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Environmental conditions in the South Atlantic (Angola Basin) during the Early Cretaceous

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ABSTRACT

The South Atlantic has experienced periods of intense anoxia and black shale deposition that form an important hydrocarbon source. Here we have investigated the depositional environment during the initial opening phase of the South Atlantic during the Early Cretaceous. The period is crucial as it is characterized by extensive source rock deposition and because it sets the stage for subsequent periods of anoxia within the northern sub-basin of the South Atlantic. Within an Aptian sequence of organic-rich sediments (up to 40% total organic carbon, TOC) from Deep Sea Drilling Project (DSDP) Site 364, we found a distinct biomarker distribution, including the presence of isorenieratane and an array of thiophenic (S-containing) compounds. Our results indicate that, during the time of deposition, corresponding to the initial phase of opening of the South Atlantic, most of the water column in the Angola Basin was hypersaline (>40‰) and euxinic, with euxinia episodically reaching the photic zone. The low relative abundance of marine biomarkers in the samples suggests that these extreme conditions were unfavourable for typical marine organisms. Stratigraphically up-section, the biomarker distribution changed as the TOC content gradually decreased (< 20 wt.%), isorenieratane and thiophenic compounds became less abundant and marine biomarkers became more abundant. We interpret the results to reflect a shift towards more open marine conditions, with less extensive euxinia/anoxia and normal marine salinity as the opening of the South Atlantic continued and the basin became less restricted. Our results demonstrate that the opening of the South Atlantic was the dominant control on the deposition of organic rich shales in the Angola Basin during the Aptian, highlighting the control of local basin geography on the depositional environment and formation of organic rich black shales during the Early Cretaceous.

1. Introduction

Although the majority of the modern ocean is well-oxygenated, certain regions are characterized by sub-oxic or anoxic water. Probably the best known example is the Black Sea, the largest present-day anoxic basin, where the vertical stratification and the restricted nature of the sea causes anoxia below ca. 100 m water depth. However, the geological past is characterized by numerous periods when the ocean was much less oxygenated. The best examples are the Oceanic Anoxic Events (OAEs) of the Mesozoic, mainly Cretaceous, when large parts of the (deep) ocean became anoxic as evidenced by the widespread deposition of organic-rich black shales (Schlanger and Jenkyns, 1976; Jenkyns, 2010). At least two Cretaceous OAEs are thought to be global: the Aptian OAE 1a (taking place around 120 Ma) and the Cenomanian/Turonian OAE 2 (around 93.5 Ma). A recent data-model comparison estimated that as much as 90% of the seafloor might have been anoxic/dysoxic during OAE 2 (Monteiro et al., 2012).

There are three different mechanisms for creating anoxia and deposition of organic rich shales: (i) silled/restricted basins in which anoxic (bottom) water forms due to density stratification (e.g. the Black Sea), (ii) a mid-depth O_2 minimum zone where the intense degradation of organic matter (OM) originally produced in the overlying photic zone consumes all available O_2 (e.g. Arabian Sea) and (iii) an upwelling region where high productivity leads to anoxic bottom water at the continental shelf (e.g. African shelf). It is likely that the breakup of the supercontinent Pangaea during the Mesozoic (Torsvik et al., 2009), with the opening of the (South) Atlantic and the resulting restricted basin geography, played an important role in facilitating the widespread anoxia, sometimes reaching the photic zone, during the OAEs (e.g. Sinninghe Damsté and Köster, 1998; Erbacher et al., 2001; Jenkyns, 2010; Monteiro

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et al., 2012; Wagner et al., 2013). Here we focus on the initial stage of the South Atlantic opening, during which a number of restricted basins such as the Cape, Argentine and Angola Basins formed. We examine the depositional environment of the Angola Basin (DSDP Site 364) and how that changed during the Aptian (Early Cretaceous) as the opening of the South Atlantic continued (Fig. 1). The Angola Basin is characterized by km thick evaporates overlain by sapropelic layers rich in OM that were deposited during the Early Cretaceous. These organic rich layers form important petroleum reservoirs (e.g. Zimmerman et al., 1987; Huc, 2004). Investigation of the environmental conditions in the Angola Basin during the first stages of the opening of the South Atlantic could provide key insight into the mechanisms and processes that operated in restricted basins during the Early Cretaceous.

2. Study area

Site 364 (11°34.32′S, 11°58.30′E, 2450 m water depth), in the Angola Basin, was drilled during DSDP Leg 40 in 1975 (Leg 40 Shipboard Scientific Party, 1978). The basin formed due to the separation of Africa and South America and the opening of the South Atlantic during the Early Cretaceous, leading to the formation of shallow-silled basins largely isolated from the ocean (Zimmerman et al., 1987; Nürnberg and Müller, 1991). During the earliest Cretaceous, the basin was so restricted that evaporates up to 3 km thick were deposited (Leg 40 Shipboard Scientific Party, 1978; Torsvik et al., 2009). Site 364 was drilled to > 1 km before the top of these Early Cretaceous evaporates was hit, and sediments of Aptian to Pleistocene age were recovered. Palaeontological evidence suggests that Site 364 was located on the continental shelf (break), with palaeodepth estimates for the latest Aptian in the range of 500–1000 m (Leg 40 Shipboard Scientific Party, 1978; Ryan et al., 1978).

3. Age control

Site 364 consists of seven units. Units five (Cores 364-25 – 20) and seven (Cores 364-46 – 39) are carbonate mixed with organic-rich sapropels (Leg 40 Shipboard Scientific Party, 1978).

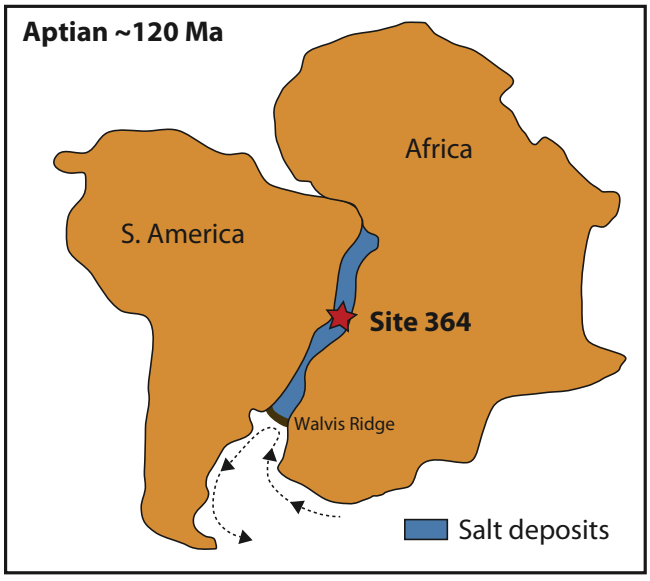

Fig. 1. Schematic overview of South Atlantic during the Aptian (based on Zimmerman et al., 1987; Huc, 2004).

Based on palynomorph, nannoplankton and foraminiferal data, unit five spans the Cenomanian to Santonian (Leg 40 Shipboard Scientific Party, 1978). Exceptionally high total organic carbon (TOC) values (> 40%) are reported for Unit seven (Bralower et al., 1994). Dating of Unit seven is more problematic due to the absence of calcareous nannoplankton and foraminifera in Cores 364-46 – 44. Even so, Bralower et al. (1994) assigned Cores 364-45 – 40 to the lower Aptian to upper Aptian/lower Albian and Cores 364-44 – 41 to the *Grantarhabdus coronadventis* nanofossil subzone (NC6B), suggesting that these organic rich-shales correspond to the global OAE 1a (ca. 120 Ma), which took place in nannofossil zone NC6 (Erba et al., 1999; Erba, 2004).

4. Material and methods

Eight samples from Cores 364-44 – 42 were sampled at the IODP core depository in Bremen. Bulk samples were freeze-dried and powdered using a mortar and pestle. Total C content and S content were analyzed using Eurovector EA 3000 and Carlo-Erba NC 2500 elemental analyzers, respectively. Total inorganic C content was determined using a Ströhlein Coulomat 702. All elemental analyses were performed in duplicate.

Ground sediment (ca. 20 g) was extracted via Soxhlet apparatus for 24 h using dichloromethane (DCM)/MeOH (2:1 v/v) to obtain lipid biomarkers. Cu cuttings were added to absorb free S during extraction. Each extract was concentrated and separated into three fractions using silica open column chromatography. Successive elution with 3 ml hexane, 4 ml hexane/DCM (3:1 v/v) and 4 ml DCM/MeOH (1:2 v/v) resulted in apolar, aromatic and polar fractions, respectively. The apolar hydrocarbon and aromatic fractions were dried under a gentle N_2 flow and dissolved in 400 µl hexane before analysis with a Finnigan Trace gas chromatography-mass spectrometry (GC–MS) instrument. After injection of 1 µl onto a Zebron-I non-polar column (50 m × 0.32 mm × 0.10 µm), the GC oven programme was: 70 °C (1 min) to 130 °C at 20 °C/min, then to 300 °C (held 24 min) at 4 °C/min. The mass spectrometer continuously scanned between *m/z* 50 and 650.

Compound specific $\delta^{13}C$ values of the alkanes were determined using an Isoprime 100 GC-combustion-isotope ratio MS (GC-C-IRMS) system. Samples were measured in triplicate and $\delta^{13}C$ values were converted to Vienna Peedee Belemnite (VPDB) by bracketing with an in-house gas (CO_2) of known $\delta^{13}C$ value. Instrument stability was monitored by regular analysis of an in-house fatty acid methyl ester standard mixture; long-term precision is ± 0.3‰. The same GC conditions were used as for GC–MS.

The polar fraction, containing the glycerol dialkyl glycerol tetraethers (GDGTs), was dissolved in hexane/*iso*-propanol (99:1, v/v) and passed through a 0.45 µm PTFE filter. Each fraction was analyzed using high performance liquid chromatography-atmospheric pressure ionization-MS (HPLC-APCI-MS) with a ThermoFisher Scientific Accela Quantum Access triple quadrupole MS instrument. Normal phase separation was achieved with an Alltech Prevail Cyano column (150 mm × 2.1 mm; 3 µm i.d.) at a flow rate of 0.2 ml/min. The initial solvent was hexane/*iso*-propanol 99:1 (v/v), eluted isocratically for 5 min, followed by a linear gradient to 1.8% *iso*-propanol over 45 min. Selective ion monitoring (SIM) was used, scanning for both isoprenoid (iso) and branched (br) GDGTs, to increase sensitivity and reproducibility and $[M+H]^+$ GDGT peaks were integrated (*m/z* 1302, 1300, 1298, 1296, 1294 and 1292 for iso-GDGTs, and *m/z* 1050, 1036, 1034, 1032, 1022, 1020, 1018 for br-GDGTs). Relative abundances for iso-GDGTs were calculated using raw peak areas. The abundance of GDGT-4, which co-elutes with crenarchaeol on a cyano column, was corrected for the abundance of the $[M+H]^+ + 2$ ion of crenarchaeol using a factor of 0.33 (Weijers et al., 2004).