

Carbon cycling and burial in the glacially influenced polar North Atlantic

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[1] We have collated published records of carbon storage (wt % calcium carbonate and organic carbon) in polar North Atlantic sediments in order to assess the role that the glacial history of Greenland and Fennoscandia may have had on carbon cycling in this oceanographically important region. The proportion of carbonate in sediment varies between 0 and ~50%, while that of organic carbon varies between 0 and ~2.0%. The spatial variation of the concentration and accumulation of both constituents is markedly different. Bulk accumulation shows a strong relationship with depth, distance offshore, and the location of major glacial outlets on neighboring landmasses. Therefore, ice sheet dynamics and erosion influence carbon (especially organic carbon) storage strongly during the late Weichselian (27-12 ^{14}C ka) via their impact on sedimentation rates and constituents. In contrast, water mass characteristics are important in determining the pattern of carbon storage during the Holocene. Carbonate fluxes to the polar North Atlantic sediment column fall by ~50% during glacial to $\sim 1.1 \times 10^{13}$ kg kyr $^{-1}$, but organic carbon storage is maintained at or greater than interglacial levels ($\sim 4.6 \times 10^{11}$ kg kyr $^{-1}$). This represents a 100% change in the ratio of preserved inorganic to organic carbon. When combined with reduced deep water ventilation, respiration of this relatively greater organic carbon flux in both the water and sediment columns provides a good explanation for the observed periodic enhanced dissolution of carbonate in polar North Atlantic late Weichselian sections, perhaps enhancing CO $_2$ storage in deep waters. *INDEX TERMS:* 4806 Oceanography: Biological and Chemical: Carbon cycling; 1050 Geochemistry: Marine geochemistry (4835, 4850); 3022 Marine Geology and Geophysics: Marine sediments—processes and transport; 9325 Information Related to Geographic Region: Atlantic Ocean; *KEYWORDS:* carbon cycling; North Atlantic; ice sheet

1. Introduction

[2] The partial pressure of atmospheric carbon dioxide ($p\text{CO}_2$) is believed to have ranged from ~200 to ~280 parts per million by volume (ppmv) during the last four glacial-interglacial cycles [Petit *et al.*, 1999]. The causes of these variations have been debated intensely over the past decade, while resolution of the fundamental mechanisms controlling CO $_2$ storage and release in the major exogenic reservoirs becomes more pressing [e.g., Petit *et al.*, 1999; Archer *et al.*, 2000; Falkowski *et al.*, 2000; Sigman and Boyle, 2000]. The primary control on carbon cycling and $p\text{CO}_2$ variation on glacial-interglacial timescales is acknowledged as changes in the composition of oceanic reservoirs [Broecker, 1982; Broecker and Peng, 1982]. Interest in specific causal mechanisms has become focused on marine organic carbon (C_{org}) cycling and its interaction with calcium carbonate (CaCO $_3$) dissolution and deposition, through increased nutrient cycling and/or reduced CO $_2$ ventilation at high (especially southern) latitudes [e.g., Keir, 1988; Howard and Prell, 1994; Elderfield and Rickaby, 2000; Stephens and Keelings, 2000], or significant alteration in the relation between calcite (CaCO $_3$) and organic carbon fluxes and their burial [Archer and Maier-Reimer, 1994; Archer, 1996]. Therefore determining the relative fluxes of organic carbon and CaCO $_3$ through time at high latitudes has become critical in assessing how $p\text{CO}_2$ variations may be related to other aspects of environmental

change. This paper seeks to redress our lack of knowledge of the fluxes of organic carbon and CaCO $_3$ in the polar North Atlantic, a series of oceanic basins strongly influenced by ice sheets and fundamentally important to the production of North Atlantic Deep Water (NADW) and the rate of thermohaline circulation.

[3] The global nonshelf flux of marine C_{org} to oceanic sedimentary storage (2.4×10^{13} g C yr $^{-1}$) is ~12% that of inorganic carbon or calcite (20×10^{13} g C yr $^{-1}$) [Smith and Hollibaugh, 1993; Milliman and Drozler, 1996]. The ratio of preserved $C_{\text{org}}/\text{CaCO}_3$ is therefore low, ~0.12, in the deep ocean [Shaffer, 1993]. Indeed, the ratio of fluxes of C_{org} and CaCO $_3$ through the water column (rain ratio) is one of the critical factors that determine carbonate preservation in the sediment column [Archer and Maier-Reimer, 1994]. Perturbation of these ratios impacts on the amount of dissolved CO $_2$ in bottom waters as follows. An increase in calcite flux to the deep ocean is associated with increased degassing of CO $_2$ from surface waters into the atmosphere. Increased C_{org} transport to depth may result from increased productivity in surface waters, which extracts CO $_2$ from the atmosphere, or greater input of labile “terrestrially derived” C_{org} . The increased flux of organic carbon charges bottom waters with CO $_2$ as a result of enhanced respiration at depth and in the oxic zone of the sediment column. These processes promote the enhanced dissolution of CaCO $_3$ both in the water column and in the sediment surface: “respiratory calcite dissolution” [Archer and Maier-Reimer, 1994]. Both of these mechanisms for bicarbonate release will promote an increase in the $p\text{CO}_2$ of the deep water. Thus raising of either the rain ratio or the ratio

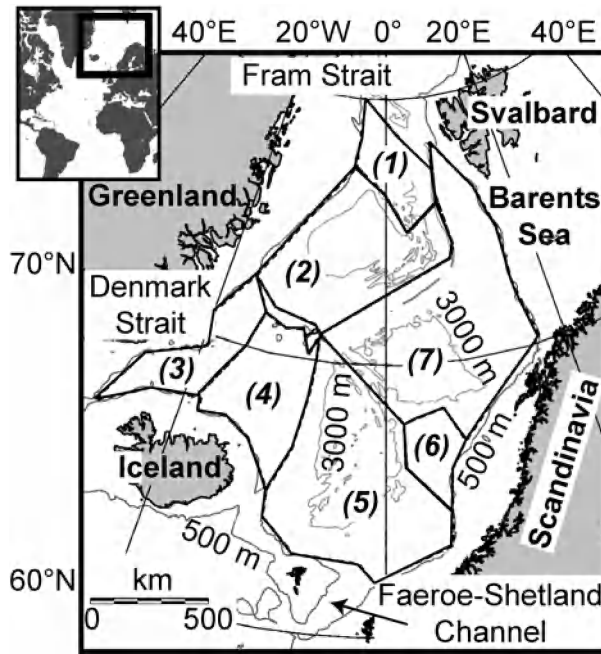


Figure 1. The polar North Atlantic constitutes seven major physiographic areas below the shelf break (thick outline): 1, Boreas Basin; 2, Greenland Basin; 3, Denmark Strait Basin; 4, Iceland Plateau; 5, Norwegian Basin; 6, Vøring Plateau; 7, Lofoten Basin. Water mass exchange is limited principally to the Fram Strait connection with the Arctic Ocean, the Barents Sea, and transport into and out of the North Atlantic via the Faeroe-Shetland Channel and the Denmark Strait.

of preserved $C_{org}/CaCO_3$, by either increasing the C_{org} flux or reducing the calcite flux promotes CO_2 release to and storage in deep waters.

[4] It follows that variations in C_{org} fluxes have potential influence on pCO_2 levels over glacial-interglacial cycles [e.g., Broecker and Peng, 1989; Archer and Maier-Reimer, 1994; Howard and Prell, 1994]. Attention to date has focused primarily on the Southern Ocean. In this paper, we examine the polar North Atlantic (Figure 1). The region is of primary importance to deep water formation in the Northern Hemisphere [Hopkins, 1991; Hansen and Østerhus, 2000]. The neighboring European landmasses are subject to large variations in ice volume and sediment delivery to the oceans in contrast to the less extreme variations of the Greenland Ice Sheet on the western margin [Elverhøi et al., 1998a]. Ice sheets are extremely efficient erosive agents [e.g., Elverhøi et al., 1998b] and are responsible for depositing great fluxes of sediment to the polar North Atlantic during the Quaternary [Sejrup et al., 1996; Dowdeswell and Siegert, 1999]. This additional sediment input is likely to impact on carbon cycling in the polar North Atlantic and may have an impact on atmospheric CO_2 concentrations. Indeed, investigations of the effect of glacial activity on the deposition of carbon in the Arctic Ocean and Labrador Sea have already demonstrated a significant but largely unquantified input of terrestrially eroded and meltwater-related organic carbon related to ice sheet erosion [Stein, 1991; Schubert and Stein, 1996; Knies and Stein, 1998].

[5] We present collations of $CaCO_3$ and C_{org} measurements from both public and published sources for the polar North Atlantic in order to determine the variability of calcite and

organic carbon fluxes for two periods during the last glacial-interglacial cycle and their relation to ice sheet dynamics. The concentrations of C_{org} and $CaCO_3$ are mapped, and fluxes are determined from these concentrations by combining mapped linear sedimentation rates with an assumed bulk density. The potential role of ice sheets as a control on global carbon cycling is addressed by comparing fluxes with the reconstructed behavior of the Eurasian ice sheet. We conclude that changes in C fluxes and rain ratios during the late Weichselian related to glacial activity result in a 100% increase in the ratio of preserved $C_{org}/CaCO_3$ in the polar North Atlantic. Such changes promote enhanced carbonate dissolution and CO_2 storage in polar North Atlantic Deep Water.

2. Methodology

[6] We will examine carbon burial during the late Weichselian (27-12 ^{14}C ka) in the polar North Atlantic. The polar North Atlantic consists of the basins and plateaux bounded by the Scotland-Iceland-Greenland Ridge to the south and the Fram Strait to the north. Exchanges of water masses are limited to the Fram Strait, the Barents Sea, and through the major sills in the Scotland-Iceland-Greenland Ridge, including the Denmark Strait and Faeroe-Shetland Channel (Figure 1). These restrictions to water exchange have important implications for thermohaline circulation at the glacial-interglacial timescale, because of their limited depth [Rasmussen et al., 1996; Whitehead, 1998]. The study region is confined to nonshelf environments deeper than 500 m water depth, divided according to major, tectonically related physiographic features of the seafloor (Figure 1). Defined in this fashion, the polar North Atlantic covers an area of 1.71×10^6 km², or $\sim 0.5\%$ of the global ocean. Water depths average $\sim 2500 \pm 600$ m. The Iceland and Vøring Plateaux and Denmark Strait Basin are the shallowest

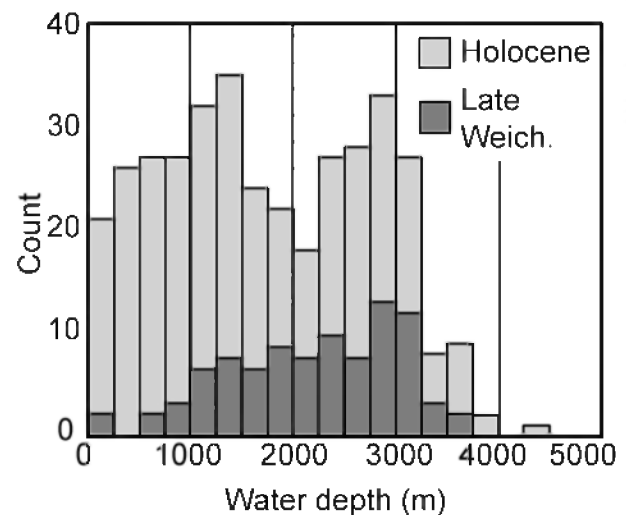


Figure 2. Depth distribution of core locations used in interpolating accumulation flux grids in the polar North Atlantic during the Holocene (light shading) and late Weichselian (dark shading). Water depths are sampled approximately equally, with lower overall sampling levels during the late Weichselian. Cores at water depths shallower than 500 m are included to allow meaningful interpolation up to the shelf break.

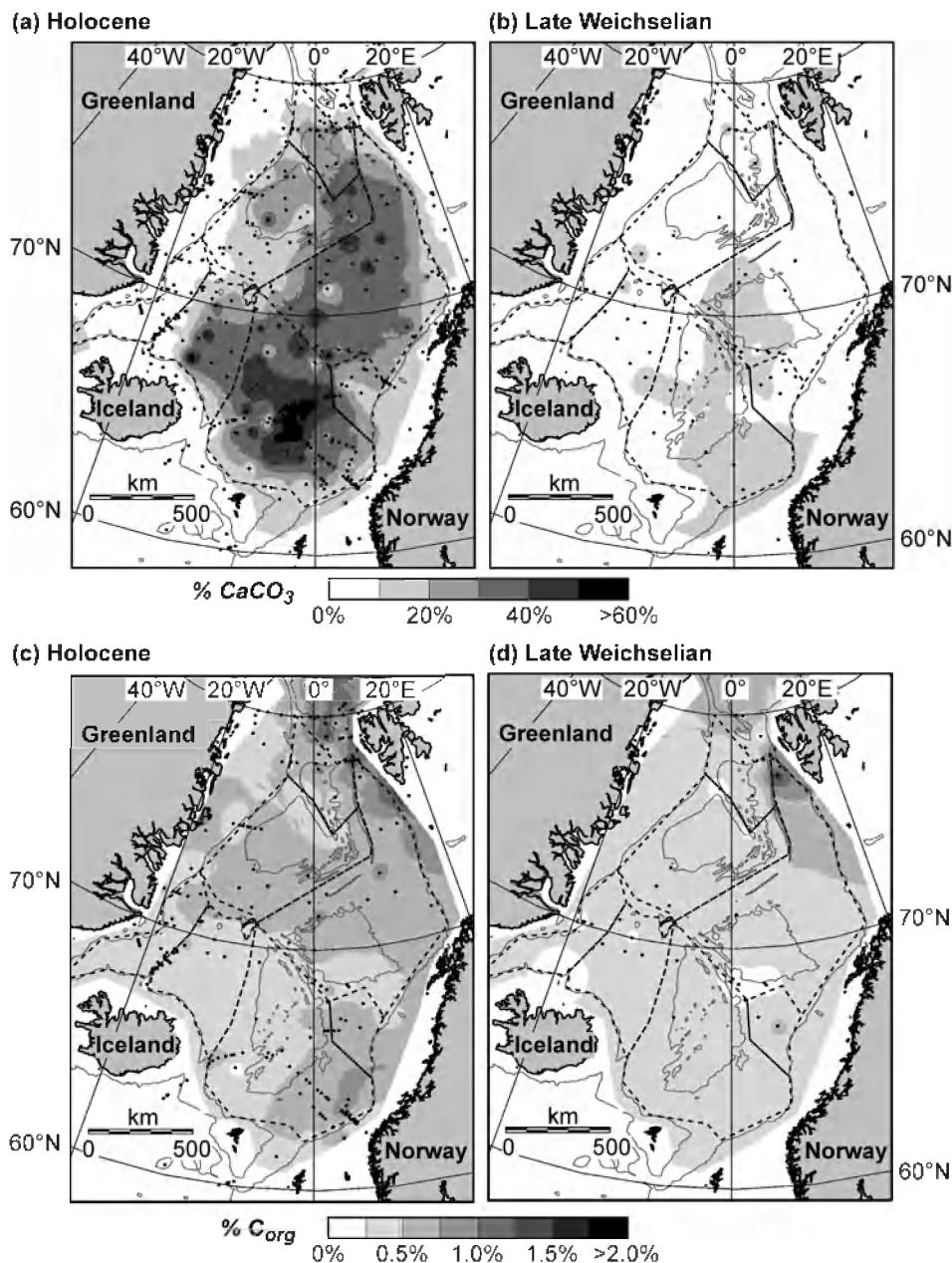


Figure 3. Holocene and late Weichselian concentrations of (a and b) CaCO_3 and (c and d) C_{org} by percentage weight in polar North Atlantic sediments. Core locations are shown by dots.

regions (100–1400 m), while the remaining basins are significantly deeper (2400–2800 m).

[7] Two periods of sedimentation are examined in order to contrast “glacial” and “interglacial” cycling, namely, the late Weichselian (27–12 ^{14}C ka) and the Holocene (12–0 ^{14}C ka), respectively. This timeframe corresponds to oxygen isotope stages (OIS) 3.1 to 2 for the late Weichselian and OIS 1 for the Holocene. We feel this division adequately captures broad-scale changes in oceanography, glaciology, tectonics, and climatology, which are significant in assessing the role of ice sheet growth and decay on carbon cycling in the region. Extremely high temporal resolution studies are unlikely to be significant in assessing the polar North Atlantic’s role in global carbon

cycling, because changes at the submillennial scale (e.g., Dansgaard-Oeschger cycles) are too short to promote large-scale changes in $p\text{CO}_2$ [Staufner *et al.*, 1998]. Assessment of the deglacial period (14–10 ^{14}C ka) may prove instructive but is for future investigation.

[8] Up to 600 core sites are used in the analysis. Core data were extracted from published records and publicly available data from the German Pangaea core database (<http://www.pangaea.de>), where much of the published European core data are archived. The following parameters were obtained for each core, where possible: location, water depth, Holocene and late Weichselian carbonate and organic carbon percentages by weight, and the thickness of sediment deposited during the Holocene and late Weichselian. Data

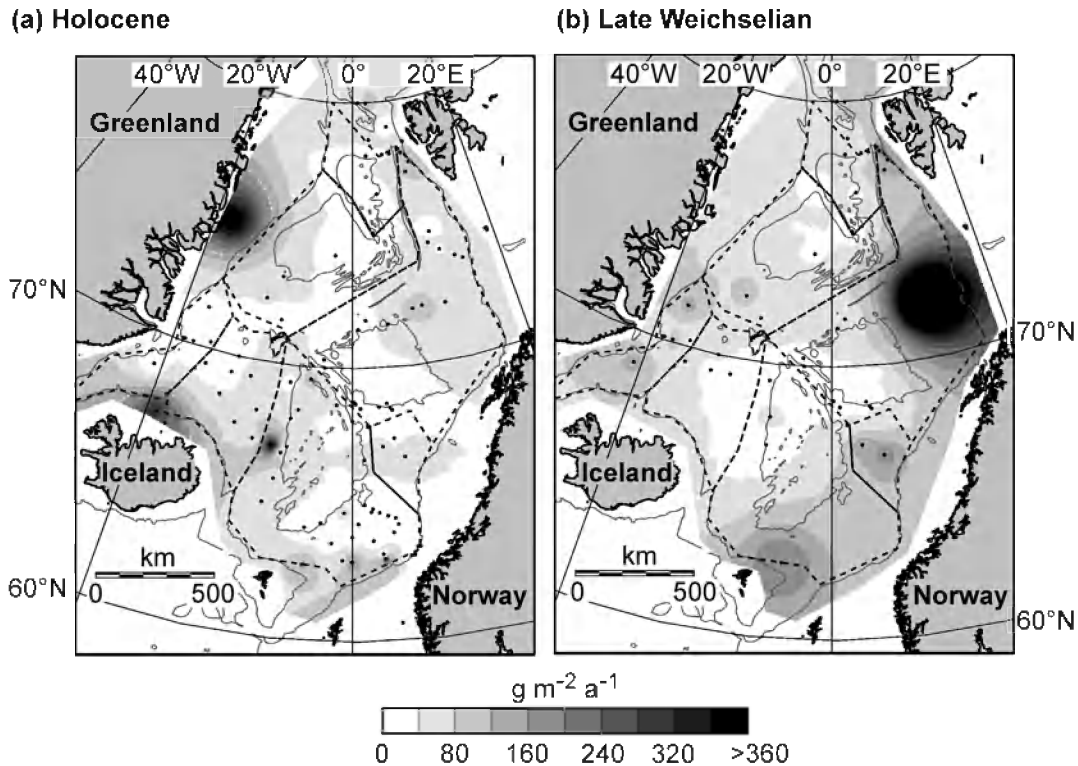


Figure 4. (a) Holocene and (b) late Weichselian bulk accumulation fields of polar North Atlantic sediments. Core locations are shown by dots.

are available electronically as Appendix 1.¹ The maximum number of data points are available for Holocene measurements of CaCO_3 and C_{org} percentages.

[9] The Holocene environment is generally well characterized in all parameters, with the glacial period being relatively under-sampled in comparison. However, all water depths are sampled approximately equally (Figure 2). Sites from the shelf are included to allow smooth interpolation of accumulation grids up to the 500 m water depth limit (Figures 3, 4, 5, and 6). We infer that the distribution and number of cores is sufficient to characterize the polar North Atlantic from gridding water depth at core locations, which reproduces well the overall morphology of the region.

[10] CaCO_3 and C_{org} are standard parameters measured on cores taken for marine studies. Typically, total carbon and total organic carbon are measured on unmodified and acid-leached or thermally decalcified samples, using either a LECO or Hereaus CHN elemental analyzer. CaCO_3 concentration is then determined by the difference between total carbon (TC) and total organic carbon (TOC), multiplied by a stoichiometric factor of 8.33:

$$\text{CaCO}_3\% = (\text{TC}\% - \text{TOC}\%) 8.33. \quad (1)$$

Older techniques rely on measuring degassed CO_2 from acidified samples containing CaCO_3 to determine the concentration of this

parameter. These earlier data are less reliable because of larger errors in measuring degassed CO_2 .

[11] The concentration of any given entity in ocean sediments is highly influenced by the total flux [e.g., *Catubig et al.*, 1998], and so the percentage of an entity in a specific sediment layer may be a poor indicator of the depositional flux [*Schneider et al.*, 2000]. Accumulation rates for CaCO_3 and C_{org} are thus determined from mapping sediment thickness and the percentage of CaCO_3 and C_{org} for each time period. Different cores have variably well constrained chronologies, and to a certain extent, this study is limited by that dependence. Chronologies are generally based on linear extrapolation between chronostratigraphic horizons, identified on the basis of ^{14}C dating, $\delta^{18}\text{O}$ stratigraphy, tephrochronology, biostratigraphy, and the concentration of ice-rafted debris (IRD). We have avoided relying on core chronologies based on carbonate stratigraphy, even though the regional coherence of the carbonate signal in many basins means that CaCO_3 concentrations have been used widely to correlate core records [e.g., *Kellogg*, 1976, 1980]. Linear sedimentation rates (LSR) (Holocene thickness/12 (kyr); late Weichselian thickness/15 (kyr)) are converted to bulk accumulation rates using a dry bulk density (DBD) of 1 g cm^{-3} , which we assume is representative of the range of wet bulk densities and porosities reported for sediments in this region [e.g., *Henrich et al.*, 1989; *Hebbeln et al.*, 1994].

[12] Errors in accumulation fields are derived as follows. Errors in the determination of calcite are assumed to lie within the range $\pm 2\%$ (to account for the use of measurements collected using degassed CO_2) and in the determination of $C_{\text{org}} \pm 0.1\%$. Thickness and linear sedimentation rates are assigned an error value of $\pm 10\%$, although in reality, this amount is almost impossible to quantify, representing a combination of laboratory measurement errors, errors

¹ Supporting Appendix 1 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.

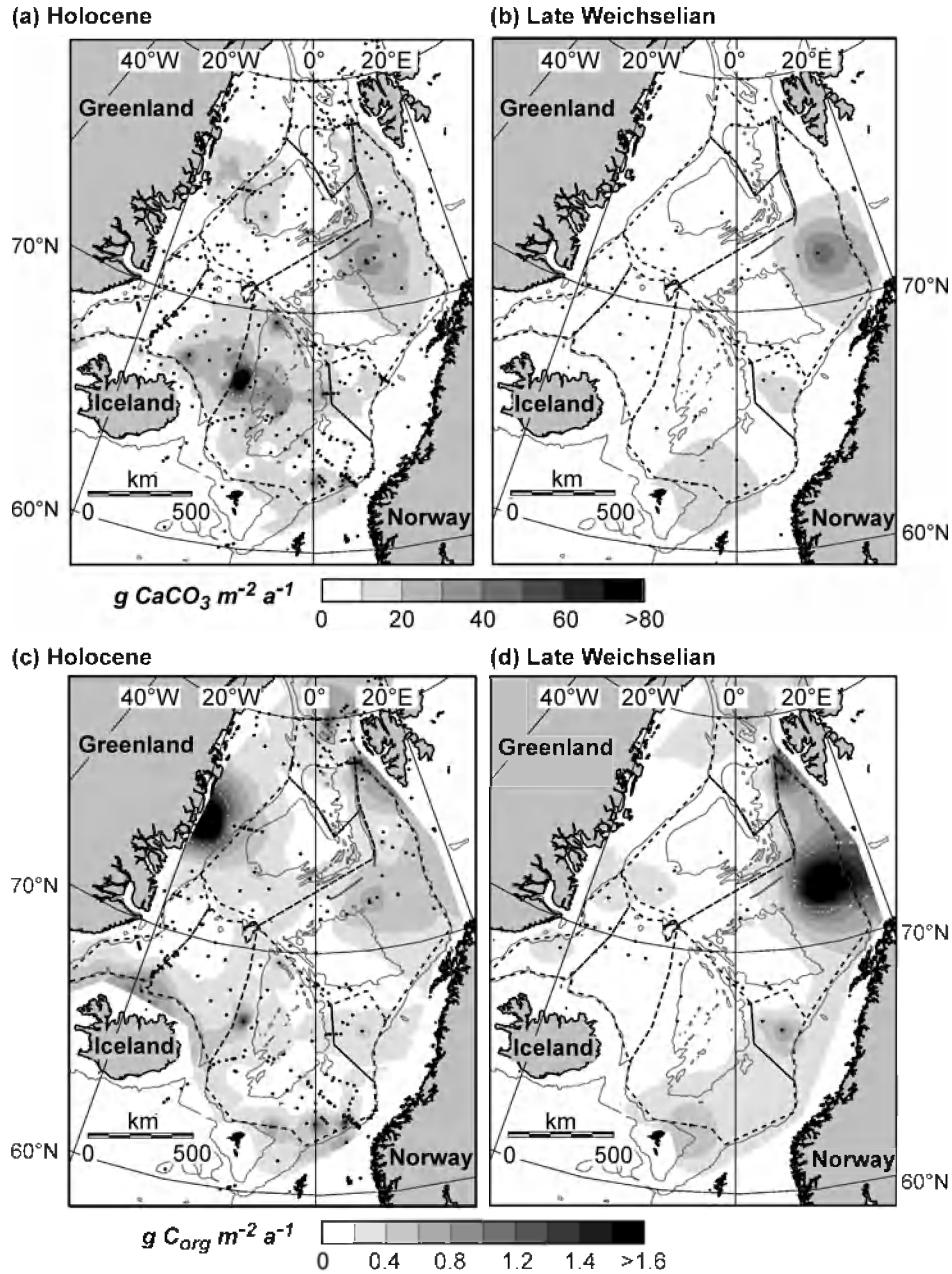


Figure 5. Holocene and late Weichselian accumulation fields of (a and b) CaCO_3 and (c and d) C_{org} in polar North Atlantic sediments. Core locations are shown by dots.

in extracting published thicknesses, and errors in determining the ^{14}C ka/OIS 2/1 boundary between glacial and interglacial. All fluxes are quoted $\pm 10\%$ because of the way in which errors are propagated through the calculations, the majority arising from uncertainty in the LSR:

$$\begin{aligned} \text{Bulk accumulation } (\pm 10\%) &= \text{DBD} \times \text{LSR} (\pm 10\%) \\ \text{CaCO}_3 \text{ accumulation } (\pm 10\%) &= (\text{DBD} \times \text{LSR} (\pm 10\%) \\ &\quad \times \% \text{CaCO}_3 (\pm 2\%)) \\ \text{C}_{\text{org}} \text{ accumulation } (\pm 10\%) &= (\text{DBD} \times \text{LSR} (\pm 10\%) \\ &\quad \times \% \text{CaCO}_3 (\pm 10\%)) \end{aligned}$$

[13] Data points are gridded using the inverse distance weighted interpolation within the ARC/INFO geographic information systems (GIS) package, using 12 neighbors and a power weighting of 2. Data are manipulated in polar stereographic projection (standard latitude 75°N , standard longitude 0°) using a 5×5 km grid.

3. Results

3.1. CaCO_3 Concentrations in Holocene Sediments

[14] The interpolated distribution of calcite concentration in Holocene sediments created through gridding of core records corresponds well with previously published maps (Figure 3a) [e.g., *Biscaye et al.*, 1976; *Kellogg*, 1976; *Hebbeln et al.*, 1998;

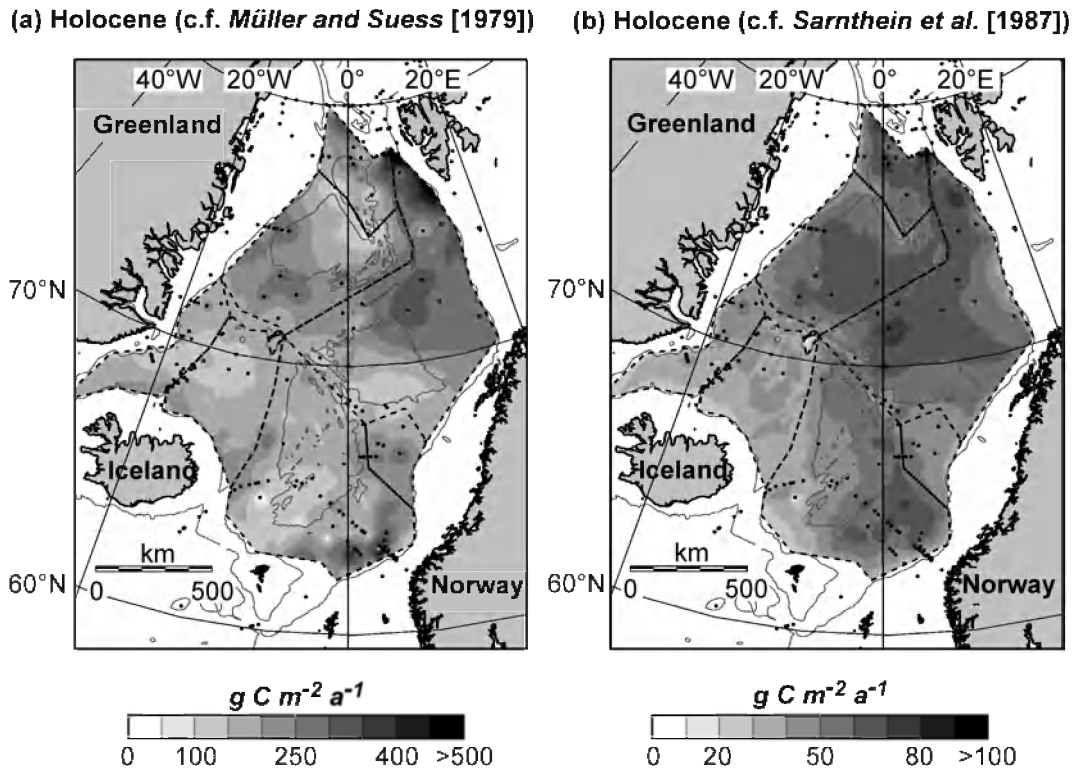


Figure 6. Reconstructed (paleo)productivities using empirical functions based on the organic carbon content of the seafloor sediments. Holocene functions according to (a) Müller and Suess [1979] and (b) Sarnthein et al. [1987] both compare well with other estimates of the patterns of productivity in the study area. Core are locations shown by dots.

Huber et al., 2000]. This gives us confidence in our methodology and results. Overall levels are somewhat lower than might be expected from other distribution maps based on core top determinations, but the values used to create our maps are averaged across the past 2–5000 years for a representative Holocene flux. The fluxes and volumes that we calculate are therefore taken as conservative estimates. The grid differs strongly from that suggested by Caubig et al. [1998]. Closer investigation reveals that the differences are due to the relatively sparse sampling of the polar North Atlantic in the latter's investigation.

[15] High concentrations of calcite (>40%) are observed beneath the warm Atlantic water masses to the east and south, while the western and northern areas are relatively devoid of CaCO_3 (10–20%) (Figure 3a), as reported by previous investigators [e.g., Biscaye et al., 1976; Kellogg, 1976]. High levels of calcite (30–40%) in Icelandic Plateau sediments are related to a combination of shallower water depths and the incorporation of warm Atlantic water masses into the Iceland gyre. Similarly, higher local levels in the Boreas Basin and northern Greenland Basin (20–30%) are related to incorporation of Norwegian Current water into the East Greenland Current through the Return Atlantic Current (Figure 3a) [Hebbeln et al., 1998; Huber et al., 2000]. Low calcite concentrations in sediments on the western margins of the polar North Atlantic (0–10%) are a result of relatively high levels of dissolution by corrosive deep water masses [Huber et al., 2000].

3.2. CaCO_3 Concentrations in Late Weichselian Sediments

[16] The proportion of CaCO_3 found in Late Weichselian sediments is much lower [Kellogg, 1976, 1980], reaching a maximum of only 20% (Figure 3b). However, calcite levels in

the majority of the basins rarely exceed 10%. Peak values (10–20%) are found in the Norwegian Basin east of the Aegir Ridge and in the southern Lofoten Basin but do not extend onto the Vøring Plateau. If elevated CaCO_3 levels are assumed to be indicative of warm water masses, as during the Holocene, the distribution of higher CaCO_3 concentrations in these southeastern basins supports the suggested repeated and frequent intrusion of warm Atlantic water into the polar North Atlantic during full glacial conditions [e.g., Veum et al., 1992; Hebbeln et al., 1994, 1998; Rasmussen et al., 1996].

3.3. C_{org} Concentrations in Holocene Sediments

[17] The Holocene distribution of organic carbon concentrations shows a strong east-west gradient (Figure 3c). The Iceland Plateau, Denmark Strait, and western Norwegian Basins display the lowest levels (0.25–0.5%), while the other basins show a higher proportion of C_{org} (>0.5%). There is a strong increase in C_{org} toward the shelf break on the eastern polar North Atlantic margins, such that peak concentrations (up to 2%) are reached offshore Svalbard, in the Fram Strait, and at the western edge of the Barents Sea (Figure 3c). There is no significant correlation between organic carbon percentage and distance from the shelf break or water depth.

3.4. C_{org} Concentrations in Late Weichselian Sediments

[18] The pattern of C_{org} concentration during the late Weichselian is similar to that of the Holocene, although overall levels are lower for any given location (Figure 3d). Levels are also more uniform, only varying below 0.25–0.5% at the base of the Vøring Plateau and northwest of Iceland. Elevated concentrations are shown on the upper slope offshore Svalbard and within the Fram Strait.

3.5. CaCO₃ and C_{org} Accumulation Fields

[19] Marked changes occur in the location of the principal foci of glacial and interglacial bulk accumulation, and these variations in bulk accumulation demonstrate clearly the dominance of margin processes in delivering sediments to the deep ocean (Figure 4). Such changes in the patterns of bulk sediment flux are also reflected in variations in the C_{org} and CaCO₃ accumulation fields (Figure 5), which are markedly different from the percentage abundance in sediments (see Figure 3). In the case of organic carbon, this pattern is especially significant because preservation is strongly influenced by bulk sediment accumulation and the rate of removal from the oxic zone, where decomposition is concentrated [e.g., Mopper and Degens, 1979; Calvert, 1987; Canfield, 1994].

[20] The focus of Holocene accumulation of calcite is the western Norwegian Basin and eastern Iceland Basin, where calcite fluxes reach in excess of 80 g CaCO₃ m⁻² yr⁻¹ (Figure 5a). These large fluxes are due to a combination of high CaCO₃ concentrations and high sedimentation rates. In the region of greatest flux, high concentrations probably reflect the elevated deposition of sediment as it is focused by the movement of deep water. Unexpectedly low calcite fluxes south of the Vøring Plateau, within the Norwegian Basin, are almost certainly linked to sediment evacuation by the Storegga Slide [Bugge *et al.*, 1988; Henrich *et al.*, 1989; Evans *et al.*, 1996]. The Bear Island Fan, located at the mouth of the southern Barents Sea, also appears as a major Holocene CaCO₃ depocenter, again due to a combination of relatively high concentrations and bulk accumulation (Figure 5a). This depocenter is also apparent in C_{org} accumulation and during the late Weichselian (Figure 5). Low accumulation fluxes in western polar North Atlantic basins are attributable directly to strong dissolution by corrosive deep water masses [Huber *et al.*, 2000]. The relatively high calcite and C_{org} fluxes on the Greenland shelf and upper slope offshore the middle northeastern coast appears to be the result of extremely high deposition rates near Shannon Island, linked to iceberg rafting from the large Storstrømmen glacier within the Greenland ice sheet [Baumann *et al.*, 1993; Funder *et al.*, 1998]. This apparently anomalous depocenter alerts us to the probable importance of ice sheets in the sequestering of carbon in the polar North Atlantic.

3.6. Paleoproductivity Estimates as a Test of C_{org} Accumulation Mapping

[21] A useful by-product of organic carbon flux mapping is the conversion of C_{org} concentration to estimates of sea surface productivity [e.g., Berger *et al.*, 1989; Rühlemann *et al.*, 1999]. Recent reviews of estimating (paleo)productivity from C_{org} records provide the means for reconstructing the primary productivity of the polar North Atlantic during the Holocene. Reconstructing Holocene productivity, and comparing this with mapped productivity, provides a useful tool for estimating the level of confidence that may be ascribed to our flux calculations. Therefore we apply two methods of reconstructing productivity, drawn from Berger *et al.* [1989] (Figure 6):

$$\text{PAP} = C_p(1 - \phi)/0.0030S^{0.3} \quad (2)$$

[Müller and Suess, 1979] and

$$\text{PAP} = 15.9 C^{0.66} S^{-0.05} [p(1 - \phi)]^{0.66} z^{0.32} \quad (3)$$

[Sarnthein *et al.*, 1987], where (paleo)productivity (PAP, g m⁻² yr⁻¹) is a function of C or organic carbon percentage, dry sediment density *p*, porosity ϕ , and sedimentation rate *S* (cm kyr⁻¹). We assume a dry bulk density of 1 g cm⁻³ and a porosity of 70%.

[22] Both methods predict similar productivity distributions across the polar North Atlantic during the Holocene (Figures 6a and 6b). The highest productivity levels, 80 g C m⁻² yr⁻¹

(Sarnthein *et al.*) to 350 g C m⁻² yr⁻¹ (Müller and Suess), are found in the southern Norwegian Basin and the Lofoten and Greenland Basins. Lowest productivities are predicted in the Iceland Plateau, Denmark Strait Basin, and western Norwegian Basin. We find both of these patterns and levels of productivity to be consistent with those reported from compiled Sea-viewing Wide Field-of-view Sensor (SeaWiFS) data (<http://seawifs.gsfc.nasa.gov/SEAWIFS.html>), compiled maps of productivity records [Berger, 1989], and the budget of C_{org} flux for the polar North Atlantic reported by Schlüter *et al.* [2000]. The close match between predicted and mapped productivities suggests that the assumptions behind our methodology are generally correct.

4. Discussion

[23] The levels and spatial patterns of fluxes of calcium carbonate and organic carbon have changed greatly from the late Weichselian to the Holocene. CaCO₃ and C_{org} depocenters have changed location, and these changes are related principally to the alteration in bulk accumulation patterns during the past 30 kyr. We suggest that these changes in carbon sequestration are related intimately with ice sheet activity and that the combination of glaciological and oceanographic variations during the late Quaternary has an influence on both long-term carbonate preservation in the polar North Atlantic and perhaps atmospheric pCO₂.

4.1. C Burial in Sediments in Relation to Ice Sheet Growth and Decay

[24] The dynamics and history of the western Fennoscandian and eastern Greenland ice sheets are relatively well constrained during the period 27-0 ka. The glacial history of the Greenland ice sheet during the late Weichselian and Holocene is one of marked stability. Drainage of the ice sheet is dominated currently by several very large outlets, including those draining through the Scoresby Sund fjord system, the Storstrømmen glacier, and Niogalvfjærd Bræ (Figure 7a) [Funder *et al.*, 1998; Bamber *et al.*, 2000]. The late Weichselian (known locally as the Flakkerhuk stade) saw the Greenland ice sheet encroach onto the inner continental shelf, during which time there was significant variability in sea ice cover (Figure 7a) [Nam *et al.*, 1995; Stein *et al.*, 1996; Funder *et al.*, 1998]. Peaks in the accumulation of IRD and the generally elevated bulk accumulation rates during the last glacial period on the western polar North Atlantic margins are therefore likely to be a result of the release of icebergs from the inner fjord and their transport into the ocean. At other times, these icebergs release their sediment load into the fjords, and margin fluxes are dominated by biological and long-distance IRD-related input [cf. Dowdeswell *et al.*, 2000].

[25] This variable pattern of iceberg release and sedimentation is seen in both bulk accumulation (Figure 5) and C_{org} fluxes through the past 30,000 years (Figures 5c and 5d). Bulk accumulation, CaCO₃, and C_{org} fluxes during the Holocene are dominated by input that appears to be focused from the Storstrømmen glacier around Shannon Island. This pattern is interpreted to indicate both the increased preservation of deposited C_{org} from the overall increase in sedimentation rate and also the extremely high likelihood that much of the C_{org} and possibly calcite in this area is, in fact, derived from a glacial source. Surprisingly, however, the Scoresby Sund system does not show such a strong influence on flux patterns. The retention of icebergs and associated products in the near-shore environment during the Flakkerhuk stade (late Weichselian) is thus shown by much reduced CaCO₃ and C_{org} fluxes despite an overall increase in bulk accumulation along this margin. The Greenland ice sheet is therefore important in modulating organic carbon and carbonate storage during the Holocene but is much less influential during glacial periods, when the dynamics of the ice sheet are isolated from polar North Atlantic basins by sea ice.

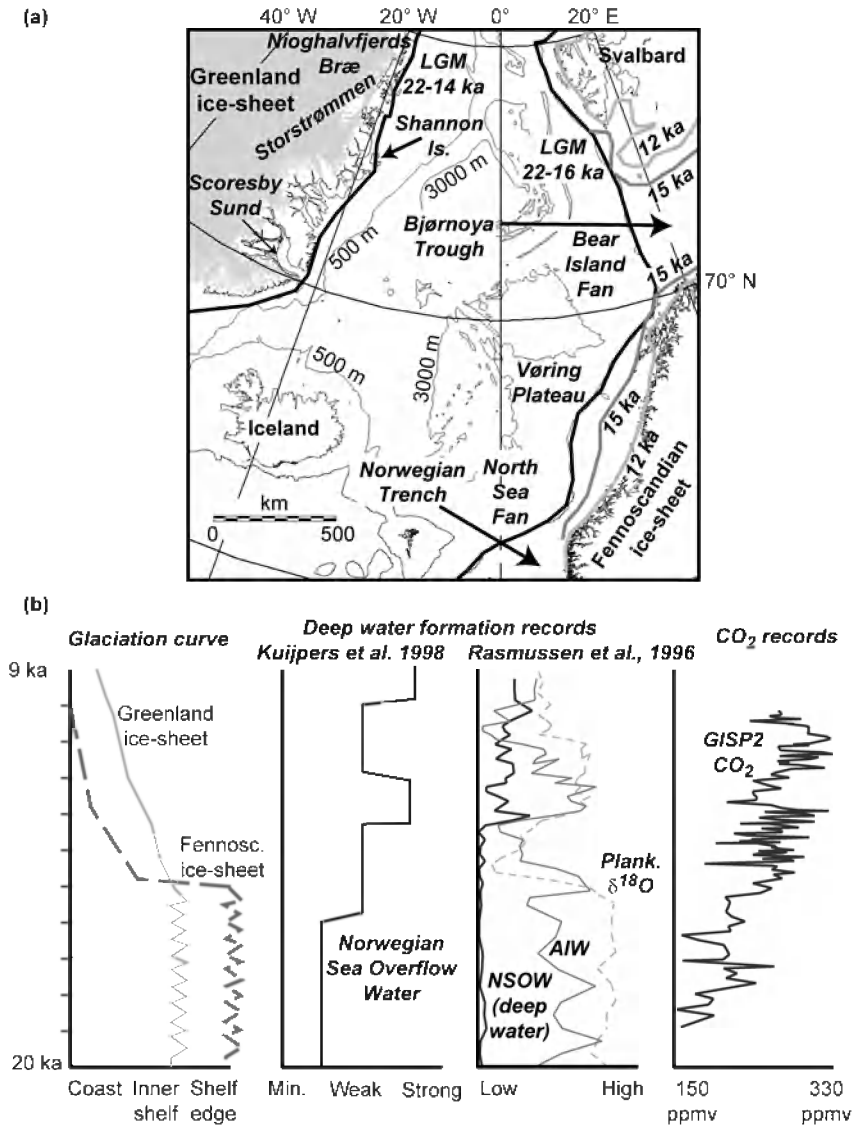


Figure 7. (a) Differences in the dynamics and responses of the ice sheets in Greenland and Fennoscandia are reflected in their Late Quaternary histories. (b) Changes in ice sheet configuration, which predate changes in atmospheric $p\text{CO}_2$. Broad-scale trends in atmospheric CO_2 do display a strong relationship with the overflow of deep water from the polar North Atlantic, as recorded south and north of the Faeroe-Shetland Channel, however (Figure 7b). Ice sheet configurations are from *Funder et al.* [1998] and *Landvik et al.* [1998] for the Greenland and Fennoscandian ice sheets, respectively. Norwegian Sea Deep Water overflow through the Faeroe Bank Channel is from *Kuijpers et al.* [1998]; the presence of Norwegian Sea Deep Water north of the Faeroes is recorded in the abundance of the benthic foraminifer *Nonion zaandamae* in core ENAM93-21. Atlantic Intermediate Water (AIW), reflecting the intrusion of Atlantic water masses, is recorded by the abundance of *Cassidulina teretis* [*Rasmussen et al.*, 1996]. Atmospheric CO_2 concentrations are those recorded at the Greenland Ice Sheet Project 2 (GISP2) ice core [*Hammer and Meese*, 1993; *Sowers et al.*, 1993; *Meese et al.*, 1994; *Anklin et al.*, 1997].

[26] Ice sheet behavior on the eastern polar North Atlantic margins has been far more dynamic in comparison, with a direct and significant impact on sedimentation rates and style [e.g., *Dowdeswell et al.*, 1996; *Landvik et al.*, 1998; *Dowdeswell and Siegert*, 1999; *Taylor et al.*, 2001]. Fennoscandian ice sheet drainage was dominated by high-velocity and sediment-laden ice streams, developed in bathymetric troughs in the continental shelves such as the Bjørnøya Trough and Norwegian Trench (Figure 7a). Elevated deposition rates during the late

Weichselian in front of ice streams are thus seen on the Bear Island Trough Mouth Fan in the Lofoten Basin, on the Vøring Plateau, and on the North Sea Fan, observed most strongly in C_{org} fluxes (Figure 5). Importantly, high-resolution core studies indicate that the ice drained from the Barents Sea is an important contributor of organic carbon to the Arctic Ocean and presumably also the polar North Atlantic, where ice fluxes are significant [*Knies and Stein*, 1998; *Fahl and Stein*, 1999; *Bouscein and Stein*, 2000].

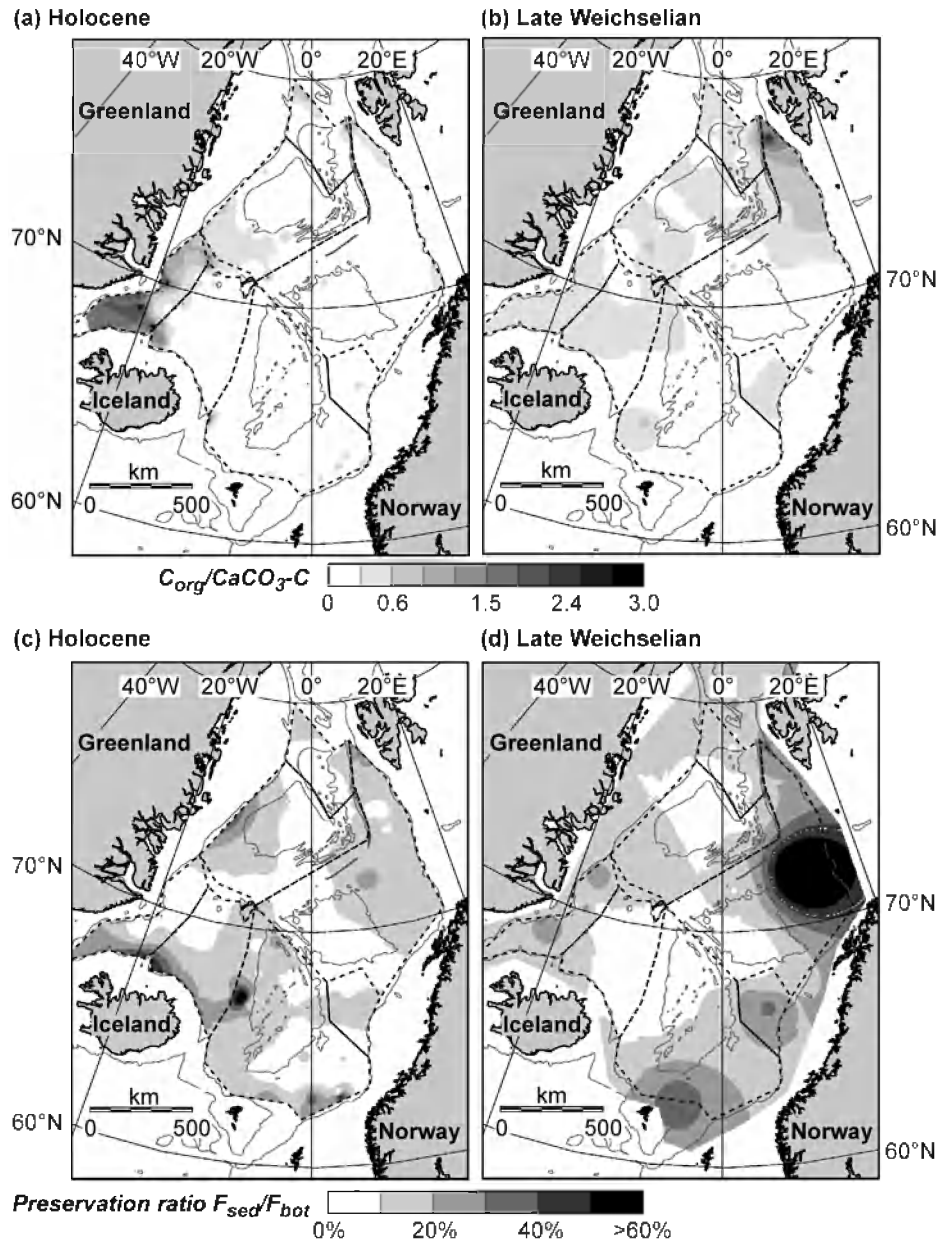


Figure 8. Changing proportions of CaCO_3 and C_{org} reflected in the differences between (a) Holocene and (b) late Weichselian rain ratio at the seafloor ($C_{\text{org}}/\text{CaCO}_3\text{-C}$). (c and d) Increased fluxes of organic carbon, in combination with generally elevated bulk accumulation, result in greater preservation of C_{org} reaching the seafloor during the late Weichselian. Preservation ratios are calculated as $F_{\text{sed}}/F_{\text{bot}} = 2.5S - S^2/50$ [Berger *et al.*, 1989], where F is flux and S represents sedimentation rate.

[27] The switching of bulk and carbon-related sediment depositories can thus be firmly related to the changes in glaciological setting. Additionally, the presence and behavior of these ice sheets results in significant additional C_{org} deposition. This latter influence is seen most strongly if we consider the rain ratio of C_{org} to CaCO_3 (Figures 8a and 8b). Deep oceanic rain ratios at the seafloor typically equal ~ 0.12 [Shaffer, 1993]. However, in areas where C_{org} input is argued to be elevated by the erosive power of ice sheets, rain ratios are much greater. Holocene rain ratios at the mouth of Scoresby Sund, which initially appears to display an

anomalously small glaciological influence, are in excess of 2.5 (Figure 8a). During the late Weichselian, elevated rain ratios are seen to occur across large areas of the Greenland, Boreas, and Denmark Strait Basins and the Iceland Plateau, while peak rain ratios in excess of 1.0 are found in front of regions associated with ice stream development in the Barents Sea and at Svalbard (Figure 8b). In addition to C_{org} fluxes being higher in many areas during the late Weichselian, overall elevated bulk fluxes led to greater preservation ratios, calculated according to Berger *et al.* [1989], in comparison with the Holocene (Figures 8c and 8d).

4.2. Importance of Glaciation

[28] The magnitude of the impact that ice sheets are interpreted to have on organic carbon fluxes and preservation may be seen by calculating total carbon-related fluxes for the polar North Atlantic during the late Weichselian and the Holocene (Table 1). The Holocene CaCO_3 flux for the polar North Atlantic is calculated to be $2.20 \pm 0.22 \times 10^{13} \text{ kg kyr}^{-1}$, compared with $1.13 \pm 0.11 \times 10^{13} \text{ kg kyr}^{-1}$ during the late Weichselian. Lower glacial fluxes of calcite are reported widely in the literature [e.g., Kellogg, 1976, 1980] and therefore come as no surprise. Significantly, however, despite this 51% reduction in flux the polar North Atlantic remains an important global depocenter for calcite during both the Holocene and late Weichselian. The basins cover $\sim 0.5\%$ of the global ocean area, yet the Holocene and late Weichselian calcite fluxes account for 2.7 and 1.2% of the global total, respectively (on the basis of total fluxes from *Catubig et al.* [1998]).

[29] The flux of C_{org} to the oceanic sedimentary store during the Holocene ($4.59 \pm 0.46 \times 10^{11} \text{ kg kyr}^{-1}$) is approximately the same as during the late Weichselian ($4.91 \pm 0.49 \times 10^{11} \text{ kg kyr}^{-1}$). Organic carbon flux during the late Weichselian is unlikely to be maintained by surface productivity because of increased sea ice coverage and reduced water temperatures. It is more likely C_{org} flux is maintained by reworking of shallow-water sediments by the Fennoscandian ice sheet, which may account for a C_{org} flux into deeper water sediments of $2.57 \pm 0.26 \times 10^{11} \text{ kg C}_{\text{org}} \text{ kyr}^{-1}$ during this period. This figure is calculated by assuming that the surface productivity-related C_{org} flux follows the 49% reduction of predominantly biogenically secreted CaCO_3 in the late Weichselian compared to the Holocene and that paleoproductivity remains dominated by carbonate producers. This calculation does not include the possible effects of increased C_{org} preservation that accompanies elevated bulk deposition of sediment [Calvert, 1987] and hence may overestimate the proportion of reworked C_{org} supplied by ice sheets. Surface production thus accounts for $2.34 \pm 0.24 \times 10^{11} \text{ kg kyr}^{-1}$ of C_{org} deposited in marine sediments during the late Weichselian, approximately equivalent to that arising from the Fennoscandian ice sheet. The extremely efficient erosiveness of ice sheets and the extensive deposition of glacial sediments in the marine environment through suspended sediment plumes and iceberg rafting are therefore fundamental in examining the carbon cycling budget of high-latitude oceans during the Quaternary.

4.3. Potential Impacts on Global Carbon Cycling

[30] The extent to which ice sheets modulate the storage of C_{org} in the polar North Atlantic during glacial periods is a striking conclusion of this study. The importance of this conclusion lies in not only the permanent drawdown of CO_2 by burial of C_{org} as it is eroded by the expanding ice sheet, which would perhaps otherwise be reworked in the shelf environment, but also in the greatly changed relation between C_{org} and CaCO_3 that these fluxes reveal and the coincidence with major reorganizations of thermohaline circulation. The search for marine mechanisms of altering atmos-

pheric $p\text{CO}_2$ levels has come to focus on organic carbon fluxes and changes in the alkalinity of deep water. While a global increase in rain ratio is not likely to have been the primary cause of glacial-interglacial CO_2 changes [Sigman and Boyle, 2000], we hypothesize that the increase in rain ratio in the polar North Atlantic, produced without an associated increase in productivity, could be important in promoting CO_2 storage in deep water within the relatively isolated basins of the Arctic Ocean. Enhanced CO_2 storage in deep water promotes the dissolution of CaCO_3 . Stored CO_2 could then be released by quasiperiodic overspill and/or after thermohaline circulation is reestablished, providing a mechanism capable of helping to explain the lagged CO_2 release to the atmosphere subsequent to δD recorded warming (Figure 9) [Mudelsee, 2001].

[31] It is important to realize that we draw no conclusions about and make no allowance for the differing makeup of organic carbon (terrestrial versus marine and labile versus refractory C_{org}) deposited in the deep ocean through time. It has been demonstrated that the constituents of C_{org} preserved on Arctic margins varies greatly through the late Quaternary [e.g., Schubert and Stein, 1996; Knies and Stein, 1998; Knies et al., 2000]. However, this debate is beyond the scope of this study, and we have assumed that C_{org} eroded and transported by ice sheets into the polar North Atlantic is generally as labile as marine-produced C_{org} in order to provide an end-member for discussion.

4.4. Explanation of Carbonate Dissolution Events in the Polar North Atlantic?

[32] During the late Weichselian, thermohaline circulation operated in several different modes, mostly associated with a massive decrease in the contribution of Norwegian Sea Deep Water to generally reduced levels of North Atlantic Deep Water, as overflow of the sills separating the polar North Atlantic from the North Atlantic was cut off (Figures 7 and 9b) [e.g., Sarnthein et al., 1994]. We suggest that the relatively constant C_{org} flux and a calcite flux of approximately half that of the Holocene together with storage of Norwegian Sea Deep Water in the polar North Atlantic was responsible for the accumulation of CO_2 in deep waters of the polar North Atlantic and more aggressive carbonate dissolution. Respiration of C_{org} in the lower water column and at the sediment-water interface results in the direct release of CO_2 to the stored Norwegian Sea Deep Water, enhancing dissolution of CaCO_3 and resulting in an increase in HCO_3^- and $p\text{CO}_2$. We suggest that Norwegian Sea Deep Water may finally become “supercharged” with CO_2 during periods when deep water production in the region is shut off or slowed down (Figure 9b).

[33] Lysocline and calcium carbonate compensation depths in the North Atlantic did not change significantly on glacial-interglacial timescales and are not at a depth (currently $\sim 3800 \text{ m}$) which affects most of the polar North Atlantic basins. Dissolution patterns in the polar North Atlantic are therefore determined at present by a combination of carbonate fluxes, water mass characteristics, deep water production, and organic carbon fluxes, which

Table 1. Fluxes and Changes in Flux of CaCO_3 and C_{org} into Polar North Atlantic Basins Below 500 m Water Depth

	CaCO_3 Flux, kg kyr^{-1}	C_{org} Flux, kg kyr^{-1}	$\text{C}_{\text{org}}/\text{CaCO}_3\text{-C}$
Holocene (12–0 ^{14}C ka)	$2.20 \pm 0.22 \times 10^{13}$	$4.59 \pm 0.46 \times 10^{11}$	0.17
Global Holocene	$83.0 \times 10^{13\text{a}}$	$1320.0 \times 10^{11\text{b}}$	(0.16)
Late Weichselian (27–12 ^{14}C ka)	$1.13 \pm 0.11 \times 10^{13}$	$4.91 \pm 0.49 \times 10^{11}$	0.36
Global Late Weichselian	$92.0 \times 10^{13\text{a}}$		
Percent change Weichselian/Holocene	51 (42–63)	110 (87–131)	210

^aGlobal Holocene and Late Weichselian CaCO_3 fluxes from *Catubig et al.* [1998].

^bGlobal Holocene C_{org} flux from review by *Munhoven* [1997] and approximately equal to values quoted by *Mopper and Degens* [1979] and *Emerson and Hedges* [1988].

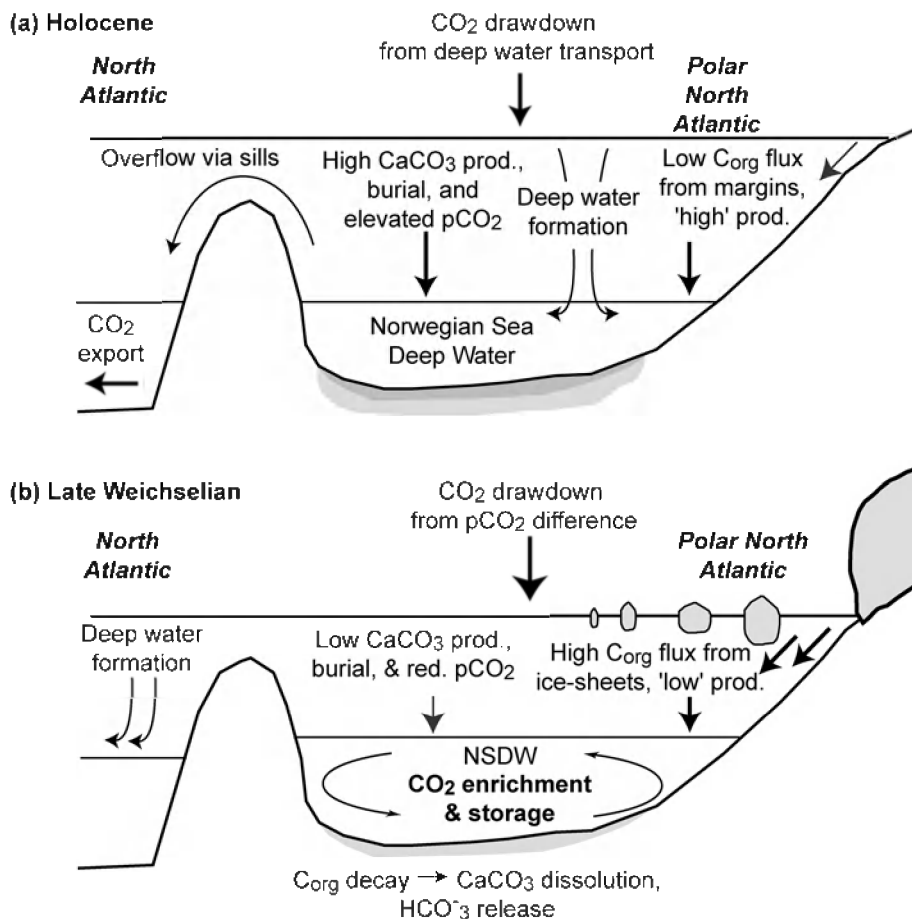


Figure 9. While the polar North Atlantic is a sink for atmospheric CO₂ during the Holocene because of both deep water convection and C_{org} production (Figure 9a), storage is temporary as deep water is convected to the North Pacific to be degassed. However, during the late Weichselian (Figure 9b), elevated C_{org} fluxes and reduced CaCO₃ accumulation lead to enhanced CO₂ storage in deep water masses in the Arctic Ocean. Water masses become more chemically aggressive and resulted in significant carbonate dissolution and further CO₂ storage, but otherwise remain isolated until deglaciation.

together change preservation conditions within the sediment column [Huber *et al.*, 2000]. Pulses of CaCO₃ dissolution are reported widely in polar North Atlantic sediments, often featured as pronounced CaCO₃ minima at the end of OIS 2 [e.g., Kellogg, 1976, 1980; Henrich, 1986; Hebbeln *et al.*, 1994, 1998; Hebbeln and Wefer, 1997]. Dissolution events are linked causally to reduced global ventilation of deep water [Henrich, 1998; Huber *et al.*, 2000, and references therein]. However, we believe that increased dissolution of CaCO₃ reported during these periods is probably linked to ice sheet behavior through organic carbon fluxes and greatly increased rain ratios, rather than simply cessation of ocean bottom ventilation by fresh, meltwater “capping” of the water column [e.g., Henrich, 1998].

[34] Evidence for reduced transport of deep water out of the basins north of the Scotland-Iceland-Greenland Ridge during the late Weichselian is widespread [e.g., Sarnthein *et al.*, 1994; Rasmussen *et al.*, 1996; Hebbeln *et al.*, 1998]. While overflow was intermittent during the glacial period, deep water circulation from polar North Atlantic sources was greatly reduced. Combined with a blocking of the Nares Strait by a merging of the Greenland and Ellesmere ice sheet during the late Weichselian [Zreda *et al.*, 1999], it is possible to emphasize the mechanism further by

invoking enhanced pCO₂ levels in the entire deep Arctic Ocean, which would have only been interacting through the Fram Strait opening for most of the late Weichselian, the Bering Strait also having become isolated through eustatic sea level changes [e.g., Svitoch and Taldenkova, 1994]. The margins of the entire Arctic Ocean are glacially influenced and subject to extensive sea ice and iceberg rafting. However, the Arctic Ocean, at $\sim 4.5 \times 10^6$ km² below 500 m water depth, covers over double the 1.7×10^6 km² of the polar North Atlantic. A slow emptying of this reservoir subsequent to the restart of interglacial modes of thermohaline circulation would also help to explain the continued low CaCO₃ levels well into the Holocene seen in many polar North Atlantic cores [e.g., Hebbeln *et al.*, 1994, 1998; Hebbeln and Wefer, 1997].

[35] A final line of evidence links Norwegian Sea Deep Water circulation directly with records of carbon cycling. Recent detailed analysis of the reservoir ages of radiocarbon prior to the Holocene in the polar North Atlantic show them to be greater, both overall and with respect to reservoir ages in the North Atlantic [Haflidason *et al.*, 2000]. This observation is consistent with enhanced storage of “old” carbon in deep water from glacially eroded C_{org} and CaCO₃ dissolved from the sediment and water columns.

5. Summary

[36] While the late Weichselian flux of CaCO_3 in the polar North Atlantic ($1.13 \pm 0.11 \times 10^{13} \text{ kg kyr}^{-1}$) is $\sim 51\%$ that of the Holocene ($2.20 \pm 0.22 \times 10^{13} \text{ kg kyr}^{-1}$), fluxes of organic carbon are maintained at least at Holocene levels ($4.91 \pm 0.49 \times 10^{11} \text{ kg kyr}^{-1}$ versus $4.59 \pm 0.46 \times 10^{11} \text{ kg kyr}^{-1}$). It is also possible that up to $2.57 \pm 0.26 \times 10^{11} \text{ kg C}_{\text{org}} \text{ kyr}^{-1}$ may be supplied by ice sheet transport. Mapping of the depocenters of CaCO_3 and C_{org} indicate clearly that the major depocenters of sediment (Figure 4) and carbon (Figures 3 and 5) in the polar North Atlantic in both the Holocene and late Weichselian are influenced strongly by the presence and dynamics of ice masses, to the extent that Fennoscandian proglacial zones are the major depocenter of C_{org} during the late Weichselian, with up to $>100\%$ greater accumulation (Figure 5d). This continued high flux of C_{org} during a period of reduced productivity has a profound effect on the preservation of C_{org} , typically increasing preservation from 0–10% to 40–50% during the late Weichselian (Figures 8c and 8d). More importantly, the proportion of C_{org} to carbon in CaCO_3 is altered considerably, both locally and regionally (Figures 8a and 8b). For example, the overall

ratio of $\text{C}_{\text{org}}/\text{CaCO}_3$ changes from 0.17 during the Holocene and 0.36 during the late Weichselian (Table 1). We have therefore been able, for the first time, to quantify fully the effect that glacial activity has on the cycling of carbon in a glacially influenced oceanic basin.

[37] The implication for these changes in carbon cycling is potentially significant when taken in concert with the major reorganization of the thermohaline circulation that also takes place over a glacial-interglacial cycle. We suggest that deep water ponded in polar North Atlantic basins and arguably throughout the Arctic Ocean as a whole becomes supercharged with CO_2 , as C_{org} decomposes and promotes dissolution of CaCO_3 in the sediment column (Figure 9b). A prolonged emptying of this CO_2 -enriched reservoir would also explain sustained low levels of CaCO_3 storage in the polar North Atlantic, which extend well into the Holocene.

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