



## Reconstruction of water column anoxia in the equatorial Atlantic during the Cenomanian–Turonian oceanic anoxic event using biomarker and trace metal proxies

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### ABSTRACT

The occurrence of the biomarker lycopane and the enrichment patterns of redox sensitive trace metals in black shales from Demerara Rise (western tropical Atlantic) reveal that bottom waters were anoxic during the upper Cenomanian and lower Turonian at this location. Bottom waters were clearly oxygen depleted already before oceanic anoxic event 2 (OAE-2), and continued to be so afterwards. Furthermore, the presence of fossil derivatives of isorenieratene and chlorobactene, pigments derived from green sulfur bacteria, demonstrates that the waters at the base of the photic zone occasionally contained sulfide (i.e., were euxinic). Before and after OAE-2, low concentrations of derivatives of these pigments are present, while much higher concentrations occur within the OAE-2 section. Stratification of the water column must have been strong to sustain euxinic conditions in the photic zone for prolonged periods. A substantial drop in the concentrations of isorenieratene and chlorobactene derivatives demonstrates that this stratification temporarily broke down during OAE-2. A simultaneous decrease in sea surface temperatures suggests that local ventilation was instrumental in this re-oxygenation event. A rapid decrease in seawater derived trace metal burial rates at Demerara Rise, occurring in phase with the onset of the anoxia related to OAE-2, suggests an approximately synchronous onset of OAE-2 in the proto-North Atlantic.

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### 1. Introduction

Recurring episodes of extensive deposition of marine, organic-rich, fine-grained, laminated, silicilastic sediments (so-called black shales) are characteristic for the mid-Cretaceous. The black shales deposited during this time are often enriched in certain trace metals (TMs) (Goldschmidt, 1954, see Brumsack, 2006 for a recent overview). These episodes of increased organic matter deposition are referred to as oceanic anoxic events (OAEs) and are primarily known from the Cretaceous (Schlanger and Jenkyns, 1976), the Jurassic (Jenkyns, 1985) and the Permian/Triassic boundary (Grice et al., 2005; Hays et al., 2007).

One of the most extreme Cretaceous OAEs is OAE-2 at the Cenomanian–Turonian boundary (93.5 My, Gradstein et al., 2004; Sageman et al., 2006), also known as the Bonarelli event. OAE-2 is characterized by a large positive carbon isotope excursion (Arthur et al., 1988) both in marine carbonates (up to 2.5‰) and organic

matter (OM) (up to 6‰) (Kuypers et al., 2002b; Tsikos et al., 2004; Erbacher et al., 2005). This positive excursion is most likely the result of the preferential removal of <sup>12</sup>C associated with the burial of OM, leaving the remaining carbon reservoir enriched in <sup>13</sup>C.

The high concentrations of organic carbon in OAE-2 black shales have been attributed to both enhanced preservation of OM by anoxic water column conditions, possibly related to a slowdown in oceanic circulation (e.g. Bralower and Thierstein, 1987; Sinninghe Damsté and Köster, 1998) and to increased productivity leading to higher OM accumulation rates (Schlanger and Jenkyns, 1976). Increased productivity will also lead to an enhanced oxygen demand for mineralization, which may overwhelm the oxidation potential of the ocean and cause water column anoxia (e.g. Schlanger and Jenkyns, 1976; Kuypers et al., 2002b). At present, the high OM content in OAE-2 black shales is therefore generally considered to be the result of a combination of increased productivity and enhanced preservation by anoxia (e.g., Kuypers et al., 2002b; Kolonic et al., 2005).

Several factors might have played a role in creating the specific environmental conditions that promoted the occurrence of OAEs during the mid-Cretaceous. Most noticeably, the climate was extraordinarily warm at the time, probably due to high atmospheric CO<sub>2</sub> concentrations caused by increased volcanism (Arthur et al., 1985; Bice et al., 2006; Sinninghe Damsté et al., 2008; Turgeon and Creaser,

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2008). The resulting warmer ocean waters possibly gave rise to halothermal rather than thermohaline ocean circulation (Horne, 1999), consequently producing lower deep water ventilation rates, as warm water contains less oxygen. Moreover, large scale deposition of evaporates in the South Atlantic during the Early Cretaceous (Wortmann and Chernyavsky, 2007) would have changed the salt balance of the ocean, creating less saline water and therefore slower circulation (Hay et al., 2006). In addition, the increased seafloor spreading, submarine volcanism and hydrothermal activity at this time would have had a strong effect on ocean circulation and TM cycling (Hays and Pitman, 1973; Paytan et al., 2004).

Specific biomarkers can be powerful tools for the reconstruction of bottom water anoxia and photic zone euxinia. The lycopane to *n*-alkane ratio ((lycopane + *n*-C<sub>35</sub>)/*n*-C<sub>31</sub>), for instance, can be used as an indicator for the palaeoxicity of the sediment/water interface (Sinninghe Damsté et al., 2003). Although the primary biological sources of lycopane are still unclear, this molecular compound is predominantly preserved in anoxic settings. The lycopane to *n*-alkane ratio, (lycopane + *n*-C<sub>35</sub>)/*n*-C<sub>31</sub>, can therefore be used as an indicator for the palaeoxicity of the sediment/water interface (Sinninghe Damsté et al., 2003). (Lycopane + *n*-C<sub>35</sub>)/*n*-C<sub>31</sub> ratios observed in sediments deposited in anoxic waters in the present-day oxygen minimum zone (OMZ) of the Arabian Sea are around 1 (Sinninghe Damsté et al., 2003). In contrast, sediments deposited in oxic bottom waters, above and below the OMZ, have ratios  $\leq 0.5$ . Elevated lycopane ratios in the sediments, therefore, demonstrate bottom waters were anoxic. Furthermore, the presence of isorenieratene or its diagenetic derivatives, indicates that at least the base of the photic zone (typically 50–150 m below sea surface; Hedgpeth, 1957) was euxinic, i.e., the water column contained free sulfide and no oxygen (Summons and Powell, 1986; Koopmans et al., 1996; Sinninghe Damsté and Köster, 1998; Kuypers et al., 2002b; Pancost et al., 2004). Isorenieratene is a carotenoid specific for Chlorobiaceae, the brown strain of the green sulfur bacteria. These photosynthetic bacteria are strict anaerobes and require both light and free sulfide, and can therefore only survive when part of the photic zone is euxinic. The presence of chlorobactene or its diagenetic derivatives points to an even shallower depth of photic zone euxinia, as chlorobactene occurs predominantly in the green coloured strain of green sulfur bacteria, which requires a higher light intensity than the brown strain (Van Gernerden and Mas, 1995). These compounds are most likely autochthonous when found in sediments, since both these aromatic carotenoids are relatively labile and rarely survive transport over longer distances (Sinninghe Damsté et al., 2001; Sinninghe Damsté and Hopmans, 2008). At several North Atlantic sites the presence of these carotenoids established that euxinia reached all the way into the photic zone during OAE-2 (Sinninghe Damsté and Köster, 1998; Kuypers et al., 2002b; Kuypers et al., 2004. See Fig. 2 for occurrences of isorenieratene and derivatives). An upward excursion of euxinic conditions in the oceans, and subsequent S out-gassing into the atmosphere, is thought to have contributed to the Cenomanian–Turonian, Permian–Triassic and Late Devonian extinction events (Grice et al., 2005; Kump et al., 2005; Hays et al., 2007). During the Cenomanian–Turonian, an estimated amount of  $8 * 10^{16}$  kg SO<sub>2</sub> along with a significant amount of H<sub>2</sub>S was introduced by plume-related volcanism (e.g. the formation of the Caribbean plateau, Kerr, 1998), which could have advanced the expansion of euxinic conditions (Sinninghe Damsté and Köster, 1998).

Records of redox sensitive TMs are useful in elucidating redox conditions of oceanic bottom waters. Generally, some redox sensitive elements (e.g., V and U) are immobilized under anoxic, non-sulfidic conditions and therefore enriched in the sediment during anoxia (Calvert and Pedersen, 1993; Brumsack, 2006). Other elements, in contrast, are mobile under anoxic, non-sulfidic conditions (e.g., Mn) and as a result become depleted in sediments deposited during anoxia. In addition, under euxinic conditions, the abundantly present

sulfide immobilizes chalcophile TMs (mainly Cu, Zn, and Cd, but also Co, Fe, and Ni) as metal sulfides, most likely by co-precipitation in pyrite (Huerta-Diaz and Morse, 1992; Tribouillard et al., 2006). Consequently, sediments deposited under euxinic conditions are usually enriched in these elements. Both Mo and As become enriched under anoxic and sulfidic conditions.

Despite intensive studies, causes and effects of OAEs are still poorly understood. To reconstruct the development of bottom water, water column and potentially photic zone anoxia during OAE-2 at Demerara Rise, we used both biomarker and TM proxies. Demerara Rise is a submarine plateau located off the coast of Suriname (Figs. 1 and 2) with excellently preserved biomarker records (e.g. Forster et al., 2004). These sediments are thus uniquely suited to compare biomarker and TM records.

## 2. Geological setting and stratigraphy

Demerara Rise is a NW–SE oriented, gently dipping submarine plateau located off the coast of Suriname (Fig. 1). During the Cenomanian–Turonian, Demerara Rise was situated in the tropics (~5°N) in the proto-North Atlantic (Fig. 2). Sediments used for this study were collected during Ocean Drilling Program (ODP) Leg 207 at Site 1260, holes A and B (Erbacher et al., 2004a). The recovered Albian to Pleistocene sequence contains a total of 509 m of sediments and includes the Cenomanian–Turonian boundary. The Cretaceous sediments at Site 1260 were most likely deposited at intermediate water depth, probably between 500 and 1500 m (Erbacher et al., 2004b; Saganuma and Ogg, 2006) but certainly below the storm wave base (200 m). The Cenomanian–Coniacian sediments of this sequence are typically laminated, dark, carbonaceous, calcareous mud- to marlstones (black shales) occasionally interbedded with sandy limestones and thin calcareous layers (Erbacher et al., 2004a). Most noticeable are a 25 cm thick carbonate layer (here referred to as the lower carbonate layer) at 425.91–425.66 m composite depth (mcd) and another thick carbonate bed above the OAE-2 interval (the upper carbonate layer, at 424.3–423.9 mcd). Both beds consist of almost pure calcium carbonate most likely of diagenetic origin (Hetzl et al., 2009), with TOC (total organic carbon) values below 1% (Fig. 3B). Apparently, the carbonate compensation depth was never shallow enough to cause appreciable carbonate dissolution at Demerara Rise.

OM from Demerara Rise is thermally immature and well preserved, mostly of marine origin with organic carbon contents of up to 20% (Erbacher et al., 2004a,b; Forster et al., 2004; Meyers et al., 2006). Both TOC and sulfur concentrations are higher than levels generally encountered in OAE-2 black shales (Brumsack, 2006; Hetzel et al., 2009). Although TOC content is already high throughout the entire sequence (with the exception of some carbonate beds), there is a clear increase from, on average, 8 to 16% TOC at the onset of OAE-2 (Forster et al., 2007) (Fig. 3B).

Stratigraphy is based on shipboard results, chemostratigraphy and nannofossil biostratigraphy (Erbacher et al., 2004a; Hardas and Mutterlose, 2006; Forster et al., 2007). The exact stratigraphic position of OAE-2 was determined by the positive isotope excursion in bulk organic carbon ( $\delta^{13}\text{C}_{\text{org}}$ ) accompanying OAE-2 (Fig. 3A) (cf. Erbacher et al., 2005; Forster et al., 2007). The OAE-2 carbon isotope excursion can be divided into three phases (cf. Kuypers et al., 2002a; Forster et al., 2007). The onset of the excursion up to the first isotopic maximum, a positive shift in  $\delta^{13}\text{C}_{\text{org}}$  values of approximately 6‰, is termed phase A (426.41–426.11 mcd). Phase A is equivalent to the “first build-up” phase used for the proposed European reference section at Eastbourne (Paul et al., 1999). Phase B (426.11–425.27 mcd) contains a decline of 2.5‰ in  $\delta^{13}\text{C}_{\text{org}}$  values, followed by a second increase of almost 3‰ and ends with an interval of steadily high  $\delta^{13}\text{C}_{\text{org}}$  values (at ca. –22‰). Phases A and B together make up OAE-2. By comparing Site 1260 to the well-dated Pueblo record of Sageman et al. (2006) an approximate duration of 550 kyr is established for OAE-2 at this site. During phase C

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