

Nd isotopic excursion across Cretaceous ocean anoxic event 2 (Cenomanian-Turonian) in the tropical North Atlantic

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ABSTRACT

Late Cretaceous fish debris from Demerara Rise exhibits a dramatic positive excursion of 8 ϵ_{Nd} units during ocean anoxic event 2 (OAE2) that is superimposed on extremely low $\epsilon_{\text{Nd}(t)}$ values (−14 to −16.5) observed throughout the rest of the studied interval. The OAE2 ϵ_{Nd} excursion is the largest yet documented in marine sediments, and the majority of the shift is estimated to have occurred over <20 k.y. Low background ϵ_{Nd} values on Demerara Rise are explained as the Nd isotopic signature of the South American craton, whereas eruptions of the Caribbean large igneous province or enhanced mixing of intermediate waters in the North Atlantic could have caused the excursion.

Keywords: ocean anoxic event 2, black shale, Demerara Rise, Nd isotopes, Cenomanian-Turonian.

INTRODUCTION

Sedimentation during the Late Cretaceous was punctuated by a series of geologically brief intervals ($\leq 10^6$ yr) characterized by widespread deposition of laminated, organic-rich calcareous mudstones or “black shales” that may have served as a negative feedback on Cretaceous greenhouse warming. These episodes represent major perturbations to the global carbon cycle and have been termed ocean anoxic events (OAEs). OAE2, spanning the Cenomanian-Turonian boundary, is particularly pronounced and globally recognized (e.g., Schlanger and Jenkyns, 1976; Arthur et al., 1987; Sageman et al., 2006).

The common presence of laminations and the scarcity of benthic fossils indicate that large portions of the seafloor became dysoxic to anoxic during OAEs. Bottom-water anoxia has traditionally been interpreted as either (1) a cause of high C_{org} concentrations due to enhanced organic matter preservation in response to decreased rates of bottom-water ventilation (Arthur et al., 1987), or (2) a consequence of high C_{org} fluxes to the seafloor due to high levels of surface productivity, resulting in benthic O_2 depletion (Pedersen and Calvert, 1990). Evidence cited in support of high productivity includes characteristically low $\delta^{15}\text{N}$ values and biomarkers of obligate anaerobic photoautotrophs, suggesting that surface productivity and accompanying organic matter degradation were high enough to drive even portions of the photic zone anoxic (Rau et al., 1987; Kuyper et al., 2004). In contrast, there are few data concerning bottom-water ventilation as a cause of benthic dysoxia and/or anoxia.

Nd isotopes are a powerful tool for tracking oceanic flow patterns (e.g., Frank, 2002; Goldstein and Hemming, 2003) and could provide an important perspective on Late Cretaceous deep-water circulation. Most seawater Nd enters the ocean from continents via rivers or wind-blown particulate material. Intermediate- and deep-water masses are imprinted with ϵ_{Nd} signatures that reflect the geology of their source regions, and they carry this signature with them as they travel through the oceans. Because the ϵ_{Nd} differences among water masses are large and because Nd has a residence time shorter than the mixing time of the oceans, it is generally possible to infer source regions and subsequent mixing of water masses, even though eolian inputs or boundary exchange can also effect ϵ_{Nd} values (Lacan and Jeandel, 2005). Fish teeth, scales, and bone fragments acquire bottom-water ϵ_{Nd} values during early seafloor diagenesis, and this value is relatively insensitive to later alteration (Martin and Scher, 2004, and references therein). Thus, stratigraphic records of ϵ_{Nd} values in fish debris provide a means to track bottom-water masses through time, but Cretaceous data are sparse. Low-resolution Late Cretaceous ϵ_{Nd} data are available for Tethyan shelf deposits (Pucéat et al., 2005; Soudry et al., 2006), and data for intermediate and deep waters are currently only available for the Maastrichtian in the Pacific (Thomas, 2004; Frank et al., 2005). No studies have examined ϵ_{Nd} changes relative to any OAE in detail.

MATERIALS AND METHODS

This paper examines Late Cretaceous ϵ_{Nd} records with emphasis on OAE2 at Demerara Rise (Fig. 1). In the Demerara sites, the Cenomanian–early Santonian is represented by 50–90 m of laminated black shale separated

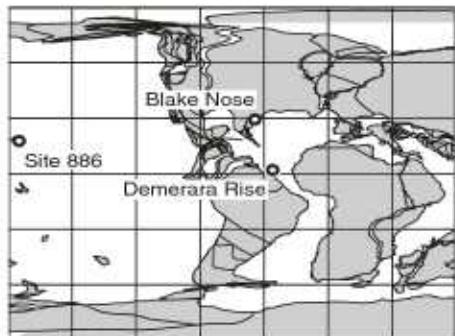


Figure 1. Approximate paleogeographic position of localities sampled in this study plotted on Ocean Drilling Stratigraphic Network (www.odsn.de) reconstruction for time of ocean anoxic event 2 (ca. 94 Ma).

from overlying late Campanian–Paleocene clayey chalk by a condensed interval and/or hiatus (Erbacher et al., 2004). The Demerara sequence is unusual in that deposition of laminated black shales began millions of years before and continued millions of years after OAE2. The OAE2 interval is clearly recognizable based on a well-documented 6‰ positive $\delta^{13}\text{C}_{\text{org}}$ excursion (Erbacher et al., 2005), but it is not lithologically distinct from sediment above and below. Fish debris is common to abundant in both the black shale and the overlying Campanian–Maastrichtian chalcs.

We measured ϵ_{Nd} values (the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio expressed relative to the chondritic uniform reservoir in parts per 10^4 ; Piepras and Wasserburg, 1987) of 45 separates of fish debris picked from the >125 μm fraction of Demerara samples. Of the 45 samples, 33 were from the black shale interval at Ocean Drilling Program (ODP) Site 1258 and 12 of those were from

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OAE2. The other 12 samples are from the Campanian and Maastrichtian chalk samples from 3 sites—1 from ODP Site 1258, 7 from ODP Site 1259, and 4 from ODP Site 1260. To provide comparative pilot data from other bathyal sites, we also analyzed 1 Albian, 2 Cenomanian, and 1 Campanian sample from Site 1050 and 6 Campanian–Maastrichtian samples from Site 886 in the Pacific (Fig. 1). Further details on sampling, sample preparation, and analytical techniques as well as tabulation of results are available in the GSA Data Repository.¹

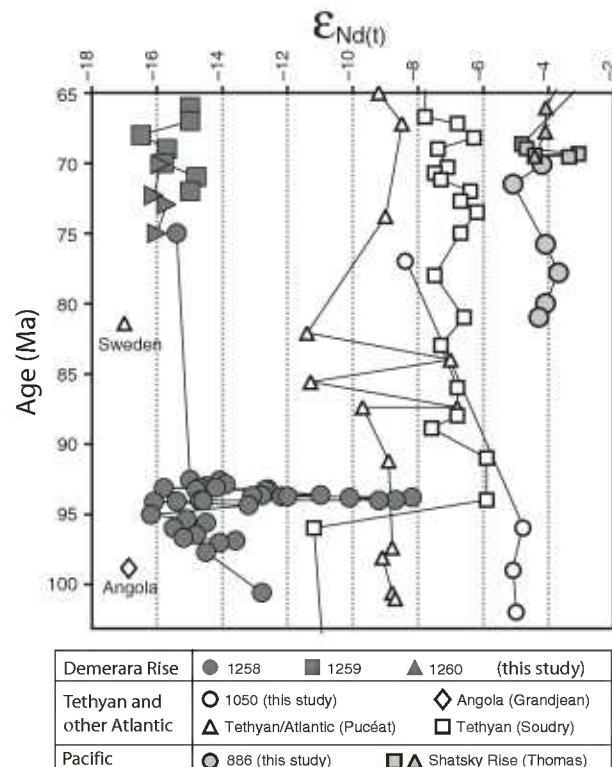
RESULTS

The $\epsilon_{\text{Nd(t)}}$ values for the majority of Demerara samples range between –14 and –16.5; however, values increased to –8.2 ϵ_{Nd} units during OAE2. At Site 1050, Albian and Cenomanian $\epsilon_{\text{Nd(t)}}$ values are close to –5, whereas the Campanian sample has a value of –8.5. The $\epsilon_{\text{Nd(t)}}$ values for Pacific Campanian and Maastrichtian samples from Site 886 range from –4 to –5, similar to earlier results from Shatsky Rise (Fig. 2).

The 8 ϵ_{Nd} unit increase at Site 1258 is closely correlated with the 6‰ increase in $\delta^{13}\text{C}_{\text{org}}$ during OAE2 (Fig. 3). The rise in $\delta^{13}\text{C}$ values at the onset of OAE2 has been estimated to have taken 120–150 k.y. (Sageman et al., 2006), and this rise spans ~1.6 m at Site 1258, suggesting an average sedimentation rate of 1.1–1.3 cm/k.y. The ϵ_{Nd} shift starts at or just below the start of the $\delta^{13}\text{C}$ excursion and increases from –16.1 at 426.88 m composite depth (mcd) to –8.7 at 425.64 mcd. However, the majority of this initial ϵ_{Nd} shift (5.5 of 7.4 units) occurs between 2 data points separated by 20 cm of core within the 1.6 m interval over which $\delta^{13}\text{C}$ values increase. Assuming approximately constant sedimentation rate and no hiatuses, the 20 cm interval would represent <20 k.y. The ϵ_{Nd} values remain high over ~2 m of section, reaching a peak value of –8.2 at 423.59 mcd, and then decrease gradually (albeit in a sawtooth pattern) to preeexcursion values over ~2.5 m of section. Stratigraphic trends in $\delta^{13}\text{C}_{\text{org}}$ are similar, but $\delta^{13}\text{C}_{\text{org}}$ values increase more smoothly than ϵ_{Nd} values at the base of OAE2 and then remain high and relatively constant for ~2.7 m before sharply returning to background values at 422.10 mcd, a level above the initiation of decreasing ϵ_{Nd} values. Estimating the rate of decrease in ϵ_{Nd} values at Site 1258 is complicated by lack of good chronostratigraphic tie points within the $\delta^{13}\text{C}$ excursion (Sageman et al., 2006) and a hiatus at Site 1258 inferred from the sharp decline in $\delta^{13}\text{C}_{\text{org}}$ values at 422.10 mcd (Erbacher et al., 2005).

¹GSA Data Repository item 2008208, methodological details and $\epsilon_{\text{Nd(t)}}$ and $\delta^{13}\text{C}_{\text{org}}$ data, is available online at www.geosociety.org/pubs/ft2008.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

Figure 2. Compilation of $\epsilon_{\text{Nd(t)}}$ values for Late Cretaceous illustrating both unusually low background values and large size of excursions in late Cenomanian (ca. 94 Ma) on Demerara Rise. Numbers refer to Ocean Drilling Program sites; Thomas refers to results from two sites on Shatsky Rise (Thomas, 2004); Pucéat refers to results from largely peri-Tethyan shelf samples with exception of the indicated point from Sweden (Pucéat et al., 2005); Soudry refers to results from Tethyan shelf deposits largely from Israel (compilation in Soudry et al., 2006); and Grandjean refers to analysis of shelfal sample from Angola (Grandjean et al., 1987).



DISCUSSION

The Demerara ϵ_{Nd} results present two surprising observations: background values that are extremely low for open-ocean sites and a well-resolved OAE2 excursion that is larger and more rapid than any previously documented ϵ_{Nd} shift in marine sediments. For comparison, during the Cenozoic, ϵ_{Nd} variation at any site or within any basin is typically ≤ 3 units, with values highest in the Pacific and lowest in the North Atlantic, and the data span only ~10 units for the entire era (e.g., O’Nions et al., 1998; Burton et al., 1999; Frank, 2002; Ling et al., 2005). Late Cretaceous Pacific values are also generally higher than Atlantic and Tethyan values, but, except during OAE2, Demerara values are an additional 4–10 units lower than most other Atlantic results (Fig. 2). Single data points from Angola (Grandjean et al., 1987) and Sweden (Pucéat et al., 2005) plot with the background values observed at Demerara, but these samples were both recovered from relatively shallow, isolated basins that likely received runoff with low ϵ_{Nd} values derived from nearby Precambrian cratons, similar to the situation in modern Baffin Bay (Stordal and Wasserburg, 1986). During the Late Cretaceous, Site 1258 would have been hundreds of kilometers from the South American coastline and is estimated to have been at depths >1000 m, with no barriers between it and the rest of the North Atlantic (Arthur and Natland, 1979; Erbacher et al., 2004; Jiménez Berrocoso et al., 2008). Isolation is therefore an unlikely explanation

for low values on Demerara Rise. Three other possible explanations for the low values are (1) a diagenetic overprint, (2) seawater-particle exchange coupled with generally sluggish circulation, or (3) sinking of a locally derived water mass imprinted with an ϵ_{Nd} value strongly influenced by Guyana shield input.

Two observations argue against extensive diagenetic alteration as an explanation for the record at Site 1258. First, pervasive alteration

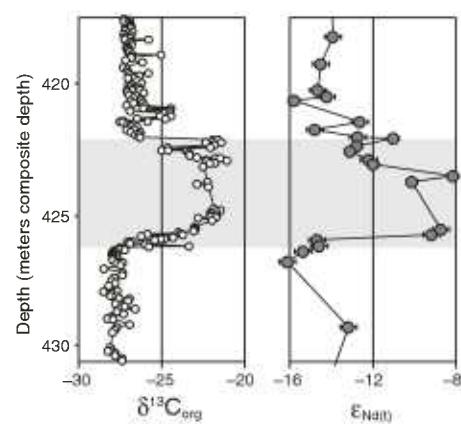


Figure 3. Cenomanian-Turonian $\epsilon_{\text{Nd(t)}}$ and $\delta^{13}\text{C}_{\text{org}}$ (Erbacher et al., 2005) values at Ocean Drilling Program Site 1258 plotted against depth across the ocean anoxic event 2 interval (shaded). Error bars for $\epsilon_{\text{Nd(t)}}$ show 2σ external precision; $\delta^{13}\text{C}_{\text{org}}$ symbols are larger than estimated error.

needed to explain the generally low values would be expected to result in a convergence of all values on the diagenetic end point, but these samples record the largest Nd isotopic excursion yet documented. Second, if the OAE2 excursion were a diagenetic artifact it would be expected to occur at a lithologic transition, whereas it actually occurs within the black shale unit, and there is no isotopic shift at the major lithologic transition and hiatus that separates black shales older than 90 Ma from chalcs younger than 75 Ma.

The seawater-particle exchange explanation for the low values is based on the modern Pacific. High Pacific ϵ_{Nd} values have been attributed to exchange between volcanic particles and seawater in a basin with relatively sluggish circulation (Goldstein and Hemming, 2003), resulting in a gradient from ϵ_{Nd} values approaching 0 in surface waters to values closer to those of inflowing circum polar waters at depth. Demerara Rise is proximal to the Precambrian Guyana shield, and sediments in rivers draining this shield have $\epsilon_{\text{Nd}(0)}$ values as low as -30 (Goldstein et al., 1997). If Cretaceous eolian input from the Guyana shield was analogous to volcanics in the modern Pacific, low ϵ_{Nd} values should be recorded for surface waters with increasing values at depth. However, we observed no separation among values in Campanian-Maastrichtian samples where results are available for three Demerara sites separated by >1 km of depth (Erbacher et al., 2004). Furthermore, contrary to the modern Pacific, the area affected by airborne material could not have been very large, because Blake Nose ϵ_{Nd} values are distinctly higher than those at Demerara Rise (Fig. 2).

The third scenario for low background ϵ_{Nd} at Demerara Rise invokes formation of an intermediate "Demerara bottom-water mass" imprinted with the nonradiogenic signature of the Guyana shield that descended to bathyal depths without appreciable mixing with other North Atlantic water masses. Implicit in this model is a prediction of excess evaporation in the southern North Atlantic that increased the density of surface water until the density flux was great enough for the waters to descend at least to bathyal depths. Low ϵ_{Nd} values might be quite localized in this scenario, and little change in ϵ_{Nd} values is predicted with depth within the water mass. The Demerara bottom-water mass model predicts very warm bottom waters on Demerara Rise, consistent with recent $\delta^{18}\text{O}$ results (Bornemann et al., 2008). A Demerara bottom-water mass could either end up in a mid-water position (analogous to modern Mediterranean Intermediate Waters) or sink to greater depths, where it might be recognized by low ϵ_{Nd} values at abyssal North Atlantic sites.

Regardless of which of these alternatives is correct, the general persistence of low ϵ_{Nd} values

from 100 to 65 Ma suggests that the source of Demerara bottom waters was relatively constant during most of the Late Cretaceous. In particular, the similarity between late Turonian and late Campanian ϵ_{Nd} values argues against initiation of unrestricted deep flow through the opening Equatorial Atlantic Gateway as the cause of the lithologic transition from black shale to chalk on Demerara Rise (Erbacher et al., 2005; Friedrich and Erbacher, 2006). On the other hand, the change from Pacific-like to North Atlantic-like ϵ_{Nd} values between the Cenomanian and Campanian at Site 1050 suggests that circulation patterns changed at Blake Nose as black shale deposition waned at Demerara Rise.

Due to its size and timing, the ϵ_{Nd} excursion at OAE2 is even more intriguing than the low background values, and the tight correlation between ϵ_{Nd} and $\delta^{13}\text{C}_{\text{org}}$ at the base of OAE2 suggests that the ϵ_{Nd} shift could reflect processes important in the initiation of OAE2 (Fig. 3). Possible end-member explanations include (1) a change in the ϵ_{Nd} values of regional continental inputs, (2) input from a new source with an unusual ϵ_{Nd} value, or (3) a change in ocean circulation.

If weathering inputs changed dramatically, the ϵ_{Nd} of seawater over Demerara Rise would shift without requiring any change in ocean processes. There are no sedimentological data supporting such a change, and any change would need to be both rapid and reversible. These conditions are difficult to reconcile with a continental weathering model. Furthermore, the direction of the ϵ_{Nd} shift (away from continental values) is opposite to what is expected if warm conditions during OAE2 enhanced continental weathering.

A possible source of new material is volcanism. Volcanic inputs could change rapidly and dramatically, and the Caribbean large igneous province (LIP) has been proposed as a causal mechanism for OAE2 (Sinton and Duncan, 1997; Snow et al., 2005; Kuroda et al., 2007). Basalts have high ϵ_{Nd} values (+10); thus, introduction of basaltic Nd would drive seawater ϵ_{Nd} values higher. In the modern ocean, Nd is quantitatively removed from hydrothermal fluids by formation of Fe and Mn hydroxides near vent sites (Halliday et al., 1992). Under anoxic conditions, however, hydrothermal fluids might carry a basaltic Nd signature far from the vents. Because oxic waters would localize any LIP ϵ_{Nd} excursion, this model predicts that the ϵ_{Nd} shift at OAE2 should follow the development of anoxia which, if productivity driven, would follow onset of the $\delta^{13}\text{C}_{\text{org}}$ excursion. Such an offset between the initiation of the ϵ_{Nd} and $\delta^{13}\text{C}_{\text{org}}$ is not observed in the Demerara Rise data; however, higher-resolution sampling will be required to precisely define the structure of the transition. The ϵ_{Nd} shift should also follow the pattern of Caribbean volcanism with a small initial pulse

near the base of OAE2 and a second larger pulse occurring ~200 k.y. later. Finally, a positive ϵ_{Nd} shift should be found consistently at OAE2 sites with evidence for LIP influence (Snow et al., 2005; Sageman et al., 2006).

The third possibility is that the ϵ_{Nd} excursion reflects a temporary change in the source or circulation of intermediate-depth bottom waters during OAE2. On Demerara Rise, peak OAE2 ϵ_{Nd} values approach Cretaceous ϵ_{Nd} values for other North Atlantic and Tethyan sites (Fig. 2). If the seawater-particle exchange model for low background values is correct, circulation would have needed to become vigorous enough that the residence time of water in the basin no longer provided sufficient time for seawater-particle exchange. If the Demerara bottom-water mass model is correct, a decrease in evaporation relative to runoff and/or precipitation is required to inhibit the formation of a dense, saline intermediate water mass during OAE2. Possible forcing mechanisms include an enhanced hydrologic cycle associated with OAE2 warming or circulation changes related to the OAE2 highstand. Regardless, circulation changes could result in higher nutrient concentrations at the depths tapped by wind-driven upwelling and, thus, promote surface productivity. Because these oceanic scenarios invoke removal of the source of the unusually low background ϵ_{Nd} values unique to Demerara Rise, other sites might show a smaller change, an opposite change, or no change at all in ϵ_{Nd} values during OAE2.

IMPLICATIONS

The Demerara ϵ_{Nd} record shows an extended interval of very low Late Cretaceous values punctuated by a large and rapid ϵ_{Nd} excursion during OAE2. Although we cannot uniquely interpret this record yet, the implications of several models proposed to explain the ϵ_{Nd} record challenge existing ideas about the Late Cretaceous. Specifically the possibility of ocean stagnation during OAE2 is difficult to reconcile with the OAE2 ϵ_{Nd} excursion. In addition, low background values support the possibility of the formation of an intermediate water mass at low latitudes during most of the Late Cretaceous and show no changes that might be explained by opening of a connection at intermediate water depths between the North Atlantic and South Atlantic.

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