PALEOCEANOGRAPHY, VOL. 20, PA3008, doi:10.1029/2004PA001102, 2005

Toarcian oceanic anoxic event: An assessment of global causes using belemnite C isotope records

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Received 19 October 2004; revised 30 March 2005; accepted 22 April 2005; published 26 August 2005.

[1] Two hypotheses have been proposed to explain simultaneous large negative excursions (up to 7‰ PeeDee belemnite) in bulk carbonate ($\delta^{13}C_{carb}$) and organic carbon isotope records ($\delta^{13}C_{org}$) from black shales marking the Toarcian oceanic anoxic event (T-OAE). The first explanation envisions recycling of dissolved inorganic carbon (DIC) with a light isotopic signature into the photic zone from the lower levels of a salinity-stratified water mass, essentially requiring a regional paleoceanographic driver of the carbon cycle. The second involves the rapid and massive dissociation of methane from gas hydrates that effectively renders the T-OAE a global perturbation of the carbon cycle. We present C isotope records from belemnites ($\delta^{13}C_{bel}$) sampled from two localities, calibrated with high-resolution ammonite biostratigraphy and Sr isotope stratigraphy, in Yorkshire (England) and Dotternhausen (Germany), that can be used to assess which model best explains the observed changes in carbon isotopes. Our records of the $\delta^{13}C$ composition of belemnite calcite do not show the large negative C isotope excursions shown by coeval records of $\delta^{13}C$ in sedimentary organic matter or bulk sedimentary carbonate. It follows that isotopically light carbon cannot have dominated the ocean-atmosphere carbon reservoir during the Toarcian OAE, as would be required were the methane release hypothesis correct. On the basis of an evaluation of available carbon isotope records we discuss a model in which the recycling of DIC from the deeper levels of a stratified water body, and shallowing of anoxic conditions into the photic zone, can explain all isotopic profiles. In particular, the model accounts for the higher C isotope values of belemnites that are characteristic of open ocean, well-mixed conditions, and the lower C isotope values of neritic phytoplankton communities that recorded the degree of density stratification and shallowing of anoxia in the photic zone.

Citation: van de Schootbrugge, B., J. M. McArthur, T. R. Bailey, Y. Rosenthal, J. D. Wright, and K. G. Miller (2005), Toarcian oceanic anoxic event: An assessment of global causes using belemnite C isotope records, *Paleoceanography*, *20*, PA3008, doi:10.1029/2004PA001102.

1. Introduction

[2] Across Europe, from England to Greece, Lower Toarcian sediments are found that are rich in organic matter, reaching nearly 20% organic carbon (TOC) in some localities [*Küspert*, 1982; *Jenkyns*, 1988; *Schouten et al.*, 2000; *Röhl et al.*, 2001; *Schmid-Röhl et al.*, 2002; *Bucefalo Palliani et al.*, 2002]. It was suggested by *Jenkyns* [1988] that these sediments, generally termed black shales, represented a global episode of enhanced organic carbon deposition, possibly as a result of anoxic conditions globally: the event is now termed the Toarcian oceanic anoxic event (T-OAE) [*Jenkyns*, 1988]. Across Europe, the Lower Toarcian black shales are often associated with a negative carbon isotope excursion, of variable magnitude up to 7‰ in $\delta^{13}C$, expressed in bulk organic matter [*Küspert*, 1982; *Jenkyns and Clayton*, 1986; *Schouten et al.*, 2000; *Hesselbo et al.*, 2000], jet (a form of highly altered wood [*Hesselbo et al.*, 2000]), organic biomarkers [*Schouten et al.*, 2000] and, in some localities but by no means all, bulk nannofossil carbonate. The excursion occurs in the *Harpoceras exaratum* subzone of the *Harpoceras falciferum* ammonite zone, or its lateral equivalents elsewhere in Europe, although some uncertainty pertains to the degree of synchrony of such ammonite zones.

[3] Two explanations have been given for the cause of the negative C isotope excursion. First, it has been attributed to the recycling of remineralized carbon from the lower levels of an intermittently stratified water column into the photic zone and its subsequent incorporation in photosynthetic phytoplankton [*Küspert*, 1982; *Sælen et al.*, 1996, 1998, 2000; *Schouten et al.*, 2000; *Röhl et al.*, 2001; *Schmid-Röhl et al.*, 2002] an explanation that requires a local driver for the C isotope excursion. Second, and more recently, *Hesselbo et al.* [2000] suggested that the negative C isotope

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0883-8305/05/2004PA001102

excursion resulted from the rapid release to the ocean and atmosphere of (biogenic) methane from methane hydrate in sediments: because biogenic methane is depleted in ^{13}C relative to ^{12}C ($\delta^{13}C \sim -60‰$), its oxidation to CO_2 in the oceans and atmosphere imparts a light carbon isotope signal on dissolved inorganic carbon (DIC), and the atmospheric CO_2, carbon reservoirs, thereby simultaneously shifting the isotopic composition of marine and terrestrial carbon toward more negative values. This explanation requires methane to be a global driver for the C isotope excursion and, if correct, the negative excursion should be seen in marine and terrestrial carbon (organic and inorganic) in sections worldwide that preserve the appropriate sediments.

[4] Here we present new records of $\delta^{13}C$ of belemnite calcite ($\delta^{13}C_{bel}$ hereinafter) across the Toarcian OAE from a section in Dotternhausen (southwest Germany) that, combined with published data from Yorkshire, allow us to distinguish between local and global causes for the negative C isotope excursion in the European *Harpoceras exaratum* subzone and its equivalents. Belemnite rostra are excellent substrates from which stable isotope (C, O, Sr) and trace element (mainly Sr/Ca and Mg/Ca) records can be derived, and are often present when other samples are absent e.g., the many Jurassic sequences lacking planktonic foraminifera. Analogous to present-day squid, belemnites were presumably nektobenthic predators, migrating into shallower waters to forage and spawn. As a negative C isotope excursion is not seen in belemnite calcite through the sections where OM and bulk sedimentary carbonate show such excursions, we conclude that the latter excursions do not reflect a global event and so were not caused by methane hydrate release. We also draw attention to published records of $\delta^{13}C$ through carbonate sequences that show no negative excursion during the *Harpoceras exaratum* subzone of the *Harpoceras falciferum* zone of the lower Toarcian.

2. Methods

[5] We collected, and analyzed for $\delta^{13}C$, belemnites from the Lower Toarcian sections exposed on the Yorkshire coast (U.K.) (for locations, see *McArthur et al.* [2000], *Bailey et al.* [2003]) and at the Rohrbach cement quarry at Dotternhausen (SW Germany) [*Küspert*, 1982]. The lithostratigraphic and biostratigraphic framework for the sections in the U.K. is documented by *Howarth* [1962, 1973] and *Hesselbo and Jenkyns* [1995]. Sample positions in Yorkshire are reported as stratigraphic heights relative to an arbitrary zero datum, placed at the base of the *Harpoceras falciferum* zone in the U.K. ammonite biostratigraphy given by *Howarth* [1962, 1973] and is the level of the base of Howarth's Bed 33 (Cannon Ball Doggers). This level coincides with the base of the *Harpoceras exaratum* subzone in the U.K. and the base of the *Eleganticeras elegantulum* subzone in Germany. We use data from *Sælen et al.* [1996], who assigned belemnite positions only by lithological unit (bed), rather than position within a bed, so we plot their data in the midpoint of the appropriate bed: the stratigraphic uncertainty arising from this procedure is generally less than 1 meter. The levels given by *Sælen et al.* [1996] refer to the same zero datum at the base of bed 33 (their Table 1) as is used by *McArthur et al.* [2000] and in this study.

[6] Sample heights in Germany are measured relative to a zero datum at the base of the *Protogrammoceras paltum* subzone in the German ammonite biostratigraphic scheme given by *Küspert* [1982], *Riegraf et al.* [1984], *Schouten et al.* [2000], *Röhl et al.* [2001] and *Schmid-Röhl et al.* [2002]. Correlation of the German section and U.K. sections was confirmed by Sr isotope stratigraphy, as described by *Bailey et al.* [2003].

[7] For determination of $\delta^{13}C_{bel}$ in new belemnites, they were reacted with 100% orthophosphoric acid at 90°C using a multiprep peripheral device and analyzed with an Optima mass spectrometer at Rutgers University. Repeat analysis of NBS19 yielded precision better than ±0.06‰ for $\delta^{13}C$ and better than ±0.08‰ for $\delta^{18}O$. Values are reported versus ‰ PDB. The same belemnite samples were also analyzed for trace element ratios (chiefly Mg/Ca, Na/Ca and Li/Ca) with ICP-MS as reported by *Bailey et al.* [2003]. Mn concentrations <30 ppm have been used to distinguish altered from nonaltered belemnite calcite and all belemnites passed our diagenetic screening. Additional values of $\delta^{13}C_{bel}$ for belemnites from Yorkshire are taken from *Sælen et al.* [1996], *McArthur et al.* [2000], and C. E. Jones (personal communication, 1995).

3. Results

[8] Data from this study, and for convenience from *Sælen et al.* [1996] and *McArthur et al.* [2000], along with the samples' stratigraphic level will be stored in the CHRONOS database (www.chronos.org). Values of $\delta^{13}C_{bel}$ are plotted against stratigraphic level for the U.K. and for Germany in Figure 1. In Figure 1, $\delta^{13}C_{bel}$ is presented alongside values of $\delta^{13}C$ in organic matter ($\delta^{13}C_{org}$) and carbonates ($\delta^{13}C_{carb}$).

3.1. Belemnites

[9] Profiles of $\delta^{13}C_{bel}$ in both the U.K. and Germany display a remarkable overall concordance of trends. In the U.K., $\delta^{13}C_{org}$ in the Yorkshire section shows a negative excursion of −6‰ [*Hesselbo et al.*, 2000] (Figure 1a), which starts in the lower *Dactylioceras semicelatum* subzone, reaches its acme in the middle of the *Harpoceras exaratum* subzone, and recovers to former values at the top of the *Harpoceras exaratum* subzone. The profile of $\delta^{13}C_{bel}$ does not record this excursion (Figure 1a): Values of $\delta^{13}C_{bel}$ increase from around +1.5‰ in the uppermost Pliensbachian *Pleuroceras spinatum* zone to around +4‰ in the *Dactylioceras semicelatum* subzone before declining to values of ∼+2‰ in the lowermost Toarcian *Harpoceras exaratum* subzone. Thereafter, they increase to around +6‰ at the top of the *Harpoceras exaratum* subzone before returning to a background value of +2‰ in the upper *Harpoceras falciferum* zone: additional fine structure in the *exaratum* excursion is discussed by *McArthur et al.* [2000]. The background value of $\delta^{13}C_{bel}$ of 1.5 to 2‰ is close to that of between 0 and 2‰ recorded in belemnites through the Pliensbachian of Spain [*Rosales et al.*, 2004], so our data record a weak positive excursion of around 1‰ that peaks in the *Dactylioceras tenuicostatum* zone before

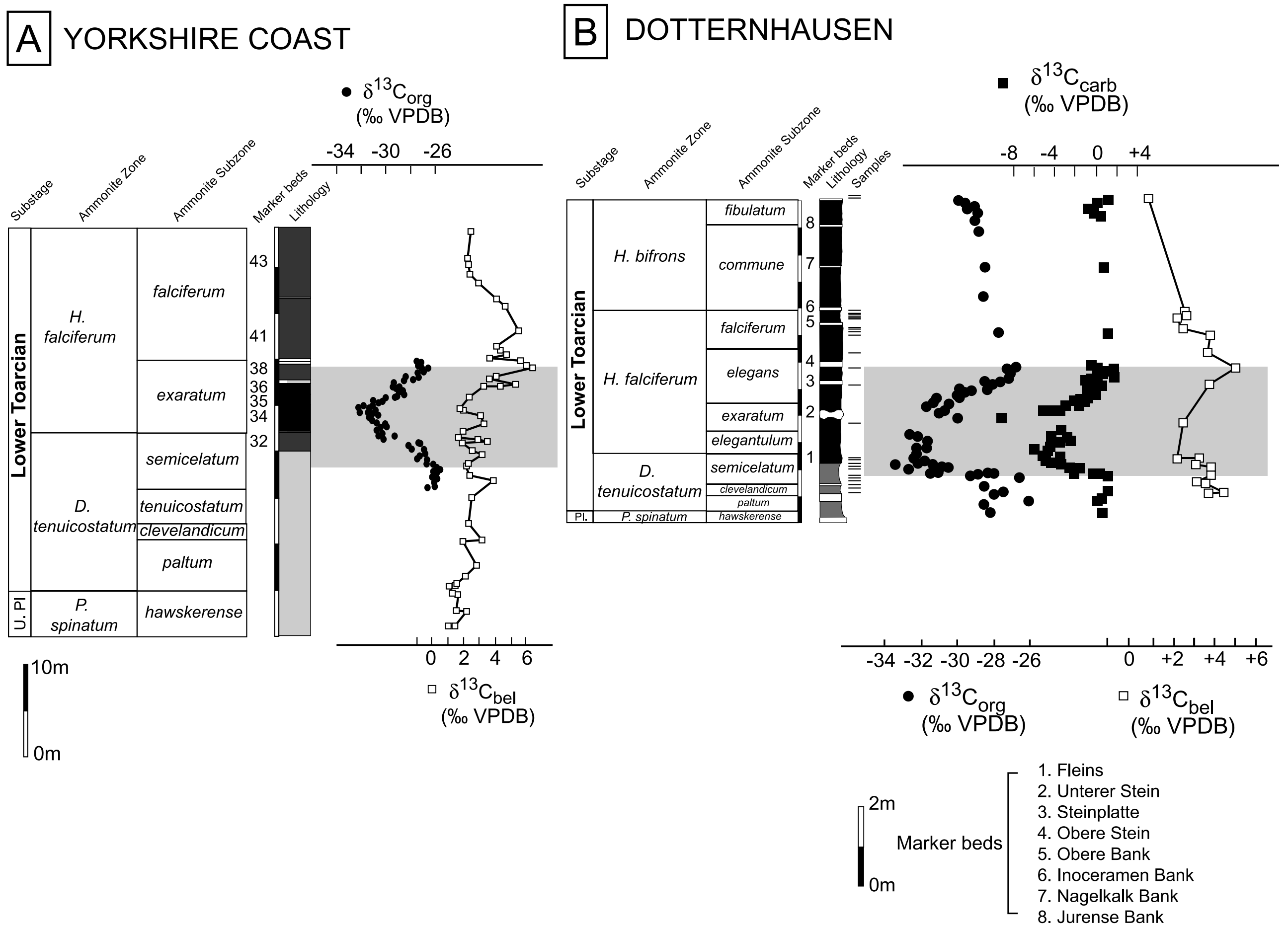

Figure 1. (a) Geochemical records from Yorkshire coast, England. Lithology, wood carbon isotope record, and bulk organic carbon isotope record ($\delta^{13}C_{org}$) are modified from *Hesselbo et al.* [2000]. Belemnite carbonate carbon isotope record ($\delta^{13}C_{bel}$) is after *McArthur et al.* [2000] and this study. (b) Geochemical records from Dotternhausen (SW Germany). Ammonite zonation and lithology are after *Riegraf et al.* [1984]. Bulk organic matter carbon isotope record ($\delta^{13}C_{org}$) is after *Schouten et al.* [2000]. Bulk rock carbonate carbon isotope record ($\delta^{13}C_{carb}$) is after *Röhl et al.* [2001]. Belemnite carbonate carbon isotope record ($\delta^{13}C$) is from Dotternhausen this study.

returning to previous values, of around +2‰, in the lower *Harpoceras exaratum* subzone. This trend through the *Dactylioceras semicelatum* and *Harpoceras exaratum* subzones is shown in more detail in Figure 2, where it can be seen that the values of $\delta^{13}C_{bel}$ return to background values of +2‰ at the point where $\delta^{13}C_{org}$ shows a maximum negative excursion of around −6‰ and TOC reaches its maximum.

[10] In Germany (Figure 1b), values of $\delta^{13}C_{bel}$ are around +4‰ in the middle of the *Dactylioceras tenuicostatum* zone and decline up section to values around +2‰ at the base of the *Eleganticeras elegantulum* subzone before showing a positive excursion up to 5‰ and a return to background values of +2‰ in the *Harpoceras falciferum* subzone.

3.2. Bulk Carbonate

[11] No profile of $\delta^{13}C$ in bulk carbonate is available for the Yorkshire sections, but elsewhere, the $\delta^{13}C$ of bulk carbonate shows a negative excursion that ranges in magnitude from −6.5‰ in Wales (Mochras Borehole), through around −2.5‰ in Porto de Mós in Portugal, to about −1‰ in Fuente de la Vidreira, Spain [*Hesselbo et al.*, 2000, Figure 2]. No negative excursion is apparent in several sections, for example in Iznalloz and Colomera, in southern Spain [*Jimenez et al.*, 1996, Figure 5], in Preston Plucknet in southern England [*Jenkyns and Clayton*, 1997] and likely in Winterbourne Kingston (ibid), where, if present, it is represented by one sample with a $\delta^{13}C$ of −2‰. In this context, it is interesting that *Hesselbo et al.* [2000, paragraph 2] state that "The negative excursion is also present, albeit very rarely, in Tethyan limestones lacking organic enrichment." Thus little evidence of negative excursions of $\delta^{13}C$ in bulk carbonate exists in Lower Toarcian sections in Kisgerecse, Hungary [*Jenkyns et al.*, 1991], or through the Scheibelberg section, of Kammerker, Austria [*Jenkyns et al.*, 1991] (although one sample at the *falciferum/tenuicostatum* boundary in Scheibelberg, with a value of +2‰, is a full 1‰ below the trend of adjacent data).

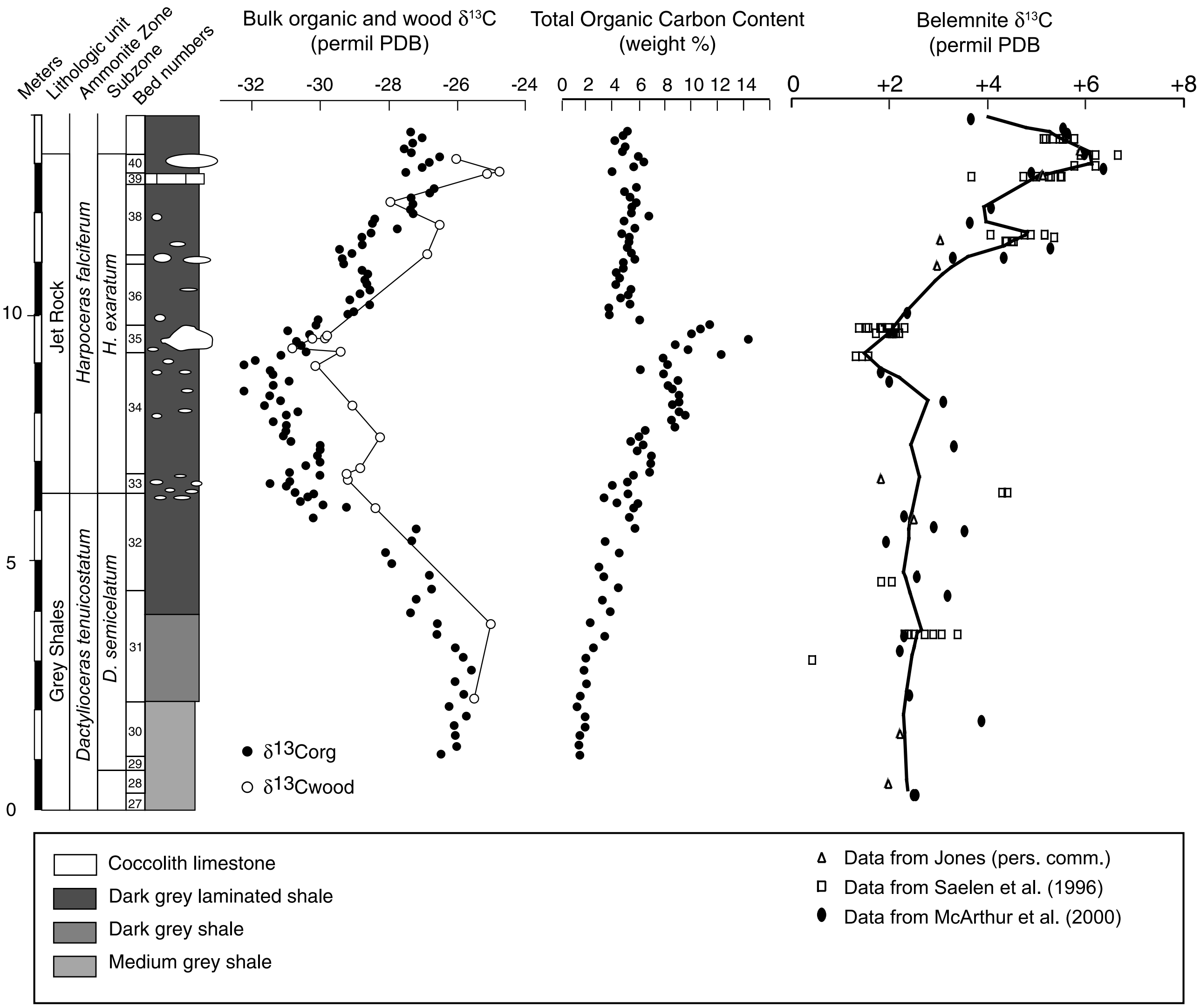

Figure 2. Detailed overview of available carbon isotope data for Yorkshire coast, England. Lithology, bulk organic matter carbon isotopes, and total organic carbon are redrawn from *Hesselbo et al.* [2000]. Belemnite carbon isotope data are from *Sælen et al.* [1996], *McArthur et al.* [2000], and C. Jones (personal communication, 1995). Curve fit to belemnite data is a 15% weighted average. Discrepancy between the $\delta^{13}C_{org}$ and $\delta^{13}C_{bel}$ records is illustrated. In contrast to organic matter, belemnites do not show a negative C isotope excursion across the T-OAE.

[12] In contrast, $\delta^{13}C$ in the data for bulk carbonate in Germany, given by *Röhl et al.* [2001] and *Schmid-Röhl et al.* [2002], shows a negative excursion, of magnitude −6‰ from a baseline of around 0‰, through the upper part of the *Dactylioceras tenuicostatum* zone and the lower part of the *Harpoceras falciferum* zone. For reasons given by *Röhl et al.* [2001] this excursion may be reflecting water column values of DIC, or may simply represent a diagenetic overprint.

3.3. Organic Matter

[13] Negative excursions in $\delta^{13}C_{org}$ are seen in sections through the *Harpoceras falciferum* zone of Yorkshire [*Küspert*, 1982; *Hesselbo et al.*, 2000] and, possibly, in the Mochras Borehole, Wales, U.K. [*Jenkyns and Clayton*, 1997]; in Germany, where they parallel trends in $\delta^{13}C$ of bulk carbonate [*Schouten et al.*, 2000; *Röhl et al.*, 2001; *Schmid-Röhl et al.*, 2002]; and in the St. Étienne-du-Valdonnez section, in France [*Küspert*, 1982]. According to *Schouten et al.* [2000] and *Röhl et al.* [2001], the excursions reflect real isotopic change, rather than changes in plankton species or differential preservation, not least because individual biomarkers show the same trends as bulk organic matter [*Schouten et al.*, 2000].

4. Discussion

[14] Records of $\delta^{13}C_{bel}$ are at odds with a putative role of methane hydrate as a cause for the negative C isotope excursion during the T-OAE, given that methane hydrate

release must affect the δ^{13}C of all carbon reservoirs, and that neither our belemnites from Germany nor those from the U.K. exhibit a negative excursion, to say nothing of a lack of such a negative excursion in other sections (see above).

[15] We consider it unlikely that belemnites do not faithfully record the δ^{13}C composition of DIC, whether in equilibrium or with constant offset from it, and that the negative excursion in δ^{13}C is therefore absent from the belemnite records we present. Belemnite calcite records the same positive excursion in δ^{13}C in middle-Valanginian (Early Cretaceous) times that is recorded by nannofossil carbonate [*McArthur et al.*, 2005a], and belemnites in the upper part of the *Harpoceras falciferum* zone record the positive excursion in δ^{13}C recorded by bulk carbonate that is present in some (not all) Tethyan sequences: these similarities support the argument that belemnites record variations in ambient δ^{13}C. Differences in habitat, or biological fractionation, may cause different species of belemnites to differ in their $\delta^{13}C_{bel}$ by as much as 1‰ [*McArthur et al.*, 2005b] but it would be fortuitous indeed were such differences to exactly counterbalance a negative shift caused by external factors. Finally, the δ^{18}O of belemnite calcite has been widely used as a paleotemperature proxy and, while its correctness for this purpose has yet to be definitively demonstrated (and the possible effect of pH on δ^{18}O in biogenic carbonate has been largely overlooked [*Zeebe*, 2001]), the concordance and sense of the interpretations that arise from such use suggest that belemnite calcite does indeed record near equilibrium values of δ^{18}O.

[16] We also discount the possibility that our samples do not record the negative excursion because they have been altered by diagenesis. First, belemnite rostra are physically robust and have a dense, impervious, microstructure composed of low-Mg calcite [*Sælen*, 1989] the most thermodynamically stable pseudomorph of calcium carbonate. Second, the C isotope composition of carbonates is widely regarded as one of the parameters most robust to alteration, and our analyzed samples (as opposed to our bulk specimens) showed no visible signs of such alteration. Third, data from *McArthur et al.* [2000] are from belemnites selected to be essentially unaltered on the basis of rigorously screening for diagenetic change, and the coherent trend they show through the section in ^{87}Sr/^{86}Sr, which reflects both long-term changes in marine ^{87}Sr/^{86}Sr and abrupt changes in sedimentation rate, is strong evidence for the high quality of the isotopic record these belemnites preserve. Fourth, data from *Sælen et al.* [1996] are from samples screened, by different but efficacious methods, to exclude those that showed signs of diagenetic alteration and they are concordant with our data and with that of *McArthur et al.* [2000]. The new data we present here were also obtained on material screened to exclude altered material being hand-picked from crushed rostra with the help of a compound microscope and guided by concentrations of Mn and Fe, two tracers for recrystallization. Finally, Ba/Ca and Cd/Ca ratios obtained from our belemnites are very low, which is consistent with measurements on modern bivalves (T. Bailey, unpublished data, 2004).

[17] Given the above, it follows that there is a high degree of certainty that the reason why our belemnite records do not show a negative excursion in δ^{13}C is because the belemnites did not live in an environment that experienced such an excursion. Because methane hydrate release must be a global event, this mechanism is not consistent with our records. Instead, our belemnite records, and all other records through the Toarcian OAE, can be fitted into the 'Küspert Model' that invokes regional or local stratification of a marine water body as a result of partial isolation, owing to changes in oceanography, followed by density stratification and the development of anoxia below a pycnocline, before gradual recovery of normal marine conditions during a subsequent rise in sea level that reestablished continuous and open marine conditions. The development of anoxia is envisaged to be repeatedly interrupted by brief returns to a fully oxygenated state following overturning of deeper waters. Below, we examine how European records of $\delta^{13}C_{bel}$, $\delta^{13}C_{org}$, and $\delta^{13}C_{carb}$, can be reconciled with this model.

4.1. "Küspert Model"

[18] In one form or another since 1901, the development of restricted circulation, and anoxia, have been a part of models for the development of organic-rich shales in the Lower Toarcian (see *Röhl et al.* [2001] for a summary). An isotopic element to the model was introduced by *Küspert* [1982], and developed by *Jenkyns* [1988], *Jenkyns and Clayton* [1997], *Sælen et al.* [1996, 1998, 2000], *Schouten et al.* [2000], *Schmid-Röhl et al.* [2002] and others cited by these authors, whereby the negative excursion in $\delta^{13}C_{org}$ through the *Harpoceras exaratum* subzone was attributed to photosynthetic uptake of isotopically light carbon, recycled from the lower levels of a water mass stratified by restriction within the semienclosed southwest German basin. In this scenario, primary production exports light carbon to levels below the pycnocline of a salinity-stratified and oxygen-depleted water body, which becomes anoxic. Bacterial degradation of exported carbon imparts a highly negative value to δ^{13}C of DIC to subpycnal waters, which, through diffusion, seasonal overturn, or mixing by major storm events, then biases overlying suprapycnal waters toward negative values of δ^{13}C in DIC. *Schmid-Röhl et al.* [2002] suggested that anoxic conditions were intermittently punctuated by week-to-year-long intervals of oxygenation, citing as evidence brief but unsuccessful attempts by epifauna to recolonize the bottom sediments.

[19] The "Küspert model" [*Küspert*, 1982] can explain both the negative excursion in $\delta^{13}C_{org}$, through the recycling of light carbon, and the intercalation within the sequence of belemnites with a C isotope composition indicating normal open ocean conditions: belemnites did not inhabit the area during times of anoxia, when these nektobenthic predators would have found food scarce and the water column unattractive, owing to photic zone anoxia [*Schouten et al.*, 2000]. The uncommon occurrence of belemnites in the black shales of Germany and Yorkshire (and Spain [*Rosales et al.*, 2004; *van de Schootbrugge et al.*, 2005]) suggests they invaded the area from well-

oxygenated surrounding seas during the brief episodes of oxygenation identified by *Röhl et al.* [2001] and *Schmid-Röhl et al.* [2002]. In Yorkshire, belemnites are very rare in bed 34 (Figure 1a). In Germany, the belemnites sampled from the black shale facies are invariably associated with the intercalated coccolithophorid limestone beds, a fact that supports our suggestion: such an association is unlikely to be caused by settling, or down mixing, of belemnite rostra through a soupy substrate to firmer, lower levels of limestone because belemnites in the *Harpoceras exaratum* subzone of Yorkshire define a good trend of increasing $^{87}Sr/^{86}Sr$ up section [*McArthur et al.*, 2000] and have C isotope values that are more similar to underlying than overlying sediments. Furthermore, the ammonite biostratigraphy seems to be in perfect order and macrofossils are generally found parallel to bedding planes: nor is there evidence for much reworking in this well-laminated, poorly burrowed, oil shale facies.

[20] The negative C isotope excursion recorded in bulk carbonate in Germany [*Röhl et al.*, 2001], the U.K. [*Jenkyns and Clayton*, 1997; *Hesselbo et al.*, 2000], Spain [*Jimenez et al.*, 1996], Portugal [*Hesselbo et al.*, 2000] and Italy (*Morettini* [1998] quoted by *Mattioli et al.* [2004]; *Jenkyns et al.* [2001]) may be because the calcifying organisms lived at a depth where they were exposed to isotopically light DIC, recycled from subpycnoclinal levels, especially during brief episodes of oxygenation or overturn of the water column, and so show depleted values of $\delta^{13}C$. Massive blooms of coccolithophorids, e.g., the ‘‘Unterer Stein’’ bed, can be traced across Germany, Switzerland and France [*Riegraf*, 1982], may have resulted from intermittent wind-driven mixing and oxygenation (see above) or episodicity on a Milankovitch timescale, causing a decrease in runoff, leading to a breakdown of salinity stratification and entrainment of nutrients from below the pycnocline [*Tyson*, 1985; *Sælen et al.*, 2000]. Maintenance of bottom anoxia during such blooms would have prevented much development of nekton, and so any food source for belemnites, which, as a consequence, did not invade the area during the peaks of coccolith production. In this respect it is also important to note that bloom organisms, such as coccolithophorids, reacted to seasonal overturn recording local conditions, whereas the belemnites, with life spans of at least several years, would primarily be influenced by open ocean conditions.

4.2. Regional Paleoceanography

[21] Photic zone anoxia (PZA) during the early Toarcian is indicated by biomarkers derived from green sulphur bacteria, such as *isorenieratane* and its diagenetic products, *aryl isoprenoids*, [*Schaeflé et al.*, 1977; *Schouten et al.*, 2000; *Frimmel et al.*, 2004; *Schwark and Frimmel*, 2004] and V porphyrins derived from either phytoplankton or phototrophic bacteria [*Sundararaman et al.*, 1993]. *Pancost et al.* [2004] have found further evidence for PZA during the Toarcian in the form of *maleimides*, degradation products of bacteriochlorophylls, which are also diagnostic for green sulphur bacteria.

[22] It is likely that PZA varied as a function of the intensity of water stratification along an onshore-offshore transect. To illustrate this variability we compare $\Delta\delta^{13}C_{carb\text{-}org}$ with $\delta^{13}C_{carb}$ records (Figure 3b) from three sections (Dotternhausen, Germany; Winterborne, U.K.; and Dogna, Italy) along a hypothetical cross section off the NW European shelf. Although not without uncertainty of interpretation [see *Kump et al.*, 1999], $\Delta\delta^{13}C_{carb\text{-}org}$ reflects relative changes in dissolved carbon dioxide concentrations $(CO_2)_{aq}$ [*Kump and Arthur*, 1999], where high values signify increased $(CO_2)_{aq}$. Across the T-OAE higher values are expected in Germany compared to Italy, because of more intense recycling of mineralized organic matter as can be deduced from generally higher organic carbon contents. Quite the opposite can be gleaned from Figure 3b. The explanation is that the $\Delta\delta^{13}C_{carb\text{-}org}$ values depend heavily on the $\delta^{13}C_{carb}$ record. The negative C isotope excursion recorded in $\delta^{13}C_{carb}$ clearly diminishes toward the less restricted conditions of the open Tethys: from Dotternhausen to Dogna, $\delta^{13}C_{carb}$ increases by nearly 8‰ in a basinward direction (Figure 3b), simultaneously shifting $\Delta\delta^{13}C_{carb\text{-}org}$ values from $\sim$25 to $\sim$33. This basinward increase reflects $\delta^{13}C(CO_2)_{aq}$ more in equilibrium with ‘‘normal’’ ocean water (and hence the atmosphere). These trends are mimicked by TOC values that also show a decrease. Although the decrease in TOC could reflect dilution of organic matter by inorganic sediment, it is well known that black shale facies are less well developed in the deeper parts of the North Tethyan basins and along the southern margin of the Tethys [*Jenkyns*, 1988; *Beaudoin et al.*, 1990; *Pancost et al.*, 2004].

[23] Instead of invoking a global mechanism, we argue, as others have done before us, for a strong regional oceanographic control on density stratification, PZA and hence carbon burial. Belemnite Mg/Ca and $\delta^{18}O$ records from Yorkshire and Dotternhausen [*McArthur et al.*, 2000; *Bailey et al.*, 2003] and northern Spain [*Rosales et al.*, 2004; *van de Schootbrugge et al.*, 2005] have been used to infer an increase in water temperature and decrease in salinity across the T-OAE, consistent with a scenario of freshening of surface waters causing density stratification. Although more data are needed to strengthen these interpretations, a survey of available data shows a salinity gradient may have existed with salinity increasing from north to south. These results fit a circulation model for the northern European shelf and Boreal Basin as presented by *Bjerrum et al.* [2001] in which low-salinity waters flowed southward through the Laurasian seaway (Figure 3c) or were transported directly by rivers from the northern Tethyan margin. By controlling density stratification, such a salinity gradient could potentially explain regional variation in organic carbon contents (Figure 3c).

[24] Density stratification on the European shelf was possibly further exacerbated by the formation of saline deep waters along the arid southern margin of the Tethys on the extended North African shelf. *Farrimond et al.* [1989] have discussed molecular evidence for highly saline bottom waters in the Tethys during the early Toarcian. The establishment of a marine connection between the Pacific and the

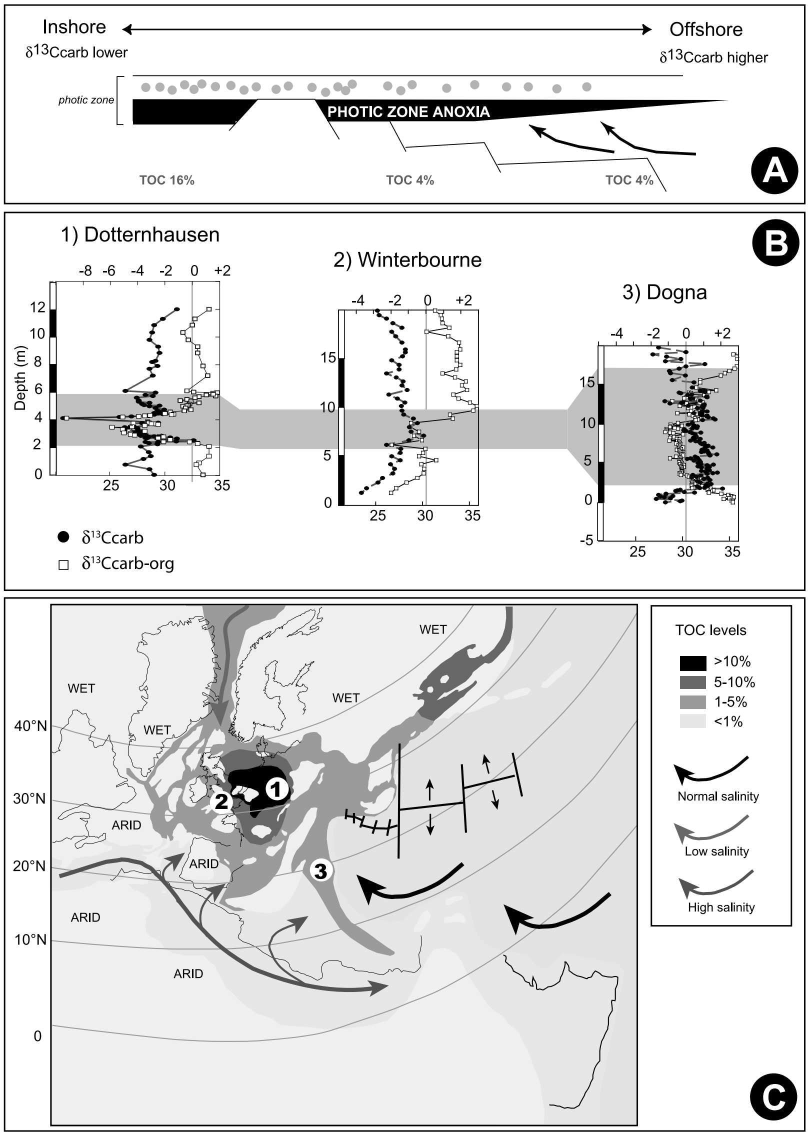

Figure 3. (a) Schematic cross section of the NW European Shelf showing relative position of three sections that serve as examples for regional variability in carbon burial and C isotope values: 1, Dotternhausen (Germany); 2, Winterborne (England); and 3, Dogna (Italy). See text for references. Maximum TOC levels are given for all three locations. Although dilution is partly responsible for decreased TOC in some sections, such as in Dogna (Italy), we suggest that decreased productivity and preservation as a result of decreased salinity stratification in more offshore waters played a dominant role. (b) Comparison of $\Delta\delta^{13}C_{carb\text{-}org}$ and $\delta^{13}C_{carb}$ records along an hypothetical inshore (Dotternhausen) to offshore (Dogna, Italy) transect. The intense salinity stratification in shallower water led to generally higher organic matter production and more intense recycling of subpycnoclinal dissolved inorganic carbon with lighter $\delta^{13}C$. Grey shaded area represents negative C isotope excursion correlated across sections. (c) Paleogeographic map for the early Toarcian (∼183 Ma) redrawn after *Beaudoin et al.* [1990] with an interpretation of paleoceanographic conditions. See color version of this figure at back of this issue.

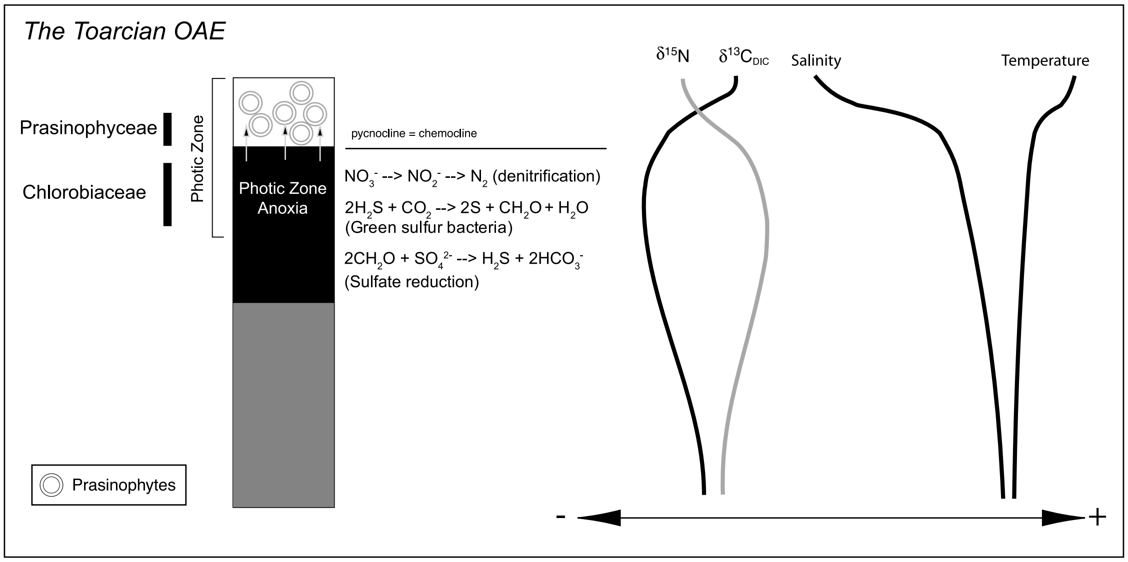

Figure 4. Schematic water column profile for Toarcian oceanic anoxic event (T-OAE). During the T-OAE, salinity stratification and probable high primary production led to shallowing of anoxic conditions into the photic zone, creating ideal conditions for phototrophic green sulfur bacteria (Chlorobiaceae) and green algae (Prasinophyceae). Cyst-forming dinoflagellates as well as calcareous nannoplankton were absent during the most intense anoxia marked by geochemical anomalies, such as the negative carbonate and organic carbon isotope excursions. This scenario explains positive nitrogen isotope excursions reported by *Jenkyns et al.* [2001], which indicate denitirification in the water column. Prasinophytes may have profited from such conditions, because they are good competitors for ammonium and nitrite. See color version of this figure at back of this issue.

Tethys, the so-called Hispanic Corridor, has received little attention in the debate on the causes for the T-OAE. After opening sometime during the late Sinemurian to early Pliensbachian, circulation became restricted during a late Pliensbachian phase of widespread sea level fall and most likely was reinvigorated again during the early Toarcian transgression. Circulation in the corridor was controlled by relatively fresh water entering on the more humid Pacific side that became progressively more saline toward the more arid Tethyan side, before flowing out into the Tethys [*Aberhan*, 2001].

[25] Our results fit a model as depicted in Figure 4. This model summarizes, in condensed form, the ideas of many previous studies [e.g., *Sælen et al.*, 2000, and references therein] and also explains many of the observed changes in the phytoplankton communities, ultimately responsible for the elevated organic carbon burial rates. During the early Toarcian, density stratification, as a result of increased fresh water inputs and higher sea surface temperatures, combined with periodic high productivity, led to upward expansion of anoxic conditions into the photic zone. In this scenario the pycnocline became coincident with both the nutricline and chemocline. The existence of PZA, including the presence of free H_2S, is consistent with the observed dramatic changes in the phytoplankton community composition. Actively swimming phytoplankton with deep dwelling and vertical migratory feeding strategies and obligate benthic life cycle stages, such as coccolithophorids and dinoflagellates, were adversely affected leading to a so-called dinoflagellate cyst "blackout" [*Bucefalo Palliani et al.*, 2002] and nannofossil disappearance event in the lower *Harpoceras falciferum* zone [*Mattioli et al.*, 2004]. Instead, these conditions were conducive to the proliferation of green algal phytoplankton (Prasinophyceae), such as *Tasmanites*, that occur abundantly in the Toarcian black shales [*Prauss et al.*, 1991; *Bucefalo Palliani et al.*, 2002]. Whereas for most phytoplankton NO_3^- is a limiting nutrient, prasinophytes are known to do well under conditions of increased availability of NH_4^+ [e.g., *Eppley et al.*, 1969; *Cochlan and Harrison*, 1991]. Diffusion of ammonium and/or nitrite is possibly indicated by positive nitrogen isotope values in Toarcian black shales, which is evidence for denitrification [*Jenkyns et al.*, 2001].

5. Conclusions

[26] Profiles of $\delta^{13}C_{(bel)}$, i.e., in belemnite carbonate, through the Lower Toarcian OAE in Germany and the U.K. do not record a negative C isotope excursion. Values of $\delta^{13}C$ in belemnite carbonate typically are heavier than 1.5‰ and, in some places record positive excursion up to +6‰. Additionally, a negative C isotope excursion is also absent from records of $\delta^{13}C$ in bulk carbonate through some European carbonate sequences. Where it is present, the magnitude of the negative excursion differs from place to place. These facts suggest that the development of the negative anomaly, where not diagenetic in origin, is related to regional paleoceanographic events, and cannot result from a massive release of methane hydrate

during the early Toarcian, since such an event would necessarily have affected simultaneously all the Earth's carbon reservoirs.

[27] Our data support the suggestions that the negative carbon isotope excursions recorded by organic matter and bulk carbonate in NW Europe were caused by a combination of restriction on circulation, coupled with local density stratification, that lead to the recycling of isotopically light DIC from the lower levels of an anoxic water mass, as proposed in a variety of ways; initially by *Küspert* [1982] and later by *Jenkyns* [1988], *Sælen et al.* [1996, 1998, 2000], *Schouten et al.* [2000], *Röhl et al.* [2001] and *Schmid-Röhl et al.* [2002].

[28] **Acknowledgments.** We thank Manfred Jaeger from Rohrbach Zement AG for access to the Dotternhausen quarry. The National Science Foundation is gratefully acknowledged for funding this research through the EREUPT-project (NSF Biocomplexity grant OCE-0084032). We thank Paul Falkowski for stimulating discussion and commenting on an earlier version of this manuscript. Paul Wignall and an anonymous reviewer provided constructive criticism, helping us to improve this paper substantially.

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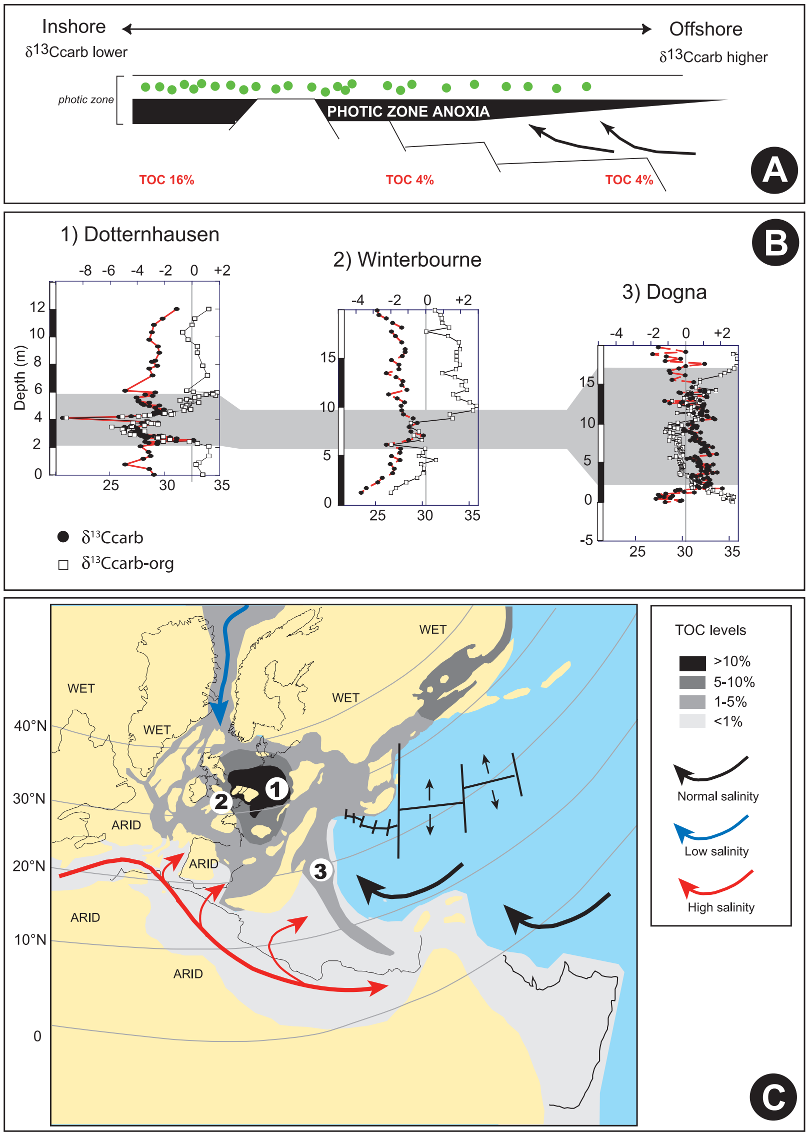

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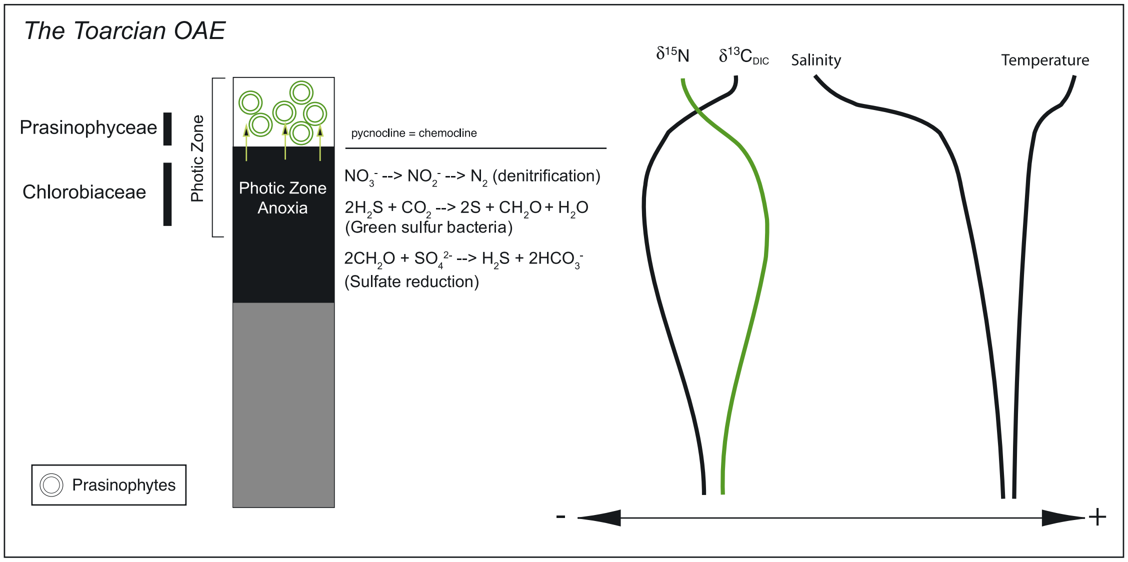

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