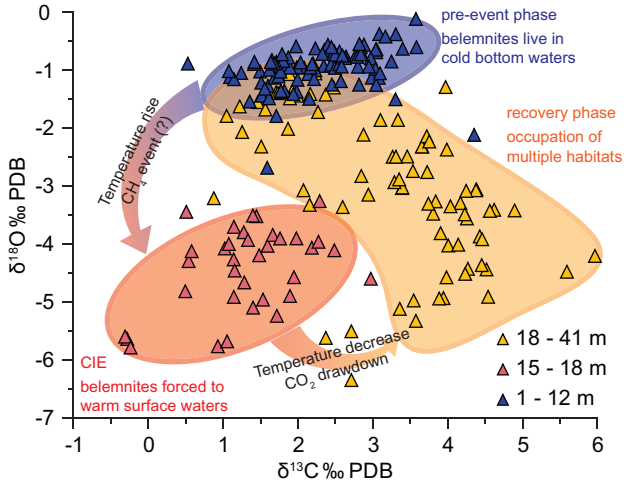

Figure 3: Crossplot of $\delta^{13}C_{bel-carb}$ and $\delta^{18}O_{bel-carb}$ values split into groups for the pre-CIE phase (1–12 m), main CIE (15–18 m), and recovery and post event phase (18–41 m). Height in meters corresponds to the values given in Fig. 2.

carbon preservation, and benthic extinctions[3, 8, 18, 19, 20]. The $\delta^{13}C_{bel-carb}$ values in the following *falciferum* subzone, which are mainly derived from *Acrocoelites*, are distinctly more variable (+1 to +5 per mil) compared to values found in *Passaloteuthis* of the *tenuicostatum* zone (+1 to +3 per mil) (Fig. 3, Supporting Information Table 1). Belemnite organic carbon-isotope values ($\delta^{13}C_{bel-org}$) follow the same overall trend as bulk organic carbon ratios, but are ~1 per mil lighter in the *tenuicostatum* zone, and ~1 per mil heavier in the *falciferum* zone (Fig. 2).

The $\delta^{18}O$ and $\delta^{13}C_{bel-carb}$ values of belemnite rostra before and during the T-OAE define well-separated fields (Fig. 3). Data from belemnites postdating the most negative carbon isotope values in the bulk organic material show a range in $\delta^{13}C_{bel-carb}$ about 1/3 larger than before and during the CIE (Figs. 2, 3). The range of $\delta^{18}O$ values of belemnites during the return to background carbon isotope values is twice as large as that of the two other groups (Figs. 2, 3). These belemnite data span a field that partly overlaps with pre-OAE belemnites and is offset from the peak OAE belemnites towards heavier $\delta^{13}C_{bel-carb}$ values (Figs. 2, 3).

Discussion

The discovery of a negative carbon isotope excursion with a magnitude of 2.5 ‰ in the organic matrix of belemnite rostra, coinciding with the negative CIEs in bulk organic carbon and carbonate (Fig. 2), counters the principal objection to the global nature of the T-OAE. It remains to be explained, however, why a corresponding CIE in the calcite of the rostra is suppressed compared to other substrates.

Relatively heavy and uniform $\delta^{18}O$ values in *Passaloteuthis* rostra preceding the T-OAE suggest a bottom-water habitat in the Cleveland Basin where temperatures were low and seasonally stable (Figs 2 and 4). The first appearance and dominance of *Acrocoelites* in belemnite assemblages after the disappearance of *Passaloteuthis* coincides with widespread ocean anoxia during the event and is characterized by a strong negative shift of ~4 ‰ in belemnite $\delta^{18}O$. Such a strong negative shift theoretically translates into a temperature increase of ~16°C[14], which appears unreasonably large as the Cleveland Basin at that time was located at subtropical latitudes[17]. It is also in strong contrast to a model-based, less extreme, prediction of 3-5°C temperature increase during the event[21]. Changes in water circulation and salinity of the Laurasian seaway may account for part of the observed signal in oxygen isotopes[17]. However, neither of these processes can simultaneously explain why the negative CIE in belemnite calcite is so subdued in comparison to the well-defined and abrupt excursions in the bulk carbonates of, for example, the Paris and Lusitanian basins[9, 10, 22, 23]. The strong decrease in $\delta^{18}O_{bel-carb}$ in the *exaratum* subzone instead suggests a combination of an overall raised water-column temperature, and a change of belemnite habitat, with *Acrocoelites* being adapted to warmer, oxygenated, surface waters (Fig. 4). This interpretation makes it possible to reconcile the $\delta^{13}C_{bel-carb}$ data across the CIE.

Surface waters are generally more enriched in ^{13}C than bottom waters because of removal of ^{12}C by photosynthesis in the photic zone and oxidation of ^{13}C-depleted organic matter in deeper waters. Our $\delta^{13}C_{bel-carb}$ record can thus be interpreted as follows: the adaptation of *Acrocoelites* to ^{13}C-enriched surface-water

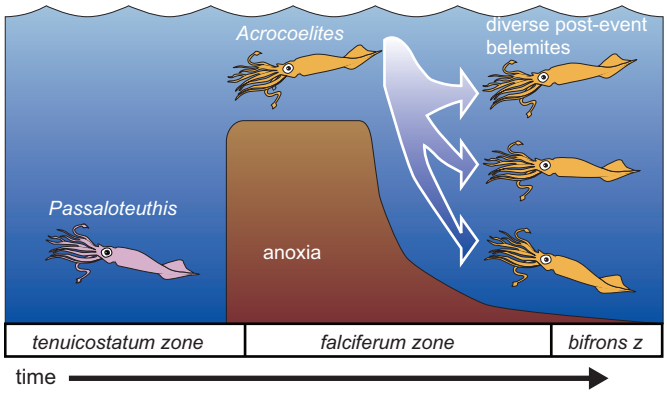

Figure 4: Tentative model for the habitat changes of belemnites in the Cleveland Basin over the T–OAE. Passaloteuthis disappears with the onset of anoxia and is succeeded by Acrocoelites that occupies the surface waters. With intermittently returning oxic bottom water conditions belemnites diversify and occupy a wider range of habitats.

shifts $\delta^{13}C_{bel-carb}$ to relatively more positive values and dampens the expression of the early Toarcian negative CIE. We attribute the increased isotopic variability and negative correlation of $\delta^{13}C_{bel-carb}$ and $\delta^{18}O_{bel-carb}$ in *Acrocoelites* after the early Toarcian negative CIE to belemnite diversification with taxa adapted to surface-water environments and returning to periodically re-oxygenated bottom-water habitats (Figs. 3, 4). Vital effects and diagenetic alteration are unlikely to have generated the observed trends, as both would have resulted in positive correlations of $\delta^{13}C$ and $\delta^{18}O$[24, 25], and partly very depleted values in the case of diagenesis[25]. Although the postulated change of habitat obscures the negative CIE in $\delta^{13}C_{bel-carb}$, the synchronous positive shifts in $\delta^{13}C_{bulk-org}$, $\delta^{13}C_{bel-org}$ and $\delta^{13}C_{bel-carb}$ after the event (Fig. 2) clearly show the recovery of early Toarcian exogenic carbon pools from the strong ^{13}C depletion.

The change in offset of $\delta^{13}C$ between belemnite and bulk organic matter through the OAE – from lighter (*Passaloteuthis*) to heavier values (*Acrocoelites*) – may reflect different feeding behaviors in the two genera. While *Acrocoelites* may have relied on food sources with a heavier carbon isotope signature than those accessible to *Passaloteuthis*, it also cannot be excluded that the contrasting carbon isotope offset is due to differences in the biosynthesis of the organic matrix between the two genera.

The concentration of dissolved CO_2 in seawater partly dictates the isotopic fractionation of carbon in the organic matter of photosynthetic marine primary producers, resulting in enhanced fractionation under higher pCO_2, whose isotopic signature is then imprinted throughout the entire food web[26]. The isotopic difference between coeval marine organic carbon and carbonate carbon through a sedimentary sequence can thus be related to changes in atmospheric CO_2. Such records can, however, only reliably represent atmospheric CO_2 if the mode of formation of both, the organic and carbonate carbon, remains the same over time. This assumption may allow for reliable interpretation of $\Delta^{13}C$ records (as proxy for changing pCO_2) in the individual *tenuicostatum* and *falciferum* subzones. However, the changing offset in $\delta^{13}C$ between bulk and belemnite organic carbon at the transition from *Passaloteuthis* to *Acrocoelites* (Fig. 2) precludes unambiguous interpretation of the belemnite

$\Delta^{13}C$ record over the early Toarcian OAE.

Taking a shift in life habits of belemnites into account can explain why the negative CIE of the T-OAE is subdued in belemnite calcite, and further strengthens the notion that the T-OAE is an event of global significance. A change in belemnite habitats is also in good agreement with benthic turnover during the widespread bottom water anoxia[19] (Fig. 2) and allows for a more realistic assessment of the geochemical signatures of rostra through the early Toarcian. Today's environmental threat to marine organisms and ecosystems through potential hyperthermia and anoxia is severe and could lead to a dramatic loss in biodiversity[2]. This is evident from the early Toarcian and other OAEs, when benthic species were strongly affected, and marine organisms showed a large turnover in species while adjusting to new habitats and available niches[19]. In some instances, however, as is the case here for belemnites, the evolutionary capabilities of past marine predators responding to extreme environmental change ultimately led to the successful occupation of a wider range of habitats.

Materials and methods

Belemnite rostra were collected from sections at Hawsker Bottoms (54°27'24" N, 0°32'20" W) and Saltwick Bay (54°29'21" N, 0°35'18" W), Yorkshire, UK. Carbon and oxygen isotope ratios as well as Mg/Ca, Sr/Ca and Mn/Ca ratios were measured at the University of Oxford and the University of Copenhagen from calcite drilled out of the rostra. In Copenhagen ~0.5 mg of calcite was processed using an IsoPrime mass spectrometer for $\delta^{13}C$ and $\delta^{18}O$ measurements and an Optima 7000 DV ICP-OES for subsequent analysis of reacted remains for element ratios. Reproducibility (2sd) of isotope ratios is better than 0.2 ‰, and better than 3 % for Mg/Ca and Sr/Ca. Reproducibility (2sd) for Mn/Ca ratios is better than 3 μmol/mol in the range of accepted Mn/Ca ratios. In Oxford carbon and oxygen isotope analyses were performed on ~50 μg of calcite powder using a Delta V mass spectrometer coupled with a Kiel IV device. Reproducibility (2sd) is better than 0.1 ‰. Element ratios were determined on ~80 μg calcite powder using an Element XR ICP-MS with reproducibility better than 1.5 % (2sd). Only results from translucent calcite showing good preservation of shell structure (Figs. S1, S2) and with Mn/Ca ratios of < 0.10 mmol/mol and Sr/Ca ratio > 1.2 mmol/mol are interpreted here.

Organic carbon was extracted from 270 to 1370 mg of calcite. For organic carbon extraction, the rostra were broken, and surfaces and visibly altered parts ground away. The clean fragments were dissolved in 6 M HCl at room temperature and insoluble organic matter from the shell matrix was extracted by five times centrifugation at 3000 rpm and disposal of the supernatant. The remaining residue was dried at 60°C and ~90 μg transferred into a tin capsule for isotopic analyses. The $\delta^{13}C$ measurements were done using an IsoPrime mass spectrometer coupled with an elemental analyzer at the University of Copenhagen. Reproducibility is better than 0.2 ‰ (2sd).

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