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The Cenomanian/Turonian oceanic anoxic event in the South Atlantic: New insights from a geochemical study of DSDP Site 530A

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ABSTRACT

One of the key objectives of Deep Sea Drilling Project (DSDP) Leg 75 was to shed light on the underlying causes of Cretaceous oceanic anoxia in the South Atlantic by addressing two major hypotheses: productivity productivity-driven anoxia vs. enhanced ocean stratification leading to preservation of organic matter and black shale deposition. Here we present a detailed geochemical dataset from sediments deposited during the Cenomanian/Turonian (C/T) transition and the global oceanic anoxic event 2 (OAE 2) at DSDP Site 530A, located off-shore Namibia (southeast Angola Basin, north of Walvis Ridge). To characterise the succession of alternating black and green shales at this site and to reconstruct the evolution of their paleoenvironmental setting, we have combined data derived from investigations on bulk organic matter, biomarkers and the inorganic fraction. The location of the C/T boundary itself is biostratigraphically not well constrained due to the carbonate-poor (but organic matter-rich) facies of these sediments. The bulk $\delta^{13}C_{org}$ record and compound-specific $\delta^{13}C$ data, in combination with published as well as new biostratigraphic data, enabled us to locate more precisely the C/T boundary at DSDP Site 530A. The compound-specific $\delta^{13}C$ record is the first of this kind reported from C/T black shales in the South Atlantic. It is employed for paleoenvironmental reconstructions and chemostratigraphic correlation to other C/T sections in order to discuss the paleoceanographic aspects and implications of the observations at DSDP Site 530A in a broader context, e.g., with regard to the potential trigger mechanisms of OAE 2, global changes in black shale deposition and climate. On a stratigraphic level, an approximation and monitoring of the syndepositional degree of oxygen depletion within the sediments/bottom waters in comparison to the upper water column is achieved by comparing normalised concentrations of redox-sensitive trace elements with the abundance of highly source specific molecular compounds. These biomarkers are derived from photoautotrophic and simultaneously anoxygenic green sulphur bacteria (Chlorobiacea) and are interpreted as paleoindicators for events of photic zone euxinia. In contrast to a number of other OAE 2 sections that are characterised by continuous black shale sequences, DSDP Site 530A represents a highly dynamic setting where newly deposited black shales were repeatedly exposed to conditions of subtle bottom water re-oxidation, presumably leading to their progressive alteration into green shales. The frequent alternation between both facies and the related anoxic to slight oxygenated conditions can be best explained by variations in vertical extent of an oxygen minimum zone in response to changes in a highly productive western continental margin setting driven by upwelling.

1. Introduction

In today's generally well mixed and oxygenated oceans and shelf seas, the formation of organic matter and sulphide-rich, fine-grained marine sedimentary deposits of characteristically dark grey to black colour is an exception rather than a rule, as almost all settling organic matter (OM) produced mainly by the marine phytoplankton is oxidised (e.g., Meyers, 2006). The establishment of long-term anoxic conditions in marine bottom waters and the sediments itself is an essential prerequisite for substantial preservation of OM on the sea floor. Upon lithification, such OM-rich sediments are eventually turned into dark

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clay- to mudstones, which are generally termed “black shales” (e.g., Arthur and Sageman, 1994). Conditions of prolonged oxygen deficiency at the sea floor can be caused by either a widely restricted water circulation, extremely high rates of sediment accumulation, or enhanced primary bioproductivity in the surface waters — or a combination of these processes (see Tyson, 2005 for a review).

Based on the Cretaceous sedimentary record, black shales are documented from a wide range of marine settings worldwide (e.g., Schlanger and Jenkyns, 1976). This raises the question of which paleoenvironmental conditions and depositional processes favoured their formation, especially during the mid-Cretaceous (Barremian through Turonian, ~130–89 million years [Myr] ago; Gradstein et al., 2004). This geologic time interval was characterised by a coincidence of intensified volcanism and oceanic crust production, elevated sea level and paleotemperatures peaking in the early Turonian (Larson, 1991a,b). The concept of global “oceanic anoxic events” (OAEs; Schlanger and Jenkyns, 1976; see Leckie et al., 2002 for a review) was postulated to explain time-slices of enhanced organic carbon burial during the Aptian to Santonian associated with the genesis of widespread marine black shales such as at the Cenomanian/Turonian (C/T) boundary (OAE 2). The OAEs reflect periods of biotic crisis, likely linked to a limited oxygen supply in already oxygen-depleted warm oceans and epeiric seas. The oxygen restriction in these marine settings could have been reinforced either by an increase in primary OM production related to transgressions (Schlanger and Jenkyns, 1976; Jenkyns, 1980) or the onset of density stratification proceeded by a decrease in oceanic circulation (e.g., Ryan and Cita, 1977; Fischer and Arthur, 1977) or a combination of both (Arthur and Schlanger, 1979; Stein, 1986).

The Cenomanian/Turonian OAE 2 is prominent regarding the amount of organic carbon (OC) deposited in different marine settings worldwide (e.g., Schlanger et al., 1987; Arthur et al., 1988; Jenkyns et al., 1994; Leckie et al., 2002). It is accompanied by a strong biotic crisis and a globally observed positive carbon isotope excursion, expressed both in carbonate and OM. Since the positive excursion is thought to be caused by the massive perturbation of the carbon cycle linked to excess burial of OC during OAE 2 (Jenkyns, 1980; Scholle and Arthur, 1980; Arthur et al., 1988) — this signal should be synchronous in both marine and terrestrial settings (e.g., Hasegawa, 1997). This positive stable carbon isotope excursion defines the Cenomanian/Turonian boundary event (CTBE) stratigraphically (e.g., Arthur et al., 1988; Kuypers et al., 2002; Jenkyns et al., 1994; Paul et al., 1999; Tsikos et al., 2004; Gale et al., 1993, 2005; Erbacher et al., 2005; Sageman et al., 2006; Jarvis et al., 2006), extending the original meaning of the term CTBE (as introduced by Thurow and Kuhnt, 1986, and Herbin et al., 1986) in the sense of chemostratigraphy.

In the marine environment, the best correlation tool should be the stable carbon isotopic record of inorganic carbon, if it is not affected by diagenetic alteration or dissolution of the carbonate phase. In the latter case, the stable isotopic composition of organic carbon ($\delta^{13}C_{org}$) could be an alternative, but this record is also sensitive to alteration and changes in the composition of the OM preserved (e.g., Sinninghe Damsté et al., 2002) and variations in primary bioproductivity (e.g., Laws et al., 1995). Compound-specific δ^{13}C records based on certain organic compounds of particular primary biological sources, i.e., biomarkers of exclusively phytoplanktonic origin, can overcome some of these problems (e.g., Tsikos et al., 2004). An organic compound that represents a well-suited proxy to assess the isotopic composition of ancient marine phytoplankton communities is the acyclic isoprenoid phytane because in most marine settings it is predominately derived from the phytol side-chain of the phytoplanktonic chlorophyll-*a* (e.g., Didyk et al., 1978; Volkman and Maxwell, 1986; Kuypers et al., 1999, 2002).

One of the main objectives of Deep Sea Drilling Project (DSDP) Leg 75 was to shed light on the paleoceanographic history of the South Atlantic with respect to the deposition of OM-rich Cretaceous black shales that had been discovered during earlier DSDP expeditions (Legs 36, 39, 40 and 71): in the Angola Basin (sites 363, 364; Fig. 1), the Cape Basin (Site 361; Fig. 1), at the Falkland Plateau (sites 327, 330 and 511) and the São Paulo Plateau/Rio Grande Rise (sites 356, 357) (see for an overview Gilbert, 1984; Dean et al., 1984a). Consequently, a key question was whether or not the black shale layers occurring in late Albian to Santonian sedimentary sequence of the South Atlantic were deposited as the result of anaerobic to euxinic conditions in the water column, analogous to today's stagnant basin setting of the Black Sea or the Cariaco Trench. Alternatively, the black shales in the Angola Basin could have formed in connection with the development of a mid-water oxygen minimum zone under highly fertile and productive surface water mass along the western African continental margin (Shipboard Scientific Party, 1984).

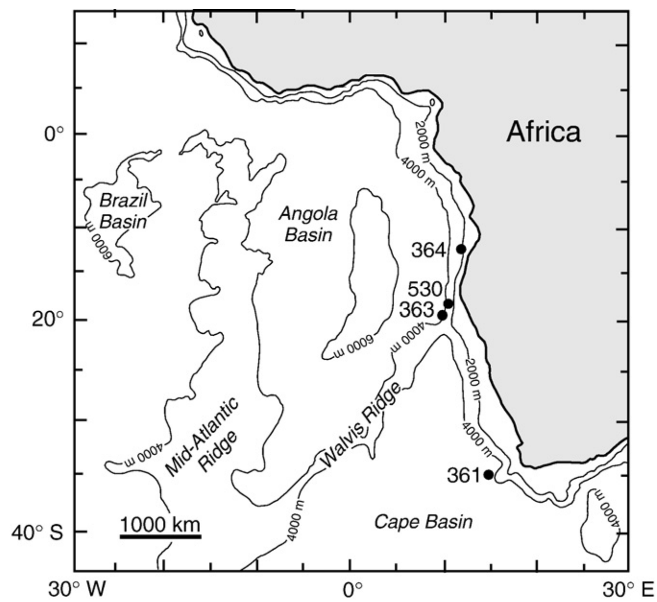

Fig. 1. Location map of Deep Sea Drilling Project (DSDP) Leg 75 Site 530A west off Namibia on Walvis Ridge (modified from Shipboard Scientific Party, 1984). Other Cretaceous black shale-bearing sites in the Angola and Cape basins (DSDP Leg 40) are indicated. Bathymetry in metres below sea level.

Initial investigations of Cretaceous black shales from DSDP Site 530A concerning their content in trace metals, OM and biomarker distributions or stable ^{13}C isotopes have been published shortly after the site was drilled in 1980 (e.g., Hay et al., 1984; Meyers et al., 1984a; Degens et al., 1986; Arthur et al., 1988). However, a systematic and combined organic and inorganic geochemical investigation spanning the C/T boundary in relatively high resolution has been missing so far.

Here, we combine geochemical data derived from investigations on bulk OM, biomarkers and trace elements to reconstruct the paleoenvironmental setting and its evolution during the OAE 2 at DSDP Site 530A. The location of the C/T boundary itself is biostratigraphically poorly constrained at this site due to the almost carbonate-free sediment facies. Our detailed bulk $\delta^{13}C_{org}$ record and compound-specific δ^{13}C dataset based on free and sulphur-bound phytane are combined with new biostratigraphic data to overcome this problem. The elaborated compound-specific δ^{13}C record presented here is the first of this kind reported from C/T black shales in the South Atlantic and represents a valuable record for correlation of the OAE 2 to other C/T sections based on chemostratigraphy.

2. Location and geological setting of DSDP Site 530A

2.1. Site location

DSDP Site 530A is located at a water depth of 4645 m below sea level (mbsl) on the southeastern margin of the Angola Basin (19°11.26′ S, 9°23.15′E; Fig. 1) approximately 15 km north of the escarpment of Walvis Ridge and 150 km west of the base of the continental slope of