Journal of the Geological Society, London, Vol. **161**, 2004, pp. 353–364. Printed in Great Britain.

Further evidence for the development of photic-zone euxinic conditions during Mesozoic oceanic anoxic events

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Abstract: Periods in Earth history characterized by extensive organic carbon deposition, so-called oceanic anoxic events (OAEs), are the subject of considerable scrutiny. Insight into the extent of anoxic conditions in the water column has been provided by the reported occurrence of derivatives of isorenieratene, a carotenoid found only in green sulphur bacteria and thus indicative of photic-zone euxinia (i.e. a water column containing free H_2S), in North Atlantic deep-sea sediments deposited during the Cenomanian–Turonian boundary OAE2 (Bonarelli Event). In this study, we have used the distributions of chlorophyll and bacteriochlorophyll degradation products, maleimides (1-*H*-pyrrole-2,5-diones) and high molecular weight porphyrins, to examine further the Cenomanian–Turonian boundary OAE2 as well as other OAEs of the early Toarcian (Posidonienschiefer Event) and early Aptian (Selli Event). In particular, methyl isobutyl (Me,*i*-Bu) maleimide, on structural grounds, appears to be diagnostic of green sulphur bacteria. This compound occurs in five of seven examined marls that record the early Toarcian OAE (Marche–Umbria, Italy), further expanding the geographical range of Toarcian sediments where evidence for photic-zone euxinic conditions has been found. Me,*i*-Bu maleimide occurs in three of six black shales spanning the Livello Selli (Marche–Umbria, Italy), the type locality for the Aptian OAE1a, providing the first evidence for photic-zone euxinic conditions during this event. With respect to the Cenomanian–Turonian OAE, maleimide evidence for photic-zone euxinic conditions was found in all the North Atlantic sites investigated, including those characterized by relatively organic-lean sediments, several Tethyan sites and one site off western Australia. These data indicate that euxinic conditions were common in the water column during Mesozoic oceanic anoxic events.

Keywords: $^{13}C/^{12}C$, Jurassic, Cretaceous, maleimides, oceanic anoxic events.

One of the most intriguing aspects of Mesozoic climate is the episodic occurrence of so-called oceanic anoxic events (OAEs). Originally, the term OAE was used to describe the phenomenon characterized by seemingly global distribution of laminated organic-carbon-rich ($>1\%$) sediments in pelagic sequences of Aptian–Albian and Cenomanian–Turonian boundary age (Schlanger & Jenkyns 1976). Since then, other episodes of widespread black-shale deposition in marine environments have been identified, and six OAEs have been proposed for the mid-Cretaceous (Arthur *et al*. 1990) and one for the Jurassic (Jenkyns 1988). These events are often associated with periods of dramatic climatic change and biotic turnover, and each apparently represents the sequestration of vast quantities of organic carbon into the geosphere (e.g. Jenkyns 1999, 2003). Consequently, black shales deposited during OAEs are among the most organic-rich marine sediments and are important petroleum source rocks. Significant positive excursions in $^{13}C/^{12}C$ ratios of marine carbonates (up to 2.5‰) and organic matter (up to 6‰) in early Aptian time (OAE1a) and at the Cenomanian–Turonian boundary (OAE2) provide additional evidence for the enhanced removal of ^{13}C-depleted organic carbon from the ocean–atmosphere reservoir (Arthur *et al*. 1988; Weissert *et al*. 1998).

Interest in OAEs has stimulated diverse investigations using sedimentological, palaeontological and geochemical approaches. However, the underlying causes and unifying characteristics of OAEs remain poorly understood. Black shales deposited during OAEs share similarities such as high organic carbon contents, lamination and impoverished benthic fauna, indicating that these sediments were deposited under oxygen-deficient bottom-water conditions (Summerhayes 1987; Bralower *et al*. 1994). Models to explain these observations typically invoke either enhanced organic matter preservation and/or enhanced primary productivity (Demaison & Moore 1980). Preservation models propose that either restricted circulation or elevated temperatures at the sites of bottom-water formation resulted in a decreased oxygen flux and decreased organic matter remineralization (e.g. Ryan & Cita 1977; Brass *et al*. 1982; Barron 1983; de Graciansky *et al*. 1984). In contrast, productivity-driven models propose that enhanced primary productivity during OAEs resulted in increased burial of organic matter (e.g. Pedersen & Calvert 1990; Erbacher *et al*. 1996; Sinton & Duncan 1997).

Given the complex changes in ocean circulation, primary productivity, redox conditions and biological populations associated with OAEs, molecular biogeochemical approaches, which can provide insight into photoautotroph and bacterial communities, are useful complements to classical inorganic and palaeontological techniques. Of particular interest in the study of OAEs are biomarkers derived from green sulphur bacteria that are diagnostic for photic-zone euxinic conditions (e.g. Summons & Powell 1986). Such biomarkers have been found in organic-rich sediments throughout the Phanerozoic (e.g. Koopmans *et al*. 1996), including those deposited during Mesozoic OAEs (Sinninghe Damsté & Köster 1998; Schouten *et al*. 2000). Identification of biomarkers for green sulphur bacteria has proved to be particularly useful in reconstructing oceanographic conditions during OAEs by helping to constrain the extent of water-column redox variations. Here, we expand on such analyses using maleimides (1-*H*-pyrrole-2,5-diones), degradation products of tetrapyrrole pigments that can be diagnostic of specific photoautrophic organisms, including green sulphur bacteria.

The origin of maleimides

Maleimides in geological samples derive from the degradation of chlorophylls, the predominant light-harvesting compounds in photoautotrophic organisms. The most abundant chlorophyll, Chl *a*, is present in all photosynthetic eukaryotes and cyanobacteria, whereas the anoxygenic prokaryotes typically contain bacteriochlorophyll (Bchl) *a* or, less commonly, Bchl *b* (e.g. Keely & Maxwell 1993, and references therein). Bchls *c*, *d* and *e* (Fig. 1, **I**) in marine settings are largely restricted to the Chlorobiaceae, the photosynthetic green sulphur bacteria. The Chlorobiaceae are of particular interest because they require both light and free hydrogen sulphide (van Gemerden & Mas 1995), and diagenetic products of their lipids are diagnostic for the specific conditions of photic-zone euxinia (e.g. Summons & Powell 1986). Specific concentrations of hydrogen sulphide are difficult to ascertain; green sulphur bacteria can apparently live at relatively low hydrogen sulphide concentrations (<1 μM) as long as O_2 is absent and light is available (e.g. Repeta *et al*. 1989).

Although most chlorophyll is degraded to lower molecular weight colourless products (Brown *et al*. 1990), a small proportion can undergo transformation to yield sedimentary porphyrins, which have a fully aromatic tetrapyrrole ring structure and exist as mainly nickel or vanadyl complexes. Such porphyrins can serve as useful tracers for ancient photoautotropic communities, with certain high-molecular-weight porphyrins apparently deriving from Bchls *c*, *d* and *e*. However, difficulties associated with identifying specific components in complex mixtures (e.g. Turner 1998) complicate the use of porphyrins as biomarkers for green sulphur bacteria and, in this paper, porphyrins are used to complement interpretations based on maleimides. Maleimides (1-*H*-pyrrole-2,5-diones) can be obtained from treatment of chlorins or porphyrins with an oxidizing agent, by photoxidation or autoxidation in ancient depositional settings or oxidation during sample storage (P. Adam, pers. comm.). Analyses of geological materials utilizing various porphyrin oxidation schemes (Hodgson *et al*. 1971; Quirke *et al*. 1980) or examination of solvent-extractable (free) maleimides (Grice *et al*. 1996) resulted in the identification of a suite of maleimides, including H,H, Me,Et (**IIa**), Me,Me (**IIb**), Et,Et (**III**), Me,*i*-Bu (**IIc**), Me,*sec*-Bu (**IId**), Me,*n*-Bu (**IIe**), Me,H (**IIf**), Me,*i*-Pr (**IIg**) and Me,*n*-Pr (**IIh**) maleimides (where Me is methyl; Et, ethyl; Pr, propyl; *i*-Pr, isopropyl; Bu, butyl; *sec*-Bu, secondary butyl; *i*-Bu, isobutyl). On structural grounds, all of these could be attributed to one or more chlorophylls; for example, Me,Et maleimide, which is particularly abundant in most sediments, probably derives from Chl *a*. Of significance are the Me,*n*-Pr and Me,*i*-Bu components, which, on structural grounds, appear to derive from Bchl *c*, *d* or *e*. At present, there is no known precursor for Me,*i*-Bu maleimide other than Bchl *c*, *d* or *e*, all of which contain an *i*-Bu side chain at C-8. There is, however, an alternative source for Me,*n*-Pr maleimide: hydrolysis of the C-17 ester in Chl *a*, followed by reduction of the resulting C_3 acid substituent (Verne-Mismer *et al*. 1986).

Hence, the relative abundances of Me,*i*-Bu maleimides can be used as a proxy for the presence of Chlorobiaceae in ancient water columns and the specific condition of photic-zone euxinia. In addition, because maleimides can be unambiguously linked to precursor chlorophylls or bacteriochlorophylls, their carbon-isotopic compositions could be useful in reconstructing changes in the carbon cycle that are often associated with OAEs (e.g. Arthur *et al*. 1988). Here, we report analyses of maleimide distributions and carbon-isotopic compositions in organic-rich sediments associated with the three most significant Mesozoic oceanic anoxic events: the early Toarcian (Posidonienschiefer Event), the early Aptian (Selli Event; OAE1a), and at the Cenomanian–Turonian boundary (Bonarelli Event; OAE2). Specifically, we illustrate the utility of maleimides in identifying photic-zone euxinia in ancient restricted basins and how this complements other organic geochemical tools (e.g. abundances of isorenieratene degradation products).

Methods

Sample extraction and fractionation

Powdered sediments (30–250 g) were extracted (×3 or ×4) by sonication (20 min) in CH_2Cl_2–MeOH (9:1, v/v). Extracts were fractionated according to methods published previously (Grice *et al*. 1997). In short, they were separated by flash chromatography into four fractions, containing: aliphatic hydrocarbons (F1); Ni porphyrins and aromatic hydrocarbons (F2); vanadyl (VO) porphyrins (F3); maleimides (F4). Another stage of flash-column chromatography was used to separate F2 into discrete aromatic and Ni porphyrin fractions and to obtain from F4 a crude maleimide fraction. The latter was purified further by thin layer

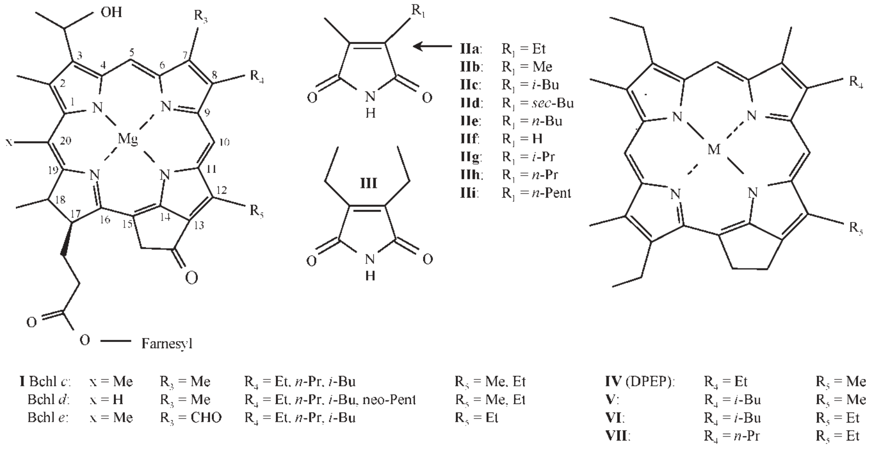

Fig. 1. Structures of bacteriochlorophylls *c*, *d*, and *e* (**I**); matelimides (**II**); including Me,*i*-Bu maleimide (**IIc**) diagnostic for green sulphur bacteria; and porphyrins (**IV–VII**) of which **V–VII** are diagnostic for green sulphur bacteria.

chromatography (TLC; modified from Grice *et al*. (1997) and described by Pancost *et al*. (2002)).

Demetallation and oxidation of porphyrins

Demetallation of metalloporphyrins was performed using the method of Chicarelli (1985) and confirmed by UV–visible spectrophotometry. Resultant free base porphyrins (typically 0.5–1 mg) were oxidized to maleimides by UV light oxidation. The mixture, in 40 ml acetone in a round-bottomed flask carrying a condenser, was irradiated until bleached (typically 12–24 h depending on the amount of starting material) using a Gallenkamp UV lamp (365 nm) with a 125 W bulb. Solvent was removed by rotary evaporation and the maleimides were purified by TLC as outlined above. Porphyrin fractions obtained by flash-column chromatography were identified as Ni, VO or free base species by UV–visible spectrophotometry using a Unicam UV2 spectrophotometer according to the methods of Chicarelli (1985). Liquid chromatography–atmospheric pressure-mass spectrometry was performed using a method similar to that of Rosell-Melé *et al*. (1996) and described by Pancost *et al*. (2002).

Gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS)

GC and GC–MS methods have been described previously (Pancost *et al*. 2002) and were conducted on both derivatized and underivatized maleimides. Underivatized maleimides were analysed using a CPWAX 52 CB column (Chrompack; 25 m × 0.32 mm i.d., 0.2 μm film) with the following temperature programme: 40°C to 100°C @ 10°C min^{-1} then to 250°C @ 4°C min^{-1} (isothermal for 25 min). Derivatized maleimides were analysed using a CPSIL 5 column (Chrompack; 25 m × 0.32 mm i.d., 0.12 μm film) with the following temperature programme: 40°C (2 min) to 80°C @ 10°C min^{-1} then to 300°C @ 4°C min^{-1} (isothermal for 20 min). Identification of the Me,Et and Et,Et components (structures in Fig. 1) was performed by comparison with standards obtained by oxidation of aetioporphyrin III and octaethylporphyrin, respectively. Other maleimides were identified by comparing retention times and mass spectra with those observed by Grice *et al*. (1996, 1997).

Results

The Toarcian OAE

Lower Toarcian organic-rich black shales are geographically widespread, occurring in Europe, North America, Asia, Japan, Australia and Madagascar (Jenkyns 1988; Jenkyns *et al*. 2002). Because of their similarity to Cretaceous black shales, the Toarcian organic-rich sediments are also thought to record an OAE (Jenkyns 1985, 1988). The event apparently lasted *c*. 0.5 Ma (Jenkyns 1988), spanning the *falciferum* ammonite biozone (specifically, the *exaratum* subzone) and is associated with emplacement of a large igneous province (Pálfy & Smith 2000; Jones & Jenkyns 2001) and relatively high sea level (Haq *et al*. 1987). Toarcian OAE sediments are characterized by a negative followed by a positive excursion in the carbon-isotope composition of organic matter and carbonate (Jenkyns & Clayton 1986, 1997; Hollander *et al*. 1991). The positive excursion is typically ascribed to the burial of ^{13}C-depleted organic matter and the consequential ^{13}C enrichment in surface-water dissolved inorganic carbon. The negative excursion has been attributed to a number of mechanisms, but its occurrence in terrestrial carbon (Hesselbo *et al*. 2000; Beerling *et al*. 2002) indicates that it records a change in the global ocean–atmosphere carbon reservoir. Another characteristic of the Toarcian OAE is the extinction and reduction in diversity of organisms such as bivalves, dinoflagellates, ostracodes, gastropods, foraminifera and ammonites (Jenkyns 1985, 1988; Little & Benton 1995).

We examined maleimide distributions in dark marls of the Marche–Umbria basin (Valdorbia near Gubbio, Marche–Umbria, Italy), which, during Toarcian times, represented part of the continental margin or proto-continental margin of the Tethys Ocean (Fig. 2). Previous work at this site (Jenkyns & Clayton 1986) revealed a positive excursion in carbonate δ^{13}C values above the black shales, and complete stratigraphic details have been previously published (Monaco *et al*. 1994; Pettinelli *et al*. 1995). A variety of maleimides is present in VAL1 (lowermost in section) and VAL4–7, including Me,H, Me,Me, Me,Et, Me,*i*-Pr, Et,Et, Me,*n*-Pr, Me,*i*-Bu and Me,*n*-Bu components. A summary of these data is shown in Table 1 (in all cases, sample numbers referred to in the text and Table 1 increase up-section). Samples VAL2 and VAL3 contain most of the same components but lack Me,*i*-Bu maleimide. As typically observed, the distributions are dominated by components of phytoplankton origin, i.e. Me,H, Me,Me and Me,Et maleimides. The Me,*i*-Bu/Me,Et ratio is highest in VAL7 (Fig. 3) and, although the sampling is sparse, there appears to be an up-section increase in the ratio. Similarly, high molecular weight porphyrins (**V**–**VII**), inferred to derive from Bchl *d* or *e*, are absent from VAL2,3, and their ratios relative to desoxophylloerythroaetioporphyrin (DPEP; **IV**, derived from Chl *a*) increase up-section.

In addition, high-molecular-weight porphyrins (**V**–**VII**), inferred to derive from Bchl *d* or *e*, are present in a variety of other southern and northern European sites. These porphyrins occur in a black shale (total organic carbon (TOC) 3.3%; total

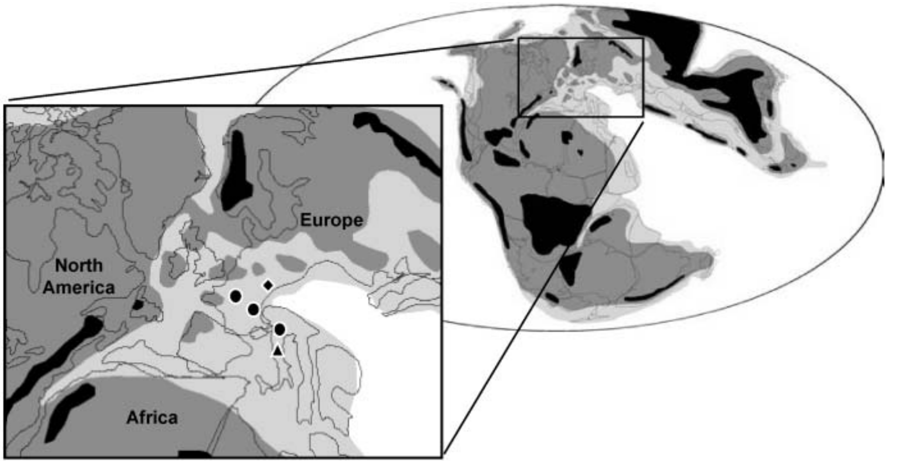

Fig. 2. Maps showing palaeogeography during the Toarcian OAE (adapted from Scotese (2001)) and the location of the Valdorbia site (▲). Also shown are sites where high-molecular-weight porphyrins thought to derive from green sulphur bacteria (●) have been recovered in Toarcian sediments. ♦, Posidonienschiefer, SW Germany, where high molecular weight porphyrins and derivatives of isorenieratene and chlorobactene have been found.

Table 1. *Geochemical data for samples; for each site, samples are listed in stratigraphic order*

Sample	TOC (%)	Sulphur (%)	Free Me,*i*-Bu maleimide	Me,*i*-Bu from porphyrin oxidation	Porphyrin evidence for PZE
C/T boundary					
367-2	29.5	8.1	+	n.d.	+
367-3	26.3	6.1	+	n.d.	+
368	9.6	2.0	+	+	+
603B-3	7.5	2.0	+	n.d.	n.d.
603B-5	3.9	1.8	+	n.d.	n.d.
551	5.8	2.1	+	n.d.	n.d.
GCLB-2	16.1	1.5	+	n.d.	+
GCLB-1	18.5	2.1	+	n.d.	+
F1	31.2	4	+	+	+
FOS5	25.3	5.8	–	n.d.	+
FOS4	29.7	4.9	–	n.d.	+
FOS3	21.1	2.9	–	n.d.	+
FOS2	15.3	1.9	–	n.d.	–
FOS1	22.4	4.7	+	n.d.	+
MP8	11.2	0.6	+	n.d.	+
MP7	18.3	2.5	–	n.d.	n.d.
MP6	22.0	3.1	–	n.d.	+
MP5	20.8	2.5	+	n.d.	+
MP4	11.0	1.2	+	n.d.	+
MP3	16.8	1.9	+	n.d.	+
MP2	17.2	1.7	+	n.d.	n.d.
MP1	2.3	1.2	–	n.d.	n.d.
CG	n.d.	n.d.	+	n.d.	+
CGQ3	5.7	1.0	–	n.d.	–
CGQ2	16.3	2.9	–	n.d.	+
CGQ1	12.4	1.3	+	n.d.	+
BG4	13.4	0.9	+	+	+
BG3	7.7	0.5	+	+	+
BG2	8.9	0.5	–	n.d.	+
BG1	6.7	0.3	–	n.d.	–
GU1	4.8	0.2	+	n.d.	+
OB6	n.d.	n.d.	+	n.d.	+
OB17	n.d.	n.d.	+	n.d.	+
OB28	n.d.	n.d.	–	n.d.	–
OB68	n.d.	n.d.	–	n.d.	–
OB 71/72	n.d.	n.d.	–	n.d.	–
763C1	2.9	1.3	+	n.d.	n.d.
763C2	25.9	1.6	+	n.d.	n.d.
763C3	9.0	3.0	+	n.d.	n.d.
Early Aptian					
GAC6	3.87	1	+	n.d.	+
GAC5	2.64	1.1	–	n.d.	–
GAC4	0.97	0.4	–	n.d.	–
GAC3	0.87	0.6	–	n.d.	–
GAC2	5.16	1.0	+	n.d.	+
GAC1	3.54	0.9	+	n.d.	+
Toarcian					
VAL7	2.66	0.1	+	n.d.	n.d.
VAL6	n.d.	n.d.	+	n.d.	n.d.
VAL5	n.d.	n.d.	+	n.d.	+
VAL4	6.52	0.4	+	n.d.	+
VAL3	n.d.	n.d.	–	n.d.	–
VAL2	3.87	0.6	–	n.d.	–
VAL1	n.d.	n.d.	+	n.d.	+

PZE, photic-zone euxinia. +, Compound present; criterion is the presence of a peak at the appropriate retention time, from which the mass spectrum of Me,*i*-Bu maleimide can be obtained; this is dependent on both the compound's abundance and co-elution with other components.–, Compound not detected. n.d., not determined.

sulphur 0.42%) that is exposed at Longarone, north of Venice (palaeoceanographically in the Belluno Trough to the east of the Trento Plateau) and that was deposited at a palaeodepth of *c.* 1 km (locality details given by Jenkyns *et al.* (1985)). These compounds were also identified in the coeval 'Schistes Carton' of the Paris Basin at sites near Semécourt (a black shale with TOC 6.8%) and Colombotte (black shale with TOC 7.9%); unfortunately, the specific horizon of the 30 m thick Schistes Carton from which these samples were collected is not known. Finally, compounds **V**–**VII** are present in two dark grey laminated shales (TOC 11.5% and 11.9%) from the Middle Lias ϵ of the southern German Basin Posidonia Shale (Posido-

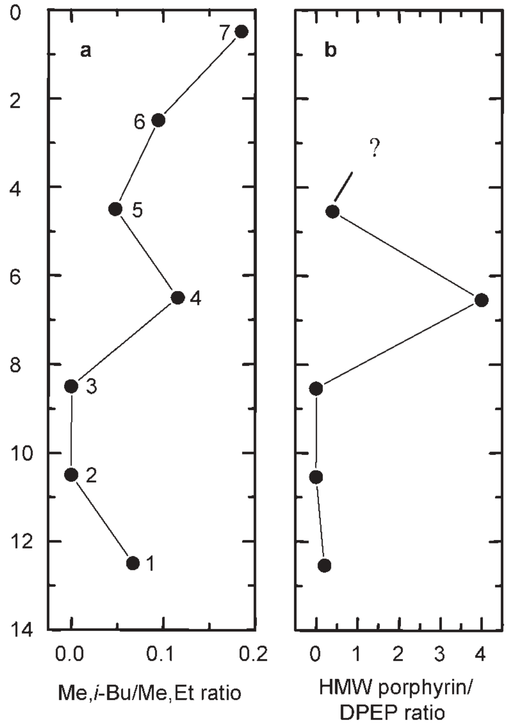

Fig. 3. Depth profiles (in metres from top of the black marl interval exposed in outcrop) of the Me,*i*-Bu/Me,Et maleimide ratio (**a**) and the abundance of high molecular weight (HMW) porphyrins (**V**–**VII**), inferred to derive from Bchl *d* or *e*, normalized against that of DPEP (**b**). The HMW porphyrin/DPEP ratios are not shown for VAL1 and VAL2 because of insufficient material for porphyrin analysis. Numbers beside data points refer to the sample names in Table 1 and the text.

nienschiefer, specifically, the Unterer Schiefer, horizon II/4 near Holzmaden; Eckardt *et al*. 1991; Waring 1991). The abundances of **V**–**VII** relative to DPEP are higher in the Schistes Carton and the Posidonia shale than in their southern European equivalents.

The Aptian OAE1a (Selli Event)

OAE1a, the earliest of the Cretaceous OAEs defined by Arthur *et al*. (1990), occurred during the early Aptian (Schlanger & Jenkyns 1976; Jenkyns 1980; Sliter 1989; Görür 1991; Bralower *et al*. 1994). Maleimide distributions were determined for black shales spanning the Livello Selli horizon at Gorgo a Cerbara, situated near Gubbio in the Umbria–Marche region of Italy (Cresta *et al*. 1989; Coccioni *et al*. 1992; Fig. 4). The Livello Selli is part of the Scisti a Fucoidi formation, which comprises cyclical interbeds of laminated, <10 cm thick black shales devoid of benthic foraminifera (Coccioni *et al*. 1992) and greenish grey to pink, homogeneous marls and limestones. Bulk carbonate and organic matter δ^{13}C values exhibit positive 2‰ shifts across the Livello Selli, as has been observed elsewhere at correlative horizons (Pratt & King 1986; Weissert 1989; Menegatti *et al*. 1998; Bellanca *et al*. 2002). Samples GAC1 (lowermost), 2 and 6 contain a variety of free maleimides, including Me,H, Me,Me, Me,Et, Me,*i*-Pr, Et,Et, Me,*n*-Pr, Me,*i*-Bu and Me,*n*-Bu components. The distributions in GAC3–5 differ in that they contain the majority of the above components but lack the specific Me,*i*-Bu maleimide. Consistent with the occurrence of Me,*i*-Bu maleimide, HMW porphyrins of inferred Chlorobiaceae origin are present in samples GAC1, 2 and 6 but not in GAC3, 4 and 5.

The Cenomanian–Turonian boundary OAE2 (Bonarelli Event)

The Cenomanian–Turonian (C/T) boundary OAE occurred *c*. 93.5 Ma ago (Gradstein *et al*. 1999) and is characterized by nearly synchronous organic-rich horizons around the world (Schlanger & Jenkyns 1976: Schlanger *et al*. 1987), particularly in the proto-North Atlantic, where organic carbon contents commonly exceed 30%. The duration of the event was probably less than 0.5 Ma (Kuhnt *et al*. 1997) and it was associated with a significant mass extinction across disparate marine realms (e.g. Kuhnt *et al*. 1986). The OAE is further defined by a positive carbon-isotope excursion recorded by carbonate (*c*. 2.5‰; Scholle & Arthur 1980; Arthur *et al*. 1988; Jenkyns *et al*. 1994), and marine and terrestrial organic carbon (*c*. 4‰; Arthur *et al*. 1988; Hayes *et al*. 1990; Hasegawa 1997; Tsikos *et al*. 2004). The difference between the inorganic and organic carbon-isotope records has been attributed to a decrease in $p\mathrm{CO}_2$ (and, thus, carbon-isotope fractionation by marine algae) as a result of extensive removal of carbon from the ocean–atmosphere reservoir (Arthur *et al*. 1988; Freeman & Hayes 1992; Kuypers *et al*. 1999). Thus, the C/T boundary OAE could have caused a brief period of global cooling (e.g. Jenkyns *et al*. 1994; Jenkyns 2003); none the less, this event occurred during a period characterized by generally very high global temperatures (e.g. Clarke & Jenkyns 1999). We investigated both free maleimides and those released by porphyrin oxidation in C/T boundary black shales from the North Atlantic, the Northern Tethys and an area off NW Australia (Fig. 5).

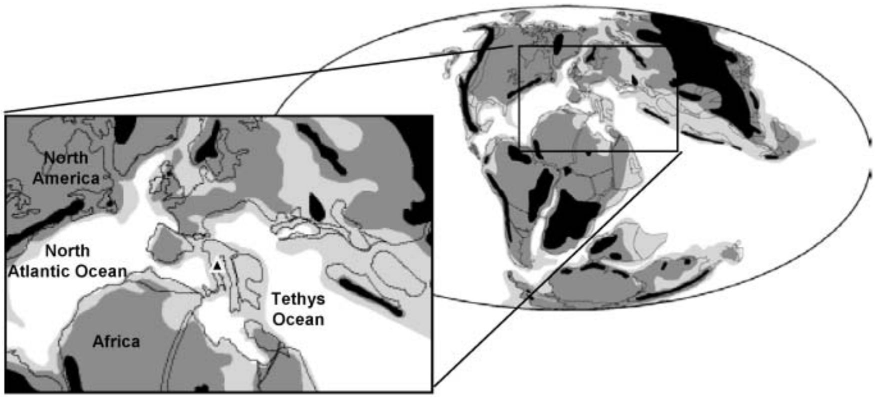

Fig. 4. Maps showing palaeogeography during the Aptian OAE1a (adapted from Scotese (2001)) and the location of the Gorgo a Cerbara site (▲).

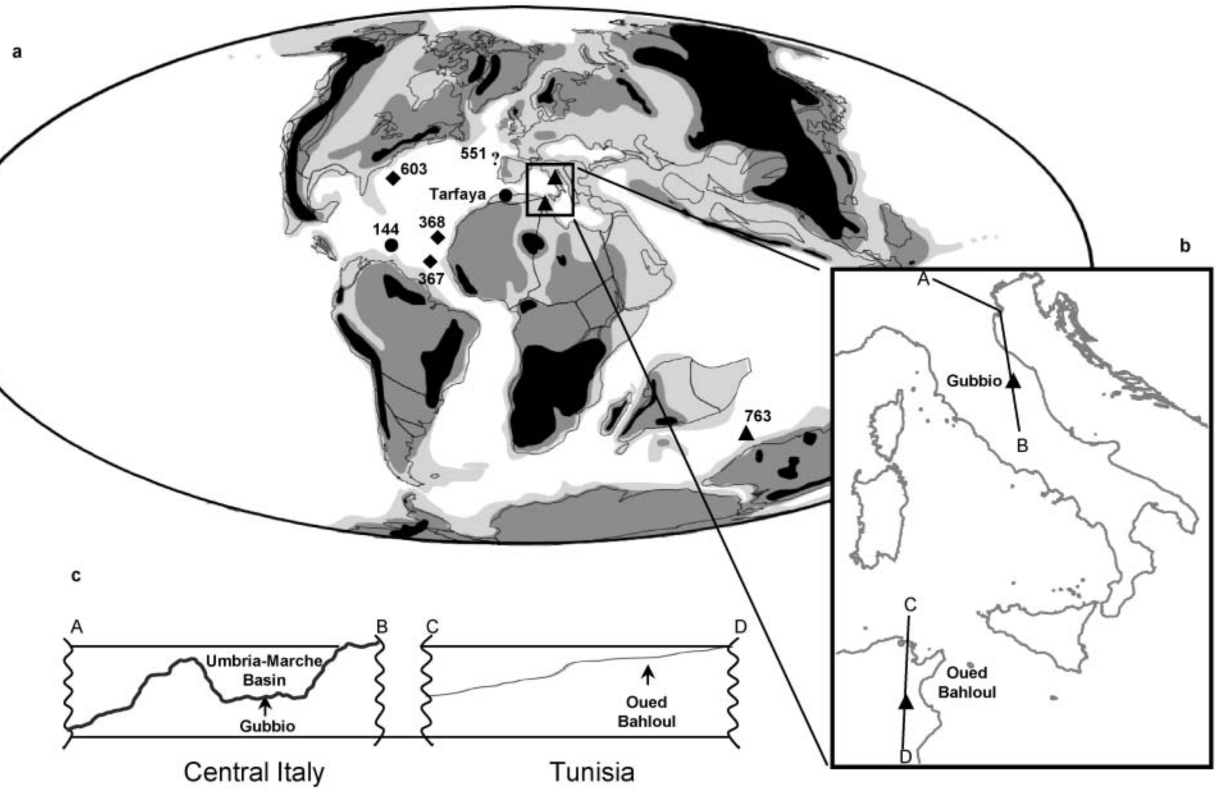

Fig. 5. Maps (**a** and **b**) and vertical profiles (**c**) showing palaeogeography during the Cenomanian–Turonian OAE (adapted from Farrimond (1987) and Scotese (2001)) and the locations of North Atlantic, Tethyan and Indian Ocean sites examined. Also shown are sites where previous workers examined the distributions of isorenieratene derivatives. ▲, Sites where Me,*i*-Bu is present but isorenieratene derivatives have either not been examined (Oued Bahloul and 763) or not found (Gubbio); ♦, sites where both Me,*i*-Bu maleimide and isorenieratene derivatives have been found; ●, sites where isorenieratene derivatives have been found but maleimides have not been examined. Site 551 is represented by a question mark because Me,*i*-Bu abundances are at the limits of detection, and therefore evidence for euxinic conditions in the photic zone is equivocal.

Northern Atlantic. Deep Sea Drilling Project (DSDP) Sites 367 and 368 are located on the Cape Verde Basin (Leg 41, Site 367, Core 18) and Cape Verde Rise (Leg 41, Site 368), situated off the coasts of Senegal and Gambia, respectively. Geochemical data on these cores have been extensively published (Brumsack & Thurow 1986; de Graciansky *et al*. 1986*b*; Herbin *et al*. 1986) and indicate that C/T boundary intervals from both cores are characterized by high TOC contents and hydrogen indices. From Site 367, core 18, two samples were analysed: Section 2, interval 91–95 cm (sample 367-2); and Section 3, interval 91–95 cm (sample 367-3). From Site 368, only one sample was examined: Core 63, Section 3, interval 120–125 cm (sample 368). Free maleimides are abundant in all three samples, with Me,Me, Me,Et, Et,Et, Me,*n*-Pr and Me,*i*-Bu components all present. Oxidation of the demetallated vanadyl porphyrins in sample 368 revealed the same components, albeit with somewhat different distributions. In all cases, maleimide distributions are dominated by the Me,Et component with lesser abundances of the Me,Me component. Consistent with the presence of maleimides of inferred Chlorobiaceae origin, cycloalkanoporphyrins inferred to derive from Bchls *d* and *e* were also observed (Fig. 1, **I**). To evaluate further the source assignments, GC–IRMS analyses were performed on 367-2 and 367-3 maleimides. Me,Et maleimide δ^{13}C values are −21.2‰ and −21.6‰ in the two samples, respectively, and Me,*i*-Bu maleimide δ^{13}C values are −7.8‰ and −7.5‰, respectively; this >12‰ difference reflects the reduced carbon-isotope fractionation associated with carbon assimilation via the reversed tricarboxylic acid (TCA) cycle and confirms a marine algal source for Me,Et maleimide and a green sulphur bacterial source for Me,*i*-Bu maleimide (e.g. Sirevag *et al*. 1977).

DSDP Site 603B (Leg 93) is situated on the continental rise off Cape Hatteras (NE USA), and sections of C/T boundary age are developed as black organic-rich claystones. The organic-rich sediments of the C/T interval (specific samples are: Core 34, Section 3, interval 65–70 cm (sample 603B-1); and Core 34, Section 5, interval 91–95 cm (sample 603B-2)) are characterized by moderate hydrogen indices (*c*. 400 mg hydrocarbon g^{-1} C), and organic matter is inferred to derive from a combination of unicellular algae (Rullkötter & Mukhopadhyay 1986) and bacterial matter (Farrimond *et al*. 1986). Such an assemblage is unusual as this site is typically dominated by terrigenous sources of organic matter (Tissot *et al*. 1980). Free maleimides were present in both samples and include the Me,H, Me,Me, Me,Et, Me,*i*-Pr, Et,Et, Me,*n*-Pr, Me,*i*-Bu and Me,*n*-Bu components. As with other C/T sediments, the Me,Et component was the most abundant maleimide in both samples.

DSDP Site 551 is located on the Goban Spur SW of Ireland, and the C/T boundary interval is represented by a thin black shale enclosed by white chalks. The shale is characterized by high TOC contents (*c*. 10% after Waples & Cunningham 1985) and contains a high proportion of siliceous material and almost no carbonate (de Graciansky *et al*. 1986*b*). It is thought to have been deposited at a depth of *c*. 1300 m (de Graciansky *et al*. 1986*a*). Only one sample of the black shale was analysed; free maleimides were recovered with the Me,Et component being most abundant, the Me,Me and Me,H components being present in subordinate abundances, and the Me,*i*-Pr, Et,Et, Me,*n*-Pr, Me,*i*-Bu and Me,*n*-Bu components occurring as very minor components.

The Tethyan Ocean. The Livello Bonarelli (Bonarelli Level) in the Gubbio area of Italy is an organic-rich *c*. 1 m thick bed consisting of radiolarian sand and interbedded laminated black shale (Arthur & Premoli Silva 1982; Schlanger *et al*. 1987). This bed lies immediately below the C/T boundary and effectively separates the Scaglia Bianca and Scaglia Rossa Formations. The Livello Bonarelli, which is carbonate-free and pyritic, has TOC contents >25% in some of its organic-rich levels (Tsikos *et al*. 2004). The organic matter, inferred to be of largely marine origin, occurs mainly as compressed amorphous wisps. Black shales from the Livello Bonarelli were collected from outcrops throughout the Gubbio area of Italy and their maleimide distributions were measured.

Two outcrop samples were analysed from the Gorgo a Cerbara (GCLB-1 and 2, the latter collected and described by Farrimond (1987)), situated by a road near Piobbico in the valley of the Torrente Candigliano (Cresta *et al*. 1989). Farrimond (1987) reported that the organic matter is composed entirely of amorphous material of low thermal maturity. The free maleimides of both samples include the Me,H, Me,Me, Me,Et, Me,*i*-Pr, Et,Et, Me,*n*-Pr, Me,*i*-Bu and Me,*n*-Bu components, with the Me,Et and Me,Me being the most abundant. The presence of Me,*i*-Bu maleimide in these (and following samples) is the first evidence for photic-zone euxinic conditions during deposition of the Livello Bonarelli.

Six samples, five of which were collected for this study (FOS1–5) and one (F1) that was collected previously (Farrimond 1987), were examined from the Livello Bonarelli, exposed in vertical outcrop near Fosto on the road between Piobbico and Secchiano (Cresta *et al*. 1989). The organic matter consists of amorphous, presumably marine, material with sparse palynomorphs and is thermally immature (Farrimond 1987; Farrimond *et al*. 1990). The free maleimides in FOS1 and F1 include the Me,H, Me,Me, Me,Et, Me,*i*-Pr, Et,Et, Me,*n*-Pr, Me,*i*-Bu and Me,*n*-Bu components. In contrast, maleimides in FOS2–5 lack the Me,*i*-Bu component. To confirm sources of maleimides, the porphyrins of F1 were combined into one fraction and oxidized. Like the free maleimides, those formed by porphyrin oxidation have a distribution consisting of the Me,H, Me,Me, Me,Et, Me,*i*-Pr, Et,Et, Me,*n*-Pr, Me,*i*-Bu and Me,*n*-Bu components.

Eight black shale samples were obtained from a 90 cm section of the Livello Bonarelli at an outcrop near the top of Monte Petrano on a dirt road SW of Cagli (MP1–8). Here, the Livello Bonarelli is characterized by black shales interbedded with siliceous radiolarian sandstones, clayey radiolarian sandstones and pyrite concretions. The free maleimides in MP2–6 and 8 include the Me,Et (most abundant), Me,Me, Me,H, Me,*n*-Pr, Et,Et, Me,*n*-Bu, Me,*i*-Pr and Me,*i*-Bu components. In contrast, MP1, 6 and 7 lack the Me,*i*-Bu maleimide. The Monte Petrano samples were further examined using GC–IRMS to determine the stable carbon-isotope composition of the Me,Et component (Fig. 6). δ^{13}C values range from −23 to −20‰, about 5‰ higher than δ^{13}C values obtained for bulk Ni-porphyrin fractions isolated from C/T boundary sediments (Greenhorn Formation) of the Cretaceous Western Interior Seaway (Hayes *et al*. 1990). Potentially, this difference reflects lower [$CO_{2(aq)}$] and/or higher algal growth rates in the Tethys than in the Cretaceous Western Interior Seaway (e.g. Bidigare *et al*. 1997). However, the two records are similar in that they both exhibit the positive carbon-isotope excursion commonly observed in C/T boundary sediments. Our record, both in terms of absolute values and temporal trends, is also consistent with inorganic and organic carbon-isotope analyses of the Livello Bonarelli (Tsikos *et al*. 2004). As δ^{13}C values of Me,Et maleimide are easy to determine as a result of the ease of maleimide preparation and the lack of significant co-elution during GC, this compound could be useful in chemostratigraphy where other diagnostic biomarkers are absent.

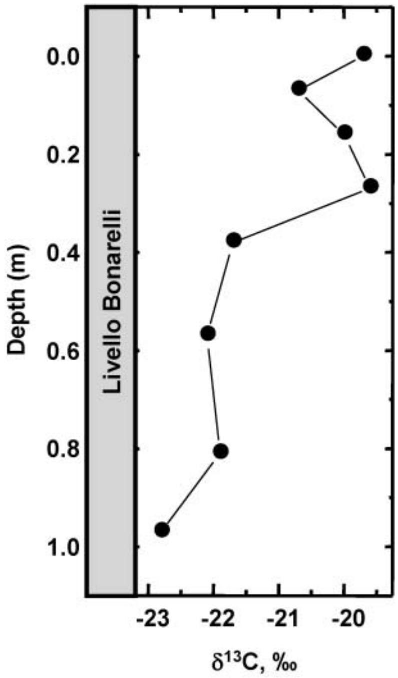

Fig. 6. Depth profile showing Me,Et maleimide δ^{13}C values through the Livello Bonarelli cropping out at the Monte Petrano section in the Gubbio region of Italy.

Three samples (CGQ1–3) were analysed from the north end of a quarry complex in the Contessa Gorge NW of Gubbio. An additional sample (CG1) collected earlier from the same locality (Farrimond 1987) was also analysed. The organic matter in CG1 is amorphous, excepting uncommon woody fragments, and is slightly more thermally mature than the organic matter in the more northern sites (Farrimond 1987; Farrimond *et al*. 1990). CGQ1 and CG1 both contain free Me,*n*-Pr and Me,*i*-Bu maleimides as well as a suite of the more common maleimides; in contrast, CGQ2 and 3, although characterized by similar distributions, did not contain the Me,*i*-Bu component.

The top 90 cm of the Bonarelli Horizon is exposed in the Bottaccione Gorge 3 km NE of Gubbio. Four samples (BG1–4) were collected, one each from four black bands interbedded with radiolarian-rich siliceous material. A fifth sample, GU1, collected from the same site by Farrimond (1987) was also analysed. The free maleimides of GU1, BG3 and BG4 had similar distributions, with the Me,H, Me,Me, Me,Et, Me,*i*-Pr, Et,Et, Me,*n*-Pr, Me,*i*-Bu and Me,*n*-Bu components present. Similar distributions were obtained by oxidation of the combined demetallated nickel and vanadyl porphyrin fractions of BG3 and BG4. In contrast, the free maleimides from BG1 and BG2 consist of the Me,H, Me,Me and Me,Et components with relatively low abundances of the Et,Et and Me,*n*-Pr maleimides. Me,*i*-Bu and Me,*n*-Bu maleimides were not detected.

The Bahloul Formation, outcropping near Oued Bahloul in NE Tunisia, is a 20–50 m unit composed of interbedded bituminous marls and limestones. The sediments were deposited in relatively deep water (Herbin *et al*. 1986; Schlanger *et al*. 1987), and the organic matter in the bituminous beds is mainly of marine origin with minor terrigenous input (Farrimond *et al*. 1990). Hydrogen indices range from 260 to 670 mg hydrocarbon g^{-1} TOC (Herbin *et al*. 1986). Five samples were analysed (OB 71/72, 68, 28, 17, 6). The free maleimides in sample OB17 and OB6 include the Me,H, Me,Me, Me,Et, Me,*i*-Pr, Et,Et, Me,*n*-Pr, Me,*i*-Bu and Me,*n*-Bu components. However, the Me,*i*-Bu and Me,*n*-Bu components were not observed in OB71/72, OB68 and OB28.

Exmouth Plateau, off Western Australia, Indian Ocean. The Exmouth Plateau, considered as formerly part of the eastern extremity of the Tethys, is situated on the NW continental margin of Australia (Fig. 5). Samples were collected from Ocean Drilling Program (ODP) Hole 763C from two thin layers of black shale, 4 cm and 12 cm thick, separated by green mottled claystone (Section 2R-1, interval 63–66 cm (sample 763C1) from the 4 cm layer; Section 2R-1, interval 29–33 cm (sample 763C2); Section 2R-1, interval 23–26 cm (sample 763C3); and Section 2R-1, interval 20–23 cm (sample 763C4) from the 12 cm layer). The sediments are thought to have been deposited at a palaeo-depth of 500–1000 m (Haq *et al*. 1992). Previous analyses of similar samples revealed TOC contents exceeding 25% (Rullkötter *et al*. 1992), whereas stratigraphically equivalent sediments at Site 762, 84 km to the north, do not exceed 2% (Haq *et al*. 1990). Organic matter, consisting of structurally degraded bituminite, is inferred to be of marine origin, has hydrogen indices of *c*. 450 mg hydrocarbon g^{-1} C_{org}, and is thermally immature (Rullkötter *et al*. 1992).

Sample 763C1 from the (lower) 4 cm thick black shale contains free Me,H, Me,Me, Me,Et, Me,*i*-Pr, Et,Et, Me,*n*-Pr, Me,*i*-Bu and Me,*n*-Bu maleimides. As is commonly observed, the Me,Et and Me,Me maleimides are the most abundant, but Et,Et maleimide is also present in significant relative abundances. Samples 763C2 and 763C3 from the (upper) 12 cm thick layer contain the same free maleimides as sample 763C1 with the exception of the Me,*n*-Bu component, which is absent. Differences in maleimide distributions include relatively higher Me,*i*-Bu abundances and lower Et,Et abundances in samples 763C2 and 763C3 compared with 763C1. In sample 763C4, only the Me,H, Me,Me, Me,Et, Et,Et and Me,*n*-Pr components were detected.

Discussion

All of the porphyrin and maleimide data are summarized in Table 1 and show evidence for photic-zone euxinic conditions during all three OAEs investigated.

Toarcian

The first evidence for the presence of Chlorobiaceae and photic-zone euxinic conditions during the Toarcian OAE was obtained from the presence of molecular fossils of the pigments isorenieratene and chlorobactene, biomarkers for the green and brown strains of green sulphur bacteria, respectively (Imhoff 1995), in the SW German Posidonienschiefer (Schouten *et al*. 2000). Our results confirm these observations. Moreover, the presence of green sulphur bacterial biomarkers in sediments from the Belluno Basin and Marche–Umbria (Valdorbia) extends the evidence for photic-zone euxinic conditions to southern Europe and, critically, the margins of the Tethyan Ocean. None the less, photic-zone euxinic conditions were probably neither as widespread nor as prolonged on the Tethyan margin as in the more northern epicontinental seas. Some Valdorbia samples contain no green sulphur bacterial biomarkers, and high-molecular-weight porphyrin to DPEP ratios are lower in Italian sections than in equivalent French and German black shales. These geographical variations in water-column redox conditions probably affected organic carbon preservation; indeed, southern European and north African sites (Italy, Greece, Tunisia) are characterized by lower organic carbon contents than northern European sites (Jenkyns 1985, 1988; Baudin *et al*. 1990), and marine organic matter in the Belluno Trough Toarcian black shales is degraded (Farrimond *et al*. 1989), suggesting at least intermittent oxygenation of the water column during deposition

Photic-zone euxinic conditions also apparently changed during the OAE. The relative abundances of Me,*i*-Bu maleimide in the Marche–Umbria Basin increase up-section (Fig. 3) as do abundances of diagnostic isorenieratene and chlorobactene derivatives (Schouten *et al*. 2000), with notably higher abundances occurring in the *falciferum* ammonite zone than in the *tenuicostatum* zone. This increase suggests that the duration of euxinic episodes in near-surface waters increased or that euxinic waters shoaled during the event, perhaps reflecting stabilization of the water column, and it is consistent with models in which black-shale deposition is caused by the impingement of a shoaling oxygen-minimum zone (as a result of either enhanced productivity or marine transgression) onto continental margin sediments (Jenkyns 1985, 1988; Jenkyns *et al*. 2001). In such a model, only during times of the most intense productivity would euxinic conditions have extended into the photic zone and resulted in the accumulation of green sulphur bacterial biomarkers. This model is also consistent with nitrogen-isotope evidence from Toarcian black shales in Italy and the UK indicating that, at times, denitrification rather than sulphate reduction was the dominant process by which organic matter was oxidized in the water column (Jenkyns *et al*. 2001).

Aptian

There is no previous evidence for photic-zone euxinic conditions during Aptian OAE1a; here, however, a combination of maleimide and porphyrin data indicates that such conditions did occur at least periodically during deposition of the Livello Selli. Given that only one locality was investigated, it is difficult to interpret these observations in the context of Aptian oceanography; however, the variable occurrence of biomarkers for green sulphur bacteria, similar to that observed in the Toarcian Valdorbia section, indicates that photic-zone euxinic conditions were episodic and perhaps related to a fluctuating oxygen-minimum zone.

Cenomanian–Turonian boundary

Previous work has clearly revealed that photic-zone euxinia was a persistent and important characteristic of the North Atlantic during the C/T boundary OAE. Sinninghe Damsté & Köster (1998) detected isorenieratene in the C/T boundary horizons at DSDP Sites 144, 367 and 368, and in a core from Morocco (Tarfaya). These results were confirmed and extended by Kuypers *et al*. (2002), who determined that these conditions also preceded the OAE. Sinninghe Damsté & Köster (1998) did not detect isorenieratene derivatives at DSDP Site 603B; however, subsequent work (Kuypers 2001) revealed that isorenieratene is indeed present in these sediments, albeit at significantly lower concentration. Sinninghe Damsté & Köster (1998) also did not detect diagnostic isorenieratene derivatives at DSDP Site 551 nor in the Livello Bonarelli.

Consistent with these results, we observed Me,*i*-Bu maleimide in C/T boundary sediments of DSDP Sites 367, 368 and 603B and the Oued Bahloul (Tunisia). However, we also detected Me,*i*-Bu maleimide in C/T boundary sediments from DSDP Site 551 and in the Livello Bonarelli, where diagnostic isorenieratene derivatives are absent; we ascribe this discrepancy to a variety of factors. First, aryl isoprenoids, degradation products of isorenieratene but also of β-carotene and, therefore, not diagnostic for green sulphur bacteria (Koopmans *et al*. 1996), are present in Livello Bonarelli samples. Thus, diagnostic derivatives of isorenieratene could have been thermally degraded whereas more stable maleimides and non-diagnostic aryl isoprenoids have been preserved. Second, the occurrence of Me,*i*-Bu maleimide in the Livello Bonarelli varies locally within the deposit, suggesting that photic-zone euxinic conditions were episodic. Third, because Me,*i*-Bu maleimide is present in only low concentrations in the DSDP Site 551 shale we are reluctant to interpret its significance. Also, such low abundances indicate that photic-zone euxinic conditions were not pronounced there; thus, all biomarkers for Chlorobiaceae are expected to be present in low abundances, compounding difficulties associated with their detection. Despite these relatively minor discrepancies, the widespread occurrence of Me,*i*-Bu, coupled with the detection of certain high-molecular-weight porphyrins and, in the case of DSDP Site 367 samples, high Me,*i*-Bu δ^{13}C values, confirms previous conclusions that photic-zone euxinic conditions occurred in the southern North Atlantic during the C/T boundary OAE. Our work extends these results by identifying evidence for a sulphidic water column in the photic zone of water masses in the Tethyan Ocean (Livello Bonarelli and Oued Bahloul) extending to the present-day Indian Ocean (Exmouth Plateau), the first evidence from the C/T boundary OAE for photic-zone euxinic conditions in the Southern Hemisphere.

The recognition of photic-zone euxinic conditions in a number of our samples and those of previous workers is of importance for understanding the chemistry of the ocean during the C/T boundary OAE. All of the analysed organic-rich shales exhibit millimetre-scale lamination, implying a lack of bioturbation by benthonic animals and, hence, bottom-water anoxia. Where the same samples show molecular evidence for green sulphur bacteria, it is apparent that free hydrogen sulphide was present in the shallow water column. Although intervening levels of the water column could conceivably have been oxygenated, the most likely hypothesis envisages a stratified water column devoid of oxygen from the photic zone to the sea floor (as proposed, for example, by Sinninghe Damsté & Köster (1998) and Kuypers *et al*. (2002)). The origin of such an extensive anoxic–euxinic layer, apparently best developed in peri-equatorial Atlantic DSDP sites, could well lie in enhanced plankton productivity given that equatorial regions today (and presumably in the past) are sites of vigorous upwelling with high nutrient availability in near-surface waters. Consistent with this explanation, Kuypers *et al*. (2002) suggested that a dramatic increase in TOC contents, isorenieratene derivative abundances and biomarker δ^{13}C values at Site 367 during the C/T boundary OAE reflects an increase in primary productivity. However, the presence of green sulphur bacterial biomarkers prior to the C/T boundary (Kuypers *et al*. 2002) suggests that euxinic conditions in the photic-zone anoxia were also related to the presence of stagnant water masses trapped by the geometry of the Cretaceous Atlantic. In contrast, for ocean regions in which organic-rich sediments occur on topographic highs but nearby deeper sites are characterized by low organic carbon contents (e.g. DSDP Sites 551 and 763, assuming their stratigraphic records are complete), it seems unlikely that the entire water column was persistently anoxic. Instead, the occurrences of Me,*i*-Bu maleimide and enhanced TOC contents in C/T boundary sediments from Sites 551 and 763 probably record regional extension of the oxygen-minimum zone. Thus, we propose that the Cretaceous North Atlantic was a stagnant ocean and an increase in primary productivity at the C/T boundary resulted in the expansion of anoxic conditions, represented by more intense photic-zone euxinic conditions in the southern North Atlantic (Kuypers *et al*. 2002) and incursion of euxinic waters into Tethyan and northernmost Atlantic shallow waters. Given this model, sporadic biomarker evidence for photic-zone euxinic conditions in the Livello Bonarelli of the Umbrian Apennines could reflect the important role of geography in moderating expansion and contraction of anoxic conditions onto the Tethyan margin. Similarly, temporal variations in local productivity probably also influenced the extent of anoxic conditions and are responsible for vertical variations in biomarker evidence for photic-zone euxinia.

Significance for interpreting causes of OAEs

There are several possible explanations for the occurrence of Chlorobiaceae biomarkers in ancient sediments. First, they could reflect a completely euxinic water column from the sea floor to at least the lower part of the photic zone, as in the Black Sea (Sinninghe Damsté *et al*. 1993). This palaeoceanographic configuration has been invoked for DSDP Sites 367 and 368 during the C/T OAE (Kuypers *et al*. 2002) on the basis of the co-occurrence of isorenieratene with trace-metal indicators of sedimentary anoxia. Importantly, this is the only situation (e.g. stratified fjords, Black Sea) where green sulphur bacteria are found in modern settings.

Second, Chlorobiaceae could have been present in a productivity-driven oxygen-minimum zone; organic matter would have been preserved in such conditions if the oxygen-minimum zone impinged on the sediments (e.g. continental shelf sites and topographic highs). Free hydrogen sulphide has been observed in the oxygen-minimum zones in the Peru upwelling region (Dugdale *et al*. 1977) and in the Indian Ocean (Ivanenkov & Rozanov 1961), but green sulphur bacteria have never been found in such a setting nor have their photosynthetic pigments been found in underlying sediments; thus, such an oxygen-minimim zone in Mesozoic oceans must have been more persistently euxinic than those found in the modern ocean.

Third, Chlorobiaceae biomarkers in abyssal marine sediments could have had an allochthonous source. For example, some organic-rich sediments have been attributed to redeposition of slope sediments; thus, the occurrence of Me,*i*-Bu maleimide in distal sediments would not necessarily record the occurrence of photic-zone euxinic conditions in the overlying water column.

It is unlikely that a single explanation accounts for the occurrence of Me,*i*-Bu maleimide (and other Chlorobiaceae biomarkers) at all the investigated sites. Certainly, the allochthonous biomarker hypothesis seems to be an unsatisfactory explanation for the occurrence of Me,*i*-Bu maleimide in sediments deposited on topographic highs and where nearby sites are characterized by low organic carbon contents (e.g. DSDP Sites 551 and 763, C/T boundary OAE); in these areas, an intensified oxygen-minimum zone seems to be the most logical explanation. However, an intensified oxygen-minimum zone alone seems inadequate to explain the very high abundances of Chlorobiaceae biomarkers and high TOC contents in deep-ocean sediments.

These results must be interpreted in the context of their specific geological settings, but they do confirm and expand on previous observations that a sulphidic water column was an important characteristic during all three major OAEs of the Jurassic and Cretaceous periods and reinforce previous work (e.g. Jenkyns 1999; Jones & Jenkyns 2001) suggesting similarities in their causal mechanisms. The results also implicate the role of anoxia as an important control on the occurrence of organic-rich units in Mesozoic sediments (e.g. de Graciansky *et al*. 1984). Photic-zone euxinic conditions, whether associated with a fully stratified water column or an oxygen-minimum zone, would have facilitated the export of organic matter from the surface ocean and enhanced the preservation of organic matter; this would have complemented associated productivity increases and fostered the sequestration of organic matter in marine sediments.

Conclusions

It is becoming increasingly apparent that photic-zone euxinic conditions were a characteristic of many ancient marine systems in which organic carbon-rich sediments were deposited. Biomarkers for Chlorobiaceae have been recovered from the Black Sea (Sinninghe Damsté *et al*. 1993), Plio-Pleistocene Mediterranean sapropels (Passier *et al*. 1999), and numerous sediments spanning the Phanerozoic (Summons & Powell 1986; Koopmans *et al*. 1996, and references therein; Joachimski *et al*. 2001). This work expands these observations by further illustrating the association of photic-zone euxinic conditions with OAEs and reveals the utility of maleimide and porphyrin distributions in palaeoceanographic investigations. Me,*i*-Bu maleimide, which, based on structural grounds and its carbon-isotope composition (in C/T sediments), derives from Bchl *d* or *e* and is an indicator for photic-zone euxinia, occurs in sediments deposited during the early Toarcian, early Aptian and Cenomanian–Turonian boundary oceanic anoxic events. Although the causes of photic-zone euxinia probably varied among the sample sites and time periods studied, the presence of hydrogen sulphide at shallow-marine levels appears to reflect a stratified water column or an intense oxygen-minimum zone modulated by productivity variations.

The authors gratefully acknowledge the donors of the Petroleum Research Fund (PRF AC-2 042402) for a grant to J.R.M., the NERC for a grant to J.R.M. and H.C.J., and the Nuffield Foundation for a grant to R.D.P. The Ocean Drilling Program provided samples from the Atlantic and Indian Oceans. We would also like to thank J. Carter for analytical support, and M. Sephton and T. Bralower for very useful suggestions that improved the final version of this paper.

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Received 13 May 2003; revised typescript accepted 19 November 2003.
Scientific editing by Anthony Cohen