GEOPHYSICAL RESEARCH LETTERS, VOL. 28, NO. 11, PAGES 2217-2220, JUNE 1, 2001

Light $\delta^{13}C$ events during deglaciation of the East Greenland continental shelf attributed to methane release from gas hydrates

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Abstract. We have documented high-resolution stable isotope records from three marine cores on the East Greenland shelf. These records exhibit three rapid light $\delta^{13}C$ events (-3 to -7‰) in benthic and planktic foraminifera during deglaciation that are spatially and temporally transgressive. The light $\delta^{13}C$ events are associated with light planktic $\delta^{18}O$, indicative of meltwater. In Kangerlussuaq Trough, the first $\delta^{13}C$ event occurs at initial deglaciation, 13.94-14.0 cal ka and the second occurs at 12.85-12.9 cal ka. A younger event at 10.3–9.3 cal ka is recorded near the mouth of Nansen Fjord during final deglaciation. The hypothesized mechanism for the light $\delta^{13}C$ is expulsion of methane from gas hydrates in the seafloor from pressure release during ice sheet retreat.

Introduction

Marine records of oxygen and carbon isotopes have recently documented $\delta^{13}C$ depletions between 3-5‰ and attributed them to rapid expulsion of methane from gas hydrates (Kennett et al., 2000; Hesselbo et al., 2000). Gas hydrates are solids formed under high pressure and low temperature in sediments that trap water and CH_4 (Kvenvolden, 1993). When overlying pressure decreases or temperature increases, gas hydrates dissociate and release methane (Dickens et al., 1995). If significant amounts of methane are released from gas hydrates, then the $\delta^{13}C$ of bicarbonate, from which foraminifera secrete their shells, decreases considerably (Rathburn et al., 2000). Comparison of living versus fossil foraminifera at cold-water seeps along the California margin show large $\delta^{13}C$ excursions near methane seeps (Rathburn et al., 2000).

Ice core records also document significant changes in methane coincident with temperature warmings (Stauffer et al., 1988; Severinghaus et al., 1998; Brook et al., 2000). The ice core methane concentration spikes are attributed to increases in tropical and boreal continental wetland methane sources. Brook et al. (2000) infer methane increases to be slower than temperature due to the lag time for the terrestrial ecosystem to respond to temperature, and they dismiss methane expulsion from gas hydrates as a significant methane source. Yet, few causes, besides methane, can explain such light $\delta^{13}C$ intervals in marine records (Dickens et al., 1995). Methane release from gas hydrates may not always impact global climate, but it cannot be dismissed as an important source of methane, especially from polar regions (Kvenvolden, 1993).

We present three events of anomalously light $\delta^{13}C$ values, -3 to –7‰, from benthic and planktic foraminifera during deglaciation of the East Greenland continental shelf, 68°N, correlative to intervals of light $\delta^{18}O$, indicative of meltwater. Evidence is presented to attribute the anomalous $\delta^{13}C$ values to the release of methane from gas hydrates by pressure release during deglaciation.

Regional Setting

The morphology of the East Greenland continental shelf, ~68°N, is marked by shallow banks and deep (upwards of 650 mwd), fault controlled, glacially modified troughs (Figure 1). Glacial, deglacial and post-glacial sediments have accumulated within these troughs (Andrews et al., 1994, 1996; Stein, 1996; Jennings and Weiner, 1996; Smith, 1997). The East Greenland current (EGC), flowing south along East Greenland from the Arctic Ocean, is composed of cold, fresh water at the surface that carries icebergs and sea ice and warm, saline Atlantic-type water at depth (Aagaard and Coachman, 1968). The inland ice expanded onto the continental shelf, filled both troughs, and extended to the shelf break during the Last Glacial Maximum (Andrews et al., 1996; Jennings et al., 1998). Ice retreated from the shelf edge prior to 14,000 ^{14}C years ago, with an inferred standstill of the ice margin on the

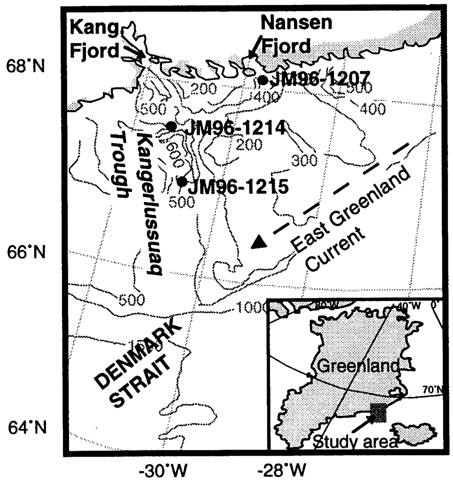

Figure 1. Bathymetric map of East Greenland, in meters, showing cores used in this study. White areas on land indicate present-day locations of glaciers.

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Paper number 2000GL012627.
0094-8276/01/2000GL012627$05.00

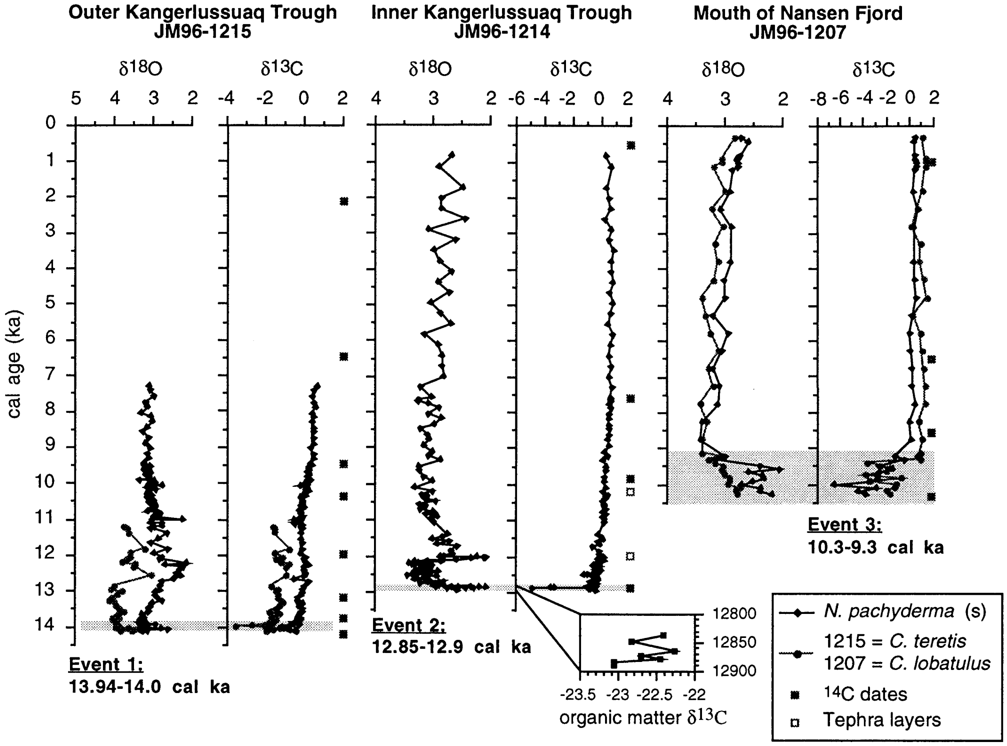

Figure 2. Stable isotope measurements of δ^{13}C and δ^{18}O from benthic and planktic foraminifera, and bulk organic matter δ^{13}C. There are three time-transgressive intervals of light δ^{13}C and δ^{18}O values, as shown by the gray lines or gray box. Benthic foraminifera isotope data are shown as circles and planktic foraminifera isotope data are shown as diamonds. Squares indicate levels of radiocarbon dates (filled squares) and tephra (open squares) used in the age models.

inner shelf during the Younger Dryas, and then final retreat into the fjords soon afterwards (Andrews et al., 1996; Jennings et al., 1998).

Methods

Sediment gravity cores, 10 cm in diameter, were raised from the East Greenland shelf in 1996 on the *R/VJan Mayen.* Two-centimeter thick samples were removed from the cores every 5 cm. The samples were wet sieved at 63 and 106 μm, and benthic and planktic foraminifera were picked from the 106-250 μm fraction for stable isotope measurements. We measured the stable isotopic composition of planktic foraminifera (*Neogloboquadrina pachyderma* (s)) from all cores and benthic foraminifera (*Cassidulina neoteretis* or *Cibicides lobatulus*) from cores with a high enough abundance of these benthic species[1]. These benthic foraminifera are typically used for isotopic analyses in paleoceanographic reconstructions on Arctic shelves (Vilks and Deonarine, 1988; D.A.R. Poole, unpublished data). Stable isotope measurements of foraminifera from cores JM96-1214 and -1215 were performed at WHOI on a Finnigan MAT 252 mass-spectrometer with an on-line Kiel Carbonate Device (Ostermann and Curry, 2000). Foraminifera samples from JM96-1207 were analyzed at the Leibniz-Laboratory for Radiometric Dating and Stable Isotope Research at Kiel University on a Finnigan MAT 251 mass-spectrometer with an on-line Kiel Carbonate Device, with a precision of ±0.05‰ for carbon and ±0.08‰ for oxygen isotopes. Selected samples with enough individuals for duplicates were measured, and the light δ^{13}C values were duplicated within machine error. Bulk sediment samples were analyzed for δ^{13}C on a Finnigan Delta-S isotope ratio mass spectrometer after preparation using the continuous flow method at the Boston University Stable Isotope Laboratory, with a precision of 0.2‰.

Age control was gained for all cores from radiocarbon dating[1] (Smith and Licht, 2000; Hagen, 1999; A.E. Jennings et al., Holocene shift in Arctic sea ice variability on the East Greenland shelf, submitted to *Holocene*, 2000), and the presence of Vedde and Saksunarvatn Ash in cores JM96-1214 and -1215 (Jennings et al., manuscript in preparation). Radiocarbon ages were calibrated using CALIB 4.1 (Stuiver and Reimer, 1986; 1993). Calibrated radiocarbon dates and tephra layers used in the age models are plotted on Figure 2.

Results

The marine cores recovered ice-proximal and postglacial sediments (Jennings et al., 1998; Hansen, 1998). Seismic stratigraphic data indicate that glacial diamicton sediments directly underlie these recovered sediments (Stein, 1996). Therefore, basal radiocarbon ages constrain the timing of glacial retreat and onset of glacial marine sedimentation. There are three intervals of light δ^{13}C and δ^{18}O values in benthic and planktic foraminifera: 13.94-14.0, 12.85-12.9, and 10.3-9.3 cal ka (Figure 2). The δ^{13}C depletions are 4-6‰ lighter than average core values. These three events are temporally and spatially distinct, and the age and location differences indicate that the events are transgressive from the mid continental shelf to the coast (Figures 1&2). Accumulation rates in these light δ^{13}C and δ^{18}O intervals range from 300 cm/ka in JM96-1214 to 200 cm/ka in JM96-

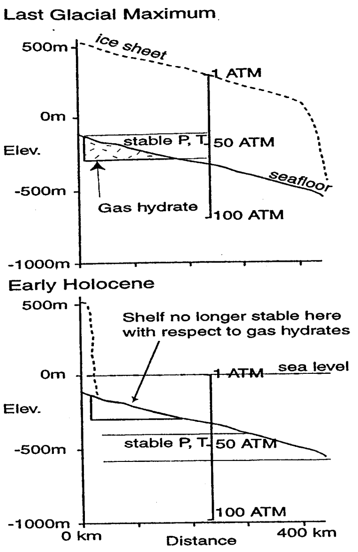

Figure 3. Conditions on the East Greenland margin at the Last Glacial Maximum (top) and immediately following ice retreat (bottom). The presence of the ice sheet on the continental shelf increased the pressure in the sediments, and maintained the temperature close to freezing, creating a broad region of the shelf that was stable with respect to gas hydrates (ca 40-60 atm, 0°C). Retreat of the ice sheet at the end of the Last Glacial Maximum reduced the pressure due to overlying ice, and allowed contact with warm AIW (3-4°C) from the EGC, destabilizing the methane from the gas hydrates.

1215 to 100 cm/ka in JM96-1207. The light $\delta^{13}C$ events are larger in the planktic than benthic foraminifera in JM96-1207, but greater in the benthic foraminifera in JM96-1215. In the JM96-1214 light $\delta^{13}C$ event, dinocyst concentrations are lower than 200 cysts per cm^3, indicating low productivity. The dinocyst assemblage is dominated by *Algisdasphaeridum(?) minutum*, and indicates that sea ice was present for 7-11 months/year and cold summer sea surface temperatures (averaging ~1.5°C in August) (deVernal and Hillarie-Marcel, 2000). Light $\delta^{18}O$ events of 0.5-1‰ are associated with each $\delta^{13}C$ depletion. Stable isotope values in bulk sedimentary organic matter from the light $\delta^{13}C$ interval in JM96-1214 ranges from -22 to -23 ‰.

Discussion

The extreme $\delta^{13}C$ depletions we observe in both planktic and benthic foraminifera (Figure 2) were most likely derived from methane expelled from gas hydrates, because methane $\delta^{13}C$ can reach -90‰ (Kvenvolden, 1993). The core sites within Kangerlussuaq and Nansen shelf troughs (>400 mwd) are sufficiently deep for gas hydrate formation (Dickens and Quinby-Hunt, 1994; Kvenvolden, 1993). Total organic carbon contents (averaging = 0.4 wt %) may be too low to produce methane via microbial activity (Kvenvolden, 1993). Based on the spatial- and time-transgressive nature of the $\delta^{13}C$ and $\delta^{18}O$ depletions (Figures 1&2), we hypothesize that ice retreat across the shelf during deglaciation is the causal mechanism for release of methane from gas hydrates (Figure 3). Ice retreat is inferred from the existence of ice-proximal glacial marine sediments overlying glacial till (Stein, 1996; Andrews et al, 1996; Jennings et al., 1998). Since the dinocyst assemblage indicates the presence of sea ice over our sites for 7-11 months of the year (deVernal and Hillaire-Marcel, 2000), the light $\delta^{18}O$ values in planktic foraminifera are attributed to both glacial meltwater and sea ice melt.

Retreat of the ice margin would have released enough pressure to dissociate the gas hydrates and expel methane into the overlying sediments and ocean water (Figure 3) (Dickens and Quinby-Hunt, 1994; Kvenvolden, 1993). A 600 m thick ice margin would produce a basal pressure of ca. 550 atm and a basal temperature near freezing. Ice retreat and associated isostatic rebound would both reduce the seafloor pressure, depending on the change in seafloor depth. Additionally, ice retreat would allow warm EGC water to flow across the site, increasing bottom water temperatures from zero to 2°-4°C. This increase in temperature would further destabilize gas hydrates (Figure 3) (Dickens and Quinby-Hunt, 1994; Kvenvolden, 1993). The low $\delta^{18}O$ values of benthic foraminifera during the $\delta^{13}C$ excursions (Figure 2) are consistent with intrusion of warm bottom waters of the EGC.

We analyzed the $\delta^{13}C$ of the bulk organic matter, primarily composed of phytoplankton, across Event 2 to determine whether phytoplankton had utilized the isotopically depleted carbon derived from methane. Because the organic matter $\delta^{13}C$ is similar to the $\delta^{13}C$ of average marine organic matter (ca. -22‰, Figure 2), we infer that the surface layer in which the phytoplankton lived did not entrain methane-derived carbon.

We excluded four alternative hypotheses as the cause of the $\delta^{13}C$ events: biological effects, vital effects, terrestrial influx of depleted carbon, and air-sea exchange. First, the light $\delta^{13}C$ values cannot be attributed to the nutrient dynamics of ocean water. The PO_4 concentration would have to double or triple to support the corresponding light $\delta^{13}C$ values, according to the Redfield Ratio (Schlesinger, 1997). Second, vital effects are dismissed because we analyzed single species of foraminifera and the vital effects in foraminifera are too small (2-3‰) to account for the large $\delta^{13}C$ depletions (McCorkle et al., 1990; D.A.R. Poole, unpublished data; Simstich, 1999). Third, if a source of isotopically depleted organic matter, such as coal from the Kangerlussuaq region (Brooks and Nielsen, 1982), were carried to the ocean by rivers or glaciers, 11-26% of the marine DIC would have to derive from that source. We cannot conceive of a mechanism by which to transport and remineralize this quantity of recalcitrant organic carbon from land to ocean[1]. Lastly, the air-sea exchange of carbon is not large enough to explain this extreme depletion of $\delta^{13}C$ in foraminifera (Lynch-Stieglitz et al., 1995). The initial invasion of isotopically-depleted atmospheric carbon is too small to create the observed $\delta^{13}C$ depletion events, and the long term effect of atmospheric exchange is to enrich the surface ocean (Lynch-Stieglitz et al., 1995).

Conclusions

We have documented a robust signal of three light $\delta^{13}C$ events, and propose a causal mechanism for these $\delta^{13}C$ events: the expulsion of methane from destabilized gas hydrates when bottom pressure decreased and bottom temperature increased

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[1] Supporting material is available via Web browser or via Anonymous FTP from ftp://kosmos.agu.org, directory "apend" (Username = "anonymous", Password = "guest"); subdirectories in the ftp site are arranged by paper number. Information on searching and submitting electronic supplements is found at http://www.agu.org/pubs/esupp_about.html.

following retreat of the East Greenland ice sheet. These three events are not documented in nearby Greenland ice core records (Brook et al., 2000), and hence, may be localized events of insufficient magnitude to impact global climate.

Our results are consistent with other studies that attribute anomalous carbon isotopic depletions in marine sediments to the release of biogenic methane from destabilized methane hydrates (Kennett et al., 2000; Hesselbo et al., 2000; Dickens et al., 1995). Our study is unique in invoking both pressure and temperature changes associated with ice shelf retreat as the mechanism for gas hydrate dissociation.

Acknowledgments. We wish to thank the scientists and crew of the *R/V Jan Mayen* (University of Tromsø) for core collection, N. Weiner for radiocarbon sample preparation, and R. Hilberman and K.V. Hansen for isotope sample preparation. This manuscript greatly benefited from reviews by G. Dickens and an anonymous reviewer. This research was supported by NSF grants OPP-9615935 and OPP-9707161, the GSA Gretchen L. Blechschmidt Grant, and the CU Beverly Sears Grant.

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(Received: November 14, 2000; Revised: February 26, 2001; Accepted: March 1, 2001)