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# Nitrogen isotope evidence for water mass denitrification during the early Toarcian (Jurassic) oceanic anoxic event

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**Abstract.** Bulk sedimentary nitrogen isotope ($\delta^{15}N_{tot}$) data have been generated from Lower Jurassic black, carbon-rich shales in the British Isles and northern Italy deposited during the early Toarcian oceanic anoxic event. A pronounced positive $\delta^{15}N_{tot}$ excursion through the *exaratum* Subzone of the *falciferum* Zone (defined by characteristic ammonites in the British Isles) broadly correlates with a relative maximum in weight percent total organic carbon and, in some sections, with a negative $\delta^{13}C_{org}$ excursion. Upwelling of a deoxygenated water mass that had undergone partial denitrification is the likely explanation for relative enrichment of $\delta^{15}N_{tot}$, and parallels may be drawn with Quaternary sediments of the Arabian Sea, Gulf of California, and northwest Mexican margin. The development of Early Toarcian suboxic water masses and consequent partial denitrification is attributed to increases in organic productivity. Approximately coincident phenomena include the following: a relative climatic optimum, realignment of major oceanic current systems, and a possible release of methane gas hydrates from continental margin sediments early in the history of the oceanic anoxic event.

## 1. Introduction

The early Toarcian oceanic anoxic event [*Jenkyns*, 1988] was registered by the global distribution of organic carbon-rich black shales across a range of environments covering the deep ocean, Tethyan continental margins, and shelf seas (Figure 1). The event itself is commonly interpreted as being triggered by a climatic optimum affecting weathering patterns, fluvial fluxes, and upwelling intensity. This latter phenomenon led to relatively high availability of certain nutrients and consequent enhanced productivity of organic-walled and siliceous plankton in near-surface waters [*Jenkyns*, 1999]. In terms of detailed biostratigraphic data [*Riegraf et al.*, 1984; *Howarth*, 1992] and chemostratigraphic data (total organic carbon (TOC), $\delta^{13}C_{carb}$, $\delta^{13}C_{org}$, and $^{87}Sr/^{86}Sr$) [*Küspert*, 1982; *Baudin et al.*, 1990; *Hollander et al.*, 1991; *Jones et al.*, 1994; *Jenkyns and Clayton*, 1997; *Schmid-Röhl et al.*, 1999; *Hesselbo et al.*, 2000; *McArthur et al.*, 2000; *Jones and Jenkyns*, 2001; *Röhl et al.*, 2001], sections in northern Europe have been studied in the greatest detail, particularly in England (Jet Rock), Germany (Posidonienschiefer), and France (Schistes Carton). Exactly coeval organic-rich facies, generally with lower values of TOC are, however, developed in many parts of southern (Tethyan) Europe [*Jenkyns*, 1988].

Biomarker studies indicate that the organic matter in all these lower Toarcian black shales is dominantly marine in origin, deriving from algal and bacterial sources [*Farrimond et al.*, 1989, 1994; *Hollander et al.*, 1991; *Schouten et al.*, 2000]. During the time of deposition of these characteristic facies, major changes in carbon isotope ratios took place in the entire shallow ocean-atmosphere system, and both negative and positive shifts in $\delta^{13}C$ values of carbonates and marine and terrestrial organic matter have been recognized [*Jenkyns and Clayton*, 1986, 1997; *Hesselbo et al.*, 2000].

Here we present bulk sedimentary nitrogen isotope data from lower Toarcian, typically millimeter-laminated organic-rich black shales (Jet Rock and coeval facies; *exaratum* Subzone of the *falciferum* Zone, as defined by ammonite occurrences) deposited in three separate basins (Wessex Basin, Cardigan Bay Basin, and Cleveland Basin) (Figure 2) in the British Isles representing part of the north European epicontinental or epeiric seaway. In addition, we present data from coeval black shales from a pelagic basin (Belluno Trough) from the Southern Alps of Italy (Figure 2). Detailed descriptions of the chemostratigraphic and biostratigraphic context of these three British sections are given by *Jenkyns and Clayton* [1997], and the general Lower Jurassic geology of these basins, in terms of structural framework and lithostratigraphy, is elucidated by *Hesselbo and Jenkyns* [1995, 1998]. The context of coeval Toarcian black shales from the Southern Alps, part of the Tethyan region of central and southern Europe where the depositional setting was a rifted continental margin and sedimentation was essentially pelagic, is discussed by *Bernoulli and Jenkyns* [1974], *Jenkyns and Clayton* [1986], and *Jenkyns* [1985, 1988]. Details of available biostratigraphy and some organic geochemical data deriving from the Toarcian of the Belluno Trough are given by *Jenkyns et al.* [1985] and *Farrimond et al.* [1988, 1989, 1994], respectively; sedimentology and inorganic geochemistry are discussed by *Claps et al.* [1995] and *Bellanca et al.* [1999].

## 2. Material and Methods

Bulk sediment samples were powdered, and ~80 mg were decarbonated using 3 *M* HCl for 8 hours at ambient temperature. Samples were then rinsed with deionized water, centrifuged, rinsed again until neutrality was reached, and then dried in an oven at 60°C. Samples of ~20 mg were then weighed out into 8 × 6 mm tinfoil cups and placed in an Europa Scientific Limited CN biological sample converter connected to a 20-20 stable-isotope gas-ratio mass spectrometer. Carbon and nitrogen isotope ratios were measured against a laboratory nylon standard ($\delta^{13}C$ = −26.1 ± 0.2‰ and $\delta^{15}N$ = −2.2 ± 0.2‰ with $n$ = 24) and expressed relative to Peedee belemnite (PDB) and atmos-

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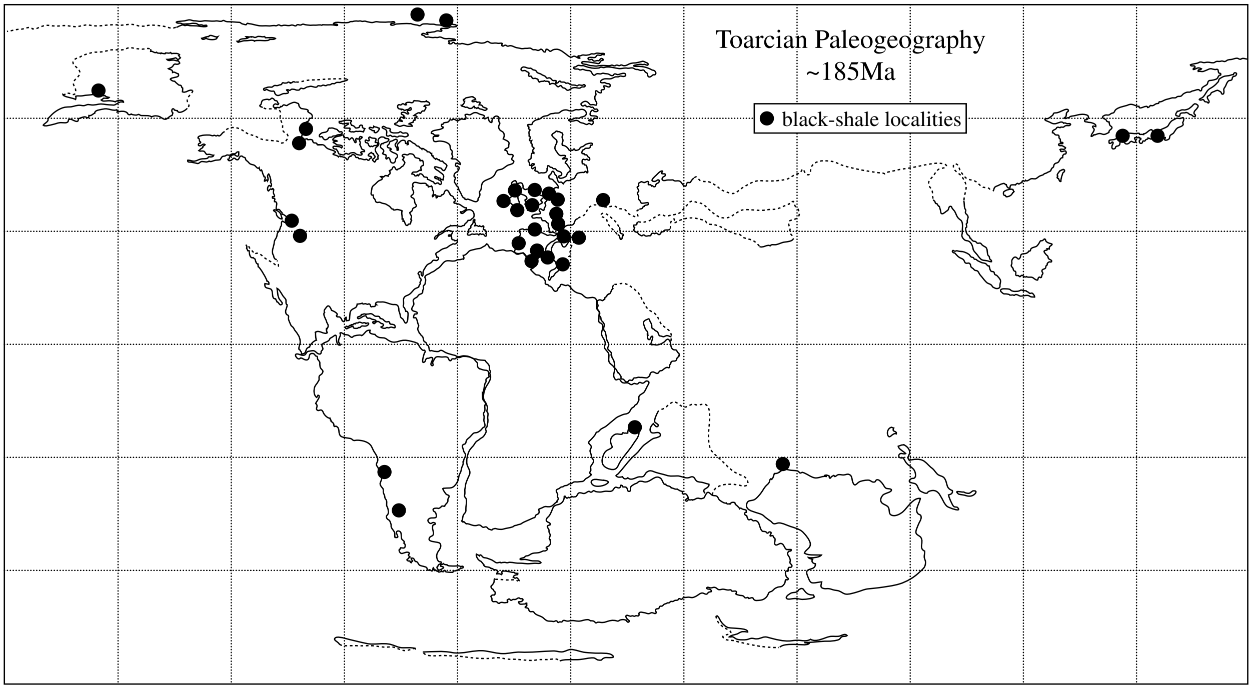


**Figure 1.** Paleogeographic map of the Toarcian (~185Ma) based on *Jenkyns* [1988] and references therein, showing localities with organic carbon-rich black shales. Additional data points are from *Baudin et al.* [1990], *Soussi et al.* [1990], *Dulai et al.* [1992], *Howarth* [1992], Nikitenko and Shurygin [1992], *Bucefalo Palliani and Mattioli* [1994], *Murphy et al.* [1995], *Parisi et al.* [1996], *Jiménez et al.* [1996], *Hori* [1997] and *Vetö et al.* [1997]. Most localities are dated as *tenuicostatum-falciferum* Zone.

pheric nitrogen (air $N_2$). Weight percent TOC values were determined using a Strohlein Coulomat 702 (details are given by *Jenkyns* [1988]).

## 3. Chemostratigraphy of Lower Toarcian Black Shales in Britain

### 3.1. Wessex Basin

The section through the lower Toarcian interval from the Wessex Basin derives from core material from the Winterborne Kingston borehole, Dorset, England (Figure 2). The lithologies present include gray, greenish-black mudstones, locally pyritic, and with included limestone nodules, and there is a distinct level of finely laminated black shales where TOC values rise to 4 wt %. Sample spacing varied according to core length but was generally in the range of one sample every 50 cm. Relevant chemostratigraphic profiles (TOC, $\delta^{15}N_{tot}$, $\delta^{13}C_{org}$, and $\delta^{13}C_{carb}$) through the lower Toarcian are illustrated in Figure 3. The biostratigraphy of the *tenuicostatum-falciferum* Zone is poorly defined because key ammonites were not obtained, but the chemostratigraphic data indicate that the level of laminated black shales pertain to the *exaratum* Subzone.

### 3.2. Cardigan Bay Basin

The section through Lower Toarcian black shales from the Cardigan Bay Basin derives from core material from the Mochras Farm borehole, Gwynedd, Wales (Figure 2). Sample spacing varied according to position in the core, ranging from one sample every 1.5 m over critical intervals to one sample every 7 m. The lithologies of the *exaratum* Subzone, the limits of which are identified biostratigraphically, include gray silty mudstones, locally calcareous, and a distinct level of black millimeter-laminated shales where TOC values rise to ~2.5%. Relevant chemostratigraphic profiles (TOC, $^{15}N_{tot}$, $\delta^{13}C_{org}$, and $\delta^{13}C_{carb}$) through the lower Toarcian are illustrated in Figure 4.

### 3.3. Cleveland Basin

The section through Lower Toarcian black shales from the Cleveland Basin derives from an outcrop at Hawsker Bottoms on the coast of Yorkshire, England (Figure 2). The lithology is dominated by highly carbon-rich (TOC values in the *exaratum* Subzone of 5–15%) millimeter-laminated black shales containing discrete levels of calcite concretions with dimensions typically in the tens-of-centimeters range. The section investigated was sampled every 10 cm across the organic-rich interval that constitutes the Jet Rock sensu stricto [*Hesselbo and Jenkyns*, 1995] and approximately every 20 cm below this unit. Relevant chemostratigraphic profiles (TOC, $\delta^{15}N_{tot}$, $\delta^{13}C_{org}$, and $\delta^{13}C_{belemnite}$) through the Lower Toarcian are illustrated in Figure 5.

## 4. Chemostratigraphy of Lower Toarcian Black Shales in North Italy (Belluno Trough)

The analyzed section through Lower Toarcian black shales from the Belluno Trough, Southern Alps, derives from core material from Dogna, near Longarone, north Italy (Figure 2). Sample spacing varied according to core length but was generally in the range of one sample every 10 cm. The ammonite biostratigraphy of this section dates the organic-rich interval (TOC values in the range 1–5%) as likely lower *falciferum* Zone [*Jenkyns et al.*, 1985]. However, we have assigned a more detailed notional north European biostratigraphy, at subzonal resolution, by reference to the characteristic carbon-isotope profile. Particularly diagnostic in this regard is the two-stage drop in values of both $\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$ at the very top of the *semicelatum* Subzone of the *tenuicostatum* Zone (Figure 6), as can be seen by reference to the detailed curve

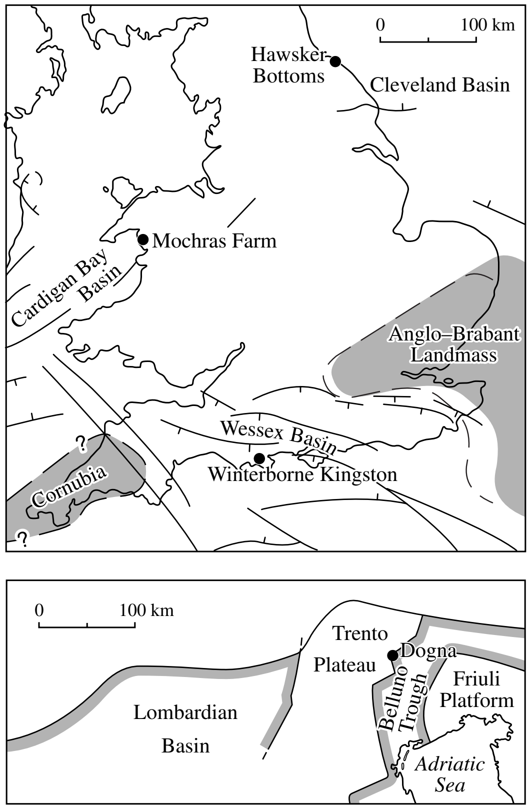


**Figure 2.** Maps showing localities investigated in this study. The Wessex, Cardigan Bay, and Cleveland Basins were situated in the north European epicontinental seaway during the Early Jurassic; the Belluno Trough was part of the Tethyan continental margin and characterized by pelagic deposition during the Toarcian interval. (Modified from *Hesselbo and Jenkyns* [1995] and *Jenkyns et al.* [1985]).

from Yorkshire, northeast England, where the ammonite zonation is well defined (Figure 5). The lithologies present in this Italian section are a little different from those in northern Europe in that the millimeter-laminated organic-rich brown shales are regularly interbedded with beds of manganoan limestones, a feature found in many coeval pelagic facies in central Europe [*Jenkyns et al.*, 1991]. Relevant chemostratigraphic profiles (TOC, $\delta^{15}N_{tot}$, $\delta^{13}C_{org}$, and $\delta^{13}C_{carb}$) through the lower Toarcian of northern Italy are illustrated in Figure 6.

## 5. Early Toarcian Nitrogen Isotope Excursion

Because thermal maturity has a negligible effect on $\delta^{15}N$ and clay minerals typically acquire their $\delta^{15}N$ signature from associated organic matter during diagenesis [*Rau et al.*, 1987; *Scholten*, 1991], the isotopic signatures documented from lower Toarcian organic-rich shales are believed primarily to reflect the original composition of the organic matter. Although the isotopic composition of modern settling organic matter is known to change, resulting in either an increase or decrease in $\delta^{15}N$ with water depth, evidence from recent organic-rich sediments suggests that nitrogen isotope ratios of sedimentary organic matter are generally little different from those of sinking particles, and these reflect the isotopic characteristics of ambient waters modified by fractionation effects as the nitrogen passes through different trophic levels of the planktonic biota [*Haug et al.*, 1998; *Holmes et al.*, 1999; *Altabet et al.*, 1999a, 1999b].

All four Lower Jurassic sections show broadly similar profiles, namely a rise in $\delta^{15}N_{tot}$ values from a background typically in the range of −2‰ to −1‰ beginning in the uppermost *tenuicostatum* Zone (Figures 3–6). Maximum $\delta^{15}N_{tot}$ values in the British sections vary from about +1.5‰ at Winterborne Kingston through about +2‰ at Hawsker Bottoms to about +2.5‰ at Mochras Farm and are registered in the lower part of the *falciferum* Zone (probably lower *exaratum* Subzone) in all three sections. Peak $\delta^{15}N_{tot}$ values of about +4‰ are similarly recorded in the lower *exaratum* Subzone of the Italian section at Dogna. Relatively high $\delta^{15}N_{tot}$ values are present in the upper *semicelatum* Subzone of the *tenuicostatum* Zone at the Hawsker Bottoms section, but this feature is not readily identifiable elsewhere. By the midpoint of the *exaratum* Subzone, $\delta^{15}N_{tot}$ values have everywhere decreased to background levels.

There is a clear relationship with other chemostratigraphic parameters. In all four sections the positive nitrogen isotope excursion occurs in sediments that are generally relatively rich in TOC. There is also some degree of correlation between the positive nitrogen isotope excursion and a negative excursion in $\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$: This relationship is seen clearly in the sections from Winterborne Kingston and Mochras, but the higher-resolution studies at Hawsker Bottoms and Dogna show the negative shift in $\delta^{13}C_{org}$ leading the positive shift in $\delta^{15}N_{tot}$. The exact relationship between TOC and $\delta^{15}N_{tot}$ is such that the rise to relatively higher nitrogen isotope ratios precedes the major rise in organic carbon values in Winterborne Kingston and Mochras, whereas the two parameters are more closely in phase at Hawsker Bottoms and Dogna. These associations indicate that values of $\delta^{15}N_{tot}$ are not simply tied to the content of organic matter in the sediment because TOC values are rather variable in the different sections. It might be argued that changing stratigraphic values of $\delta^{15}N_{tot}$ relate to changes in the relative abundance of different organic compounds or different terrigenous fractions with different isotopic ratios. Although these possibilities cannot be totally ruled out, the similarity in the stratigraphic patterns of $\delta^{15}N_{tot}$ across Europe during this period of Jurassic time leads us to favor a paleoceanographic interpretation in the context of the early Toarcian oceanic anoxic event.

The mechanisms for enrichment of a water mass in $^{15}N$ relative to $^{14}N$ have been clarified through oceanographic studies in modern oceans and on modern sediments [e.g., *Calvert et al.*, 1992; *Altabet and Francois*, 1994; *Altabet et al.*, 1995; *Holmes et al.*, 1997, 1998; *Brandes et al.*, 1998; *Naqvi et al.*, 1998]. In a given water mass, nitrate utilization will selectively withdraw the lighter nitrogen isotope into planktonic organic matter. This process will go hand in hand with progressive depletion of the nitrate pool [*Miyake and Wada*, 1967; *Wada and Hattori*, 1976; *Farrell et al.*, 1995]. The effect of these processes is to produce nitrate-poor waters that are typically characterized by higher $\delta^{15}N$ values than are nitrate-rich waters.

Alternatively, in an oxygen-depleted or suboxic water mass, bacterial denitrification (reduction of nitrate to gaseous nitrogen) takes place through the following steps:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

In this reaction series, $^{14}N$-rich nitrate is preferentially employed as an oxidizing agent for falling organic matter, again leading to relative enrichment of $^{15}N$ in the residual nitrate pool [*Richards*, 1965; *Cline and Kaplan*, 1975; *Liu and Kaplan*, 1989; *Naqvi et al.*, 1998]. Because the gaseous product, elemental dinitrogen, is largely transferred to the atmosphere, this process causes loss of oceanic nitrate [*Codispoti*, 1995]. Theoretically, if denitrification were total, as in the euxinic layers of the Black Sea, there should be negligible residual nitrate left to cause relative enrichment of the water mass in $^{15}N$ [*Fry et al.*, 1991; *Sachs and Repeta*, 1999].

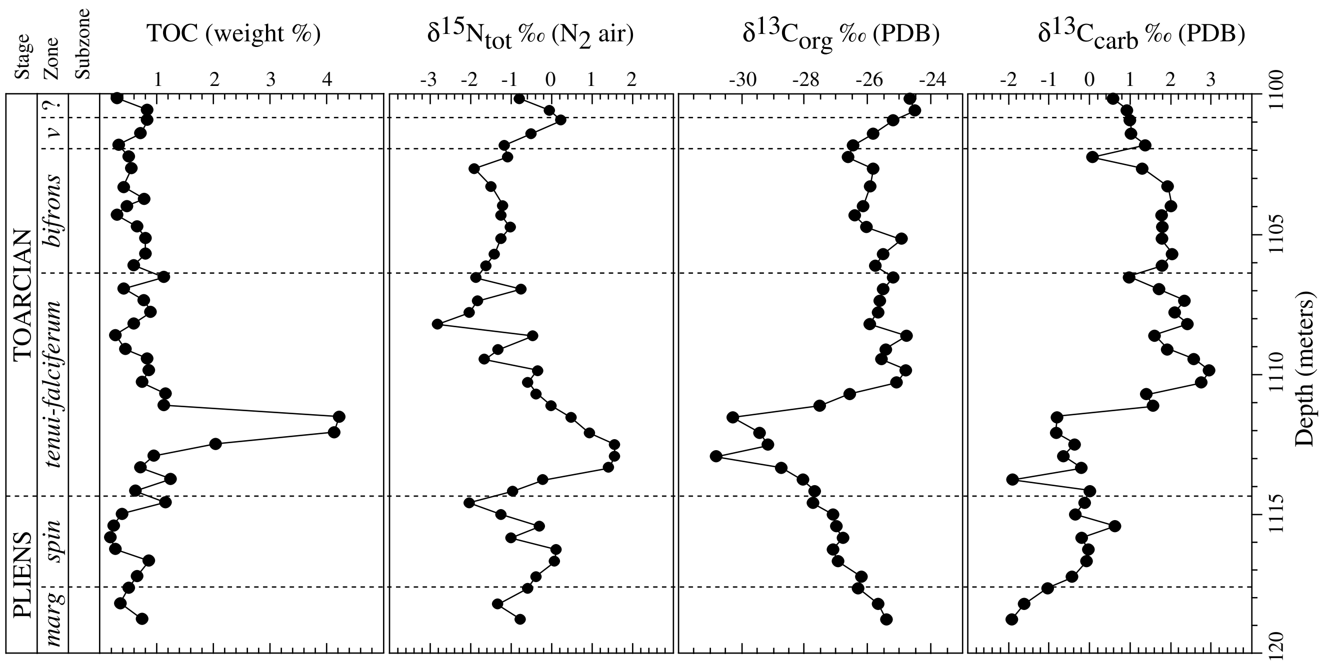


**Figure 3.** Chemostratigraphic data (total organic carbon (TOC), $\delta^{15}N_{tot}$, $\delta^{13}C_{org}$, and $\delta^{13}C_{carb}$) for Winterborne Kingston Borehole, England. Ammonite zonal boundaries in the *tenuicostatum-falciferum* Zone interval are poorly constrained. Ammonite biostratigraphy is after *Ivimey-Cook* [1982]. TOC and $\delta^{13}C_{carb}$ data are from *Jenkyns and Clayton* [1997]. Abbreviations are as follows: *marg*, *margaritatus* Zone; *spin*, *spinatum* Zone (Pliensbachian); *tenui*, *tenuicostatum* Zone; *v*, *variabilis* Zone (Toarcian).

Hence a positive $^{15}N$ anomaly formed under these conditions implies partial dentrification or a supply of fresh nitrate into the suboxic zone at a rate greater than its removal.

These two oceanographic models indicate that the positive $\delta^{15}N_{tot}$ excursion in the *exaratum* Subzone could be registering (1) the isotopic signature of a water mass that became progressively nitrate depleted because plankton productivity extracted $NO_3^-$ faster than it was replenished either from below or laterally or (2) the isotopic signature of a water mass that had undergone partial denitrification. In the latter case, nutrient supply from the zone of denitrification into the photic zone by upwelling would have been required to transfer the $^{15}N$-enriched waters to levels where they could be utilized by organic-walled plankton [cf. *Saino and Hattori*, 1987]. Under such conditions the processes of upwelling with attendant increase in productivity and settling biogenic particle flux, and generation of an intensified oxygen minimum zone with associated partial denitrification, could have been consequential phenomena, as suggested for the Arabian Sea at the present time [*Altabet et al.*, 1995]. Whether or not high rates of organic carbon flux correlate with relatively high values of $\delta^{15}N$ in zones of denitrification varies according to oceanographic conditions and the structure of the phytoplankton community. In the Arabian Sea, zones of higher organic carbon fluxes are associated with relatively lower $\delta^{15}N$ values of the settling particles [*Schäfer and Ittekkot*, 1993]; these sediment trap data, however, must record short-term processes. Quaternary sedimentary records in this area, and in eastern Pacific sites where highly oxygen deficient water masses are present, show a positive correlation between $\delta^{15}N$ values and TOC [*Ganeshram et al.*, 1995, 2000; *Reichart et al.*, 1998]. This is discussed in more detail in section 6. A significant difference between productivity-related $\delta^{15}N$ enrichment and denitrification is that the former results in depletion of virtually all nutrients utilized by phytoplankton, whereas denitrification depletes the water mass only of nitrate.

## 6. Relation Between TOC and $\delta^{15}N_{tot}$

If relatively elevated values of TOC in the lower *exaratum* Subzone of the Toarcian (which here roughly correlate with relatively high $\delta^{15}N_{tot}$ values) (Figures 3–6) are taken as the prime chemostratigraphic index, this suggests at first sight that both must record a time of enhanced productivity, at least of organic-walled plankton. As noted in section 5, such a relationship (high TOC and high $\delta^{15}N_{tot}$) is the opposite of what is generally observed today under normal oxic conditions because depletion of the nitrate pool is the dominant effect, and withdrawal of this nutrient suppresses productivity. A possible illustration of these processes in ancient deposits is shown by the correlation between Quaternary Mediterranean sapropels and relatively light nitrogen isotope ratios in the contained organic matter when compared with enclosing organic-poor sediments [*Calvert et al.*, 1992; *Milder et al.*, 1999; cf. *Sachs and Repeta*, 1999]. A similar relationship is also seen in alternating organic-rich and organic-poor sediments from the Cretaceous Atlantic and the Devonian-Carboniferous of North America [*Rau et al.*, 1987; *Calvert et al.*, 1996; *Caplan and Bustin*, 1998].

Admittedly, direct measure of productivity and/or flux rates of organic carbon is not necessarily given by weight percent TOC because this quantity is affected by variable preservation and dilution by other constituents, primarily clay minerals and carbonate in the case of the lower Toarcian. There is, however, no correlation between weight percent TOC and weight percent $CaCO_3$ and/or weight percent clay (derived as 100 − (wt % $CaCO_3$ + wt % organic matter)) in the *exaratum* Subzone in any of the four sections examined (data from the U. K. sections are given by *Jenkyns and Clayton* [1997]), suggesting broad independence of these variables.

Sedimentation rates may also have varied across the organic-rich interval and between stratigraphically adjacent strata: The more

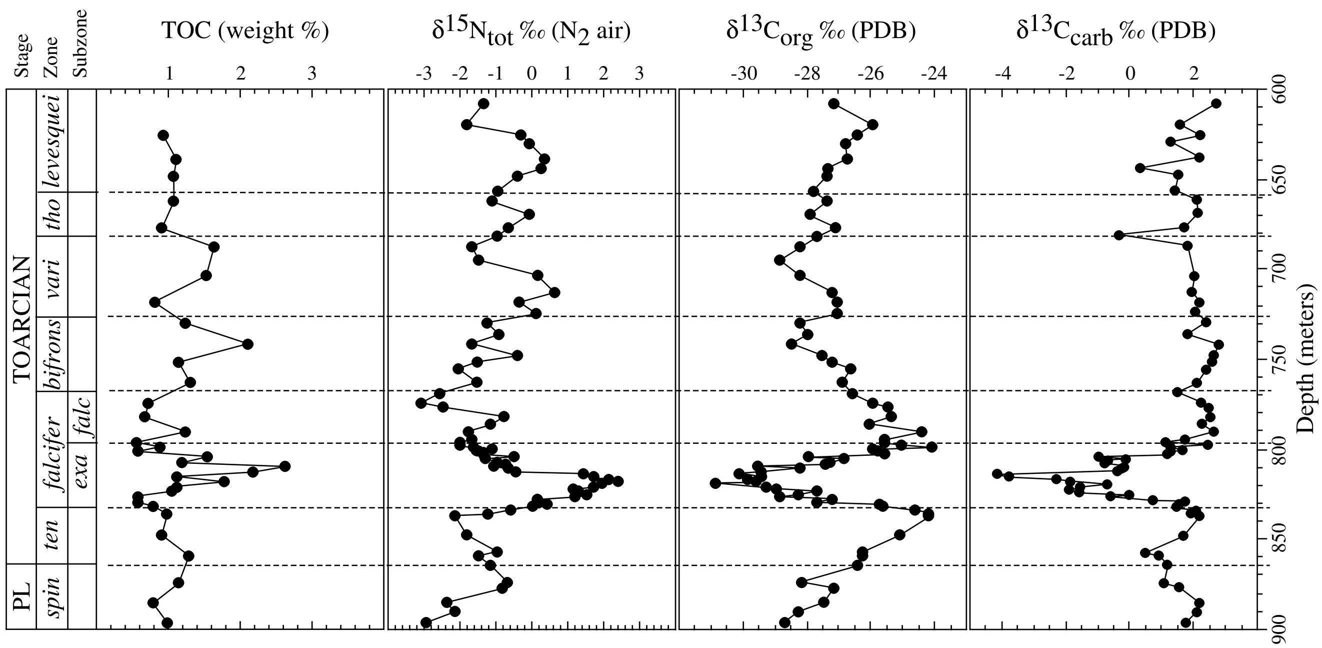


**Figure 4.** Chemostratigraphic data (TOC, $\delta^{15}N_{tot}$, $\delta^{13}C_{org}$, and $\delta^{13}C_{carb}$) for Mochras Farm borehole, Wales. Ammonite biostratigraphy is after *Ivimey-Cook* [1971]. TOC, $\delta^{13}C_{org}$, and $\delta^{13}C_{carb}$ data are partly from *Jenkyns and Clayton* [1997]. Abbreviations are as follows: *spin*, *spinatum* Zone (Pliensbachian); *ten*, *tenuicostatum* Zone; *falcifer*, *falciferum* Zone; *exa*, *exaratum* Subzone; *falc*, *falciferum* Subzone; *vari*, *variabilis* Zone; *tho*, *thouarsense* Zone (Toarcian).

condensed the section, the smaller the paleoflux of preserved organic matter for a constant value of TOC. However, strontium isotope data from belemnites in Yorkshire sections (Cleveland Basin) suggest that, if anything, condensation is more extreme in the upper *exaratum* Subzone, where values of $^{87}Sr/^{86}Sr$ rise extremely steeply, than it is in the more organic-rich lower *exaratum* Subzone [*McArthur et al.*, 2000]. Furthermore, the regional development of carbon-rich Toarcian black shales of identical age across northern and southern Europe, coupled with a local relative abundance of radiolarians, implies an increase in the productivity of siliceous and organic-walled microfossils during the early Toarcian oceanic anoxic event [*Vetö et al.*, 1997; *Ebli et al.*, 1998; *Jenkyns*, 1999]. Relatively high Ba/Rb ratios in Italian black shales from the Belluno Trough (essentially the same section illustrated in Figure 6) equally suggest heightened biological productivity [*Bellanca et al.*, 1999; cf. *Dymond et al.*, 1992].

These relationships suggest that the early Toarcian oceanic anoxic event was productivity related and that we need to explain high flux and high burial rate of organic-walled plankton accompanied by relatively heavy nitrogen isotope values. The difference in absolute values of TOC compared with rather similar $\delta^{15}N$ values in all four sections probably reflects not only differences in primary productivity across the region but differences in water depth, affecting transit times of suspended organic matter through the water column, and sedimentary rate.

Quaternary sediment cores with coincident high TOC concentrations and relatively elevated $\delta^{15}N$ values are known from the northwestern continental slope south of the Gulf of California [*Ganeshram et al.*, 1995], the Peru margin [*Ganeshram et al.*, 2000], and the northern Arabian Sea [*Reichart et al.*, 1998], where they are attributed to intense upwelling of $^{15}N$-enriched nitrate from the underlying suboxic zones of denitrification. Thus in these locales the conditions that favored accumulation of organic matter (enhanced productivity and/or enhanced preservation [*Demaison and Moore*, 1980]) also allowed transmission of a denitrification signature into the sedimentary record. Similar relationships are recorded from Quaternary cores within the Gulf of California itself where laminated opal-rich sediments are relatively enriched in $\delta^{15}N$ [*Pride et al.*, 1999] and in the Santa Barbara Basin where sediments with relatively high $\delta^{15}N$ values are laminated and those with relatively low $\delta^{15}N$ values are bioturbated [*Emmer and Thunell*, 2000].

## 7. Relation Between $\delta^{15}N_{tot}$ and $\delta^{13}C$

The stratigraphic evolution of carbon isotope signatures of organic matter and carbonate through the *tenuicostatum* and *falciferum* Zones are not necessarily very helpful in resolving key paleoceanographic parameters controlling nitrogen isotope ratios. The negative excursion in $\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$ was originally interpreted by *Küspert* [1982] as being related to vigorous recycling of waters rich in oxidized organic matter, an interpretation largely endorsed by *Sælen et al.* [1996], *Schouten et al.* [2000], and *Röhl et al.* [2001]. However, the recognition by *Hesselbo et al.* [2000] that this excursion is equally registered in terrestrial higher-plant material indicates that the isotopic disturbance was not related to local oceanographic phenomena, but rather it recorded the behavior of the entire exchangeable carbon reservoir. The negative carbon isotope excursion interrupts a much longer lasting positive excursion, in $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$, that extended over the *tenuicostatum* and *falciferum* Zones (particularly well displayed in the Mochras profile, Figure 4). This positive carbon isotope excursion has been conventionally interpreted as being related to excess burial of marine organic carbon during the oceanic anoxic event [*Jenkyns and Clayton*, 1986; *Jenkyns*, 1988].

The stratigraphical association of the negative $\delta^{13}C$ excursion with the positive $\delta^{15}N_{tot}$ excursion (Figures 3–6) led us initially to interpret the $\delta^{15}N$ signatures in terms of local upwelling of a deoxygenated water mass that carried the isotopic imprint of both oxidation of organic matter and denitrification [*Gröcke and Jen-*

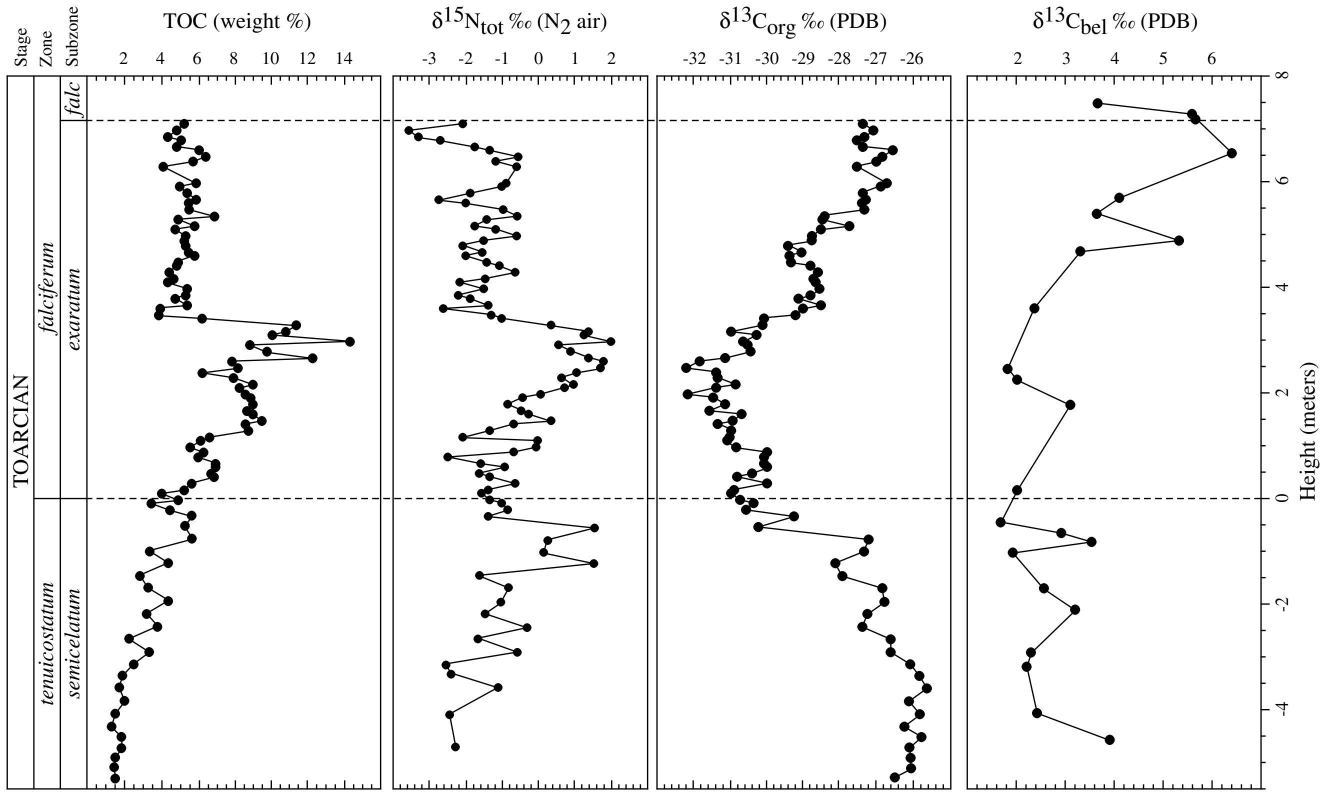


**Figure 5.** Chemostratigraphic data (TOC, $\delta^{15}N_{tot}$, $\delta^{13}C_{org}$, and $\delta^{13}C_{belemnite}$) for Hawsker Bottoms, England. Ammonite biostratigraphy is after *Howarth* [1962, 1992]. TOC and $\delta^{13}C_{org}$ data are from *Jenkyns and Clayton* [1977] and *Hesselbo et al.* [2000]. Values for $\delta^{13}C_{belemnite}$ (screeened for diagenesis by rejection of all belemnite calcite with Fe values >150 ppm, as suggested by *Jones et al.* [1994]) are from *McArthur et al.* [2000]. The abbreviation *falc* is *falciferum* Subzone (Toarcian).

*kyns*, 1999]. Because the whole of the ocean-atmosphere system was apparently influenced by the negative $\delta^{13}C_{org}$ excursion, this line of argumentation would only be tenable if the reservoir of upwelled deoxygenated waters were of oceanic dimensions. Such, for example, has been suggested as an explanation for the negative carbon isotope excursion around the Permo-Triassic boundary [*Knoll et al.*, 1996]. However, detailed study of a range of Toarcian isotopic profiles containing both marine organic carbon and terrestrially derived wood led *Hesselbo et al.* [2000], rather, to relate this negative $\delta^{13}C$ excursion to dissociation, release, and oxidation of methane from gas hydrates along continental margins during a period of global warmth, realignment of major oceanic water masses, and regional extensional activity. If this view is correct, the association of the negative $\delta^{13}C$ excursion with the positive $\delta^{15}N_{tot}$ excursion is not necessarily genetically significant, unless large-scale oxidation of methane in the water column promoted anoxic conditions. However, the abrupt two-stage drop in $\delta^{13}C_{org}$ values seen across the *tenuicostatum-falciferum* Zone boundary (*semicelatum-exaratum* Subzone boundary) in the sections from the Mochras Borehole, Gwynedd, Wales (Figure 4), Hawsker Bottoms, Yorkshire (Figure 5), and Dogna, north Italy (Figure 6), suggests that major release of gas hydrates was a transient phenomenon early in the history of the oceanic anoxic event and not directly related to an increase in $\delta^{15}N$ values, which took place somewhat later in time. However, all the illustrated sections show that $\delta^{15}N$ values increased before the most negative $\delta^{13}C_{org}$ values were attained, so the phenomena of methane release to the water column (somewhere) and denitrification in the European epicontintental and marginal seas may have overlapped in time.

## 8. Favored Model for Nitrogen Isotope Excursions

The correlation of high $\delta^{15}N_{tot}$ with low values of TOC in lower Toarcian black shales is interpreted as the chemostratigraphic signature of partial denitrification and upwelling, by reference to the geochemistry of Quaternary sediments from the Arabian Sea and eastern Pacific margin [*Ganeshram et al.*, 1995, 2000; *Reichart et al.*, 1998]: In both cases the magnitude of the positive excursions (2–4‰) is similar. Comparison between the TOC and $\delta^{15}N_{tot}$ profiles (Figures 3–6) suggests that the impact of partial denitrification was locally (Mochras and Winterborne Kingston) felt in near-surface waters before the major increase in burial and preservation rate of organic carbon. Such relationships are consistent with upwelling-related phenomena: Chemostratigraphic signals in the water mass will not necessarily exactly match those recorded in the sediments, particularly in the case of total organic carbon whose values are controlled by several variables [*Demaison and Moore*, 1980; *Pedersen and Calvert*, 1990].

Additional support for the role of denitrification comes from evidence for water column sulfate reduction in the north European seaways during *exaratum* Subzone time because sulfate follows nitrate as an electron acceptor during oxidation of organic matter by anaerobic bacteria [e.g., *Richards*, 1965; *Demaison and Moore*, 1980]. Hence denitrification must have preceded sulfate reduction.

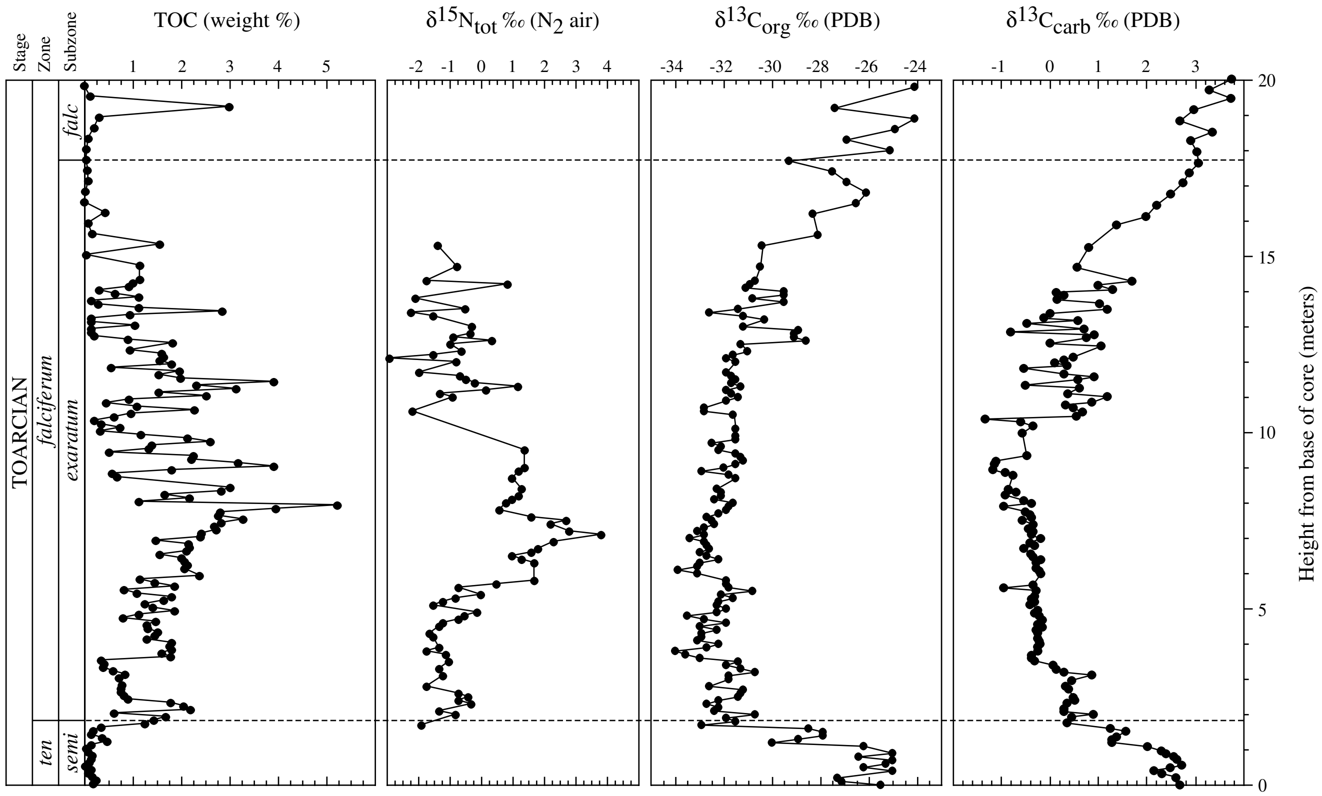


**Figure 6.** Chemostratigraphic data (TOC, $\delta^{15}N_{tot}$, $\delta^{13}C_{org}$, and $\delta^{13}C_{carb}$) for Dogna, north Italy. Biostratigraphy is after *Jenkyns et al.* [1985]; additional stratigraphic resolution is obtained by reference to the $\delta^{13}C_{org}$ curve from Hawsker Bottoms, Yorkshire (Figure 5). Abbreviations are as follows: *ten*, *tenuicostatum* Zone; *semi*, *semicelatum* Subzone; *falc*, *falciferum* Subzone (Toarcian).

The evidence for sulfide-rich waters in the photic zone of the early Toarcian seaway comes from the presence of isorenieratane (derived from anoxigenic phototrophic sulfur bacteria [*Schouten et al.*, 2000]) in the Jet Rock and German correlatives. In a number of Italian sections through Toarcian black shales, including an example from the Belluno Trough, there is also evidence from porphyrins and other biomarkers for the former presence of green sulfur bacteria, indicating photic zone euxinic conditions [*Turner*, 1998]. The local presence of small (<10 μm) pyrite framboids in laminated carbon-rich shales from the Belluno Trough also likely testifies to euxinic conditions in the water column [*Bellanca et al.*, 1999; cf., *Wilkin et al.*, 1996]. Thus paleoceanographic conditions may have alternated between dysoxic and euxinic.

It is probable that denitrification and subsequent sulfate reduction was largely a function of enhanced productivity, with oxidation of planktonic organic matter causing extreme oxygen depletion. For the nitrogen isotope signature of denitrification to be encoded in the sedimentary record would have required upwelling into the photic zone of a $^{15}N$-rich water mass whose residual nitrate could be utilized by organic-walled plankton. In order for high productivity to be sustained for a considerable length of time (duration of *exaratum* Subzone is estimated as 0.15–1.1 Ma [*Cope*, 1998; *McArthur et al.*, 2000]) the net rate of nitrate export from the zone of dentrification must have been less than its rate of supply into the same water mass [cf. *Sachs and Repeta*, 1999].

The northern and southern European partly denitrified water masses would, during *exaratum* Subzone time, have had a relatively high P:N ratio, and injection of such fluids into the photic zone could well have influenced the nature and skeletal composition of the planktonic biota. Biotic changes across the *exaratum* Subzone in northern and southern Europe involve a relative increase, within the organic-walled plankton, of prasinophyte green algae at the expense of dinoflagellates and acritarchs [*Loh et al.*, 1986; *Bucefalo Palliani and Riding*, 1999]. Although such changes have been interpreted as being related to reduced salinity, a change in nutrient balance is an equally attractive explanation, particularly as prasinophytes are apparently able to use reduced nitrate (nitrite and ammonium) more efficiently than other algal groups [*Cochlan and Harrison*, 1991; *Prauss*, 1996]. In the eastern tropical Pacific and elsewhere, relatively nitrite-rich levels, formed by nitrate reduction, have been identified in zones of denitrification [*Cline and Kaplan*, 1975; *Codispoti and Christensen*, 1985; *Liu and Kaplan*, 1989]; ammonium can also be produced in anoxic water masses but is generally low in this area because of rapid assimilation by bacteria [*Lipschultz et al.*, 1990].

## 9. Mesozoic Versus Quaternary Nitrogen Isotope Ratios

Available nitrogen isotope data on Jurassic and Cretaceous black shales dominated by marine organic matter record $\delta^{15}N$ values typically between −2.5 and 4‰, generally lower than those of most Quaternary sediments ($\delta^{15}N$ typically 0–12‰). Cretaceous examples include the Toolebuc Formation from the Eromanga Basin, Queensland, Australia, of early late Albian age [*Bralower et al.*, 1993], whose $\delta^{15}N$ values lies in the range −0.5 to −2.5‰ [*Rigby and Batts*, 1986], Cenomanian–Turonian black shales from the South Atlantic ($\delta^{15}N$ = −1.0 to −2.7‰) analyzed by *Rau et al.* [1987], and coeval material from the Bonarelli Level from the Marche-Umbrian Apennines in Italy ($\delta^{15}N$ = −2.0 to −0.6‰)

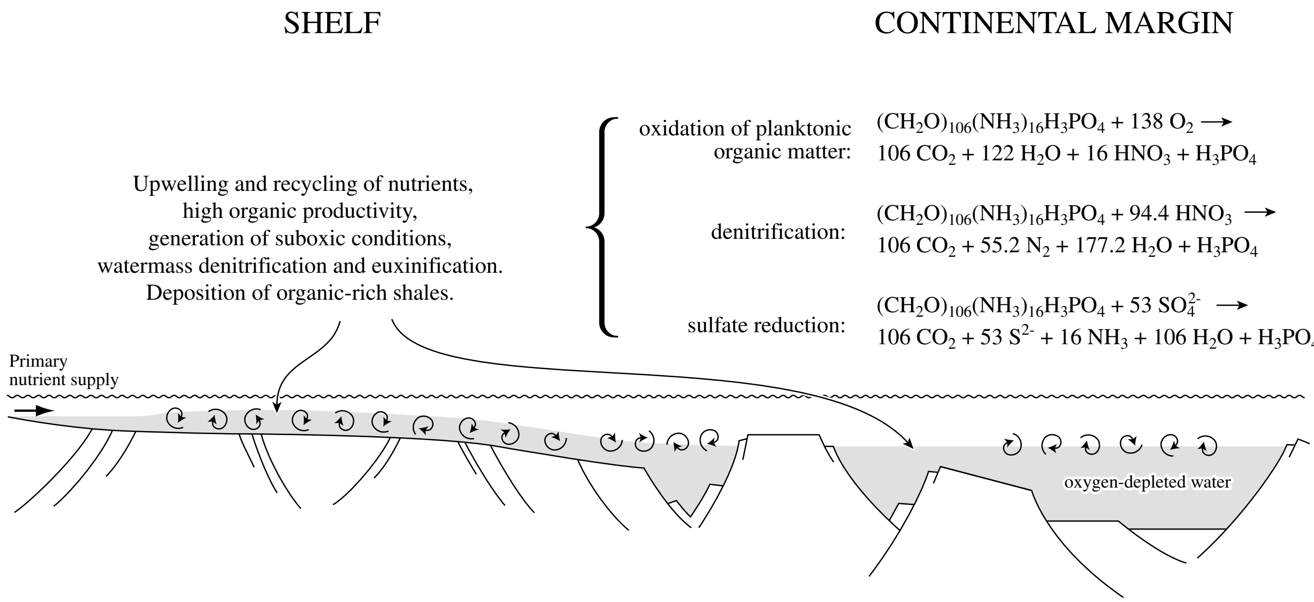


**Figure 7.** Paleoceanographic model, modified from *Jenkyns* [1985, 1988], showing suggested processes and reactions on the north European shelf and Tethyan continental margin during the early Toarcian oceanic anoxic event. Evidence from laminated black shales (implying lack of bioturbation) and from biomarkers indicative of photic zone anoxia is taken as implying that much of the water column below the near-surface mixed layer was generally oxygen depleted. The absence of black shales in some basinal sections may be ascribed to erosion or nondeposition. Reactions characteristic of such poorly oxygenated/anoxic/euxinic water masses are taken from *Richards* [1965]. The relatively positive $\delta^{15}N$ values of *exaratum* Subzone organic matter are attributed to injection into the photic zone of a partially denitrified water mass subsequently utilized by various types of phytoplankton. The presence, at this time, of relatively high sea levels and extended European shelf seas [*Hallam*, 1981; *Hesselbo and Jenkyns*, 1998] may have changed recycling patterns of water masses to aid denitrification [cf. *Bertrand et al.*, 2000].

analyzed by *Ohkouchi et al.* [1997]. These examples reflect the sedimentary record of Cretaceous oceanic anoxic events, similar in kind to that of the early Toarcian [*Jenkyns*, 1999]. Nitrogen isotope data on the Kimmeridge Clay (Upper Jurassic) from southern England shows $\delta^{15}N$ values typically in the range $-2$ to 2‰ [*Sælen et al.*, 2000].

These relatively $^{15}N$ depleted values, typically lower than those found in adjacent organic-lean sediments, have been taken to suggest that atmospheric nitrogen fixers, such as cyanobacteria, have played a major role in the development of certain Mesozoic organic-rich deposits [*Rigby and Batts*, 1986; *Rau et al.*, 1987; *Ohkouchi et al.*, 1997; *Sælen et al.*, 2000]. Organisms that can utilize the superabundant atmospheric dinitrogen when dissolved nitrate is scarce relative to phosphate will have a competitive advantage [*Haug et al.*, 1998; *Tyrrell*, 1999], and their $\delta^{15}N$ signatures approximate that of atmospheric nitrogen [*Wada and Hattori*, 1976; *Saino and Hattori*, 1987; *Capone et al.*, 1997; *Karl et al.*, 1997]. Blooms of nitrogen-fixing cyanobacteria have been recorded from the Arabian Sea at times when the nitrate abundance in near-surface waters is extremely low [*Capone et al.*, 1998]. Hence the values of $\delta^{15}N$ in lower Toarcian black shales ($\delta^{15}N$ typically between $-2$ and 4‰) could record a significant admixture of planktonic cyanobacterial matter; such has been suggested for the Jet Rock of Yorkshire by *Sælen et al.* [2000].

The problem resides, however, in the fact that the $\delta^{15}N$ values in sediments above and below the lower Toarcian black shales are low relative to those generally found today, and there is no evidence for particularly high productivity which might have caused nitrate depletion sufficient to encourage invasion of atmospheric nitrogen fixers into the environment at these times. Quite the reverse is true, in fact, because the TOC values are low relative to the black shales themselves. In this context the early Toarcian nitrogen isotope excursions are best viewed as operating from a $\delta^{15}N$ baseline of about $-1$‰. Although typical $\delta^{15}N$ values of present-day deep oceanic oxygenated waters are $\sim$5–6‰ [*Wada et al.*, 1975; *Liu and Kaplan*, 1989], values in the Mediterranean are close to $-1$‰ because of a lack of significant denitrification and low levels of nitrate utilization [*Sachs and Repeta*, 1999]. This oligotrophic basin perhaps offers the best paleoceanographic model for conditions before and after the early Toarcian oceanic anoxic event in the north European epicontinental seaway and Tethyan continental margin. During the event itself, particularly when denitrification had gone to completion and waters were locally euxinic, nitrogen-fixing cyanobacteria may have added to the planktonic population; such a phenomenon would have reduced, to some degree, the dominant signal (increased values of $\delta^{15}N$) of high productivity, upwelling, generation of suboxic water masses, and partial denitrification.

## 10. Conclusions

Data from lower Toarcian sections in northern and central Europe, from both epicontinental and pelagic facies, indicate a broad correlation between relatively elevated values of both total organic carbon (weight percent TOC) and $\delta^{15}N$. This key association suggests that regional upwelling, high productivity, and expansion of the oxygen-minimum layer, likely triggered by a climatic optimum, were responsible for promoting partial denitrification in the water column and transferring this chemostratigraphic signature into planktonic organic matter and subsequently into the sediment during the early Toarcian oceanic anoxic event (Figure 7).

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## References

Altabet, M. A., and R. Francois, Sedimentary nitrogen isotopic ratio as a recorder for surface ocean nitrate utilization, *Global Biogeochem. Cycles*, *8*, 103–116, 1994.

Altabet, M. A., R. Francois, D. W. Murray, and W. L. Prell, Climate-related variations in denitrification in the Arabian Sea from $^{15}N/^{14}N$ ratios, *Nature*, *273*, 506–509, 1995.

Altabet, M. A., D. W. Murray, and W. L. Prell, Climatically linked oscillations in Arabian Sea denitrification over the past 1 m.y.: Implications for the marine N cycle, *Paleoceanography*, *14*, 732–743, 1999a.

Altabet, M. A., C. Pilskaln, R. Thunell, C. Pride, D. Sigman, F. Chavez, and R. Francois, The nitrogen isotope biogeochemistry of sinking particles from the margin of the eastern North Pacific, *Deep Sea Res., Part I*, *46*, 655–679, 1999b.

Baudin, F., J.-P. Herbin, J.-P. Bassoulet, J. Dercourt, G. Lachkar, H. Manivit, and M. Renard, Distribution of organic matter during the Toarcian in the Mediterranean and Middle East, in *Deposition of Organic Facies, Stud. Geol.*, vol. 30, edited by A. Y. Huc, pp. 73–91, Am. Assoc. Pet. Geol., Tulsa, Okla., 1990.

Bellanca, A., D. Masetti, R. Neri, and F. Venezia, Geochemical and sedimentological evidence of productivity cycles recorded in Toarcian black shales from the Belluno Basin, Southern Alps, northern Italy, *J. Sediment. Res.*, *69*, 466–476, 1999.

Bernoulli, D., and H. C. Jenkyns, Alpine, Mediterranean and central Atlantic Mesozoic facies in relation to the early evolution of the Tethys, in *Modern and Ancient Geosynclinal Sedimentation*, edited by R. H. Dott, Jr. and R. H. Shaver, *Spec. Publ. Soc. Econ. Paleontol. Mineral.*, *19*, 129–160, 1974.

Bertrand, P., T. F. Pedersen, P. Martinez, S. Calvert, and G. Shimmield, Sea level impact on nutrient cycling in coastal upwelling areas during deglaciation: Evidence from nitrogen isotopes, *Global Biogeochem. Cycles*, *14*, 341–355, 2000.

Bralower, T. J., W. V. Sliter, M. A. Arthur, R. M. Leckie, D. J. Allard, and S. O. Schlanger, Dysoxic/anoxic episodes in the Aptian-Albian (Early Cretaceous), in *The Mesozoic Pacific: Geology, Tectonics, and Volcanism, Geophys. Monogr. Ser.*, vol. 77, edited by M. S. Pringle et al., pp. 5–37, AGU, Washington, D. C., 1993.

Brandes, J. A., A. H. Devol, T. Yoshinari, D. A. Jayakumar, and S. W. A. Naqvi, Isotopic composition of nitrate in the central Arabian Sea and eastern tropical North Pacific: A tracer for mixing and nitrogen cycles, *Limnol. Oceanogr.*, *43*, 1680–1689, 1998.

Bucefalo Palliani, R., and E. Mattioli, Enrichment in organic matter within the Early Toarcian Marne di Monte Serrone Formation: A synchronous event in the Umbria-Marche Basin (Central Italy), *Palaeopelagos*, *4*, 129–140, 1994.

Bucefalo Palliani, R., and J. B. Riding, Relationships between the early Toarcian anoxic event and organic-walled phytoplankton in central Italy, *Mar. Micropaleontol.*, *37*, 101–116, 1999.

Calvert, S. E., B. Nielsen, and M. R. Fontugne, Evidence from nitrogen isotope ratios for enhanced productivity during formation of eastern Mediterranean sapropels, *Nature*, *359*, 223–225, 1992.

Calvert, S. E., R. M. Bustin, and E. D. Ingall, Influence of water column anoxia and sediment supply on the burial and preservation of organic carbon in marine shales, *Geochim. Cosmochim. Acta*, *60*, 1577–1593, 1996.

Caplan, M. L., and R. M. Bustin, Palaeoceanographic controls on geochemical characteristics of organic-rich Exshaw mudrocks: Role of enhanced primary production, *Org. Geochem.*, *30*, 161–188, 1998.

Capone, D. G., J. P. Zehr, H. W. Paerl, B. Bergman, and E. J. Carpenter, *Trichodesmium*, a globally significant Cyanobacterium, *Science*, *276*, 1221–1229, 1977.

Capone, D. G., A. Subramaniam, J. P. Montoya, M. Voss, C. Humborg, A. M. Johansen, R. L. Siefert, and E. J. Carpenter, An extensive bloom of the $N_2$-fixing cyanobacterium *Trichodesmium erythraeum* in the central Arabian Sea, *Mar. Ecol. Prog. Ser.*, *172*, 281–292, 1998.

Claps, M., E. Erba, D. Masetti, and F. Melchiorri, Milankovitch-type cycles recorded in Toarcian black shales from the Belluno Trough (Southern Alps, Italy), *Mem. Sci. Geol.*, *47*, 179–188, 1995.

Cline, J. D., and I. R. Kaplan, Isotopic fractionation of dissolved nitrate during denitrification in the Eastern Tropical North Pacific Ocean, *Mar. Chem.*, *3*, 271–299, 1975.

Cochlan, W. P., and P. J. Harrison, Kinetics of nitrogen (nitrate, ammonium and urea) uptake by the picoflagellate *Micromonas pusilla* (Prasinophycea), *J. Exp. Mar. Biol. Ecol.*, *153*, 129–142, 1991.

Codispoti, L. A., Is the ocean losing nitrate?, *Nature*, *376*, 724, 1995.

Codispoti, L. A., and J. P. Christensen, Nitrification, denitrification and nitrous oxide cycling in the eastern tropical South Pacific Ocean, *Mar. Chem.*, *16*, 277–300, 1985.

Cope, J. C. W., Discussion on estimates of the amount and rate of sea-level change across the Rhaetian–Hettangian and Pliensbachian–Toarcian boundaries (latest Triassic to Early Jurassic), *J. Geol. Soc. London*, *154*, 421, 1998.

Demaison, G. J., and G. T. Moore, Anoxic environments and oil source bed genesis, *AAPG Bull.*, *64*, 1179–1209, 1980.

Dulai, A., Z. Suba, and S. Szarka, Toarcian (Lower Jurassic) organic-rich black shale in the Réka Valley (Mecsek Hills, Hungary), *Földt. Közl.*, *122*, 67–87, 1992.

Dymond, J., E. Suess, and M. Lyle, Barium in deep-sea sediments: A geochemical proxy for paleoproductivity, *Paleoceanography*, *7*, 163–181, 1992.

Ebli, O., I. Vetö, H. Lobitzer, C. Salgó, A. Demény, and M. Hetényi, Primary productivity and early diagenesis in the Toarcian Tethys on the example of the Mn-rich black shales of the Sachrang Formation, Northern Calcareous Alps, *Org. Geochem.*, *29*, 1635–1647, 1998.

Emmer, E., and R. C. Thunell, Nitrogen isotope variations in Santa Barbara Basin sediments: Implications for dentrification in the eastern tropical North Pacific during the last 50,000 years, *Paleoceanography*, *15*, 377–387, 2000.

Farrimond, P., G. Eglinton, S. C. Brassell, and H. C. Jenkyns, The Toarcian black shale event in northern Italy, in *Advances in Organic Geochemistry*, edited by L. Mattavelli and L. Novelli, *Org. Geochem.*, *13*, 823–832, 1988.

Farrimond, P., G. Eglinton, S. C. Brassell, and H. C. Jenkyns, Toarcian anoxic event in Europe: An organic geochemical study, *Mar. Petrol. Geol.*, *6*, 136–147, 1989.

Farrell, J. W., T. F. Pedersen, S. E. Calvert, and B. Nielsen, Glacial-interglacial changes in nutrient utilization in the equatorial Pacific Ocean, *Nature*, *377*, 514–517, 1995.

Farrimond, P., D. P. Stoddart, and H. C. Jenkyns, An organic geochemical profile of the Toarcian anoxic event in northern Italy, *Chem. Geol.*, *111*, 17–33, 1994.

Fry, B., H. W. Jannasch, S. J. Molyneaux, C. O. Wirsen, J. A. Muramoto, and S. King, Stable isotope studies of the carbon, nitrogen and sulfur cycles in the Black Sea and Cariaco Trench, *Deep Sea Res., Part A*, *38*, 1003–1019, 1991.

Ganeshram, R. S., T. F. Pedersen, S. E. Calvert, and J. W. Murray, Large changes in oceanic nutrient inventories from glacial to interglacial periods, *Nature*, *376*, 755–758, 1995.

Ganeshram, R. S., T. F. Pedersen, S. E. Calvert, G. W. McNeill, and M. R. Fontugne, Glacial–interglacial variability in denitrification in the world's oceans: Causes and consequences, *Paleoceanography*, *15*, 361–376, 2000.

Gröcke, D. R., and H. C. Jenkyns, Denitrification during the Toarcian Oceanic Anoxic Event as recorded by nitrogen isotope ratios of bulk marine organic matter, abstract presented at Ninth Annual V. M. Goldschmidt Conference, Geochem. Soc. and Eur. Soc. of Geochem., Cambridge, Massachusetts, Aug. 22–27, 1999.

Hallam, A., A revised sea-level curve for the Early Jurassic, *J. Geol. Soc. London*, *138*, 735–743, 1981.

Haug, G. H., T. F. Pedersen, D. M. Sigman, S. E. Calvert, B. Nielsen, and L. C. Peterson, Glacial/interglacial variations in production and nitrogen fixation in the Cariaco Basin during the last 580 kyr, *Paleoceanography*, *13*, 427–432, 1998.

Hesselbo, S. P., and H. C. Jenkyns, A comparison of the Hettangian to Bajocian successions of Dorset and Yorkshire, in *Field Geology of the British Jurassic*, edited by P. D. Taylor, pp. 105–150, Geol. Soc. of London, 1995.

Hesselbo, S. P., and H. C. Jenkyns, British Lower Jurassic sequence stratigraphy, in *Mesozoic-Cenozoic Sequence Stratigraphy of European Basins*, edited by P.-C. de Graciansky et al., *Spec. Publ. SEPM Soc. Sediment. Geol.*, *60*, 561–581, 1998.

Hesselbo, S. P., D. R. Gröcke, H. C. Jenkyns, C. J. Bjerrum, P. Farrimond, H. S. Morgans Bell, and O. R. Green, Massive dissociation of gas hydrate during a Jurassic oceanic anoxic event, *Nature*, *406*, 392–395, 2000.

Hollander, D. J., G. Bessereau, S. Belin, and A. Y. Huc, Organic matter in the Early Toarcian shales, Paris Basin, France: A response to environmental changes, *Rev. Inst. Fr. Pet.*, *46*, 543–562, 1991.

Holmes, M. E., P. J. Müller, R. R. Schneider, M. Segl, and G. Wefer, Reconstruction of past nutrient utilization in the eastern Angola Basin based on sedimentary $^{15}N/^{14}N$ ratios, *Paleoceanography*, *12*, 604–614, 1997.

Holmes, M. E., P. J. Müller, R. R. Schneider, M. Segl, and G. Wefer, Spatial variations in euphotic zone nitrate utilization based on $\delta^{15}N$ in surface sediments, *Geo Mar. Lett.*, *18*, 58–65, 1998.

Holmes, M. E., C. Eichner, U. Struck, and G. Wefer, Reconstruction of surface ocean nitrate utilization using stable nitrogen isotopes in sinking particles and sediments, in *Use of Proxies in Palaeoceanography: Examples From the South Atlantic*, edited by G. Fischer and G. Wefer, pp. 447–468, Springer-Verlag, New York, 1999.

Hori, R. S., The Toarcian radiolarian event in bedded cherts from southwestern Japan, *Mar. Micropaleontol.*, *30*, 159–169, 1997.

Howarth, M. K., The Jet Rock Series and the Alum Shale Series of the Yorkshire coast, *Proc. Yorks. Geol. Soc.*, *33*, 381–422, 1962.

Howarth, M. K., *The ammonite family Hildoceratidae in the Lower Jurassic of Britain: Part 1, Monogr. Palaeontogr. Soc. London*, vol. 145, pp. 1–106, Palaeontogr. Soc., London, 1992.

Ivimey-Cook, H. C., Stratigraphical palaeontology of the Lower Jurassic of the Llanbehr (Mochras Farm) Borehole, in *The Llanbehr (Mochras Farm) Borehole*, edited by A. W. Woodland, *Rep. Inst. Geol. Sci. U. K.*, *71*(18), 87–92, 1971.

Ivimey-Cook, H. C., Biostratigraphy of the Lower Jurassic and Upper Triassic (Rhaetian) rocks of the of the Winterborne Kingston Borehole, in *The Winterborne Kingston Borehole, Dorset, England*, edited by G. H. Rhys, G. K. Lott, and M. A. Calver, *Rep. Inst. Geol. Sci. U. K.*, *81*(3), 97–106, 1982.

Jenkyns, H. C., The early Toarcian and Cenomanian–Turonian anoxic events in Europe: Comparisons and contrasts, *Geol. Rundsch.*, *74*, 505–518, 1985.

Jenkyns, H. C., The early Toarcian (Jurassic) anoxic event: Stratigraphic, sedimentary, and geochemical evidence, *Am. J. Sci.*, *288*, 101–151, 1988.

Jenkyns, H. C., Mesozoic anoxic events and palaeoclimate, *Zentralbl. Geol. Palaeontol. Teil 1*, *1997*, 943–949, 1999.

Jenkyns, H. C., and C. J. Clayton, Black shales and carbon isotopes in pelagic sediments from the Tethyan Lower Jurassic, *Sedimentology*, *33*, 87–106, 1986.

Jenkyns, H. C., and C. J. Clayton, Lower Jurassic epicontinental carbonates and mudstones from England and Wales: Chemostratigraphic signals and the early Toarcian anoxic event, *Sedimentology*, *44*, 687–706, 1997.

Jenkyns, H. C., M. Sarti, D. Masetti, and M. K. Howarth, Ammonites and stratigraphy of Lower Jurassic black shales and pelagic limestones from the Belluno Trough, Southern Alps, Italy, *Eclogae. Geol. Helv*, *78*, 299–311, 1985.

Jenkyns, H. C., B. Géczy, and J. D. Marshall, Jurassic manganese carbonates of central Europe and the early Toarcian anoxic event, *J. Geol.*, *99*, 137–149, 1991.

Jiménez, A. P., C. Jiménez de Cisneros, P. Rivas, and J. A. Vera, The Early Toarcian anoxic event in the westernmost Tethys (Subbetic): Paleogeographic and paleobiogeographic significance, *J. Geol.*, *104*, 399–416, 1996.

Jones, C. E., and H. C. Jenkyns, Seawater strontium isotopes, oceanic anoxic events, and seafloor hydrothermal activity in the Jurassic and Cretaceous, *Am. J. Sci.*, *301*, 112–149, 2001.

Jones, C. E., H. C. Jenkyns, and S. P. Hesselbo, Strontium isotopes in Early Jurassic seawater, *Geochim. Cosmochim. Acta*, *58*, 1285–1301, 1994.

Karl, D., R. Letelier, L. Tupas, J. Dore, J. Christian, and D. Hebel, The role of nitrogen fixation in biogeochemical cycling in the subtropical North Pacific Ocean, *Nature*, *388*, 533–538, 1997.

Knoll, A. H., R. K. Bambach, D. E. Canfield, and J. P. Grotzinger, Comparative Earth history and Late Permian mass extinction, *Science*, *273*, 452–457, 1996.

Küspert, W., Environmental changes during oil shale deposition as deduced from stable isotope ratios, in *Cyclic and Event Stratification*, edited by G. Einsele and A. Seilacher, pp. 482–501, Springer-Verlag, New York, 1982.

Lipschultz, F., S. C. Wofsy, B. B. Ward, L. A. Codispoti, G. Friedrich, and J. W. Elkins, Bacterial transformations of inorganic nitrogen in the oxygen-deficient waters of the Eastern Tropical South Pacific Ocean, *Deep Sea Res., Part A*, *37*, 1513–1541, 1990.

Liu, K.-K., and I. R. Kaplan, The eastern tropical Pacific as a source of $^{15}N$-enriched nitrate in seawater off southern California, *Limnol. Oceanogr.*, *34*, 820–830, 1989.

Loh, H., B. Maul, M. Prauss, and W. Riegel, Primary production, maceral formation and carbonate species in the Posidonia Shale of NW Germany, in *Biogeochemistry of Black Shales*, edited by E. T. Degens, P. A. Meyers, and S. C. Brassell, *Mitt. Geol. Palaeontol. Inst. Univ. Hamburg*, *60*, 397–421, 1986.

McArthur, J. M., D. T. Donovan, M. F. Thirlwall, B. W. Fouke, and D. Mattey, Strontium isotope profile of the Early Toarcian (Jurassic) Oceanic Anoxic Event, the duration of ammonite biozones, and belemnite palaeotemperatures, *Earth Planet. Sci. Lett.*, *179*, 269–285, 2000.

Milder, J. C., J. P. Montoya, and M. A. Altabet, Carbon and nitrogen stable isotope ratios at sites 969 and 974: Interpreting spatial gradients in sapropel properties, in *Proc. Ocean Drill. Program Sci. Results*, *161*, 401–411, 1999.

Miyake, Y., and E. Wada, The abundance of $^{15}N/^{14}N$ in marine environments, *Rec. Oceanogr. Works Japan*, *9*, 37–53, 1967.

Murphy, N. J., M. J. Sauer, and J. P. Armstrong, Toarcian source rock potential in the North Celtic Sea Basin, offshore Ireland, in *The Petroleum Geology of Ireland's Offshore Basins*, edited by P. F. Croker and P. M. Shannon, *Geol. Soc. Spec. Publ.*, *93*, 193–207, 1995.

Naqvi, S. W. A., T. Yoshinari, J. A. Brandes, A. H. Devol, D. A. Jayakumar, P. V. Narvekar, M. A. Altabet, and L. A. Codispoti, Nitrogen isotopic studies in the suboxic Arabian Sea, *Proc. Indian Acad. Sci.*, *107*, 367–378, 1998.

Nikintenko, B. L., and B. N. Shurygin, Lower Toarcian black shales and Pliensbachian-Toarcian crisis of the biota of Siberian paleoseas, in *Proceedings International Conference on Arctic Margins*, edited by D. K. Thurston and K. Fujita, pp. 39–44, U. S. Dep. of the Inter., Anchorage, Alaska, 1992.

Ohkouchi, N., K. Kawamura, E. Wada, and A. Taira, High abundances of hopanols and hopanoic acids in Cretaceous black shales, *Ancient Biomol.*, *1*, 183–192, 1997.

Parisi, G., M. Ortega-Huertas, M. Nocchi, I. Palomo, P. Monaco, and F. Martinez, Stratigraphy and geochemical anomalies of the early Toarcian oxygen-poor interval in the Umbria-Marche Apennines (Italy), *Geobios*, *29*, 469–484, 1996.

Pedersen, T. F., and S. E. Calvert, Anoxia vs. productivity: What controls the formation of organic-carbon-rich sediments and sedimentary rocks?, *AAPG Bull.*, *74*, 454–466, 1990.

Prauss, M., The Lower Toarcian Posidonia Shale of Grimmen, northeast Germany: Implications from the palynological analysis of a near-shore section, *Neues Jahrb. Geol. Palaeontol. Abh.*, *200*, 107–132, 1996.

Pride, C., R. Thunell, D. Sigman, L. Keigwin, and M. Altabet, Nitrogen isotopic variations in the Gulf of California since the last deglaciation: Response to global climate change, *Paleoceanography*, *14*, 397–409, 1999.

Rau, G. H., M. A. Arthur, and W. E. Dean, $^{15}N/^{14}N$ variations in Cretaceous Atlantic sedimentary sequences: Implication for past changes in marine nitrogen biogeochemistry, *Earth Planet. Sci. Lett.*, *82*, 269–279, 1987.

Reichart, G. J., L. J. Lourens, and W. J. Zachariasse, Temporal variability in the northern Arabian Sea Oxygen Minimum Zone (OMZ) during the last 225,000 years, *Paleoceanography*, *13*, 607–621, 1998.

Richards, F. A., Anoxic basins and fjords, in *Chemical Oceanography*, vol. 1, edited by J. P. Riley and G. Skirrow, pp. 611–645, Academic, San Diego, Calif., 1965.

Riegraf, W., G. Werner, and F. Lörcher, *Der Posidonienschiefer. Biostratigraphie, Fauna und Fazies des südwestdeutschen Untertoarciums* (*Lias* ε), 195 pp., F. Enke, Stuttgart, 1984.

Rigby, D., and B. D. Batts, The isotopic composition of nitrogen in Australian coals and oil shales, *Chem. Geol.*, *58*, 273–282, 1986.

Röhl, H.-J., A. Schmidt-Röhl, W. Oschmann, A. Frimmel, and L. Schwark, The Posidonia Shale (Lower Toarcian) of SW Germany: An oxygen-depleted ecosystem controlled by sea level and palaeoclimate, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *165*, 27–52, 2001.

Sachs, J. P., and D. J. Repeta, Oligotrophy and nitrogen fixation during eastern Mediterannean sapropel events, *Science*, *286*, 2485–2488, 1999.

Sælen, G., P. Doyle, and M. R. Talbot, Stable-isotope analyses of belemnite rostra from the Whitby Mudstone Fm., England: Surface water conditions during deposition of a marine black shale, *Palaios*, *11*, 97–117, 1996.

Sælen, G., R. V. Tyson, N. Telnæs, and M. R. Talbot, Contrasting watermass conditions during deposition of the Whitby Mudstone (Lower Jurassic) and Kimmeridge Clay (Upper Jurassic) formations, UK, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *163*, 163–196, 2000.

Saino, T., and A. Hattori, Geographical variation of the water column distribution of suspended particulate organic nitrogen and its $^{15}N$ natural abundance in the Pacific and its marginal seas, *Deep Sea Res., Part A*, *34*, 807–827, 1987.

Schäfer, P., and V. Ittekkot, Seasonal variability of $\delta^{15}N$ in settling particles in the Arabian Sea and its palaeogeochemical significance, *Naturwissenschaften*, *80*, 511–513, 1993.

Schmid-Röhl, A., J. Röhl, W. Oschmann, and A. Frimmel, Der Posidonienschifer (Lias ε) Südwestdeutschlands: Hochauflösende geochemische, palökologische und sedimentologische Untersuchungen, *Zentralbl. Geol. Palaeontol., Teil 1*, *1997*, 989–1004, 1999.

Scholten, S. O., The distribution of nitrogen isotopes in sediments, *Geol. Ultraiectina*, *81*, 1–101, 1991.

Schouten, S., H. van Kaam Peters, W. I. C. Rijpstra, M. Schoell, and J. Sinninghe Damste, Effects of an oceanic anoxic event on the stable carbon isotopic composition of Early Toarcian carbon, *Am. J. Sci.*, *300*, 1–22, 2000.

Soussi, M., M. H. Ben Ismail, and A. M'Rabet, Les "black shales" toarciens de Tunisie centrale: Témoins d'événement anoxique sur la marge sud téthysienne, *C. R. Acad. Sci., Ser. II*, *310*, 591–596, 1990.

Turner, A. D., Recognition of photic zone anoxia from LC-MS studies of porphyrin distributions in ancient sediments, Ph.D. thesis, 245 pp., Univ. of Bristol, Bristol, England, 1998.

Tyrrell, T., The relative influences of nitrogen and phosphorus on oceanic primary productivity, *Nature*, *400*, 525–531, 1999.

Vetö, I., A. Demény, E. Hertelendi, and M. Hetényi, Estimation of primary productivity in the Toarcian Tethys — a novel approach based on TOC, reduced sulphur and manganese contents, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *132*, 355–371, 1997.

Wada, E., and A. Hattori, Natural abundance of $^{15}N$ in particulate organic matter in the North Pacific Ocean, *Geochim. Cosmochim. Acta*, *40*, 249–251, 1976.

Wada, E., T. Kadonaga, and S. Natsuo, $^{15}N$ abundance in naturally occurring substances and global assessment of denitrification from isotopic viewpoint, *Geochem. J.*, *9*, 139–148, 1975.

Wilkin, R. T., H. L. Barnes, and S. L. Brantley, The size distribution of framboidal pyrite in modern sediments: An indicator of redox conditions, *Geochim. Cosmochim. Acta*, *60*, 3897–3912, 1996.

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