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Variable Eocene-Miocene sedimentation processes and bottom water redox conditions in the Central Arctic Ocean (IODP Expedition 302)

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ABSTRACT

In 2004, Integrated Ocean Drilling Program Expedition 302 (Arctic Coring Expedition, ACEX) to the Lomonosov Ridge drilled the first Central Arctic Ocean sediment record reaching the uppermost Cretaceous (~430 m composite depth). While the Neogene part of the record is characterized by grayish–yellowish siliciclastic material, the Paleogene part is dominated by biosiliceous black shale-type sediments. The lithological transition between Paleogene and Neogene deposits was initially interpreted as a single sedimentological unconformity (hiatus) of ~26 Ma duration, separating Eocene from Miocene strata. More recently, however, continuous sedimentation on Lomonosov Ridge throughout the Cenozoic was proclaimed, questioning the existence of a hiatus. In this context, we studied the elemental and mineralogical sediment composition around the Paleogene–Neogene transition at high resolution to reconstruct variations in the depositional regime (e.g. wave/current activity, detrital provenance, and bottom water redox conditions). Already below the hiatus, mineralogical and geochemical proxies imply drastic changes in sediment provenance and/or weathering intensity in the hinterland, and point to the existence of another, earlier gap in the sediment record. The sediments directly overlying the hiatus (the Zebra interval) are characterized by pronounced and abrupt compositional changes that suggest repeated erosion and re-deposition of material. Regarding redox conditions, euxinic bottom waters prevailed at the Eocene Lomonosov Ridge, and became even more severe directly before the hiatus. With detrital sedimentation rates decreasing, authigenic trace metals were highly enriched in the sediment. This continuous authigenic trace metal enrichment under persistent euxinia implies that the Arctic trace metal pool was renewed continuously by water mass exchange with the world ocean, so the Eocene Arctic Ocean was not fully restricted. Above the hiatus, extreme positive Ce anomalies are clear signs of a periodically well-oxygenated water column, but redox conditions were highly variable during deposition of the Zebra interval. Significant Mn enrichments only occur above the Zebra interval, documenting the Miocene establishment of stable oxic conditions in the Arctic Ocean. In summary, extreme and abrupt changes in geochemistry and mineralogy across the studied sediment section do not suggest continuous sedimentation at the Lomonosov Ridge around the Eocene–Miocene transition, but imply repeated periods of very low sedimentation rates and/or erosion.

1. Introduction

The Arctic region is highly sensitive to climate changes, making its sedimentary record a unique archive of past environmental conditions. However, our knowledge about the pre-Quaternary Arctic Ocean is very limited due to the scarcity of long sediment cores. In 2004, Expedition 302 (Arctic Coring Expedition, ACEX) of the Integrated Ocean Drilling Program (IODP) recovered a composite sediment record of ~430 m length, to date representing the only Late Cretaceous to Holocene marine archive of the Arctic Ocean (Backman et al., 2006; Backman and Moran, 2009; Moran et al., 2006). The most pronounced and abrupt changes in lithology, geochemistry and microfossil inventory within the ACEX record occur at ~200 m composite depth (mcd). Based on palynological dating, a sedimentation hiatus created a gap of ~26 Ma in the ACEX record, covering the middle Eocene (44.4 Ma) to lower Miocene (18.2 Ma), eliminating much of the Eocene and the complete Oligocene sediment material (Backman et al., 2006; Moran et al., 2006; Sangiorgi et al., 2008). The existence of this hiatus was related to a period of non-sedimentation or even erosion on the Central Lomonosov Ridge (CLR; Moore et al., 2006; Jakobsson et al., 2007; Kaminski et al., 2009; O'Regan et al., 2008; Sangiorgi et al., 2008, 2009). The lithological expressions of this tentative hiatus are changes in sediment color and texture which defined the boundary between the mostly homogenous, dark gray Middle Eocene sediments (Unit 1/6) and the light–dark banded lower Miocene clay section (Unit 1/5), the "Zebra interval" (Backman

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et al., 2006; for core photos, see Suppl. 1). Paleoenvironmental interpretations related to hiatus formation included a relative sea level fall, either induced by glacio-eustatic processes or tectonic uplift of the CLR.

In the Eocene, despite the first signs of perennial sea ice formation (St. John, 2008; Stickley et al., 2009), the Arctic Ocean was most probably a subtropical, semi-enclosed basin with a fresh/brackish surface layer and anoxic to sulfidic deep-water masses similar to the modern Black or Baltic Seas (Backman et al., 2006; Knies et al., 2008; März et al., 2010; Ogawa et al., 2009; Onodera et al., 2008; Stein et al., 2006; Stickley et al., 2008). Shortly after formation of the hiatus, the opening of the Fram Strait supposedly led to flushing of the Arctic basin with oxygen-rich Atlantic waters, stratification and anoxic bottom water conditions terminated, and the fully marine well-ventilated modern Arctic Ocean developed (Jakobsson et al., 2007).

Recently, the previous age model established by Backman et al. (2008), including the existence of a sedimentological hiatus, was questioned by Poirier and Hillaire-Marcel (2009, 2011). They argued for continuous sedimentation on the CLR from the middle Eocene though lower Miocene, and proposed a connection of the Atlantic to the Arctic Ocean (including oxygenation of its water masses) as early as 36 Ma BP. Continuous Eocene to Miocene sedimentation on the CLR was also suggested by Kim and Glezer (2007) based on the seismic correlation of Siberian onshore stratigraphic sections containing siliceous microfossils and dinoflagellate cysts to the ACEX site. These fundamentally different interpretations of the ACEX record highlight the necessity to study this peculiar interval in more detail. Apart from this specific controversy, the interval around 200 mcd can also provide more general insights into the pre-Quaternary history of the Arctic Ocean.

Published inorganic geochemical data indicate that drastic changes in detrital sediment provenance, bottom water redox conditions, and diagenetic processes occurred before and after the palynologically defined hiatus (Backman et al., 2006; Krylov et al., 2008; Martinez et al., 2009; März et al., 2010; Ogawa et al., 2009; Sangiorgi et al., 2008; Vogt, 2009). In this manuscript we want to specifically study the variability or detrital sediment sources, sedimentation processes, and redox conditions in the lower water column and sediments between 193 and 205 mcd in the ACEX record. We will discuss our results in the context of paleoenvironment changes in the Arctic, and provide a geochemical and mineralogical perspective on the argument of continuous versus non-continuous sedimentation between the Eocene and the Miocene on the CLR.

2. Material and methods

Sample material was partly obtained from cooperating scientists (AWI Bremerhaven, R. Stein; University Utrecht, H. Brinkhuis) to generate a high-resolution geochemical data set for the interval between 193 and 205 mcd. Samples were frozen, freeze-dried and ground in an agate ball mill for subsequent analyses. Total organic carbon (TOC) contents were published by Stein (2007a,b) and are available for download from PANGAEA (www.pangaea.de, doi:10.1594/PANGAEA.548674). Inorganic carbon contents are not provided here because the studied sediment interval is overall very carbonate-poor (Backman et al., 2006). Sample aliquots were prepared for element analysis with Wavelength-Dispersive X-ray Fluorescence Spectrometry (WD-XRF, Panalytical PW 2400). A detail method description is given by März et al. (2010), as well as more general interpretation of element patterns.

Selected trace metals (TM), including Cd, Mo, Re, U, and rare earth elements (REE), were analyzed via Inductively Coupled Plasma Mass Spectrometry (ICP-MS, ThermoFisher, Element 2) from total acid digestion solutions. For acid digestions, 50 mg of sample was oxidized in polytetrafluoroethylene (PTFE) vessels with distilled HNO_3 (either with 2 ml overnight at ambient temperature, or with 0.5 ml at 180 °C for 2 h). Subsequently, samples were heated with 3 ml HF (40%) and 3 ml $HClO_4$ (70%) in closed PTFE autoclaves (PDS-6) for 8 h at 180 °C. After evaporating the acid mixture on hot plates at 180 °C to incipient dryness, 3 ml 6 N HCl aliquots were added three times and evaporated again to prevent precipitation of insoluble Al and Ti oxides. The wet residue was re-dissolved in 1 ml distilled HNO_3, diluted to 10 ml with deionized water, and heated in closed PTFE autoclaves (PDS-6) for 2 h at 180 °C. The acid digestions were diluted to 25 ml, and one drop of HF was added for stabilization of light rare earth elements (LREE). Most of the acids used (HNO_3, HCl, and $HClO_4$) were purified by subboiling distillation, HF was of Suprapure (Merck) quality. Prior to analysis the clear solutions were diluted 10-fold with 2% v/v HNO_3. Analytical precision was better than 8% (for detailed information see Schnetger et al., 2000). The accuracy of acid digestion method and ICP-MS analysis was better than 5%, as checked with suitable, extensively tested inhouse reference materials (Posidonia Shale PS-S, Black Sea BS, Demerara Rise Black Shale DR-BS).

To correct for variable dilution by biogenic or diagenetic components, elemental records are normalized to Al. This element is abundant in hemipelagic marine sediments, does not undergo diagenetic reactions, and is largely unrelated to biogenic processes. Element data are given in wt.% and ppm, and normalization to Al is displayed in%/% and ppm/% for major and minor elements, respectively (Supplement 2).

Element/Al ratios are further compared to respective average shale values (AS; after Wedepohl, 1971, 1991), and enrichment factors (EFs) are calculated for each element (Supplement 3) according to the following equation:

$$\mathrm{EF(element)} = \mathrm{Element/Al(sample)/Element/Al(AS)}.$$

The resulting EFs provide information if an element is enriched (EF>1) or depleted (EF<1) in a sample relative to AS, providing information about depositional processes (sorting and winnowing), redox conditions of bottom water and sediment, and the degree of restriction of the Arctic basin.

In addition, we calculated Mo/U ratios that were recently reported as proxies for restriction of silled anoxic basins, and for tracing mechanisms of trace element enrichment (Algeo and Tribovillard, 2009).

Reconstruction of paleoredox conditions via REE composition requires the calculation of the Ce anomaly after De Baar et al. (1988):

$$\mathrm{Ce/Ce^*} = 3(\mathrm{Ce/Ce_{shale}})/(2(\mathrm{La/La_{shale}}) + (\mathrm{Nd/Nd_{shale}}))$$

The North American Shale Composite (NASC; Gromet et al., 1984) is applied to normalize REE concentrations, as it is regarded to represent the lithology and REE composition of the circum-Arctic hinterland (Beeskow and Rachold, 2003).

Aliquots of the ground samples were analyzed for mineralogical composition by X-ray Diffraction (XRD), using the full quantification technique according to Vogt et al. (2002) that normalizes all determined mineral contents to 100%. Main mineral phases are displayed as wt.%, and include quartz, the sum of phyllosilicates, plagioclase, K-feldspar, as well as zeolites, amphiboles plus cordierite, and pyrite. In addition, as grain size data are not available, a grain size proxy was calculated based on the quartz + feldspars to phyllosilicates ratio. Quartz and feldspars are usually dominant in the sand + silt fraction, while phyllosilicates are mostly in the clay fraction, thus a higher ratio indicates coarser grain sizes (Müller, 1999; Vogt, 1997). Respective data sets are available for download from Pangaea (Vogt, 2010: www.pangaea.de, doi:10.1594/PANGAEA.747735).

3. Results

Based on geochemical and mineralogical results, the studied ~12 m thick sediment section is subdivided into four intervals. The layer from 202.0 to 203.4 mcd (brick signature in Figs. 1–4 and 6–8) represents a diagenetic front within Unit 1/6 (März et al., 2010; Sangiorgi et al., 2008; Stickley et al., 2008) that will not be described and discussed in