



HAL
open science

Isorenieratane record in black shales from the Paris Basin, France: Constraints on recycling of respired CO₂ as a mechanism for negative carbon isotope shifts during the Toarcian oceanic anoxic event

Yvonne van Breugel, Marianne Baas, Stefan Schouten, Emanuela Mattioli,
Jaap S. Sinninghe Damsté

► To cite this version:

Yvonne van Breugel, Marianne Baas, Stefan Schouten, Emanuela Mattioli, Jaap S. Sinninghe Damsté. Isorenieratane record in black shales from the Paris Basin, France: Constraints on recycling of respired CO₂ as a mechanism for negative carbon isotope shifts during the Toarcian oceanic anoxic event. *Paleoceanography*, 2006, 21, pp.1-8. 10.1029/2006PA001305 . hal-00152813

HAL Id: hal-00152813

<https://hal.science/hal-00152813>

Submitted on 3 May 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Isorenieratane record in black shales from the Paris Basin, France: Constraints on recycling of respired CO₂ as a mechanism for negative carbon isotope shifts during the Toarcian oceanic anoxic event

Yvonne van Breugel,¹ Marianne Baas,¹ Stefan Schouten,¹ Emanuela Mattioli,² and Jaap S. Sinninghe Damsté¹

Received 19 April 2006; revised 13 July 2006; accepted 19 July 2006; published 22 December 2006.

[1] The prominent negative stable carbon isotope excursion in both carbonate and organic carbon recorded in organic-rich sediments deposited during the Toarcian oceanic anoxic event (OAE) has commonly been explained by recycling of ¹³C-depleted CO₂ (the so-called Küspert model). More recently, the massive release of ¹³C-depleted methane or other forms of ¹³C-depleted carbon was also proposed to account for the observed negative δ¹³C excursions in organic carbon of terrigenous as well as of marine origin. The occurrence of diagenetic products of the carotenoid isorenieratene (isorenieratane and other aryl isoprenoids) in Toarcian black shales has been regarded as supporting evidence for the Küspert hypothesis as they point to strong stratification of the epicontinental seas. A section of a drill core straddling the Toarcian of the Paris Basin (Cirfontaine-en-Ornois) contained intact isorenieratane, providing evidence that photosynthetic green sulphur bacteria were present at the time of deposition, even prior to the OAE. However, the isorenieratane abundances are very low in the section where the negative δ¹³C excursion in organic carbon and phytane, a chemical fossil derived from chlorophyll, occurs. The abundance of the isorenieratene derivatives increases, once the δ¹³C records have shifted to more positive values. The δ¹³C of isorenieratane (generally circa −13.1 ± 0.5 ‰) indicates that the respired CO₂ contribution at the chemocline was low and is thus not likely to be the main cause of the prominent up to 7‰ negative δ¹³C shift recorded in Toarcian organic carbon records.

Citation: van Breugel, Y., M. Baas, S. Schouten, E. Mattioli, and J. S. Sinninghe Damsté (2006), Isorenieratane record in black shales from the Paris Basin, France: Constraints on recycling of respired CO₂ as a mechanism for negative carbon isotope shifts during the Toarcian oceanic anoxic event, *Paleoceanography*, 21, PA4220, doi:10.1029/2006PA001305.

1. Introduction

[2] The early Toarcian (~183 million years ago) was characterized by widespread deposition of organic carbon-rich sediments, as evidenced from the sedimentary record at many European locations and also from areas such as western Canada, Japan, Madagascar, Argentina and the Arctic slope [Jenkyns, 1988; Jenkyns *et al.*, 2002]. Lower Toarcian strata of the *falciferum* Zone are, in some cases, also characterized by substantially ¹³C-depleted organic carbon (−31 to −32‰) [Jenkyns and Clayton, 1986; Jenkyns, 1988; Vetö *et al.*, 1997], a feature which is inconsistent with the concept of organic carbon burial during oceanic anoxic event (OAEs), which typically results in a positive carbon isotope excursion [Arthur *et al.*, 1990]. In fact, isotopic profiles from selected, shallow marine epicontinental sedimentary successions of the Toarcian of Europe

exhibit striking, negative δ¹³C excursions in bulk organic carbon and/or carbonate [Jiménez *et al.*, 1996; Jenkyns and Clayton, 1997; Röhl *et al.*, 2001; Kemp *et al.*, 2005]. Concomitantly with the marine isotopic records, negative shifts in δ¹³C are also recorded in fossil wood from Toarcian sections in Whitby, UK and Bornholm, Denmark [Hesselbo *et al.*, 2000]. These records have led to the hypothesis that this widespread negative δ¹³C shift was caused by massive methane release from sedimentary gas hydrates [Hesselbo *et al.*, 2000] or by thermal metamorphism of preexisting organic deposits [McElwain *et al.*, 2005], in a similar fashion with prevailing hypotheses for the Paleocene-Eocene thermal maximum [Dickens *et al.*, 1995; Svensen *et al.*, 2004]. Such models imply that the negative δ¹³C excursion of the early Toarcian is a globally occurring phenomenon. However, no evidence of such an excursion has hitherto been reported from outside the northwestern Tethys epicontinental seas. Moreover, the excursion is absent in the Toarcian belemnite δ¹³C record of Yorkshire, UK and Dotternhausen, SW Germany [van de Schootbrugge *et al.*, 2005].

[3] It has been suggested that sharp negative isotopic excursions in marine sediments can also be produced as a direct consequence of recycling of ¹²C-rich CO₂, accumu-

¹Royal Netherlands Institute for Sea Research, Department of Marine Biogeochemistry and Toxicology, Den Burg (Texel), Netherlands.

²Université Lyon 1, UMR 5125 CNRS-Laboratoire PEPS, UFR Sciences de la Terre, Villeurbanne, France.

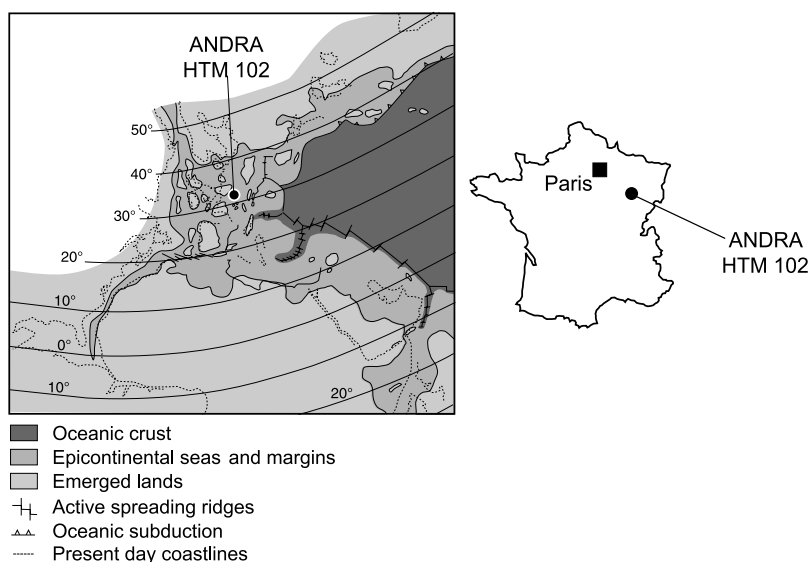


Figure 1. Paleogeographical frame of the drill core site [Mattioli *et al.*, 2004] and the location of the drill site in France (inset).

lated in a stratified marine system by anaerobic respiration of organic matter [Küspert, 1982]. The presence of biomarkers derived from the specific pigments of green sulphur bacteria (GSB) [see *Sinninghe Damsté and Schouten*, 2006, and reference therein] in black shales representing the Toarcian OAE reveal that marine anoxia extended well into the photic zone, a fact that could be interpreted to support the recycling model of Küspert [Schouten *et al.*, 2000; Schwark and Frimmel, 2004; Pancost *et al.*, 2004]. GSB are photosynthetic organisms and require both light and hydrogen sulfide. The carotenoid isorenieratene has only been detected in GSB and is thus an unambiguous biomarker for photic zone anoxia. Its diagenetic product, the C₄₀ diaryl isoprenoid isorenieratane, can be found in sediments as old as Proterozoic, as long as the organic material is not too thermally mature [Koopmans *et al.*, 1996a; Brocks *et al.*, 2005]. Catagenetic (higher temperature) processes yield small-chain aryl isoprenoids due to C-C bond cleavage of the C₄₀ compounds derived from isorenieratene [Koopmans *et al.*, 1996a]. Evidence for the formation of aryl isoprenoids from the common algal β -carotene [Koopmans *et al.*, 1996b] limits their use as biomarkers for GSB, and unequivocal evidence for photic zone anoxia is therefore limited to (aromatized) C₄₀ diaryl isoprenoid compounds. However, the occurrence of photic zone anoxia in the Toarcian has been based on the findings of mainly aryl isoprenoids in a black shale of Dotternhausen [Schwark and Frimmel, 2004], whilst only very low abundances of isorenieratane, due to the relatively high maturity level, have been observed in the same section [Schouten *et al.*, 2000]. Therefore, the occurrence of photic zone euxinia during the deposition of Toarcian black shales needs further confirmation.

[4] In this paper, we examine a drill core section from the Paris Basin that is likely to contain organic carbon of lower thermal maturity, similar to other Toarcian sites in the Paris Basin [Farrimond *et al.*, 1989; Hollander *et al.*, 1991], and

hence is more liable to contain the C₄₀ diaryl isoprenoids. Detailed analyses of the relative abundance and $\delta^{13}\text{C}$ record of isorenieratane were used in conjunction with isotopic records of bulk organic carbon and phytane (a phytoplankton-derived biomarker), in order to shed further light on stratification conditions during the Toarcian OAE, and by extension, on the applicability of the Küspert model for this event.

2. Material and Methods

2.1. Core Material

[5] Core material was analyzed from borehole HTM 102 drilled in 1994 by the Agence Nationale pour la gestion des Déchets Radioactifs (ANDRA) in the northeast of the Paris Basin (Cirfontaine en Ornois, Lorraine). The Paris Basin was part of a shallow northern epicontinental sea (Boreal Realm; Figure 1) [Jenkyns, 1988]. Because of the occurrence of tempestites (i.e., erosional surface at the base of the core, followed by chaotic fossil accumulation, and overlain by ripples with low angle cross lamination between 805.7 and 806 m), the estimated maximum water depth for the studied setting was between 50 and 100 m.

[6] The Toarcian core section comprises 18 m of mainly laminated mudstone, overlying a lowermost part that comprises wackestone and packstone (limestone characterized by a mud-supported and a grain-supported texture, respectively, together with a lime-mud matrix), both rich in bivalves, belemnites and ammonites (Figure 2). According to sedimentological and biostratigraphic evidence, an important condensation event seems to have affected the basal part of the core. The section below 806.15 m belongs to the nannofossil subzone *Lotharingius sigillatus*, predating the Toarcian OAE (NJT 5b) [Mattioli and Erba, 1999]. The boundary between this subzone and the following NJT 6 *Carinolithus superbus* Zone (or NJ 6 of Bown and Cooper

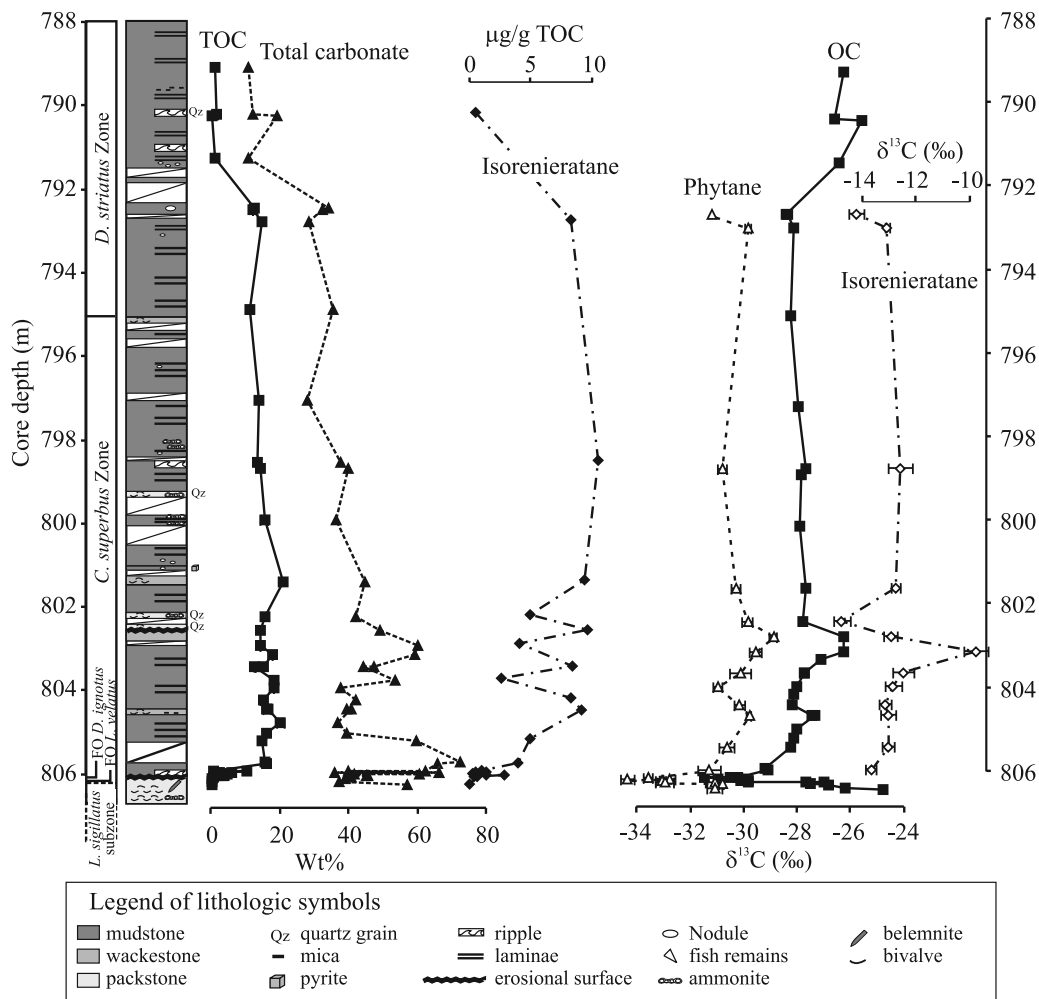


Figure 2. Lithostratigraphy with nanofossil zones of the ANDRA Core HTM 102 at Cirfontaine-en-Ornois (Lorraine, France). Also shown are stratigraphic records for TOC and bulk carbonate content (in wt% of sediment), isorenieratane abundances and stable carbon isotope ratio of TOC, phytane and isorenieratane. FO: first occurrence.

[1998]) is slightly questionable, as the species marker occurs very sporadically in the studied samples from 806.03 m upwards. Nevertheless, the first occurrence (FO) of *Lotharingius velatus*, which in many other sections occurs in the same stratigraphic level as *C. superbus*, can be of biostratigraphic use in locating the base of NJT 6. The FO of *Discorhabdus ignotus* (806.09 m in the HTM 102 core) is commonly recorded in the interval corresponding to the second half of the isotopic negative excursion, where the bulk organic matter content in the sediments decreases [Bucefalo Palliani and Mattioli, 1998; Bucefalo Palliani et al., 2002; Mattioli et al., 2004]. This record therefore places the core section in a biostratigraphic interval comparable to other early Toarcian Tethyan sections. It was recently estimated, based on the recognition of four precession cycles, that between the base and top of the negative isotope excursion, 80 kyr elapsed [Kemp et al., 2005].

2.2. Bulk Analyses

[7] Powdered rock samples were acidified with dilute HCl at ambient temperature to remove carbonate. Depending

on the original TOC contents of each sample, between 0.2–1.6 mg of the washed and dried carbonate-free residues were weighed in tinfoil cups. Organic carbon contents and carbon isotope ratios were measured against a benzoic acid laboratory standard (%C = 68.80, $\delta^{13}\text{C}$ value of -27.8‰), calibrated against the NBS22 standard ($\delta^{13}\text{C}$ value of $-29.5 \pm 0.02\text{‰}$), on a Flash elemental analyzer coupled to a Delta^{PLUS} mass spectrometer. All analytical results are presented in the usual δ notation, in ‰ relative to the VPDB (Vienna Pee Dee Belemnite) standard.

2.3. Biomarker Analysis

[8] Powdered samples were extracted with a dichloromethane (DCM)/methanol mixture (9:1, v/v) using an accelerated solvent extractor (ASE), in three cycles under conditions of 100°C and 1000 Psi (5 min static, 100% flush, 90 s purge). Total lipid fractions, to which the internal standard C₂₂ ante-iso alkane was added for quantitative analyses, were separated on a column (volume circa 20 ml) packed with Al₂O₃ (activated for 2 h at 150°C), via successive elution with hexane/DCM (9:1, v/v; 4 × column

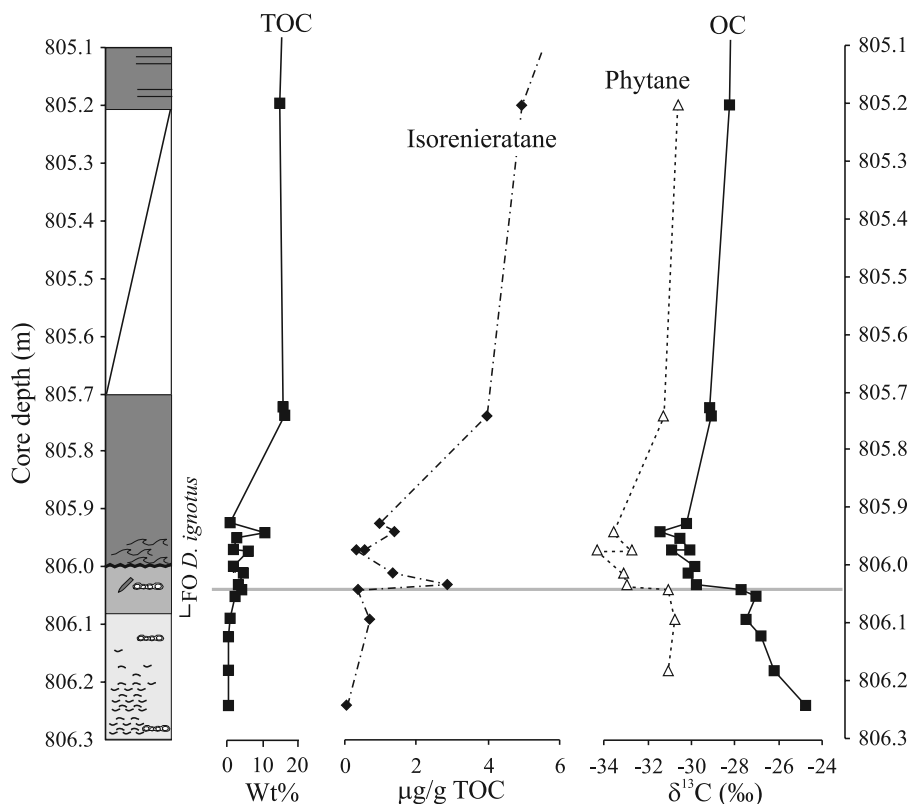


Figure 3. Detailed view of the negative $\delta^{13}\text{C}$ excursion at the onset of the organic carbon rich sediments, accompanied by corresponding TOC and isorenieratane abundances. Legend as in Figure 2.

volume) and methanol/DCM (1:1, v/v; $3 \times$ column volume), to yield apolar hydrocarbon fractions and polar fractions, respectively. The apolar fractions were analyzed by gas chromatography–mass spectrometry (GC-MS), for identification of the apolar compounds and quantification of isorenieratane, and subsequently separated and purified for isotope-ratio-monitoring (irm)-GC-MS. To that end, the apolar fractions were separated over an Ag^+ -impregnated silica column (circa 1 ml) with hexane/DCM (9:1, v/v), hexane/DCM (1:1, v/v) and DCM, to yield an aliphatic hydrocarbon fraction containing phytane and the third fraction containing isorenieratane. The aliphatic and aromatic hydrocarbon fractions were analyzed using isotope-ratio-monitoring (irm)-GC-MS.

2.4. Gas Chromatography–Mass Spectrometry

[9] GC-MS analyses were performed using a ThermoFinnigan TRACE gas chromatograph using an on-column injector. A fused silica capillary column (25 m \times 0.32 mm) coated with CP-Sil 5 (film thickness 0.12 μm) was used with helium as carrier gas. The oven was programmed at a starting (injection) temperature of 70°C, which rose to 130°C at 20°C/min and then to 320°C at 4°C/min, at which it was maintained for 20 min. The column was directly inserted into the electron impact ion source of a ThermoFinnigan DSQ quadrupole mass spectrometer, scanning a mass range of m/z 50–800 at a rate of 3 s^{-1} and an ionization energy of 70 eV. The selective ion mode moni-

toring m/z values 57, 133–134 was used for quantification. The peak intensities of the internal standard C_{22} ante-iso alkane and isorenieratane were determined with the m/z 57 and m/z 133 + 134 traces, respectively, and these were compared after correction. The correction factors were calculated with the ratio between the SIM-mode peak intensities and the peak intensities in separate full-scan GC-MS analyses of the C_{22} ante-iso alkane and an isorenieratane standard.

2.5. Isotope-Ratio-Monitoring Gas Chromatography–Mass Spectrometry

[10] The irm-GC-MS system used was a ThermoFinnigan Delta C with an HP 5890 GC, and GC conditions being the same with those described above for the GC-MS analyses. The $\delta^{13}\text{C}$ values for individual compounds are reported in the standard delta notation against the VPDB standard and are the means of duplicate runs with a reproducibility 0.5% or better.

3. Results

[11] The $\delta^{13}\text{C}$ values of total organic carbon (TOC) record an overall 6.5‰ shift to more negative values within the basal packstone-wackestone interval (Figures 2 and 3). TOC contents increase from ~ 0.5 wt% in the preexcursion (i.e., pre-OAE) interval, to a range of 1 to 10 wt% around the negative $\delta^{13}\text{C}_{\text{TOC}}$ shift and up to 20 wt% thereafter. The

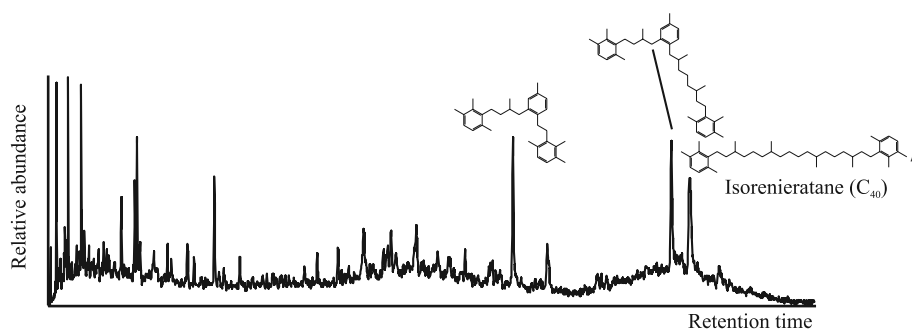


Figure 4. Mass chromatogram (m/z 133 + 134) of the apolar fraction of a representative (HTM 102, 805.74 m) black shale from the ANDRA core section. Major isorenieratene derivatives are indicated.

carbonate content fluctuates between 40 and 70 wt% in the lowest 4 m of the section (Figures 2 and 3) and decreases to less than 20 wt% at the top 2 m of the core section, where TOC also decreases and $\delta^{13}\text{C}_{\text{TOC}}$ increases (Figure 2).

[12] The apolar fractions of the analyzed sediments contain mainly pristane, phytane, *n*-alkanes, lycopane and a complex mixture of steroids and hopanoids. The $\delta^{13}\text{C}$ record of phytane varies in a similar fashion with that of TOC for most part of the section, except for the portion preceding the rapid shift at 806.04 m (grey line; Figure 3) where TOC reveals a gradual shift in $\delta^{13}\text{C}$ of almost 3‰.

[13] The aromatic fractions contain mainly (poly)aromatic steroids, chroman, diaryl isoprenoids and aryl isoprenoids. Free isorenieratane and other aromatic isorenieratene derivatives (Figure 4) appear to be present across the entire section (Figure 2). Isorenieratane abundances are, however, very low in the lowest 30 cm of the section around the negative $\delta^{13}\text{C}_{\text{TOC}}$ spike. Abundances of short-chain aryl isoprenoid increase relative to isorenieratane in the latter section, but their concentrations are also low. Above the interval containing the negative $\delta^{13}\text{C}$ spike, isorenieratane abundances increase substantially, in concert with the upward increase in TOC wt% (Figure 3). $\delta^{13}\text{C}$ values for isorenieratane could only be measured in the interval above the negative carbon isotope spike, where abundances were sufficient compared to the background matrix. The values across this latter interval fluctuate narrowly between $-13.1 \pm 0.5\text{‰}$, except for two values that correspond to stratigraphic depths of 802.9 (-9.8‰) and 802.2 m (-14.8‰ ; Figure 2).

4. Discussion

[14] Biostratigraphic data based on nanofossil occurrences suggest that the negative excursion in $\delta^{13}\text{C}_{\text{org}}$ recorded in the examined section lies in the *C. superbis* zone, and is therefore biostratigraphically comparable to other Tethyan settings (NJT 6 [Mattioli and Erba, 1999] or NJ 6 [Bown and Cooper, 1998]). In addition, the FO of *D. ignotus* commonly occurs towards the "recovery" point of the negative isotopic excursion which commonly coincides with the decrease of organic-rich strata marking the OAE [Bucefalo Palliani and Mattioli, 1998; Bucefalo Palliani et al., 2002; Mattioli et al., 2004]. The stratigraphic position of the negative $\delta^{13}\text{C}$ excursion at the base of the organic-rich

sediments is also comparable to that of another section from the Paris Basin described by Hollander et al. [1991].

[15] Distinctly negative $\delta^{13}\text{C}_{\text{org}}$ excursions are frequently used to infer a marked $\delta^{13}\text{C}$ shift in the marine dissolved inorganic carbon (DIC) reservoir. OM, however, contains an abundance of different constituents, each with a characteristic carbon isotopic composition influenced by a wide variety of environmental and physiological parameters. The use of molecular fossils specific to primary producers greatly reduces the possible effects of source mixing, preservation and diagenesis on the $\delta^{13}\text{C}$ values. Phytane is a nonspecific biomarker, mainly derived from the phytol moiety of phytoplanktonic chlorophyll [Didyk et al., 1978; Koopmans et al., 1999]. The covariation of the $\delta^{13}\text{C}$ of phytane with that of TOC ($R^2 = 0.78$) in the examined section, suggests that the negative $\delta^{13}\text{C}$ excursion can be ascribed to changes in the $\delta^{13}\text{C}$ of water column DIC, assuming that phytoplankton used CO₂ as the carbon source and average carbon isotope fractionation remained the same before and during the event. However, the initial gradual shift from -25 to -28‰ in the $\delta^{13}\text{C}_{\text{org}}$ record of the packstone (below the grey line of Figure 3) is not discernible from the $\delta^{13}\text{C}$ record of phytane. The partly tempestitic origin of this lower unit suggests that oxygenated water column conditions were prevalent during its deposition. It is, therefore, likely that contributions of refractory (allochthonous) organic material (OM) to the sedimentary OC were relatively greater than those of autochthonous marine OM. Terrestrial OM (usually more refractory than marine OM) was also generally ^{13}C enriched compared to marine OC in the Toarcian [Vetö et al., 1997]. An increased terrestrial contribution to the organic matter at the base of the section is not apparent from the biomarker distribution. The negative $\delta^{13}\text{C}$ shift starting at 806.03 m is recorded both in the phytane record (-3.3‰) and in the bulk organic carbon record (-3.7‰), indicating that this likely represents a change in the $\delta^{13}\text{C}$ of DIC.

[16] Isorenieratane is present in low abundances even in the packstone underlying the interval recording the negative $\delta^{13}\text{C}_{\text{TOC}}$ shift. This packstone-wackestone unit also contains abundant winnowed bivalves that indicate a well-mixed water column, whilst the isorenieratane itself requires euxinic water column conditions during deposition. This paradox was also reported for the Kimmeridge Clay For-

mation and the Peterborough member of the Oxford Clay Formation, and has been explained by intermittent euxinia [van Kaam-Peters *et al.*, 1998; Kenig *et al.*, 2004]. Sedimentological observations in the examined section suggest that even during the OAE (as represented by the organic carbon-rich interval), laminated black shale deposits are interrupted by benthic colonization events and bioturbated horizons, similar to the lower Toarcian Posidonia Shale in Germany [Röhl *et al.*, 2001]. It seems that the conditions of a well-mixed water column with intermittent euxinia were replaced by long-term stagnant conditions and bottom water anoxia, interrupted by short-term oxygenated bottom-water conditions. Such conditions are collectively favorable for recycling of respired CO₂ ('Küspert model'), in the form of alternate events of build-up of ¹³C depleted, respired CO₂ below the chemocline, and uptake thereof by phytoplankton during mixing events [Küspert, 1982; Hollander and Smith, 2001]. A likely mixing mechanism could be related to periodic storm events, as suggested by sedimentological features such as ripples observed within intervals in the mudstone, notably where the organic carbon is also most ¹³C depleted (Figure 2). However, the relative abundance of isorenieratane increases only after the ¹³C of TOC and phytane return to more positive values. If recycling of respired CO₂ is indeed the main cause for the negative ¹³C values, an increase in isorenieratane abundance would be expected either synchronously with or even prior to the negative ¹³C excursion. This is not the case.

[17] The isorenieratane ¹³C record can be used to estimate the degree of contribution of respired CO₂ at the chemocline [cf., van Breugel *et al.*, 2005]. Van Breugel *et al.* found that the ¹³C of this carotenoid covaried with the strong variations in ¹³C of CO₂ (aq) and was independent of the CO₂ and isorenieratane concentration. The observed constant isotopic fractionation (ϵ_p) of isorenieratane versus CO₂, $4 \pm 1\%$ [van Breugel *et al.*, 2005] can, thus, in combination with the ¹³C values of isorenieratane (Table 1) be used to calculate the ¹³C of CO₂ at the chemocline ($\delta^{13}\text{C}_{\text{CO}_2\text{-chemocline}}$) in the Toarcian shelf sea according to the following equation:

$$\delta^{13}\text{C}_{\text{CO}_2\text{-chemocline}} = \left[\frac{1.004 \cdot (1000 + \delta^{13}\text{C}_{\text{isorenieratane}})}{1000} \right] \quad (1)$$

[18] The contribution of remineralized organic carbon to the dissolved inorganic carbon (DIC) pool at the chemocline can subsequently be estimated with the following isotopic and concentration mass balance equations:

$$\delta^{13}\text{C}_{\text{chem}} \times [\text{DIC}_{\text{chem}}] = \delta^{13}\text{C}_{\text{atm}} \times [\text{DIC}_{\text{atm}}] + \delta^{13}\text{C}_{\text{resp}} \times [\text{DIC}_{\text{resp}}] \quad (2)$$

$$[\text{DIC}_{\text{chem}}] = [\text{DIC}_{\text{atm}}] + [\text{DIC}_{\text{resp}}] \quad (3)$$

with DIC_{chem} = chemocline DIC, DIC_{atm} = DIC in equilibrium with atmospheric CO₂ and DIC_{resp} = DIC

Table 1. Calculated Percentage of Recycled Dissolved Inorganic Carbon (DIC) at the Chemocline in the Toarcian Epicontinental Sea Based on Measured ¹³C Values of Isorenieratane at Various Intervals of the Studied Section of the Paris Basin

Average Depth in Core, m	$\delta^{13}\text{C}$ -TOC, ‰	$\delta^{13}\text{C}$ Isorenieratane, ‰ ^a	$\delta^{13}\text{C}_{\text{CO}_2}$ at Chemocline, ‰	Percentage Recycled DIC, %
792.45	-28.37	-14.2 ± 0.3	-10.3	11–19
792.75	-28.14	-13.1 ± 0.1	-9.1	7–16
798.52	-27.67	-12.6 ± 0.5	-8.6	6–15
801.38	-27.68	-12.8 ± 0.2	-8.8	6–15
802.20	-27.80	-14.8 ± 0.3	-10.8	13–22
802.55	-26.24	-13.0 ± 0.3	-9.0	7–17
802.89	-26.24	-9.8 ± 0.4	-5.8	0–6
803.41	-27.72	-12.5 ± 0.4	-8.5	5–14
803.73	-28.03	-12.8 ± 0.3	-8.9	6–15
804.19	-28.20	-13.1 ± 0.2	-9.2	7–16
804.45	-27.31	-13.1 ± 0.3	-9.1	7–16
805.18	-28.24	-13.1 ± 0.2	-9.1	7–16
805.73	-29.06	-13.7 ± 0.2	-9.8	9–17

^aRange indicates the standard deviation of the measurement based on 3–4 irr-GC/MS runs.

formed by remineralization of organic carbon ('respired' DIC). Equations 2 and 3 can be rearranged to yield the following equation (Equation 4) to calculate the respired DIC contribution.

$$\begin{aligned} \text{Respired DIC contribution} &= \frac{[\text{DIC}_{\text{resp}}]}{[\text{DIC}_{\text{chem}}]} \times 100\% \\ &= \frac{\delta^{13}\text{C}_{\text{chem}} - \delta^{13}\text{C}_{\text{atm}}}{-\delta^{13}\text{C}_{\text{atm}} + \delta^{13}\text{C}_{\text{resp}}} \times 100\% \quad (4) \end{aligned}$$

With estimates for the ¹³C of CO₂ in surface waters in equilibrium with atmospheric CO₂ and the ¹³C of CO₂ formed by respiration of organic matter, the contribution of respired CO₂ to CO₂ at the chemocline can be estimated. The stable carbon isotopic composition of sedimentary organic carbon ($\delta^{13}\text{C}_{\text{TOC}}$; Table 1) is used as an estimate for the isotopic composition of respired DIC. The $\delta^{13}\text{C}$ -CO₂ chemocline (Table 1) is converted into $\delta^{13}\text{C}$ -DIC chemocline [Mook *et al.*, 1974] with a temperature range of 15–25°C based on palaeotemperature estimations for the European Toracian shelf sea [Rosales *et al.*, 2004], and the assumption that $\delta^{13}\text{C}\text{-DIC} \sim \delta^{13}\text{C}\text{-HCO}_3^-$. The $\delta^{13}\text{C}_{\text{DIC}}$ of surface waters in equilibrium with atmospheric CO₂ was estimated using the average ¹³C values of carbonate minerals, by correcting for the average isotopic depletion of carbonate minerals relative to DIC (~1.2‰). As the carbonate ¹³C record of our section is not particularly robust (large fluctuations between -1.4 and 2.1‰ and standard deviation up to 1.1‰; van Breugel, unpublished results), we use the range 2–4‰ in which most ¹³C values of belemnites unaffected by diagenesis and present in the Yorkshire and Dotternhausen lower Toarcian sections fall [van de Schootbrugge *et al.*, 2005]. Belemnite ¹³C values probably reflect $\delta^{13}\text{C}_{\text{DIC}}$ values of open ocean surface waters.

[19] With the ranges in water temperatures (15–25°C) and carbonate ¹³C values (2 to 4‰), minimum and

maximum contributions of respired DIC at the chemocline were calculated (Table 1) and vary between 0 and 22% with an average value of 11%. When compared to other contemporary and ancient stratified marine basins [van Breugel *et al.*, 2005, and references therein], this contribution is relatively small. For example, much higher respired DIC contributions at the chemocline of circa 40% were measured for a shallow Norwegian anoxic fjord, Kyllaren fjord, and a number of contemporary lakes [van Breugel *et al.*, 2005]. Considering the substantially lower contribution of respired DIC at the chemocline of the Toarcian epicontinental sea (11% on average), it seems unlikely that the process of recycling of respired DIC caused the large negative shift in the lower Toarcian $\delta^{13}\text{C}_{\text{TOC}}$ record as $\delta^{13}\text{C}_{\text{DIC}}$ at the chemocline is more affected by this process than $\delta^{13}\text{C}_{\text{DIC}}$ of surface waters. However, at one interval recycling of respired DIC may have had an effect: the respired DIC contribution changes from 0–6 to of 13–22% when the $\delta^{13}\text{C}$ value of isorenieratane shifts from -9.8‰ to -14.8‰ between 802.9 and 802.2 m. It may be that the observed relatively small 1.5‰ negative shift in the $\delta^{13}\text{C}_{\text{TOC}}$ record (and corresponding 1‰ shift in the $\delta^{13}\text{C}$ record for phytane) at this specific depth, was caused by recycling of respired DIC.

5. Conclusion

[20] The new isotopic and molecular records presented in this study provide firm indication that, during the early Toarcian of the Paris Basin, water column anoxia extended into the photic zone. Corresponding sedimentological and palaeontological evidence, however, also requires that either regular or occasional mixing of the water column took place during deposition. Although these processes may collectively have had a bearing on the observed $\delta^{13}\text{C}$ records of marine organic carbon, it seems that recycling of respired CO₂ as originally proposed by Küspert [1982] is unlikely to have been the main cause for the large negative $\delta^{13}\text{C}$ shift recorded at the onset of OC-rich sediment deposition during

the early Toarcian. Firstly, stratification of the lower Toarcian epicontinental sea was much weaker at times when $\delta^{13}\text{C}_{\text{TOC}}$ values are most negative. Secondly, the calculated contribution of DIC formed by remineralization of organic matter at the chemocline is relatively low, indicating that DIC bearing a negative carbon isotope signal is unlikely to have been taken up by phytoplankton as proposed in the Küspert model.

[21] We conclude that a clear-cut mechanism for the lower Toarcian negative isotope excursion is still lacking. An abrupt and massive release of ^{13}C -depleted carbon, perhaps methane as proposed by Hesselbo *et al.* [2000], Beerling *et al.* [2002], Kemp *et al.* [2005], and McElwain *et al.* [2005] would explain the large negative $\delta^{13}\text{C}$ shift in both carbonate and TOC at the onset of OC-rich sediment deposition during the early Toarcian and importantly also explains the negative $\delta^{13}\text{C}$ excursion observed in fossil wood records [Hesselbo *et al.*, 2000]. However, the lack of a negative shift in belemnite $\delta^{13}\text{C}$ was recently used as an argument against the gas hydrate theory [van de Schootbrugge *et al.*, 2005] and the Küspert model was used to explain the negative shifts in the European carbon isotope records for the Toarcian OAE. However, our data presented here and studies recycling of isotopically light DIC in a contemporary model for stratified epicontinental seas [van Breugel *et al.*, 2006] do not provide support for the Küspert model. Perhaps, positive $\delta^{13}\text{C}$ shifts due to relative changes in burial rates of organic matter versus carbonate potentially obscures the preservation of negative isotope signals such as the one characterizing many early Toarcian sites [Cramer and Kent, 2005]. Therefore, it remains a distinct possibility that the negative carbon isotope anomaly may in fact have been caused by a confluence of mechanisms.

[22] **Acknowledgments.** We thank ANDRA for making the core material available. J. Ossebaar (NIOZ) is thanked for analytical assistance with the bulk organic carbon determinations. Stephen Hesselbo, Lorentz Schwark, Rich Pancost, Jerry Dickens, and an anonymous referee are thanked for their helpful reviews. This research was financed by a grant of the Netherlands Organization for Scientific Research (NWO) to JSSD.

References

- Arthur, M. A., H. C. Jenkyns, H.-J. Brumsack, and S. O. Schlanger (1990), Stratigraphy, geochemistry, and paleoceanography of organic carbon-rich Cretaceous sequences, in *Cretaceous Resources, Events and Rhythms*, edited by R. N. Ginsburg and B. Beaudoin, pp. 75–119, Springer, New York.
- Berling, D. J., M. R. Lomas, and D. R. Gröcke (2002), On the nature of methane gas-hydrate dissociation during the Toarcian and Aptian oceanic anoxic events, *Am. J. Sci.*, *302*, 28–49.
- Bown, P. R., and M. K. E. Cooper (1998), Jurassic, in *Calcareous Nannofossil Biostratigraphy*, edited by P. R. Bown, pp. 34–85, Springer, New York.
- Brooks, J. J., G. Love, R. E. Summons, A. H. Knoll, G. A. Logan, and S. A. Bowden (2005), Biomarker evidence for green and purple sulphur bacteria in a stratified Palaeoproterozoic sea., *Nature*, *437*, 866–870.
- Bucefalo Palliani, R., and E. Mattioli (1998), High resolution integrated microbiostratigraphy of the Lower Jurassic (late Pliensbachian early Toarcian) of central Italy, *J. Micropaleontol.*, *17*, 153–172.
- Bucefalo Palliani, R., E. Mattioli, and J. B. Riding (2002), The response of marine phytoplankton and sedimentary organic matter to the early Toarcian (Lower Jurassic) oceanic anoxic event in northern England, *Mar. Micropaleontol.*, *46*, 223–245.
- Cramer, B. S., and D. V. Kent (2005), Bolide summer: The Paleocene/Eocene thermal maximum as a response to an extraterrestrial trigger, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *224*, 144–166.
- Dickens, G. R., J. R. O'Neil, D. K. Rea, and R. M. Owen (1995), Dissociation of oceanic methane hydrate as a cause of the carbon isotope excursion at the end of the Paleocene, *Paleoceanography*, *10*, 965–971.
- Didyk, B. M., B. R. T. Simoneit, S. C. Brassell, and G. Eglinton (1978), Organic geochemical indicators of palaeoenvironmental conditions of sedimentation, *Nature*, *272*, 216–222.
- Farrimond, P., G. Eglinton, C. Brassell, and H. C. Jenkyns (1989), Toarcian anoxic event in Europe: an organic geochemical study, *Mar. Pet. Geol.*, *6*, 136–147.
- Hesselbo, S. P., D. R. Gröcke, H. C. Jenkyns, C. J. Bjerrum, P. Farrimond, H. S. Morgans Bell, and O. R. Green (2000), Massive dissociation of gas hydrate during a Jurassic oceanic anoxic event, *Nature*, *406*, 392–395.
- Hollander, D. J., and M. A. Smith (2001), Microbially mediated carbon cycling as a control on the $\delta^{13}\text{C}$ of sedimentary carbon in eutrophic Lake Mendota (USA): New models for interpreting isotopic excursions in the sedimentary record, *Geochim. Cosmochim. Acta*, *65*, 4321–4337.

- Hollander, D. J., G. Bessereau, S. Belin, A. Y. Huc, and J. P. Houzay (1991), Organic matter in the early Toarcian Shales, Paris Basin, France: A response to environmental changes, *Rev. Inst. Fr. Pet.*, **46**, 543–562.
- Jenkyns, H. C. (1988), The early Toarcian (Jurassic) anoxic event: stratigraphic, sedimentary, and geochemical evidence, *Am. J. Sci.*, **288**, 101–151.
- Jenkyns, H. C., and C. J. Clayton (1986), Black shales and carbon isotopes in pelagic sediments from the Tethyan Lower Jurassic, *Sedimentology*, **33**, 87–106.
- Jenkyns, H. C., and C. J. Clayton (1997), Lower Jurassic epicontinental carbonates and mudstones from England and Wales: chemostratigraphic signals and the early Toarcian anoxic event, *Sedimentology*, **44**, 687–706.
- Jenkyns, H. C., C. E. Jones, D. R. Gröcke, S. P. Hesselbo, and D. N. Parkinson (2002), Chemostratigraphy of the Jurassic System: Applications, limitations and implications for palaeoceanography, *J. Geol. Soc. London*, **159**, 351–378.
- Jiménez, A. P., C. Jiménez de Cisneros, P. Rivas, and J. A. Vera (1996), The early Toarcian anoxic event in the westernmost Tethys (Subbetic): Paleogeographic and paleobiogeographic significance, *J. Geol.*, **104**, 399–416.
- Kemp, D. B., A. L. Coe, A. S. Cohen, and L. Schwark (2005), Astronomical pacing of methane release in the Early Jurassic period, *Nature*, **437**, 396–399.
- Kenig, F., J. D. Hudson, J. S. Sinninghe Damsté, and B. N. Popp (2004), Intermittent euxinia: Reconciliation of a Jurassic black shale with its biofacies, *Geology*, **32**, 421–424.
- Koopmans, M. P., J. Köster, H. M. E. van Kaam-Peters, F. Kenig, S. Schouten, W. A. Hartgers, J. W. de Leeuw, and J. S. Sinninghe Damsté (1996a), Diagenetic and catagenetic products of isorenieratene: Molecular indicators for photic zone anoxia, *Geochim. Cosmochim. Acta*, **60**, 4467–4496.
- Koopmans, M. P., S. Schouten, M. E. L. Kohnen, and J. S. Sinninghe Damsté (1996b), Restricted utility of aryl isoprenoids as indicators for photic zone anoxia, *Geochim. Cosmochim. Acta*, **60**, 4873–4876.
- Koopmans, M. P., W. I. C. Rijpstra, M. M. Klapwijk, J. W. de Leeuw, M. D. Lewan, and J. S. Sinninghe Damsté (1999), A thermal and chemical degradation approach to decipher pristane and phytane precursors in sedimentary organic matter, *Org. Geochem.*, **1089**–1104.
- Küspert, W. (1982), 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, New York.
- Mattioli, E., and E. Erba (1999), Synthesis of calcareous nannofossil events in Tethyan Lower and Middle Jurassic successions, *Riv. Ital. Paleontol. Stratigr.*, **105**, 343–376.
- Mattioli, E., B. Pittet, R. Bucefalo Palliani, H.-J. Röhl, and E. Morettoni (2004), Phytoplankton evidence for the timing and correlation of palaeoceanographical changes during the early Toarcian oceanic anoxic event (Early Jurassic), *J. Geol. Soc.*, **161**, 685–693.
- McElwain, J. C., J. Wade-Murphy, and S. P. Hesselbo (2005), Changes in carbon dioxide during an oceanic anoxic event linked to intrusion into Gondwana coals, *Nature*, **435**, 479–482.
- Mook, W. G., J. C. Bommerson, and W. H. Staverman (1974), Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide, *Earth Planet. Sci. Lett.*, **22**, 169–176.
- Pancost, R. D., N. Crawford, S. Magness, A. Turner, H. C. Jenkyns, and J. R. Maxwell (2004), Further evidence for the development of photic-zone euxinic conditions during Mesozoic oceanic anoxic events, *J. Geol. Soc.*, **161**, 353–364.
- Röhl, H.-J., A. Schmid-Röhl, W. Oschmann, A. Frimmel, and L. Schwark (2001), The Posidonia Shale (lower Toarcian) of SW-Germany: An oxygen-depleted ecosystem controlled by sea level and palaeoclimate, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **165**, 27–52.
- Rosales, I., S. Quesada, and S. Robles (2004), Paleotemperature variations of Early Jurassic seawater recorded in geochemical trends of belemnites from the Basque-Cantabrian basin, northern Spain, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **203**, 253–275.
- Schouten, S., H. M. E. van Kaam-Peters, W. I. C. Rijpstra, M. Schoell, and J. S. Sinninghe Damsté (2000), Effects of an oceanic anoxic event on the stable carbon isotopic composition of early Toarcian carbon, *Am. J. Sci.*, **300**, 1–22.
- Schwark, L., and A. Frimmel (2004), Chemostratigraphy of the Posidonia Black Shale, SW-Germany II: Assessment of extent and persistence of photic-zone anoxia using aryl isoprenoid distributions, *Chem. Geol.*, **206**, 231–248.
- Sinninghe Damsté, J. S., and S. Schouten (2006), Biological markers for anoxia in the photic zone of the water column, in *Marine Organic Matter: Biomarkers, Isotopes and DNA, The Handbook of Environmental Chemistry*, vol. 2, *Reactions and Processes*, part 2N, edited by J. K. Volkman, pp. 127–163, Springer, New York.
- Svensen, H., S. Planke, A. Malthes-Sørensen, B. Jamtveit, R. Myklebust, T. R. Eidem, and S. S. Rey (2004), Release of methane from a volcanic basin as a mechanism for initial Eocene global warming, *Nature*, **429**, 542–545.
- van Breugel, Y., S. Schouten, M. Paetzel, J. Ossebaer, and J. S. Sinninghe Damsté (2005), Reconstruction of delta $\delta^{13}\text{C}$ of chemocline CO₂ (aq) in past oceans and lakes using the $\delta^{13}\text{C}$ of fossil isorenieratene, *Earth Planet. Sci. Lett.*, **235**, 421–434.
- van Breugel, Y., S. Schouten, M. Paetzel, and J. S. Sinninghe Damsté (2006), Seasonal variation in the stable carbon isotopic composition of algal lipids in a shallow anoxic fjord: Evaluation of recycling of respired CO₂ as a cause for the negative isotope excursion in sedimentary records of carbonate and organic matter, *Amer. J. Sci.*, **306**, 367–387.
- 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.
- van Kaam-Peters, H. M. E., W. I. C. Rijpstra, J. W. de Leeuw, and J. S. Sinninghe Damsté (1998), A high resolution biomarker study of different lithofacies of organic sulfur-rich carbonate rocks of a Kimmeridgian lagoon (French southern Jura), *Org. Geochem.*, **28**, 151–177.
- Vetö, I., A. Demeny, E. Hertelendi, and M. Hetényi (1997), 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.

M. Baas, S. Schouten, J. S. Sinninghe Damsté, and Y. van Breugel, Royal Netherlands Institute for Sea Research, Department of Marine Biogeochemistry and Toxicology, P.O. Box 59, 1790 AB, Den Burg (Texel), Netherlands. (damste@nioz.nl)

E. Mattioli, Université Lyon 1, UMR 5125 CNRS-Laboratoire PEPS, UFR Sciences de la Terre, 2 rue Dubois, 69622 Villeurbanne, France.