Short-term euxinia coinciding with rotaliporid extinctions during the Cenomanian-Turonian transition in the middle-neritic eastern North Atlantic inferred from organic compounds

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ABSTRACT
Oceanic anoxic event 2 (OAE2), which occurred during the Cenomanian-Turonian (C-T) transition and lasted 1 m.y., is characterized by a positive global carbon isotopic excursion and stepwise extinctions in marine biota. To examine temporal variations in the dissolved oxygen content of the water column, shallow-marine C-T sediments from northern Spain were analyzed for concentrations of dibenzothiophenes, which are indicators of euxinic depositional environments, and 2,3,6-trimethylarylisoprenoids, which probably indicate photic-zone euxinia. The positive excursion in δ13C values of carbonates is accompanied by short-term (103–104 yr) and long-term (105 yr) increases in dibenzothiophene and 2,3,6-trimethylarylisoprenoid concentrations, suggesting that the bottom water and photic zone of the eastern marginal sea of the North Atlantic Ocean were euxinic. Two of the short-term increases in organic compound concentrations took place just after the last occurrence of the planktonic foraminifers Rotalipora greenhornensis and R. cushmani. These transient maxima indicate that the extinction of both planktonic foraminifers was due to short-term OAEs lasting 103–104 yr.

INTRODUCTION
The mid-Cretaceous was generally a time of extraordinarily warm climates, high sea levels, and high atmospheric pCO2 levels (e.g., Schlanger et al., 1987; Haq et al., 1987; Clarke and Jenkyns, 1999; Huber et al., 2002; Wilson and Norris, 2001). Certain intervals during the mid-Cretaceous were characterized by extensive deposition of organic-carbon–rich black shale across a wide range of marine settings. Because deposition of black shale is favored in oxygen-limited to oxygen-free (anoxic) environments, these intervals have been interpreted as oceanic anoxic events (OAEs; Schlanger and Jenkyns, 1976). The most prominent and widespread of the Cretaceous OAEs spans the Cenomanian-Turonian (C-T; ca. 93.5 Ma) boundary and is called OAE2, or the C-T boundary event. The beginning of OAE2 is marked by an increase in the stable carbon isotopic ratio of marine sediment, in both carbonate and organic matter (e.g., Arthur et al., 1988; Kuyper et al., 1999, 2002; Scopelliti et al., 2008).

OAE2 induced major changes in the marine biota, as indicated by an estimated global extinction rate across the C-T boundary of 26% at the generic level and 33%–53% at the species level (Sepkoski, 1989, 1996). A study of benthic and planktonic foraminifera across the C-T boundary showed that ~50% of deep-water foraminifera, but <20% of surface-dwelling foraminifera, became extinct (Kaiho, 1994). The morphology of the calcareous benthic foraminifera showed that the extinction horizon was consistent with low oxygen conditions, and the main cause of this extinction was suggested to be the formation of dysoxic intermediate water (Kaiho and Hasegawa, 1994).

Recent organic geochemical studies have sought to provide evidence for anoxic and/or euxinic conditions in the water column and at the seafloor during OAE2, especially in the area of what was then the North Atlantic Ocean. Molecular fossils (sedimentary derivatives of characteristic biomolecules) of specific pigments (isorenieratene) biosynthesized by green sulfur bacteria were detected in C-T samples from Deep Sea Drilling Project (DSDP) cores from various sites in the North Atlantic Ocean (Sinninghe Damsté and Köster, 1998; Kuyper et al., 2002, 2004) and exploration well cores in northwestern Africa (Sinninghe Damsté and Köster, 1998; Kuyper et al., 2002; Kolonic et al., 2005). Given that green sulfur bacteria require both light and hydrogen sulfide (H2S) for inorganic carbon fixation, and are therefore indicators of photic-zone euxinia, these studies concluded that photic-zone euxinia developed in the North Atlantic during the C-T transition. Sediment cores through the C-T interval in northwestern Africa exhibit a high S/C ratio (>0.36) and an abundance of organic sulfur compounds, reflecting deposition in anoxic depositional environments (Nzoussi-Mbassani et al., 2005). C-T boundary event black shale is also present in South Atlantic and Tethyan settings and has been studied using organic geochemical methods (Forster et al., 2008; Sepúlveda et al., 2009). However, the relation between foraminifer extinction and water-column anoxia and/or euxinia has not been addressed from an organic geochemical point of view.

This study addresses variations in water-column euxinia during the C-T transition in sediment from what was then the middle-neritic eastern North Atlantic Ocean, using organic geochemical methods. The timing of short-term euxinic events relative to the extinction of rotaliporid planktonic foraminifers is also investigated. The study section is located east of Oviedo, at Arobes, in the province of Asturias, northern Spain (Fig. 1). The sedimentary succession consists of limestone, marl, and mudstone (Fig. 2). Analytical methods are detailed in the GSA Data Repository.1

RESULTS AND DISCUSSION

Water Depth
Benthic foraminiferal assemblages in the Arobes section are characterized by Rosalina, Fursenkoina, Praebulimina, Textularia, Haplophragmoides, and Lenticulina (see the Data Repository). This assemblage implies a shallower depositional environment than that of benthic foraminiferal assemblages (Praebulimina, Textularia, Haplophragmoides, and Lenticulina) present in South Atlantic and Tethyan settings (>0.36) and an abundance of organic sulfur compounds, reflecting deposition in anoxic depositional environments (Nzoussi-Mbassani et al., 2005). C-T boundary event black shale is also present in South Atlantic and Tethyan settings and has been studied using organic geochemical methods (Forster et al., 2008; Sepúlveda et al., 2009). However, the relation between foraminifer extinction and water-column anoxia and/or euxinia has not been addressed from an organic geochemical point of view.

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1GSA Data Repository item 2011169, analytical methods and stratigraphic distribution of benthic and planktonic foraminifers, is available online at www.geosociety.org/pubs/ft2011.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.
Rosalinia, Gynoidinooids, Gavelinella, and Bolivina) in the Ganausa section, which accumulated in a middle to outer shelf environment (Colin et al., 1982; Lamolda and Peryt, 1995). Together with the abundance of brachiopods, the foraminiferal assemblage indicates that the Arobes C-T section was deposited on a middle-lower neritic shelf in the eastern North Atlantic Ocean.

Stable Carbon Isotope and Total Organic Carbon Content

The δ13C values of bulk carbonates show a pronounced positive excursion between the base and top of the measured section at Arobes (Fig. 2A). This excursion has been suggested to be global and divisible into three principal phases (Kuypers et al., 2002): phase A, a rapid return to preexcursion values. It is commonly accepted that the positive δ13C excursion (phases A and B) reflects a prominent change in the global atmospheric-oceanic pool of inorganic carbon resulting from a global increase in the burial rate of 13C-depleted organic carbon (Arthur et al., 1988). According to Kuypers et al. (2002), OAE2 is the main phase of enhanced carbon burial and should be coeval with phases A and B of the carbon isotope excursion (a span of ~0.7 m.y., as estimated by the occurrence of planktonic foraminifers and calcareous nannoplankton; Fig. 2).

The depth profile of δ13C values of brachiopod shells from the Arobes section is similar to that of carbonates (Fig. 2A); the detailed brachiopod δ13C profile of the interval between beds 15A and 19 (top) cannot be determined due to the absence of brachiopods. The absence of brachiopods during this interval suggests that they were unable to survive in this area owing to bottom-water anoxia. This interval can be presumed to have undergone the most anoxic conditions of OAE2.

The total organic carbon (TOC) content of the sediment ranges between 0.11% and 0.53% (Fig. DR1; see the Data Repository). The TOC content of mudstone is higher than that of limestone. The vertical profile of TOC content indicates that TOC in beds 1, 2, and 16 is relatively high (>0.4%). No difference is evident between the TOC contents of phases A, B, and C.

Organic Molecules

Dibenzothiophene (DBT) and alkyl DBTs (C1–C3) and 2,3,6-trimethylarylisoprenoids, ranging from C14 to C21 with the exception of C14, are present in all sediment samples from the Arobes section (Figs. 2B and 2C; Fig. DR2). The vertical profiles of DBTs and the arylisoprenoids are shown in Figures 2B and 2C, respectively. The vertical trend of
concentrations normalized by TOC is similar to concentrations normalized by sediment weight. Elevated DBT concentrations are present in OAE2, particularly between beds 17 (top) and 21 (an interval of ~0.4 m.y., assuming a constant sedimentation rate). In addition, two short-term increases in concentrations of these compounds, each ~10^3 to 10^4 yr long, are just above each last occurrence (LO) of R. greenhornensis and R. cushmani (Fig. 2D). The vertical profile of the total concentration of arylisoprenoids roughly resembles that of DBTs (Figs. 2B and 2C).

DBTs are known to be present in various types of sediment and petroleum (e.g., Hughes et al., 1995). Organic sulfur–containing compounds such as DBTs are most commonly formed by the reaction of reduced inorganic sulfur species with functionalized organic molecules during sediment deposition and early diagenesis (Hughes, 1984; Simmings Damsté and de Leeuw, 1990). The presence of DBTs probably reflects the concentration of HS at the sediment surface (Hughes et al., 1995), implying the presence of sulfur-rich anoxic (i.e., euxinic) bottom waters. Increased DBT concentration during OAE2 indicates that euxinic conditions expanded. The two short-term increases in the concentrations of DBTs, just after the LOs of both R. greenhornensis and R. cushmani (the upper bed or layer over the LO is the bed in which extinction occurred), reflect ephemeral but strongly euxinic depositional environments. These rotaliporids were deep-water species that lived at or below the thermocline for most of their life cycles (Norris and Wilson, 1998; Keller et al., 2001). Their extinction may have been caused by the short-term euxinic events that occurred during deposition of bed 3B and just above the base of bed 16 (10–15 cm). The relatively elevated concentrations of DBTs from bed 17 (top) to bed 21 suggest that the benthic euxinic conditions of this interval were the most stable and persistent of OAE2, consistent with the temporary absence of all brachiopods (Fig. 2A).

The arylisoprenoids identified are thought to have been derived from carotenoids that are specific to photosynthetic green sulfur bacteria (Chlorobiaceae; Summons and Powell, 1987). These organisms are phototrophic anaerobes (Chlorobiaceae; Summons and Powell, 1987). Their presence in OAE2 indicates that euxinic conditions expanded. The two short-term increases in the concentrations of DBTs, just after the LOs of both R. greenhornensis and R. cushmani (the upper bed or layer over the LO is the bed in which extinction occurred), reflect ephemeral but strongly euxinic depositional environments. These rotaliporids were deep-water species that lived at or below the thermocline for most of their life cycles (Norris and Wilson, 1998; Keller et al., 2001). Their extinction may have been caused by the short-term euxinic events that occurred during deposition of bed 3B and just above the base of bed 16 (10–15 cm). The relatively elevated concentrations of DBTs from bed 17 (top) to bed 21 suggest that the benthic euxinic conditions of this interval were the most stable and persistent of OAE2, consistent with the temporary absence of all brachiopods (Fig. 2A).

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Notes

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