and enthalpies of mixing are predicted for garnet along the pyrope-grossular join. Simulations such as these can shed additional light on the link between mineral behaviour at the atomic level and macroscopic thermodynamic properties. For simulation techniques of this type to become sufficiently accurate for direct use in geological applications, there is an urgent need for improved experimental determinations of several key quantities, such as the enthalpies of mixing along both garnet joins.

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A 26 million year gap in the central Arctic Ocean Cenozoic record: why and how?

Introduction

The first marine deep-time Cenozoic record from the central Arctic Ocean was recently acquired during Integrated Ocean Drilling (IODP) Expedition 302 (the Arctic Coring Expedition, ACEX). About 430 m of sediments were partially recovered through drilling of the Lomonosov Ridge, in water depths of ~1300 m, 250 km from the North Pole (Fig. 3.12 a, b).

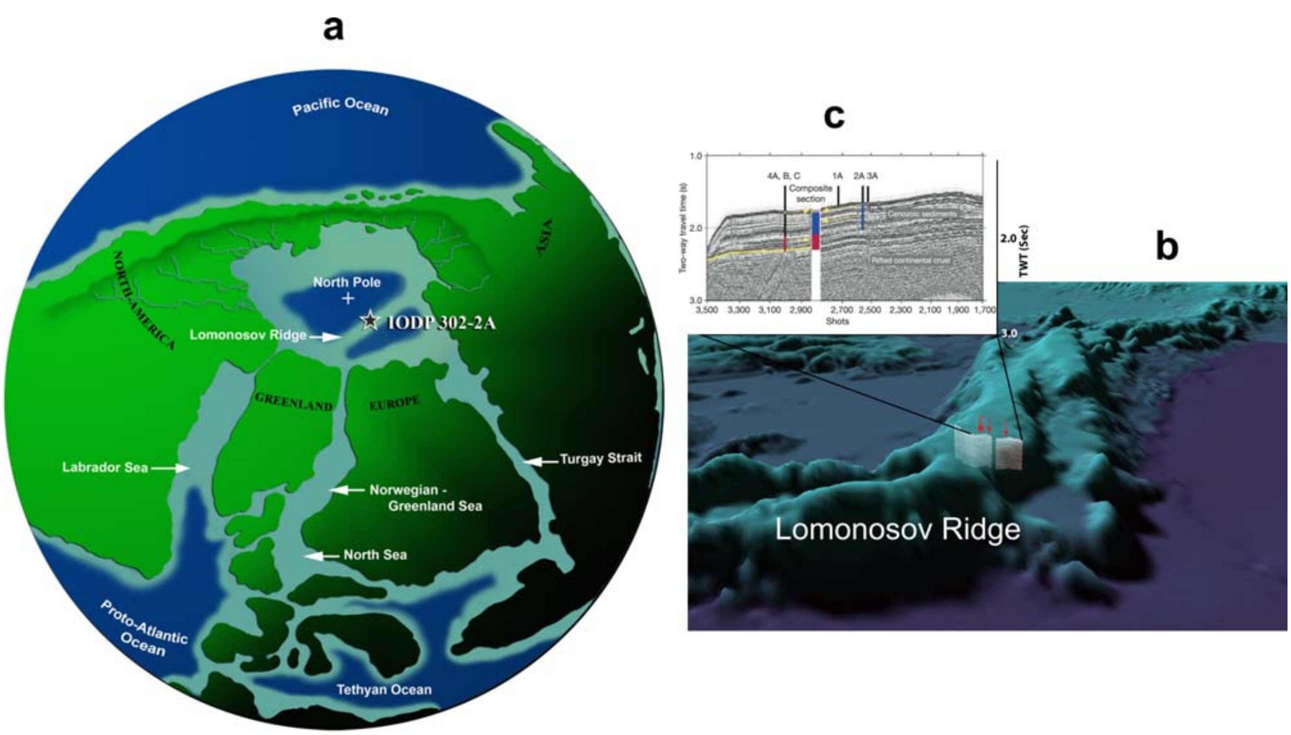

Figure 3.12: a – Drilling location on the Lomonosov Ridge (modified from Brinkhuis et al., 2006); b - detailed 3D bathymetry of the Lomonosov Ridge (courtesy of M. Jakobsson) with indication of the 4 drilled sites; c- Seismic profile of the LR with indication of the 4 sites drilled, and the composite section derived from the spliced cores

The Lomonosov Ridge is a fragment of continental crust rifted from the Barents-Kara shelf in the late Paleocene (~58 Ma ago) when sea floor spreading began along the Gakkel Ridge (Vogt et al., 1979). Sediments were recovered from four different and closely spaced holes (M0001, M0002, M0003 and M0004, Figure 3.12c) with scarce overlapping. Based on seismic profile correlations, chemostratigraphy, lithostratigraphy, and biostratigraphy, the four holes were spliced into a single stratigraphic section as best as possible (Fig. 3.12 c, Fig. 3.13). Recovery was about 80% in the upper 270 m, < 50% in the remaining part of the sequence. Overlying an Upper Cretaceous (Campanian) basement, sediments were deposited on the Lomonosov Ridge after its rifting from the Eurasian continental margin (Expedition 302 Scientists, 2006; Moran et al., 2006).
The sediments provide a unique record of the geological, paleoceanographical and paleoenvironmental evolution of the Arctic Ocean during the Cenozoic. Recovered sediments were divided into four major lithologic Units (Fig. 3.13), mostly based on geochemical and textural properties (Expedition 302 Scientists, 2006; Moran et al., 2006).

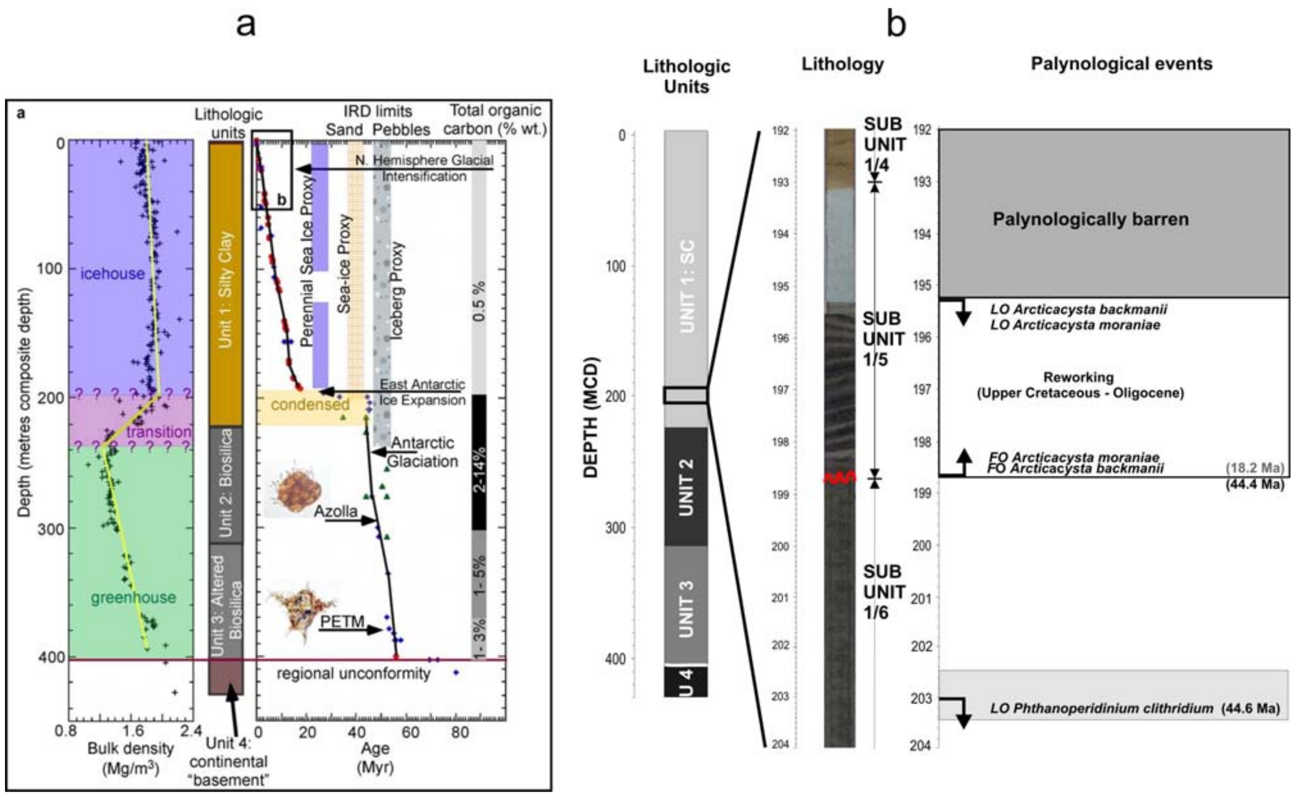

Figure 3.13: a) Age model for the ACEX core based on shipboard results and lithologic units (from Moran et al., 2006); b) Lithostratigraphic column, with the indication of the 4 lithologic units recognized in the ACEX section (Expedition 302 Scientists, 2006; Moran et al., 2006) and image of the core section, which contains the hiatus (red wiggled line) and the ‘zebra’ interval above it. Dinocyst events, which permitted the identification of the hiatus and its duration, are also reported: Last Occurrence (LO) of Phthanoperidinium clithridium (44.6 Ma), First Occurrence (FO) of the dinocysts belonging to the genus Arcticacysta marking the palynological break at 198.70 mcd (18.2 Ma) [Sangiorgi et al., 2008a, b].

Palaeogene sediments (Units 2 and 3) are very dark, partly laminated siliciclastic claystones rich in organic carbon (TOC up to 5%), pyrite and microfossils. They indicate a relative shallow marine setting, with frequent brackish or even fresh surface waters during the latest Palaeocene and the early Eocene (Brinkhuis et al., 2006). Neogene sediments (Unit 1, further subdivided in 6 subunits) are generally organic carbon and fossil poor silty muds with abundant dropstones and sand lenses (Expedition 302 Scientists, 2006; Moran et al., 2006).

Unexpectedly, preliminary biostratigraphical analysis of the ACEX record reported the occurrence of a "presumed condensed and possibly partially missing section at the transition between the Greenhouse and the Icehouse worlds, in the interval from ~44 to ~16 Myr ago" (Moran et al., 2006, Fig. 3.13a). Detailed biostratigraphical analyses, particularly based on dinoflagellate cysts (dinocysts), have then proved the existence of a hiatus, spanning ~26 million years from the middle Eocene (~44.4 Ma) to the late early Miocene (~18.2 Ma; Figure 3.13b). The hiatus, masked in the seismic profile, occurs at an abrupt change in sediment color, between subunit 1/6 and subunit 1/5 (core 2A 46X 1W, at 198.70 meters composite depth, mcd) of the ACEX record (Figure 3.13). Subunit 1/6 is characterized by dark brown sediments and contains the last occurrence (LO) of a middle Eocene marker dinocyst species (*Phthanoperidinium clithridium*). Lower subunit 1/5 is characterized by ~ 2.5 m black to dark grey centimeter-wide alternation, "zebra-like" bands, by Total Organic Carbon (TOC) contents up to 15% (Stein et al., 2006) and by a very distinctive dinocyst assemblage totally dominated by the new dinocyst genus Arcticacysta (with the species *A. backmanii* and *A. moraniae*) likely of early Miocene (Burdigalian) age. This interval also contains sparse reworked dinocysts of Cretaceous to Oligocene age (Expedition 302 Scientists, 2006; Figure 3.13 b).

The hiatus also marks an abrupt decrease in sedimentation rates, between 24.3 m/Ma in the middle Eocene to 8.0 m/Ma in the early Miocene (Backman et al., 2008, in press).

To unravel the nature of the hiatus, we performed a high resolution multiproxy palynological (dinocysts, pollen and spores), micropaleontological (siliceous microfossils), inorganic and organic geochemical study of sediments below and above the hiatus.

Material and methods

Samples were taken from lithological subunits 1/6, 1/5 and 1/4 (cores 2A 47X 3W to 2A 44X 1W, from 203.70 to 191.99 mcd; Figure 3.13 b). The sediments change from homogeneous dark into a cm-scaled alternation black and grey bands (called 'zebra') to light grey, blue and reddish-brown (Fig. 3.13 b).

For dinocyst and other palynomorph analysis, other than pollen and spores, samples were processed without oxidation, as outlined in Wood et al. (1996). For pollen and spores analysis, samples were also oxidized with 35% HNO_3 and stained with Bismarck Brown. Assemblages were counted using a light microscope at a magnification of 400X.

Methods and results for siliceous microfossil analysis for subunit 1/6 are provided by Stickley et al. (2008, in press). Quantitative X-ray fluorescence (XRF) measurements were performed on freeze-dried and homogenized (agate ball mill) sample powders. These were analyzed for major and minor elements using a Philips PW 2400 X-ray spectrometer, following standard methodology. Selected trace metals (TM), including Rare Earth Elements (REE), were analyzed by an "Element 2" ICP-MS (Finnigan MAT, Germany). Glycerol dibiphytanyl glycerol tetraethers (GDGTs) analyses to derive TEX86 (Tetra Ether IndeX of lipids with 86 carbon atoms) were performed following the procedure outlined in Schouten et al. (2007). HPLC/MS analyses were performed according to Hopmans et al. (2000 and 2004) and Schouten et al. (2007). The TEX86 was calculated according to Schouten et al. (2002) and converted to temperatures using these authors' equation:

TEX86 = 0.015*T + 0.28

Results

Fig. 3.14 present a selection of the proxies analysed, which will be discussed with the aim of unravelling the nature of the hiatus. A more complete reconstruction of the central Arctic Ocean environment at the Greenhouse to Icehouse transition can be found in Sangiorgi et al. (2008b).

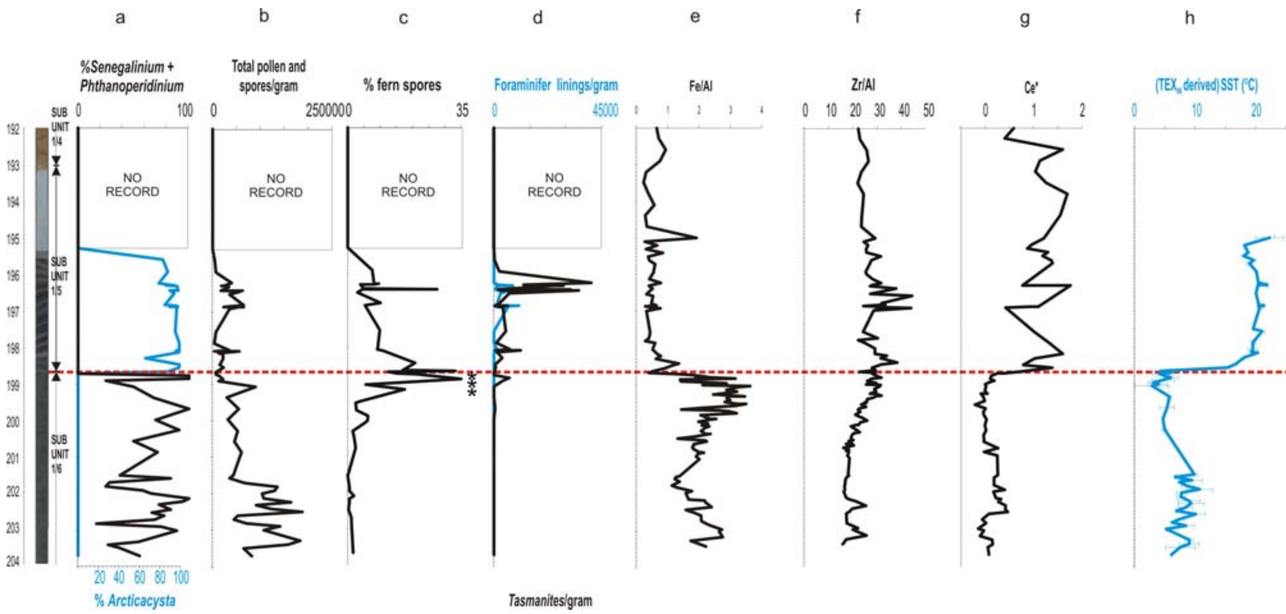

Figure 3.14 – selected proxies, which permitted the understanding of the nature of the hiatus (see text)

Below the hiatus (at 198.70 mcd), in the middle Eocene part of the record, dinocysts in subunit 1/6 are dominated by the taxa Senegalinium and Phthanoperidinium (Figure 3a). They are most concentrated in the interval 203.70 and 201.91 mcd. They represent cysts of fresh to brackish tolerant dinoflagellates (e.g., Brinkhuis et al., 2006). Terrestrial palynomorphs (pollen and spores) are also abundant in subunit 1/6, with the highest concentrations between 203.70 and 201.91 mcd (Fig. 3.14 b). Subunit 1/6 contains abundant warm temperate species (i.e., *Quercus* [oak], *Juglans* [walnut], *Ulmus* [elm]), and common occurrence of pollen of *Taxodium* (cypress) in the lower part. Fern spore abundance increases progressively throughout this interval, comprising 13-35% of assemblages between 198.92 and 198.70 mcd (Fig. 3.14 c). This part of the record immediately below the hiatus contains also abundant fungal spores (Fig. 3.14 c).
Siliceous microfossil (primarily diatoms, chrysophyte cysts, and ebridians) are abundant in the interval ~203.4 - 202.5 mcd. Freshwater chrysophyte cysts are the most abundant group. Above this interval siliceous microfossils are sparse (see Stickley et al., 2008, in press for details).
Large shifts in geochemical composition occur in the record analyzed. At around 202 mcd a very marked increase in K/Al ratio within a 2-samples interval, 16 cm apart indicates a drastic change in provenance. Above the K/Al shift from ~202 to 198.70 mcd is a pyrite-rich interval, as indicated by very high Fe/Al (Fig. 3.14 e), and S/Al. The increase in Fe/Al just below the hiatus indicates progressive freshwater influence (Figure 3.14 e). Above 202 mcd, Ti/Al, Zr/Al (Fig. 3.14 f), and Si/Al ratios steadily increase. This geochemical signal points towards increased current velocities and/or a shallower

environment, because the above elements are enriched in heavy minerals or quartz (Dellwig et al., 2000).

Sea surface temperatures (SSTs) reconstructed using TEX86 [Schouten et al., 2002]. Below the hiatus, temperatures were relatively constant with an average of 8.2 ±1.4ºC (Fig. 3.14 g). Toward the hiatus SSTs were lower averaging 4.7±1.0ºC (Fig. 3.14 h).

Above the hiatus, in lower subunit 1/5, the ‘zebra’ interval (198.70 – 195.30 mcd), dinocysts are usually abundant and the new early Miocene genus *Arcticacysta* [Sangiorgi et al., 2008a, in press] dominates the assemblages (Fig. 3.14 a). The ecological preference of the genus is unknown. However, the existence of monogeneric assemblages is suggestive of restricted environmental conditions. In this subunit there are also sparse reworked dinocysts, ranging in age from the Cretaceous to the Oligocene (see also Expedition 302 Scientists, 2006). Above 195.30 mcd, the record is palynologically barren, and dinocysts are not preserved. Freshwater algae are still present in lower subunits 1/5 and Tasmanites becomes very abundant in the upper meter of the zebra interval (Fig. 3.14 d). Freshwater indicators are still present in the sediments above the hiatus. However, fluctuating but fairly abundant concentrations of organic remains of agglutinated benthic foraminifers found in the ‘zebra’ interval (Fig. 3.14 d), imply that marine water ingression occurred at this time. The presence of deep water benthic foraminifera indicates that oxygenation at depth occurred, at least intermittently. At 198.70 mcd a drastic change is seen in Cerium (Ce)- anomalies (Fig. 3.14 g). Strong positive Ce-anomalies are evident are most likely related to the development of a more oxic environment.

Pollen assemblages of subunit 1/5 between the hiatus at 198.70 mcd and the palynologically barren zone at 195.30 mcd are dominated strongly by bisaccate pollen, suggesting colder atmospheric temperatures. The hiatus is clearly marked by a sharp change in TEX86-derived Sea Surface Temperatures. SSTs show an initial abrupt increase from 4 to 15°C followed by a rapid rise to relatively stable values of 19.7±1.5ºC (Fig. 3.14 h). The interval above 195.30 mcd is palynologically barren (no record, in Fig. 3.14)

Discussion

Our multiproxy reconstruction of central Arctic Ocean sediments from Lomonosov Ridge provides insights into factors related to the 26 million years hiatus in the mid-Cenozoic (from ~44.4 to ~18.2 Ma).

Very pronounced shifts in the dinocyst assemblages, inorganic geochemical ratios and TEX86-derived SST values clearly underline the position of the hiatus in the ACEX sediment record. This is placed at 198.70 mcd.

Below the hiatus increases in the Ti/Al and Zr/Al (Fig. 3.14 f) may indicate either enhanced current velocity and/or shallow environments. However, the lack of evidence for major changes in grain size and the high TOC values (~4-5%) below and above the hiatus (Expedition 302 Scientists, 2006; Stein et al., 2006) lead to the hypothesis of a progressive shoaling of the Lomonosov Ridge depositional site. This is confirmed by peaks in fern spores, most common in near-shore sites (e.g., Mudie, 1980) and the occurrence of fungal spores just below the hiatus (Fig. 3.14 c). Fern spores are still abundant above the hiatus, implying a shallow water environment. Consequently, the missing sediment record can be explained by erosion and/or non deposition of sediments in a site, which remained close to or at sea level for several million years. The sparse dinocyst reworking in the zebra interval (Fig. 3.14 b) is also a clear indication that older sediments were deposited somewhere around the site and later re-deposited when the Lomonosov Ridge started subsiding. Interplaying sea-level changes and tectonic activity (possibly uplift) must be invoked as possible causes for such a long gap in the sediment record, although a shallow water setting for the Lomonosov Ridge in the mid Cenozoic is inconsistent with classical post-rifting thermal subsidence models for passive margins (McKenzie, 1978) as well as the published model describing the subsidence of the ridge based on similar 'thermal cooling' assumptions (Moore et al., 2006).

Conclusions

Paleoenvironmental reconstructions based on dinocysts, pollen and spores, benthic foraminifera, inorganic and organic geochemistry and siliceous remains reveal conspicuous changes, suggesting a transition from brackish-fresh shallow water to open marine environments (see also Sangiorgi et al, 2008b in press). These environmental turnovers, coupled with the occurrence of such a large hiatus, cannot be due to climatic shifts alone, but suggest that major tectonic rearrangements coupled with sea level variations changed the depositional setting. The hiatus is likely the result of erosion and/or non deposition of sediments in a site, which remained close to or at sea level for several million years.

Beside unravelling the nature of the hiatus, the environmental reconstruction performed on this interval of the ACEX core tracks the development of the Arctic Ocean from its 'lake' phase in the middle Eocene (see also Brinkhuis et al., 2006) to its estuarine and marine phases in the early Miocene (see also Jakobsson et al., 2007). The warm SSTs (~20ºC) in the zebra interval immediately above the hiatus can be partly explained with the onset of the ingression of warmer north Atlantic waters. Above 195.30 mcd, sediments bare proofs of a well ventilated environment (lack of palynomorphs and extreme oxic conditions as testified by the Cerium anomaly, Figure 3). This interval, in the early Miocene, is coeval to the complete opening of the Fram Strait between Svalbard and Greenland, which led to a well-ventilated Arctic Ocean (Jakobsson et al., 2007).

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