Upper ocean circulation in the glacial North Atlantic from benthic foraminiferal isotope and trace element fingerprinting

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Abstract. Benthic Cd/Ca and δ^{13} C records from the midlatitude and northern North Atlantic are used to derive nutrient inventories and water mass distribution patterns for the past 50,000 years. Inferred Holocene water column Cd concentrations (CdW') and δ^{13} C values are 0.17-0.24 nmol kg⁻¹ and 1.0-1.3‰ Peedee belemnite (PDB), which document the dominance of nutrient-depleted Mediterranean Outflow Water (MOW) and Upper North Atlantic Deep Water (UNADW). Glacial benthic Cd/Ca and δ^{13} C indicate a continued contribution of UNADW to the northern North Atlantic and upper Portuguese margin (CdW'=0.08 nmol kg⁻¹; δ^{13} C=+1.86‰ PDB). At the upper Moroccan margin, glacial CdW' (0.23 nmol kg⁻¹) is higher, and δ^{13} C (+1.44‰ PDB) is lower. During "Heinrich" events, benthic δ^{13} C decreases by up to 1.3‰, and peak Cd/Ca increases by 0.1-0.14 µmol mol⁻¹; water column phosphorus equivalents are 1.8-2.8 µmol kg⁻¹. The combined Cd/Ca and δ^{13} C pattern indicates that during mean glacial conditions Antarctic Intermediate Water, (AAIW) reached the midlatitude northeast Atlantic (30°N). During Heinrich events, AAIW contribution maximized so that Southern Hemisphere waters filled the North Atlantic basin from bottom water to middepth levels.

1. Introduction

Orbital and suborbital ocean circulation changes have been recorded in a variety of proxy records from middepth to deepocean sites throughout the world ocean [Duplessy et al., 1988; Imbrie et al., 1992; Keigwin and Jones, 1994; Behl and Kennett, 1996; Schulz et al., 1998]. In the North Atlantic, a close connection of convection changes with millennial-scale variability of surface-ocean hydrography has been inferred from faunal and geochemical data bases both for the last glacial and the glacial-interglacial transition [Labeyrie et al., 1992; Oppo and Lehman, 1993; Sarnthein et al., 1995; Marchitto et al., 1998]. Sporadic incursions of meltwater and concomitant drawdown of salt in the surface layer have led to a spin-down, reorganization, or even complete halt of thermohaline overturn. Numerical paleocean modeling predicts significant convective instability at only small freshwater inputs and lends further credence to the high sensitivity of the North Atlantic's thermohaline overturn to changes in its salinity balance [Stocker et al., 1992; Paillard and Labeyrie, 1994; Rahmstorf, 1994, 1995; Weaver and Hughes, 1994; Manabe and Stouffer, 1995; Tziperman, 1997; Ganopolski et al., 1998]. The apparent connection of deep-ocean variability and millennial-scale climatic oscillations in the North Atlantic region as inferred from Greenland ice core studies is commonly

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taken as evidence that thermohaline overturn in the northern North Atlantic played a leading role in determining deep-ocean chemical inventories during the last glacial.

Here we present a suite of isotopic and geochemical time series from sediment cores in the midlatitude and northern North Atlantic that monitor the convective response to changing climatic conditions during the past 50,000 years. The apparent disparate pattern between benthic $\delta^{13}C$ and Cd/Ca provides evidence for distinctive changes of water mass patterns that went along with meltwater surges during "Heinrich" events. Enhanced geochemical gradients between the upper Portuguese and Moroccan margins during the last glacial are indicative of an upper ocean hydrological front in the midlatitude northeast Atlantic that separated North Atlantic from Southern Ocean water masses.

2. Materials and Methods

Records of stable oxygen (§18O) and carbon isotopes (§13C) and of cadmium/calcium (Cd/Ca) ratios in benthic foraminifera have been established along sediment cores from the Moroccan and Portuguese margins and from the Rockall Plateau and Reykjanes Ridge in the northern North Atlantic (Figure 1 and Table 1). The depth range of the cores, 1.1-2.2 km, covers middepth to upper deep water levels. Core sites were chosen to monitor ventilation changes close to the sites of convection in the northern North Atlantic (cores M23414 and SO82-05) and downstream from the convection sites at intermediate water depths in the midlatitude northeast Atlantic (cores SO75-26KL and M16004).

For isotope analyses, between 1 and 21 specimens of epibenthic foraminifera *Cibicidoides wuellerstorfi*, *C. pseudoungerianus*, and *C. mollis* were picked from the >250 μ m sediment fraction. These species are believed to live at the sediment-water interface and directly record δ^{13} C signals of

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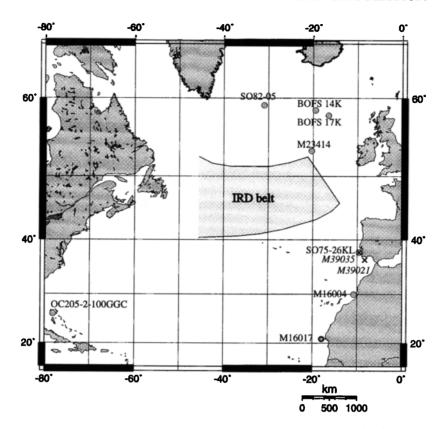


Figure 1. Location of sediment cores (circles) in the northern and midlatitude North Atlantic. Also shown (crosses) are stations of GoFlo hydrocasts used to calibrate benthic Cd/Ca to water column CdW1. For positions of sediment cores and water stations see Table 1.

ambient bottom water total dissolved carbon [Belanger et al., 1981; Curry and Lohmann, 1982; Duplessy et al., 1984; Zahn et al., 1986; McCorkle et al., 1990]. Within the sandy horizons of ice-rafted debris (IRD) Heinrich layer abundances of benthic foraminifera were reduced but still high enough to allow one to pick at least six specimens per isotope sample to ensure statistical robustness of the isotope values in these intervals. Samples were cleaned in methanol in an ultrasonic bath for a minimum of 10 s. Methanol was carefully siphoned off afterward and the samples were dried at 40° C. Isotope measurements were done using a Finnigan 252 gas mass spectrometer that was linked online to a CARBO Kiel carbonate preparation line. Long-term reproducibility of δ^{18} O and δ^{13} C was 0.08 and 0.05, respectively.

All isotope values are referred to the Peedee belemnite (PDB) scale.

For Cd/Ca analysis, between 3 and 20 specimens of benthic foraminiferal species *Uvigerina* spp., *C. wuellerstorfi, C. lobatulus*, *C. kullenbergi*, *C. pseudoungerianus*, and *Bulimina striata mexicana* were picked from the size fraction 250-500 µm. Sample preparation for Cd/Ca measurements followed standard laboratory protocols given by *Boyle and Keigwin* [1986] and *Rosenthal et al.* [1995]: (1) multiple ultrasonic cleaning to clean the fragments from detrital sediment particles, (2) reductive cleaning to remove metal oxides, (3) oxidative cleaning to reduce remaining organic matter, and (4) weak acid leaching to dissolve the outer carbonate layer, which may contain impurities that

Table 1. Location of Sediment Cores and Water Stations Used and Referred to in This Study

Core/GoFlo	Geographic Position Latitude, °N Longitude, °W		Water Depth, m	Data Source			
				Stratigraphy	Stable Isotopes	Cd/Ca	
SO75-26KL	37° 49.3'	09° 30.2'	1099	Zahn [1997]	Zahn [1997]	this work	
BOFS 17K	58° 00.2'	16° 29.8'	1150	Manighetti et al. [1995]	Bertram et al. [1995]	Bertram et al. [1995]	
SO82-05	59° 11.3'	30° 54.5'	1416	Moros et al. [1997]	Jung [1996]	this work	
M16004	29° 58.8'	10° 39.0'	1512	Zahn et al. [1987]	Zahn et al. [1987]	this work	
BOFS 14K	58° 37.2'	19° 26.2'	1756	Manighetti et al. [1995]	Bertram et al. [1995]	Bertram et al. [1995	
M23414	53° 32.2'	20° 17.3'	2196	Sarnthein et al. [1994]	Jung [1996]	this work	
OC205-2-100GGC	26° 03.1'	78° 01.1'	1045	Slowey and Curry [1995]	Slowey and Curry [1995]	tias work	
M39035-2	37°49.4'	09°30,2'	1083		this work	this work	
M39021-2	36° 36.5'	08° 14.3'	900		this work	this work	

would distort the trace element ratios. Cleaned fragments were dissolved in subboiled 0.075 M nitric acid shortly before analysis. Cd and Mn concentrations were determined on a GF-AAS (Perkin-Elmer 4100 ZL), and Ca concentrations were determined on a flame AAS (Perkin-Elmer 1100B or 5000). Triple Cd and Ca analyses were carried out on sample solutions from the larger samples containing > 0.5 mg of foraminiferal carbonate and were dissolved in 100 μ L nitric acid. Single Cd and Ca measurements were performed on smaller sample solutions which contained < 0.2 mg carbonate and were dissolved in only 50 μ L nitric acid. Statistical robustness of the measurements was further enhanced by preparing paired samples of different benthic foraminiferal species from individual sediment samples wherever possible.

Reproducibility of the trace element measurements was checked through an internal foraminiferal carbonate standard, which consisted of a pool of U. mediterranea shells that were picked from the Holocene section of Meteor core M16017 from the perennial coastal upwelling zone off Cape Blanc, NW Africa (21°15' N, 17°48' W, 821 m water depth). For Cd/Ca analyses, subsamples of 0.2-0.5 mg were prepared and were cleaned in batches of 10-40 individuals following the same cleaning procedure as was applied for core samples. Initially, 0.2-0.5 mg carbonate subsamples were prepared individually, but later on, larger subsamples of 3-4 mg carbonate were pooled, and the 0.2-0.5 mg subsamples for the standard runs were split from these larger sets. The mean Cd/Ca ratio of the foraminiferal laboratory standard is $0.055 \pm 0.015 \,\mu\text{mol mol}^{-1}$ (83 replicate analyses) and lies in the upper range of dissolved water column Cd equivalents of the global foraminiferal Cd/Ca distribution [see Boyle 1988a]. The standard deviation of the pooled foraminiferal Cd/Ca values reflects both analytical reproducibility and "noise" from an apparently imperfectly homogenized foraminifera pool containing shells that were admixed by bioturbation from deeper and shallower core depths. The pooled foraminiferal laboratory standard was run at 10-20 sample intervals, and blank solution was run at 20 sample intervals to monitor purity of chemicals and consistency of sample preparation procedures. Measurements of Mn concentrations provided further control on potential diagenetic distortion [Boyle, 1983]. Samples yielding Mn/Ca ratios above 150 µmol mol-1 were rejected as they may carry secondary carbonate crusts with possible inclusions of particulate Cd. Using a Mn/Ca cutoff of 150 µmol mol-1, 11% of all measurements were discarded from our database (65% C.

wuellerstorfi, 18% Uvigerina spp., and 5-8% C. kullenbergi and C. pseudoungerianus).

Benthic Cd/Ca ratios were transformed into water column dissolved Cd equivalents using a global mean ocean Ca concentration of 4.12x102 mg kg-1 and applying an empirical Cd partition coefficient between foraminiferal calcite and water. Cd partition coefficients were calculated using up to 24 benthic Cd/Ca measurements of 4-10 Holocene samples and published water column data and in situ water Cd measurements from GoFlo hydrocasts at two stations at the Portuguese margin and the outer Gulf of Cadiz (Figure 1); [Danielsson et al., 1985; Willamowski, 1999]. The Holocene Cd/Ca values were calculated using data from multiple measurements of up to 10 different samples (Table 2). For cores SO75-26KL and M16004 from the Portuguese and Moroccan margins we arrive at partition coefficients of 3.1 (SO75-26KL, 1099 m) and 2.1 (M16004, 1512 m) (Table 2). Using published water column Cd values from the northern North Atlantic [Danielsson et al., 1985] and Holocene benthic Cd/Ca values from cores M23141 and SO82-05, we arrive at partition coefficients of 4.2 (SO82-05, 1416 m) and 3.3 (M23414, 2196 m) at these sites. These coefficients are different from depth-dependent coefficients of Boyle [1992] which for our sites would increase from 1.5 to 2.2 (Table 2). We cannot offer a satisfying explanation for the discrepancy between our partition coefficients and those published by Boyle [1992] other than that regional variability may exist in the global ocean that on occasion makes application of globally uniform partition coefficients difficult. In the later discussion of our benthic Cd/Ca data we use the partition coefficients derived from our measurements to estimate water column CdW concentrations. That is., CdW is calculated the same way as by Boyle [1992] but using our own partition coefficients. To discern between Boyle's [1992] and our own CdW estimation procedure, we use here the term CdW'. To ensure that the water mass patterns drawn from our data are not an artifact of the choice of partition coefficients, we also calculate CdW estimates using Boyle's [1992] partition coefficients for comparison.

For trace element measurements, core SO75-26KL was sampled every 10 cm, equivalent to time steps of 0.5-1.5kyr. Sample intervals were decreased to 1-1.5 cm, corresponding to 0.01-0.5ky time steps, at the Last Glacial Maximum (LGM) and in Heinrich events. Core M16004 was sampled at 5-10 cm intervals, corresponding to time steps of 2-5kyr; in core sections

Table 2. Mean Holocene Benthic Foraminiferal 8¹³C and Cd/Ca, Water Column Cd and Phosporus Concentrations, and Calculated Foraminiferal Water Column Cd Partition Coefficients

Core	Section Age, kyr	Water Depth, m	Samples/ Replicates ^a	δ ¹³ C, ‰ PDB	Cd/Ca, [µmol mol ⁻¹]	Cdwater, [nmol kg ⁻¹]	P, µmol kg ⁻¹	D_d	
								this study	Boyle [1992]
SO75-26KL	Hol (3.0-8.5)	1099	8/14	1.015	0.047	0.17 ^b	0.86	3.1c	1.3
SO82-05	Hol (0-9)	1416	4/8	1.347	0.103	0.24d	n.a.	4.3°	1.5
M16004	Hol (0.6-9.6)	1512	4/8	1.030	0.036	0.17 ^b	1.21	2.1c	1.6
M23414	Hol (3.0-8.9)	2196	10/24	1.120	0.081	0.24 ^d	n.a.	3.3°	2.2

a Number of sample depths/number of analyses.

^b In situ GoFlo water column samples, hydrocast stations M39035 and M39065, western Iberian margin.

From in situ water olumn Cd and Ca measurements (stations M39035 and M39065) and Holocene benthic Cd/Ca.

d from Danielsson et al. [1985].

e From water date of Danielsson et al. [1985] and Holocene benthic Cd/Ca.

containing the LGM and Heinrich events, sampling intervals were decreased to 0.5-5 cm, equivalent to time steps of 0.1-1.5kyr. Core M23414 from the slope of Rockall Plateau was sampled at 2.5-10 cm intervals, equivalent to 0.1-3.5kyr (mean is 1 kyr) time steps. Benthic foraminifera were very rare in samples from core SO82-05 and many samples had to be rejected because of high Mn/Ca ratios, so that we arrive at a mean sampling interval of 2.5-25 cm, equivalent to time steps of 0.3-3kyr (mean is 1.6kyr).

Stratigraphies, ¹⁴C accelerator mass spectrometry (AMS) dates, age models, and benthic isotope records for all cores were available from previous studies [Zahn et al., 1987; Sarnthein et al., 1994; Manighetti et al., 1995; Slowey and Curry, 1995; Moros et al., 1997; Zahn et al., 1997] (Table 1). Published ages for the North Atlantic Heinrich events which were applied to discrete IRD maxima along some cores were used as additional chronostratigraphic markers.

3. Results

3.1. The $\delta^{18}O$ Records

Of the four δ^{18} O records shown in Figure 2a, the benthic δ^{18} O records from cores SO75-26KL and M16004 from the upper Portuguese and Moroccan margins display the lowest values during the past 50kyr. Today, Mediterranean waters provide a substantial contribution to the hydrography at both sites (~ 30% as estimated from temperature-salinity profiles near site SO75-26KL [Zenk and Armi, 1990]). On the basis of the combined benthic $\delta^{18}O$ and $\delta^{13}C$ evidence it has been inferred that during the last glacial, Mediterranean waters were replaced by middepth waters from the open North Atlantic with a contribution of a warm glacial North Atlantic Central Water [Zahn et al., 1997]. The δ¹⁸O values along cores SO82-05 (Reykjanes Ridge) and M23414 (Rockall Plateau) are at the heavy end of the δ^{18} O range displayed by the four cores. At water depths of 1416 and 2196 m. cores SO82-05 and M23414 are located in the advection paths of cold upper North Atlantic Deep Water (UNADW) with possible recirculated contributions of cold Labrador Sea Water (LSW), which shifts benthic δ18O to increased, i.e., "cold" values.

In core SO82-05 a first abrupt step toward lighter values occurs during the early Termination I, at 15ka. A similar step is seen in the δ^{18} O record from core M23414. At this time, the δ^{18} O and δ¹³C records (Figures 2a and 2b) of both cores converge with those of cores SO75-26KL and M16004 off Portugal and Morocco. The shifts in benthic $\delta^{18}O$ and $\delta^{13}C$ at the two cores from the northern North Atlantic conceivably indicate an abrupt decrease in LSW formation with a potential contribution of meltwaters during the early Termination I. A similar pattern is observed during the two negative (δ¹⁸O anomalies in core SO82-05 at 23ka and 21ka, i.e., immediately prior to and during Heinrich event H2 when δ¹⁸O overlaps with that in "warm" cores M16004 off Morocco and SO75-26KL off Portugal (Figure 2a). This overlap in δ^{18} O correlates with negative anomalies in δ^{13} C in which the δ^{13} C records of the four cores converge (Figure 2b). These periods of converging $\delta^{18}O$ and $\delta^{13}C$ are indicative of periods during the last glacial when LSW formation was substantially decreased in response to glacial meltwater flow. Enhanced contribution of brines has been inferred as a mechanism to deplete benthic δ^{18} O during these periods [Jansen and Veum, 1990; Vidal et al., 1997]. However, on the basis of converging $\delta^{18}O$ and $\delta^{13}C$ signals from the northern and midlatitude North Atlantic sites a stronger influence of a lesser ventilated, warmer middepth water mass throughout the North Atlantic basin in response to reduced LSW formation appears likewise conceivable during these periods.

3.2. δ¹³C Records

Glacial benthic δ¹³C values in middepth cores SO82-05, M23414, SO75-26KL, and M16004 are elevated over or similar to Holocene δ¹³C values (Figure 2b). This pattern documents enhanced ventilation of upper deep water and intermediate water levels in the glacial North Atlantic as is also documented in basin-wide synoptic mapping of benthic δ13C from northeast Atlantic core sites [Duplessy et al., 1988; Sarnthein et al., 1994]. Most positive full-glacial δ13C values at and above +1.6% PDB are recorded in cores SO82-05 and SO75-26KL from the Reykjanes Ridge and upper Portuguese margin. Full-glacial δ¹³C in both cores is increased over Holocene δ^{13} C values by >0.5%. Glacially elevated $\delta^{13}C$ in core SO82-05 in conjunction with increased $\delta^{18}O$ values indicates that the core was in the advection path of a young, cold middepth water mass, presumably coming from the Labrador Sea [Lackschewitz et al., 1998]. Glacial δ¹³C values in core M23414 are around +1.0% PDB, i.e., 0.6-0.4% more negative than glacial δ^{13} C in core SO82-05 to the north and in core SO75-26KL to the southeast. In fact, glacial $\delta^{13}C$ (and Cd/Ca, see below) in core M23414 is not much different from Holocene values. Core M23414 at 2196 m is located 800-1100 m deeper in the water column than cores SO82-05 (1416 m) and SO75-26KL (1099 m). The close similarity in glacial and Holocene δ¹³C values in core M23414 is in contrast to glacially increased values at shallower core sites and depleted values at deeper cores in the North Atlantic region and points to variable mixing ratios between Antarctic Bottom Water (AABW) and North Atlantic water masses at this depth level. The stronger glacial advection of AABW to the northern North Atlantic [Duplessy et al., 1988; Sarnthein et al., 1994] and its upward mixing to the depth level of core M23414 apparently counterbalanced the influence of better ventilated middepth water masses above. Enhanced northward advection of southern ocean water masses at middepths is also consistent with the observation of a stronger meridional δ^{13} C gradient between the northern North Atlantic and the tropical Atlantic during the last glacial [Matsumoto and Lynch-Stieglitz, 1999].

Glacial δ^{13} C of +1.1% PDB in core M16004 from the Moroccan margin is 0.5% more negative than that in core SO75-26KL only a short distance to the north. This strong gradient is not seen today in water column data and implies that the boundary between Southern Hemisphere and North Atlantic middepth water masses passed between the Portuguese and Moroccan margins. Meridional benthic δ^{13} C transects across the east Atlantic basin indeed suggest the presence of a 13 C-depleted water mass at upper deep water depths during the last glacial [see Sarnthein et al., 1994, Figure 9]. Whereas the depletion may have been caused by an enhanced flux of organic debris to the seafloor underneath the northwest African upwelling system, the disparate δ^{13} C-Cd/Ca pattern of cores SO75-26KL and M16004 rather points to a water mass effect, i.e., a hydrographic front (see below).

The δ^{13} C records indicate the presence of well-ventilated middepth and upper deep water masses during the last glacial. During the early Termination I an abrupt decrease in δ^{13} C is seen

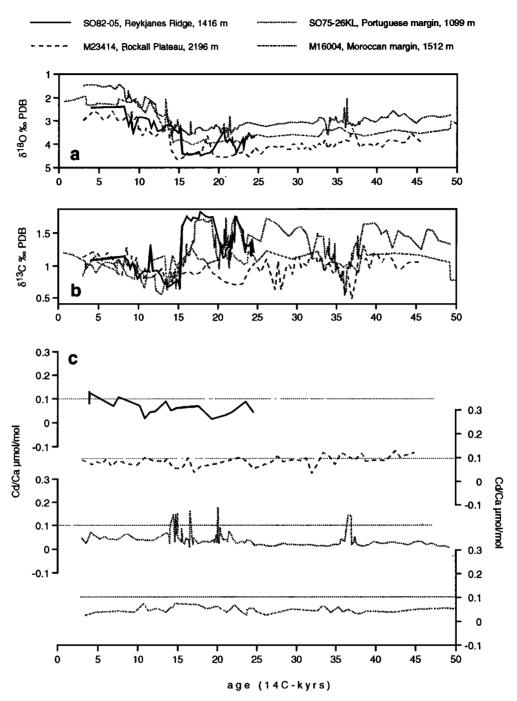


Figure 2. (a) Oxygen isotope, (b) carbon isotop, and (c) Cd/Ca records. The records from middepth core sites document better ventilation and lower nutrient concentrations during the last glacial. Note marked Cd/Ca maxima in core SO75-26KL which correlate with Heinrich events.

in the shallow cores SO82-05 and SO75-26KL (Figure 2b). The decrease starts about 2kyr earlier in core SO75-26KL off Portugal than in Reykjanes Ridge core SO82-05. As a result of the δ^{13} C decrease, δ^{13} C values from the two shallow cores converge with those from shallow middepth core M16004 and core M23414 from within UNADW. During the Bölling/Alleröd warm period the middepth and UNADW δ^{13} C records indicate a more homogenous water mass distribution in the North Atlantic. Convergence of δ^{13} C records from the shallow cores and the

subsequent coherent δ^{13} C increase reflect the deglacial decrease in convective overturn in the northern North Atlantic and subsequent onset of Holocene circulation patterns with increased contributions of overflow waters from the Nordic Seas.

The glacial sections of the $\delta^{13}C$ records are punctuated by negative $\delta^{13}C$ anomalies. These have been linked to slowdown of convection and decreased ventilation during meltwater surges that went along with Heinrich meltwater events and caused enhanced buoyancy stratification at convection sites in the northern North

Atlantic [Sarnthein et al., 1994; Jung, 1996; Zahn et al., 1997; see also Maslin et al., 1995]. The δ¹³C anomalies are most strongly developed in cores SO82-05 and SO75-26KL, which both display strongly increased glacial δ¹³C values. In both cores, δ¹³C during Heinrich events H2 and H4 decreases by 0.7-1.0‰ below mean glacial δ^{13} C levels, indicating substantial ventilation decreases. The δ^{13} C anomaly during H1 is masked by the 1.0% δ¹³C decrease during early Termination I and is therefore not well developed in cores SO82-05 and SO75-26KL. It is important to note that benthic foraminiferal abundances in Heinrich layers 1 and 2 in core SO75-26KL remained virtually unchanged during these episodes [Allenstein, 1995]. Therefore we believe that the benthic δ¹³C anomalies (as well as Cd/Ca anomalies, see below) in this core directly mirror water column signals. At the northern North Atlantic sites where sedimentation rates are lower and concentrations of IRD grains are higher, bioturbational dampening of the anomaly amplitudes cannot be ruled out.

The δ^{13} C records of middepth cores M23414 from Rockall Plateau and M16004 from the Moroccan margin display only subtle δ^{13} C depressions during the Heinrich events and only small δ^{13} C shifts during Termination I. According to the age models, sedimentation rates at both sites are similar, 3-7 cm/kyr, an order of magnitude lower than at the site of core SO75-26KL (15-35 cm/kyr) but similar to sedimentation rates at core SO82-05 (7-11 cm/kyr). Thus stratigraphic resolution is lower in cores M23414 and M16004, but the subdued δ^{13} C changes during the Heinrich events and during Termination I may still contain true water mass signals which indicate that ventilation changes during these events were smaller at these sites (see discussion further below).

3.3. Cd/Ca Records

Middepth cores SO75-26KL and M16004 at the upper Portuguese and Moroccan margins which are today in the advection path of Mediterranean Outflow Water (MOW) display mean Holocene Cd/Ca ratios of 0.047 and 0.037 µmol mol-1 (Figure 2c). These low values reflect the presence of nutrientdepleted MOW and North Atlantic middepth waters (mainly Labrador Sea water) which originate from oligotrophic source regions in the Mediterranean and in the northern North Atlantic. Mean glacial ratios in both cores are 0.025 µmol mol-1 (SO75-26KL) and 0.049 μ mol mol⁻¹ (M16004). That is, glacial Cd/Ca values at the upper Portuguese margin are depleted, whereas at the upper Moroccan margin they are increased over mean Holocene levels. The lower Cd/Ca values fit well to the glacially increased 813C values in core SO75-26KL in that both point to decreased nutrient concentrations. Glacially increased Cd/Ca values, however, in core M16004 are in antiphase to glacially increased benthic δ^{13} C. This divergent proxy pattern between both cores has some bearing on water mass chemistry and circulation patterns, which will be discussed below. Cd/Ca ratios in core M23414 from the Rockall Plateau are likewise increased over those of the middepth cores with Holocene and glacial values averaging to 0.081 (± 0.009 , n=11) and 0.089 μ mol mol⁻¹ $(\pm 0.02, n=37)$, respectively, which within the standard deviation, are virtually identical. Middepth core SO82-05 from the Reykjanes Ridge again displays more depleted glacial Cd/Ca values, 0.053 µmol mol-1, while Holocene values are increased to 0.103 µmol mol-1.

The Cd/Ca (and δ¹³C) records of core SO75-26KL show increased variability owing to denser sample spacing and higher

sedimentation rates (Figure 2c). Records from the other cores shown in Figure 2c are of lower resolution because benthic foraminifera were less abundant for Cd/Ca measurements and because an increased number of Cd/Ca measurements at the northern North Atlantic sites had to be discarded owing to contamination problems as indicated by increased Mn/Ca ratios. In general, however, Cd/Ca values at upper deep water site M23414 from Rockall Plateau are increased over those at middepth sites, which fits well to today's and inferred glacial circulation patterns in the area [Duplessy et al., 1988; Sarnthein et al., 1994] with more rapid ventilation of the upper water column with nutrient-depleted water masses and a stronger contribution of nutrient-increased AABW during the last glacial at depth.

Outstanding features in the benthic Cd/Ca record of core SO75-26KL are abrupt increases during Heinrich events H1, H2, and H4. Cd/Ca ratios increase to values of 0.14-0.18 µmol mol-1, far above the glacial-interglacial range of values. Amplitudes of the Cd/Ca anomalies are ~6 times the glacial-interglacial Cd/Ca change in the same core. The maximum Cd/Ca ratios are converted into CdW' values of 0.46-0.58 nmol kg-1, which applying global Cd-nutrient correlations [Boyle, 1994], translate into water column phosphorus concentrations between 1.8 µmol kg-1 (high-nutrient water column Cd:P correlation) and 2.8 µmol kg-1 (low-nutrient water column Cd:P correlation [Boyle, 1988a]), for the Heinrich event anomalies. Applying Boyle's partition coefficients, the Cd/Ca maxima convert into even higher water column Cd concentrations of 1.1-1.4 nmol kg-1 which translate into water column phosphorus concentrations >3.5 µmol kg-1. No matter which conversion we use (our own partition coefficients or Boyle's [1992] global coefficients), the data clearly show that nutrient concentrations in the North Atlantic must have been extremely high during the Heinrich events. Converting the negative δ^{13} C anomalies into nutrient equivalents by applying an upper ocean δ¹³C-phosphate relation [Zahn and Keir, 1994], we derive phosphorus concentrations of only 0.3-1.9 µmol kg⁻¹. From the apparent offset between both nutrient estimates we infer a thermodynamic imprint on benthic δ^{13} C in association with (partial) equilibration of seawater $\delta^{13}C_{\Sigma CO}$ with the overlying atmosphere at the convection sites [Broecker and Maier-Reimer, 1992; Lynch-Stieglitz et al., 1995].

4. Discussion

4.1. Proxy-Proxy Patterns as Indicators of Glacial Water Mass Distribution

Water column $\delta^{13}C_{\Sigma CO_2}$ and dissolved Cd on a global scale are both linked to ocean dissolved phosphorus distribution [Kroopnick, 1985; Boyle, 1988a] in that both proxies are driven by biological nutrient cycling. Secondary effects exist from isotope fractionation during air-sea gas exchange and from enzymatic reactions which regulate the uptake of trace metals by marine phytoplankton [Mook et al., 1974; Cullen et al., 1999]. Air-sea gas exchange exerts control on $\delta^{13}C_{\Sigma CO_2}$ in that it is temperature dependent and increases surface water $\delta^{13}C_{\Sigma CO_2}$ by some 0.1% per 1°C temperature decrease [Mook et al., 1974]. The net effect of this fractionation pattern is that $\delta^{13}C_{\Sigma CO_2}$ is regionally decoupled from its mean global nutrient correlation [Charles and Fairbanks, 1990; Broecker and Maier-Reimer, 1992; Charles et al., 1993; Lynch-Stieglitz et al., 1994; 1995].

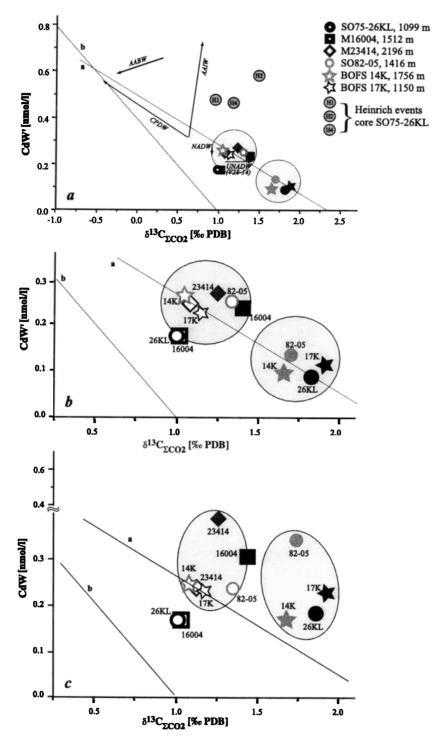


Figure 3. (a) CdW':δ¹³C_{ΣCO2} diagram showing proxy coordinates as computed from benthic records along sediment cores used in this study. Open symbols give mean Holocene values, and solid symbols are mean glacial values. Arrows define glacial-interglacial shifts in CdW':δ¹³C_{ΣCO2} coordinates of NADW, UNADW, AAIW, AABW, and CPDW [from Boyle, 1992 and Lynch-Stieglitz et al., 1996]. They are used as reference for comparison to the proxy coordinates from our sediment cores. Solid lines give the link between CdW' and δ¹³C as defined by global proxy-nutrient correlations (line a is for nutrient-poor conditions, and line b is for nutrient-rich conditions). (b) Close-up view of the lower right part of Figure 3a for better visual inspection. Glacial δ¹³C is corrected by -0.32‰ to account for ocean reservoir effects. No correction was applied for Cd/Ca as the inferred reservoir effect of 13% is within the reproducibility limits of Cd/Ca measurements. (c) Same as in Figure 3b except that glacial water column Cd concentrations are estimated using Cd partition coefficients of Boyle [1992]. Data of BOFS cores 14 and 15 are from Bertram et al. [1995].

Water column Cd concentrations, on the other hand, may be modulated independently from nutrient cycling by changes in seawater PCO2 and micronutrient concentrations which regulate Cd uptake by phytoplankton [Cullen et al., 1999]. However, lacking extensive regional to global surveys on the proposed PCO₂-Cd connection, we assume here that on a global scale, dissolved Cd, in the absence of an atmospheric link, behaves more conservatively than does δ13C_{ΣCO2} and that benthic Cd/Ca can be used in connection with benthic δ¹³C to trace paleoceanographic water mass patterns and origins [Lynch-Stieglitz et al., 1994]. Most importantly, along water mass advection paths through the ocean biological cycling affects both δ13C_{ΣCO2} and dissolved Cd equally therefore maintaining the original δ13C-Cd offset which a given water mass acquired at its source of origin. The δ^{13} C-Cd offset thus behaves like a conservative tracer which is altered only by mixing with other water masses [Lynch-Stieglitz et al., 1994].

Proxy-proxy (CdW': δ^{13} C, Figure 3) plots that show δ^{13} C Σ CO2 and CdW' as estimated from benthic foraminiferal $\delta^{13}C$ and Cd/Ca ratios reveal a systematic glacial-interglacial pattern. "Biofractionation" lines that link δ^{13} C and CdW' are shown for reference to indicate the correlation between both proxies were they strictly driven by biological cycling. Mean Holocene and glacial proxy coordinates of main end-member water masses in the Atlantic are taken from Boyle [1992] and Lynch-Stieglitz et al. [1996] and are used as references for comparison to the glacialinterglacial data from our sediment cores. Glacial CdW':813C coordinates were determined from glacial benthic δ^{13} C, which was corrected by -0.32‰ to account for ocean reservoir effects. No correction was applied for glacial Cd/Ca as the inferred reservoir effect of 13% is in the same order as the reproducibility of the Cd/Ca measurements [Boyle, 1992]. Largest glacialinterglacial end-member proxy shifts are indicated for Southern Hemisphere water masses (AAIW, AABW and Circumpolar Deep Water, (CPDW)); shifts for NADW and UNADW are moderate to small (Figure 3a). Glacial-interglacial shifts of proxy coordinates computed from the benthic δ^{13} C and Cd/Ca records display a disparate pattern (Figure 3b). Glacial coordinates of northern North Atlantic cores SO82-05, BOFS 14K, and BOFS 17K as well as of core SO75-26KL from the upper Portuguese margin display distinctly higher δ¹³C and lower CdW' values compared to the Holocene. Cores M16004 (upper Moroccan margin) and M23414 (middepth Rockall Plateau) also display increased glacial 813C values, but CdW' at both sites is slightly increased.

Mean Holocene proxy values are well within the range of modern water column $\delta^{13}C_{\Sigma CO_2}$ and dissolved Cd values of NADW and UNADW $\delta^{13}C_{\Sigma CO_2}$: 0.8-1.3% PDB; CdW': 0.2-0.3 nmol kg⁻¹ [Danielsson et al. 1985]; Kroopnick [1985]; Bertram et al. [1995]). Mean glacial proxy values at our core sites remain in the Northern Hemisphere domain of the $\delta^{13}C$ -CdW' field in that $\delta^{13}C$ remains positive and CdW' is low, and none of the glacial core coordinates display the substantial $\delta^{13}C$ decrease and CdW' increase indicated for Southern Hemisphere water mass endmembers (Figures 3a and 3b). An important feature is the divergence of glacial proxy coordinates between cores SO75-26KL and M16004 at the upper Portuguese and Moroccan margins. Mean Holocene values for $\delta^{13}C$ and CdW' at both sites are identical ($\delta^{13}C=1.0\%$ PDB; CdW'=0.17 nmol kg⁻¹), which is in agreement with the dominance of nutrient-depleted MOW at

both locations. Mean glacial values are offset at both sites. The northern core, SO75-26KL, shows substantially increased δ^{13} C (1.9% PDB, corrected by 0.32% for glacial carbon pool) and decreased CdW' values (0.08 nmol kg⁻¹), whereas in the southern core, M16004, the δ^{13} C increase is less than half of that at the northern site (1.4% PDB) and CdW' is increased (0.23 nmol kg⁻¹).

The shift of the proxy coordinates toward higher δ^{13} C and lower CdW' at the northern North Atlantic core sites during the last glacial confirms previous observations that middepth water masses in the North Atlantic were more nutrient depleted than today [Duplessy et al., 1988; Sarnthein et al., 1994]. However, the divergence between glacial proxy coordinates of cores SO75-26KL and M16004 is a clear indication that the upper Portuguese and Moroccan margins despite their close geographic proximity, were influenced by different water masses. Glacial δ^{13} C at both locations was increased, so that the glacial decrease in CdW' at the northern core site off Portugal is well in line with the glacial δ^{13} C increase. The glacial CdW' increase at the southern location off Morocco, however, is opposite to what is expected from the smaller but still distinctive glacial δ^{13} C increase at this core site.

Figure 3c compares Holocene proxy coordinates with glacial values that were calculated using Boyle's [1992] partition coefficients to convert foraminiferal Cd/Ca to water column CdW estimates. Other than our CdW' estimates (Figure 3b), are the glacial CdW estimates similar to or, as in the case of core SO82-05 from Reykjanes Ridge, increased over Holocene values (note that the Holocene values in Figure 3c were still calculated using our own partition coefficients; using Boyle's [1992] depthdependent coefficients results in unreasonably high CdW estimates for the northern North Atlantic of up to 0.7 nmol kg⁻¹, i.e., values that are typically found in the Pacific). In this case, glacial nutrient concentrations (as inferred from CdW) throughout the shallow northern North Atlantic would have approached values similar to those in today's South Atlantic and Southern Ocean, an inference which we consider unreasonable given that convection of young nutrient-depleted waters still occurred in the region. Nevertheless, glacial shifts of CdW, the same as for CdW', estimated from cores M23414 and M16004 are offset from those at our other North Atantic core sites in that the glacial CdW equivalents are shifted toward the Southern Ocean data field. The fact that application of the global partition coefficients result in vast overestimations of modern and also of conceivable glacial water column Cd concentrations at our core sites leads us to trust our own partition coefficients as the more reliably values for converting benthic Cd/Ca values into water column Cd equivalents at our core sites.

4.2. Constraints on Middepth Circulation in the North Atlantic: Last Glacial and Heinrich Events

Glacial $\delta^{13}C_{\Sigma CO2}$:CDW' proxy coordinates of core SO75-26KL fall into the proxy field of the northern North Atlantic as defined by glacial data from cores SO82-05, BOFS 14K, and BOFS 17K (Figure 3). Glacial proxy values of core M16004 are moved away from this field toward the proxy distribution inferred for Southern Hemisphere water masses (Figure 3a). Using CdW' as nutrient reference and applying global nutrient correlations for water column Cd concentrations and $\delta^{13}C_{\Sigma CO2}$ [Boyle, 1988a, 1988b; Zahn and Keir, 1994], we arrive at $\delta^{13}C$ anomalies ($\delta^{13}C_{\text{excess}}$) of 0.2% for core SO75-26KL and 0.49% for core M16004. We define $\delta^{13}C_{\text{excess}}$ here as the $\delta^{13}C$ increase which is

not supported by decreases in nutrient concentrations, thus pointing to thermodynamic imprints from air-sea gas exchange. Upper deep water core M23414 (2196 m water depth) from Rockall Plateau displays mean glacial values of 0.26 nmol kg⁻¹ (CdW') and 1.3% PDB δ¹³C) from which similar δ¹³C_{excess} of 0.47‰ is inferred. Glacial δ13Cexcess for UNADW and AAIW end-members as estimated from core data by Boyle [1992] (V28-14, Denmark Strait, 1855 m water depth) and Lynch-Stieglitz et al. [1996] both are around 0.5%. The close similarity of δ¹³C_{excess} for AAIW and UNADW precludes the use of the anomaly as a unique water mass indicator. It either points to similar thermal histories during air-sea gas exchange in the highlatitude North and South Atlantic or to similar oceanographic regimes in both regions involving upwelling of nutrient-rich deeper water into the surface layer and (partial) carbon isotope equilibration with the overlying atmosphere. The fact, however, that glacial CdW':813C coordinates for cores M23414 and M16004 are moved away in the proxy-proxy diagram from the northern North Atlantic domain toward higher CdW' and lower δ¹³C (Figure 3) indicates that both cores were influenced by a nutrient-enriched water mass. From this data pattern we infer that core M23414 during the LGM received some contribution from AABW that shoaled into upper deep water levels along the southern slopes of Rockall Plateau. The glacial maximum hydrography at the upper Moroccan margin, on the other hand, obviously was influenced by a nutrient-enriched water mass as indicated by higher CdW' and lower δ^{13} C values than are documented in core SO75-26KL at the upper Portuguese margin. From this we infer that during the last glacial, AAIW penetrated into the midlatitude eastern North Atlantic. The benthic δ¹³C and Cd/Ca gradients between the upper Moroccan and Portuguese margins as displayed in proxy offsets between cores SO75-26KL and M16004 indicate that an upper ocean hydrographic front existed in the midlatitude northeast Atlantic, separating UNADW from AAIW

The inference of a middepth hydrographic front between AAIW and UNADW in the midlatitude North Atlantic has some bearing on glacial circulation patterns in the region. Current paleoceanographic concepts postulate a shoaling of convection depths in the northern North Atlantic during the last glacial because of lower density fluxes in response to cooler SST and lower surface salinities [Boyle and Keigwin, 1987; Duplessy et al., 1988; Sarnthein et al., 1994]. Judging by the pattern of benthic δ¹³C along meridional transects alone [Duplessy et al., 1988; Sarnthein et al., 1994] indeed suggests that the dominant upper deep and middepth water masses in the glacial maximum North Atlantic were of Northern Hemisphere origin. The benthic Cd/Ca data from the upper Moroccan margin, however, suggest that glacial water masses there were enriched in nutrients despite the positive benthic δ^{13} C imprints. With the constraint of benthic Cd/Ca as a further nutrient and circulation proxy we thus infer that the Southern Hemisphere contribution to the glacial North Atlantic hydrography was stronger than has previously been estimated on the basis of benthic δ13C alone. Our data suggest that AAIW in the eastern North Atlantic reached as far north as the northern Moroccan margin, i.e., to immediately south of the Gulf of Cadiz (Figure 4).

Numerical paleocirculation modeling lends credence to our inferred circulation scheme. Using glacial maximum surface ocean conditions as estimated from paleoceanographic databases, Seidov et al. [1996] infer a slowdown of thermohaline overturn

by some 30% and reductions in marine northward heat transfer, much in line with other model predictions [Stocker et al., 1992; Rahmstorf, 1994, 1995; Weaver and Hughes, 1994; Manabe and Stouffer, 1995; Ganopolski et al., 1998]. Most importantly, the model predicts a reversed gyre circulation for the glacial maximum middepth North Atlantic [Seidov et al., 1996]. In the model a strong UNADW current flows along the western Iberian margin, is deflected to the west across the North Atlantic at midlatitudes (~30°N), and turns south upon approaching the western Atlantic margin to form a strong southward current in the western basin [Seidov et al., 1996, Figure 7c]. This circulation path of UNADW would constitute an effective barrier against the northward penetration of AAIW in the western North Atlantic but would still allow AAIW to spread northward in the eastern basin to the Moroccan margin (Figure 4). This water mass asymmetry between the eastern and western Atlantic is also picked up by benthic 813C in cores SO75-26KL from off Portugal and OC205-2-100GGC from the upper Bahama slope (1045 m water depth [Slowey and Curry, 1995]), which is similar in both cores during the last glacial but is offset to more positive values from core M16004 at the upper Moroccan margin (Figure 5).

Marked benthic Cd/Ca maxima are observed in core SO75-26KL during Heinrich events (Figure 2). The δ¹³C-CdW' coordinates for these events are exceptional in the proxy-proxy diagram in that they fall far outside the North Atlantic domain (Figure 3a). The δ¹³C values in core SO75-26KL during the Heinrich events are depleted below mean glacial levels by as much as 1.3%, and estimated CdW' values are increased by a factor of 2-3 to values between 0.46 and 0.58 nmol kg⁻¹. Such elevated CdW' values in today's ocean are well above Atlantic deep and middepth CdW' concentrations (0.1-0.3 nmol kg-1 [Danielsson et al., 1985; Boyle, 1992; Willamowski, 1999]) and are typically found in the Southern Ocean [Nolting et al., 1991; Boyle, 1992; Frew and Hunter, 1992]. In the global CdW:P correlation [Boyle, 1988a, 1994] these values are equivalent to 2.0-2.2 µmol kg-1 phosphorus. Applying Boyle's [1992] partition coefficients, inferred CdW estimates are even higher, between 1.10 and 1.38 nmol kg-1. Using CdW' (as derived from benthic Cd/Ca and our partition coefficients) as nutrient reference for normalization of benthic δ^{13} C, we arrive at δ^{13} C_{excess} values of 0.6% (H4) to 1.7% (H2) for Heinrich events H1, H2, and H4. Temperature as the sole driving force behind the δ^{13} C excess values appears unreasonable because δ13C excess values of up to 1.7% would indicate temperature decreases by some 17°C [Mook et al., 1974; Broecker and Maier-Reimer, 1992]. Conceivably, equilibration of surface waters during these episodes with the overlying atmosphere was more efficient in response to increased water column stability and longer residence times of waters at the surface.

Changes in dissolved Cd inventories or ocean $\delta^{13}C_{\Sigma CO2}$ are viable means to alter water mass $Cd\delta^{13}C$ signals. There are no high-resolution benthic Cd/Ca and $\delta^{13}C$ records available from the high-latitude North and South Atlantic which would allow one to estimate water column Cd and $\delta^{13}C$ signals during Heinrich events. Possible mechanisms to cause nonanalog $Cd:\delta^{13}C$ would be changes in Cd/P ratio through Cd input from continental margins as in today's Southern Ocean [Frew, 1995] or more efficient nutrient cycling in conjunction with stronger carbon isotope fractionation during photosynthetic carbon fixation [e.g., Rau et al., 1989; Rau, 1994]. However, from sediment core evidence it has been concluded that Southern

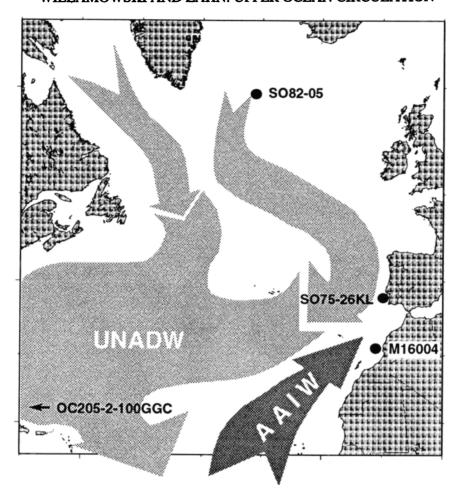


Figure 4. Upper ocean circulation scheme for the glacial North Atlantic. A strong flow of UNADW from the northern North Atlantic to the south and across the basin to the west is inferred from paleocean modeling [Seidov et al., 1996]. A northward penetration of AAIW to the midlatitude northeast Atlantic is inferred from benthic δ^{13} C (see Figure 5) and Cd/Ca data which indicate a middepth hydrographic front between the Moroccan and Portuguese margins. Positions of sediment cores with δ^{13} C records shown in Figure 5 are indicated.

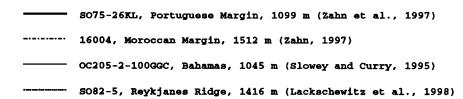
Ocean Cd and nutrient budgets have been reasonably stable on glacial-interglacial timescales [Boyle, 1992; Boyle and Rosenthal, 1996], so that it is not immediately obvious how a potential increase in Cd during Heinrich events should have been generated there. Taking the Heinrich event CdW':δ¹³C proxy coordinates at face value and using mean glacial Cd:δ¹³C end-member signals of AAIW and UNADW for comparison (Figure 3a), the position of Heinrich event proxy coordinates suggests that North Atlantic middepth water masses during the meltwater events consisted of >60% of Southern Hemisphere waters. If so, this implies that during these events the North Atlantic was filled with southern source waters from bottom water depths to upper ocean levels (1000 m) and perhaps even shallower.

In the absence of reliable information on end-member water mass proxy patterns during Heinrich events, this estimate must be considered conservative. As can be seen from Figure 3a, estimated AAIW contributions are fairly insensitive to potential changes in AAIW $\delta^{13}C_{\Sigma CO_2}$. If dissolved Cd concentrations in AAIW were increased over their modern values as would be required to explain the high positive $\delta^{13}C_{excess}$ values, a contribution of some other low-nutrient water mass is needed to

explain the Heinrich event proxy coordinates. Whatever the ultimate cause for the nonanalog proxy pattern during the Heinrich events was, the extremely high CdW' values and inferred nutrient estimates for these episodes are unlikely driven by reduced middepth ventilation from North Atlantic sources alone but must have been caused by a contribution of Southern Hemisphere water masses.

5. Conclusions

Benthic Cd/Ca and δ^{13} C along sediment cores from middepth core sites in the North Atlantic trace glacial-interglacial water mass changes and finer-scale variability linked to Heinrich meltwater events. Glacial benthic δ^{18} O and δ^{13} C of +4.5% PDB (Cibicides scale) and +1.6% PDB document the presence of cold well-ventilated Upper North Atlantic Deep Water (UNADW) in the middepth northern North Atlantic. Off Portugal, benthic δ^{13} C is also positive, but δ^{18} O is more negative, indicating advection of well-ventilated warmer central waters. Benthic Cd/Ca supports the presence of nutrient-depleted UNADW during the last glacial but also points to distinctive contributions of Southern



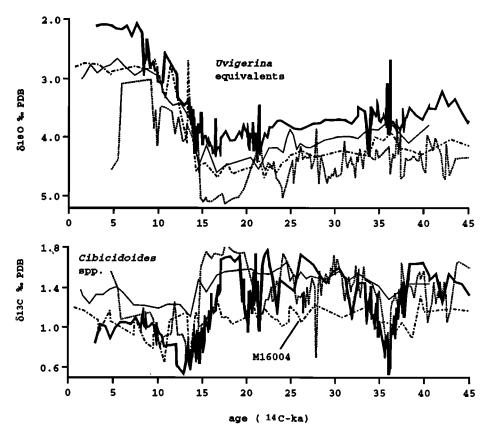


Figure 5. Benthic isotope records from middepth core sites in the subtropical and northern North Atlantic. During the last glacial the δ^{13} C record of core OC205-2-100GGC from the Bahamas [Slowey and Curry, 1995] is similar to those from the northern North Atlantic and the Portuguese margin and offset from that of core M16004 from the Moroccan margin, which displays more negative δ^{13} C values. This asymmetric pattern at midlatitudes is indicative of an influx of AAIW into the glacial northeast Atlantic at the same time when the western and northern North Atlantic were dominated by UNADW. See also Figure 4 and text for discussion.

Hemisphere waters to lower UNADW and middepth water masses off Morocco. Water column CdW' was estimated from benthic Cd/Ca using partition coefficients which we calulated from our own in situ water column Cd data and published data [Danielsson et al., 1985] and mean Holocene benthic Cd/Ca. Our partition coefficients deviate from Boyle's [1992] depthdependent coefficients and point to regional variability in water column-to-foraminifer Cd distributions. Inferred CdW' (and also CdW as calculated using Boyle's [1992] partition coefficients) shows a disparate pattern between the upper Portuguese and Moroccan margins. The discrepancy in glacial δ¹³C and water column Cd concentrations between the upper Portuguese (+1.54‰ PDB; 0.08 nmol kg-1 CdW') and Moroccan margins (+1.1% PDB; 0.23 nmol kg-1 CdW') is indicative of a middepth hydrographic boundary, which is also implied by numerical modeling [Seidov et al., 1996]. This boundary separated

UNADW from AAIW, which penetrated northward in the glacial northeast Atlantic to ~30°N.

During Heinrich events and during Termination I, $\delta^{13}C$ decreases and Cd/Ca increases abruptly. The $\delta^{13}C$ decreases by as much as 1.3% during these episodes, and peak Cd/Ca maxima are increased to 0.14-0.18 µmol mol⁻¹. The Cd/Ca increases amount to 6 times the glacial-interglacial amplitude and indicate nonanalog conditions in which water column Cd concentrations reached 0.5-0.6 nmol kg⁻¹, equivalent to water column phosphorus concentrations of 2 to >3 µmol kg⁻¹. Such high concentrations are today found in the Southern Ocean and Pacific. Benthic $\delta^{13}C$ remains reasonably positive, between +0.5 and +1.2% PDB (compared to +1.7% PDB at the same core site, SO75-26KL), in direct contrast to the inferred high nutrient concentrations, but the records from the different core sites converge. The combined benthic $\delta^{13}C$ and Cd/Ca patterns signify

nonanalog conditions which cannot be explained by a slowdown of thermohaline overturn alone in the North Atlantic. The data indicate the presence of a more homogenous water mass during these episodes with distinctive contributions of Southern Hemisphere waters.

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