



Deep water mass geometry in the glacial Atlantic Ocean: A review of constraints from the paleonutrient proxy Cd/Ca

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[1] Paleonutrient proxies currently provide the strongest constraints on the past spatial distribution of deep water masses. We review the state of knowledge derived from the trace metal proxy Cd/Ca for the Atlantic Ocean during the Last Glacial Maximum (LGM). We compile published benthic foraminiferal Cd/Ca data, supplemented with new data, to reconstruct meridional Cd sections through the Holocene and LGM Atlantic. Holocene Cd/Ca reflects the modern water masses North Atlantic Deep Water (NADW), Antarctic Bottom Water (AABW), and Antarctic Intermediate Water (AAIW) reasonably well, except for anomalously high values in the intermediate to mid-depth far North Atlantic. LGM Cd/Ca clearly shows that NADW was replaced by the shallower Glacial North Atlantic Intermediate Water (GNAIW), with significant northward expansion of AABW. The boundary level between GNAIW and AABW was very abrupt, occurring between ~2200 and 2500 m modern water depth. Combined Cd/Ca and *Cibicidoides* $\delta^{13}\text{C}$ data allow us to also calculate the air-sea signature of $\delta^{13}\text{C}$ ($\delta^{13}\text{C}_{\text{as}}$). The LGM Atlantic can be explained entirely by mixing between high- $\delta^{13}\text{C}_{\text{as}}$ GNAIW and low- $\delta^{13}\text{C}_{\text{as}}$ AABW. Negative $\delta^{13}\text{C}_{\text{as}}$ values in glacial AABW were likely caused by poor ventilation during formation, probably associated with extensive sea ice coverage. Overall, our knowledge base would benefit from improved data coverage in the South Atlantic and Southern Ocean, and a better understanding of ancillary effects on the Cd/Ca proxy itself.

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1. Introduction

[2] Past changes in the ocean's Meridional Overturning Circulation (MOC) are believed to have

significantly impacted regional climates by altering patterns of ocean heat transport. In particular, changes in the strength and/or location of North Atlantic Deep Water (NADW) formation likely

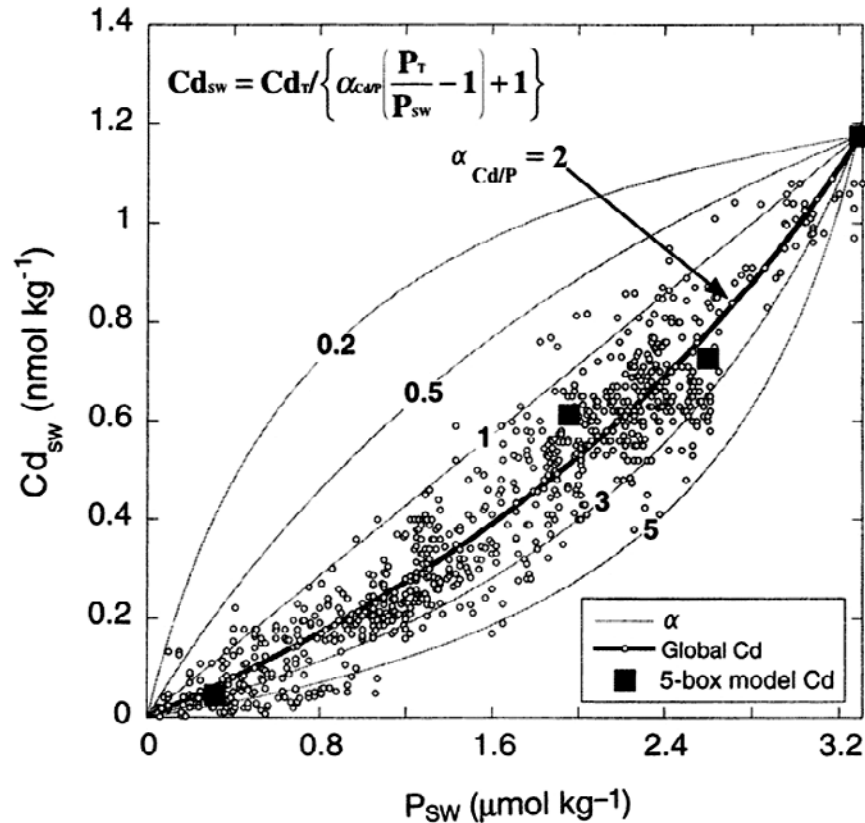


Figure 1. Dissolved Cd versus dissolved phosphate in the global ocean, reproduced from *Elderfield and Rickaby* [2000]. Curves show different solutions to the inset equation (equation (1)) with $Cd_T = 1.2$ and $P_T = 3.3$ that can explain regional relationships between the two nutrients. Bold line is the best fit to the global data set, with $\alpha_{Cd/P} = 2$. Reprinted by permission from Macmillan Publishers Ltd.

caused the abrupt millennial-scale warmings and coolings that characterized the climate of the North Atlantic region during the last glaciation [e.g., *Broecker et al.*, 1985; *Stocker and Wright*, 1991; *Ganopolski and Rahmstorf*, 2001; *Rahmstorf*, 2002]. The climatic footprint of these so-called Dansgaard-Oeschger events was large, including notable impacts on the position of the Atlantic Intertropical Convergence Zone (ITCZ) [*Peterson et al.*, 2000], the strength of the Asian monsoons [*Schulz et al.*, 1998; *Wang et al.*, 2001], and the intensity of the northeastern tropical Pacific oxygen minimum zone [*Behl and Kennett*, 1996; *Ortiz et al.*, 2004]. In addition, glacial modes of deep ocean circulation may have fundamentally altered large-scale patterns of nutrient upwelling, biological production, and $CaCO_3$ preservation, thereby contributing to the drawdown of atmospheric CO_2 [e.g., *Broecker and Peng*, 1987; *Toggweiler*, 1999; *Sigman and Boyle*, 2000; *Marchitto et al.*, 2005; *Toggweiler et al.*, 2006].

[3] Most of what paleoceanographers know about the past distribution of deep water masses is derived from paleonutrient proxies. Such passive tracers offer no direct information about deep water formation rates or fluxes [*LeGrand and Wunsch*, 1995], but may be used to constrain conceptual and numerical models of the MOC. The most widely applied paleonutrient tracer is benthic foraminiferal $\delta^{13}C$, which is inversely correlated with the labile nutrient phosphate [*Kroopnick*, 1985; *Duplessy et al.*, 1988; *Sarnthein et al.*, 1994; *Curry and Oppo*, 2005]. Boyle and colleagues developed benthic foraminiferal Cd/Ca as a deep water tracer at about the same time that $\delta^{13}C$ was first applied to the problem, in the early 1980s [*Boyle and Keigwin*, 1982, 1985/1986]. Cd/Ca was therefore instrumental in codifying the view of a glacial-age shoaling of low-nutrient NADW and northward expansion of nutrient-rich Antarctic Bottom Water (AABW) into the North Atlantic [*Boyle and Keigwin*, 1987; *Oppo and Fairbanks*, 1987] (note that we use AABW to include Circumpolar Deep Water

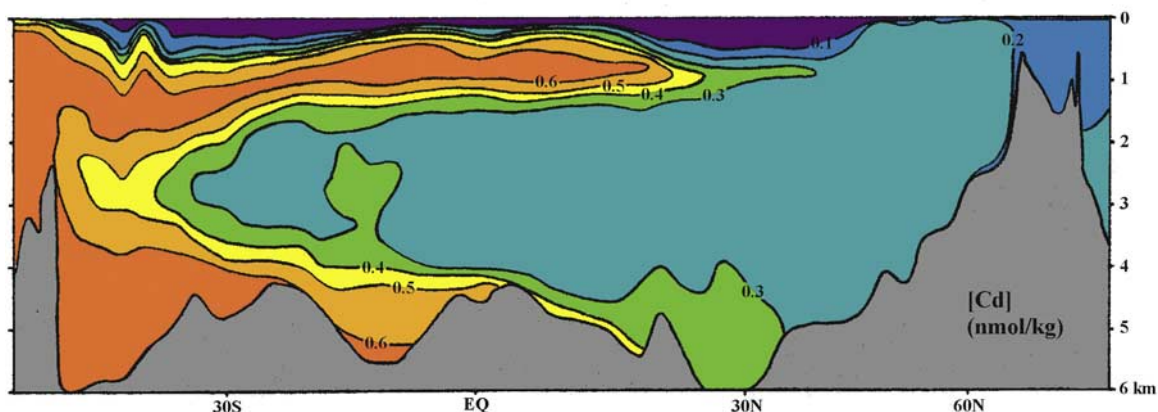


Figure 2. Inferred dissolved Cd concentrations in the modern western Atlantic Ocean, estimated from GEOSECS dissolved phosphate measurements [Bainbridge, 1981] and the Cd:phosphate global relationship of Boyle [1988]. Low-Cd NADW lies between high-Cd AABW below and AAIW above. After Marchitto *et al.* [2002].

(CPDW); the glacial version of AABW/CPDW has also sometimes been referred to as Southern Ocean Water). Benthic foraminiferal Ba/Ca [Lea and Boyle, 1989, 1990; Martin and Lea, 1998] and Zn/Ca [Marchitto *et al.*, 2000, 2002] have since been developed as complementary paleonutrient tracers, though their application has been very limited in comparison to Cd/Ca.

2. Cd/Ca Systematics

[4] Numerous dissolved trace elements in the ocean exhibit vertical profiles that resemble those of major nutrients [Nozaki, 1997]. That is, they are at low concentrations in surface waters and greater concentrations at depth. In some cases, this behavior is linked to the element's importance as a micronutrient. In other cases, nutrient-like behavior may simply result from adsorption onto particulate organic matter in the photic zone and co-mineralization in the deep sea. Regardless of biogeochemical mechanisms, such elements may be useful as nutrient and water mass tracers. Paleocceanographic applications rely on the observation that various elements are accidentally incorporated into benthic foraminiferal CaCO₃ during precipitation. In particular, divalent cations are believed to substitute for Ca in the CaCO₃ crystal matrix.

[5] Dissolved Cd has an oceanic distribution very similar to that of the nutrient phosphate [Boyle *et al.*, 1976; Boyle, 1988; Elderfield and Rickaby, 2000] (Figures 1 and 2). Both are efficiently removed from most surface waters and regenerated at depth, with an intermediate-depth concentration maximum near 1000 m. Cd therefore behaves like a labile nutrient, and its concentration increases

about five-fold between the deep North Atlantic and North Pacific. Although Cd has been linked to at least one important algal metalloenzyme, carbonic anhydrase [Cullen *et al.*, 1999; Morel *et al.*, 2003], it is not clear if this use is sufficient to explain its ocean-wide nutrient-like behavior. The global correlation between Cd and phosphate follows a slight curve that may be explained by preferential uptake of Cd relative to phosphate, either actively by phytoplankton or passively by adsorption onto particulate organic matter [Elderfield and Rickaby, 2000] (Figure 1):

$$\text{Cd} = 1.2 / (\alpha_{\text{Cd/P}}(3.3/\text{P} - 1) + 1) \quad (1)$$

where $\alpha_{\text{Cd/P}}$ is the ratio of Cd/P in particulate organic matter relative to Cd/P in seawater, and averages ~ 2 for the global data set. Historically, however, the Cd:phosphate relationship has been described simply by two line segments [Boyle, 1988]:

$$\text{Cd} = 0.208\text{P} \quad (\text{for } \text{P} < 1.34 \mu\text{mol kg}^{-1}) \quad (2)$$

$$\text{Cd} = 0.398\text{P} - 0.254 \quad (\text{for } \text{P} > 1.34 \mu\text{mol kg}^{-1}) \quad (3)$$

[6] Benthic foraminiferal Cd/Ca ratios reflect seawater dissolved Cd concentrations, with partition coefficients:

$$D_{\text{Cd}} = (\text{Cd/Ca})_{\text{foram}} / (\text{Cd/Ca})_{\text{seawater}} \quad (4)$$

that vary with water depth in calcitic species, from a minimum of 1.3 above 1150 m to a maximum of 2.9 below 3000 m [Boyle, 1992]. The aragonitic benthic foraminifer *Hoeglundina elegans* has a partition coefficient of 1.0, apparently invariant with water depth [Boyle *et al.*, 1995]. Cd incorporation into benthic foraminifera does not

appear to be significantly affected by water temperature [Marchitto, 2004].

3. Challenges and Uncertainties

[7] Several ancillary effects may complicate the reconstruction of past Cd concentrations in seawater. First, many published records rely on combinations of benthic foraminiferal taxa, including epifaunal genera like *Cibicidoides* and infaunal genera like *Uvigerina*. Microhabitat is known to affect the $\delta^{13}\text{C}$ of infaunal taxa because of organic matter degradation within sediment pore waters [Zahn *et al.*, 1986; McCorkle *et al.*, 1997]. Yet Boyle [1992] has shown that there is no consistent Cd/Ca offset between the various calcitic taxa, regardless of microhabitat. Tachikawa and Elderfield [2002] suggest that infaunal species usually record Cd/Ca values similar to *Cibicidoides*, despite elevated pore water Cd, because they have lower partition coefficients. If true, it would seem to be fortuitous that *Cibicidoides* and *Uvigerina* have successfully been used interchangeably in paleoceanographic reconstructions. Our own compilation of published data (section 5.1) indicates that there is no significant bias if infaunal species are included. Nevertheless, improved understanding of possible species-level differences and microhabitat effects is essential.

[8] Benthic foraminiferal trace metal partition coefficients are further affected by seawater saturation state with respect to calcite (ΔCO_3^{2-}). D_{Cd} , D_{Ba} , and D_{Zn} may be reduced by 50% or more in the severely undersaturated abyssal Indo-Pacific [McCorkle *et al.*, 1995; Marchitto *et al.*, 2000, 2005]. Limited measurements on recently living (Rose Bengal-stained) foraminifera, laboratory dissolution experiments, and theoretical biomineralization considerations implicate reduced trace metal incorporation during growth, rather than post-mortem preferential dissolution [Boyle, 1988; Elderfield *et al.*, 1996; Marchitto *et al.*, 2000]. Benthic foraminifera are believed to be more chemically homogenous than planktonic foraminifera, and therefore not subject to the same dissolution artifacts [Boyle and Rosenthal, 1996]. For Cd the ΔCO_3^{2-} effect is limited to undersaturated waters, but D_{Ba} and D_{Zn} appear to be reduced in even mildly supersaturated waters.

[9] Past changes in deep sea saturation state may therefore overprint benthic foraminiferal trace metal records, especially in regions that are poorly saturated today. In the deep Pacific, where glacial-

interglacial changes in deep circulation are believed to have been small, ΔCO_3^{2-} was probably the dominant control on Zn/Ca (and to a lesser extent Cd/Ca) records [Marchitto *et al.*, 2005]. In the North Atlantic, glacial intrusion of low- CO_3^{2-} AABW may have lowered D_{Zn} slightly, but D_{Cd} was not likely affected [Marchitto *et al.*, 2002]. It is possible that Cd/Ca records from the deep South Atlantic are overprinted by changes in saturation state, but paleo- CO_3^{2-} is difficult to estimate. CaCO_3 accumulation in a South Atlantic core currently bathed by AABW suggests better preservation during glacial intervals, with highest inferred CO_3^{2-} levels during glacial terminations [Hodell *et al.*, 2001]. Farther north within the South Atlantic, CO_3^{2-} changes were likely dominated by the waxing and waning of AABW. Tropical paleo- CO_3^{2-} records based on planktonic foraminiferal shell weights show dissolution events during Marine Isotope Stage (MIS) 5/4 glacial intensifications [Broecker and Clark, 2003]. However, attempts to use shell weights to reconstruct South Atlantic paleo- CO_3^{2-} have been hampered by the complicating effects of variable growth conditions and pore water dissolution [Broecker and Clark, 2004]. Paired Cd/Ca and Zn/Ca data could theoretically provide insight because of the different sensitivities of these proxies to ΔCO_3^{2-} [Marchitto *et al.*, 2000, 2005]. There is also some indication that Cd/Ca in the benthic species *Nuttallides umbonifera* is immune to the saturation effect [Boyle and Rosenthal, 1996; Mackensen, 1997].

[10] An additional challenge arises from within-sample heterogeneity. Boyle [1995] noted that the Cd/Ca scatter between triplicate picks (~ 15 – 20 individuals each) from a sediment sample is more than double that derived from equivalent-sized splits of crushed and homogenized individuals. The pooled standard deviation of the former approach ($\pm 0.023 \mu\text{mol mol}^{-1}$) is similar to the average within-core scatter of the Cd/Ca measurements compiled here. This error is equivalent to about $\pm 0.08 \text{ nmol Cd per kg seawater}$ (at maximum D_{Cd} of 2.9), which is relatively large compared to the modern whole-Atlantic gradient of $\sim 0.5 \text{ nmol kg}^{-1}$ (Figure 2). Hence our reconstructed meridional sections (section 5.1) contain considerable noise, and individual data points must be viewed with caution. Possible causes for heterogeneity include: bioturbational mixing of non-contemporaneous individuals; variable microhabitats, even within the same species; unknown factors such as age or growth rate that may affect Cd uptake; and sedimentary contamination.



Table 1. Compilation of Published Holocene and LGM Benthic Foraminiferal Cd_w Data^a

Core	Lat., deg	Long., deg	Depth, m	Hol. Cd _w , nmol/kg	LGM Cd _w , nmol/kg	References
AII107-65	-32.03	-36.19	2795		0.44	1
AII107-131	-30.88	-38.05	2925		0.36	1
BOFS11K	55.19	-20.35	2004	0.39	0.25	2
BOFS14K	58.62	-19.44	1756	0.37	0.17	2
BOFS17K	58.00	-16.50	1150	0.54	0.23	2
BOFS28K	24	-22	4900	0.35	0.54	3
BOFS29K	20	-21	4000	0.31	0.54	3
BOFS31K	19	-20	3330	0.34	0.46	3
CHN82-4	41.72	-32.85	3427	0.27	0.42	1, 4
CHN82-11	42.38	-31.80	3209	0.22	0.43	1, 4
CHN82-15	43.37	-28.23	2153	0.32	0.21	1, 4
CHN82-20	43.50	-29.87	3070	0.26	0.36	1, 4
EN66-10	6.65	-21.90	3527	0.42	0.68	1
EN66-16	5.47	-21.13	3152	0.37	0.72	1
EN66-32	2.47	-19.73	5003	0.34	0.48	1
EN66-38	4.92	-20.50	2931	0.45	0.71	1
EN120-GGC1	33.67	-57.62	4450	0.25	0.71	5
IOS82-PC-SO1	42.38	-23.52	3540	0.29	0.47	1
KNR64-5	16.52	-74.80	1800	0.25	0.13	1, 5
KNR110-82	4.34	-43.49	2816		0.32	1
KNR159-5-36	-27.51	-46.47	1268	0.50	0.40	6
M12328	21	-19	2778	0.29	0.42	3
M12392	25.17	-16.83	2573		0.30	1
M16004	29.98	-10.65	1512	0.22	0.30	7
M23414	53.54	-20.29	2196	0.37	0.40	7
M35003	12.08	-61.25	1299	0.47	0.30	8
NEAP-3K	62.83	-23.95	1510		0.21	9
NEAP-4K	61.48	-24.17	1627	0.35	0.28	9, 10
NEAP-8K	59.78	-23.90	2360		0.49	9
NEAP-15K	56.35	-27.80	2848		0.49	9
NEAP-17K/18B	54.68	-28.35	2880	0.34	0.40	9
NEAP-18K/19B	52.75	-30.33	3275	0.33	0.58	9
OC205-2-7JPC	26.14	-77.74	1320	0.37	0.19	11
OC205-2-33GGC	26.22	-77.69	783	0.37	0.17	11
OC205-2-103GGC	26.07	-78.06	965	0.35	0.16	11
OC205-2-106GGC	25.98	-78.18	654	0.39	0.25	11
OC205-2-108GGC	25.98	-78.18	743	0.39	0.20	11
OC205-2-149JPC	26.26	-77.67	423	0.17	0.15	11
ODP 980	55.48	-14.70	2168		0.24	4
RC12-267	-38.68	-25.78	4144	0.52	0.42	1
RC12-294	-37.27	-10.10	3308	0.44	0.51	1, 12
RC13-228	-22.33	11.20	3204	0.34	0.36	1, 12
RC13-229	-25.50	11.33	4191	0.49	0.50	1, 13, 14
RC16-84	-26.70	-43.33	2438	0.21	0.47	15
RC16-85	-29.92	-43.42	3909	0.69	0.70	15
RC16-86	-32.17	-43.93	3759	0.63	0.59	15
RC16-119	-27.70	-46.52	1567	0.41	0.29	15
SO75-26KL	37.82	-9.50	1099	0.36	0.19	7
SO82-05	59.19	-30.91	1416	0.67 ^b	0.35 ^b	7
V19-240	-30.58	-13.28	3103		0.56	1
V22-174	-10.07	-12.82	2630	0.34	0.36	1
V22-197	14.17	-18.58	3167	0.39	0.39	1
V23-100	22.68	-21.30	4579		0.52	1
V24-1	30.50	-73.50	3012		0.25	1
V24-253	-26.95	-44.68	2069	0.24	0.42	15
V25-59	1.37	-39.48	3824	0.26	0.45	1, 12
V26-176	36.00	-72.00	3942		0.32	1
V28-14	64.78	-29.57	1855		0.24	1
V28-73	57.18	-20.87	2063	0.57	0.30	4
V29-179	44.00	-24.53	3331	0.31	0.37	1
V29-193	55.40	-18.73	1326	0.50	0.28	4
V29-202	60.38	-20.97	2658	0.31	0.38	4



Table 1. (continued)

Core	Lat., deg	Long., deg	Depth, m	Hol. Cd _w , nmol/kg	LGM Cd _w , nmol/kg	References
V29-204	61.18	-23.02	1849	0.22	0.20	4
V30-40	0.20	-23.13	3706		0.52	1
V30-49	18.43	-21.08	3093	0.25	0.56	1, 16
V30-51	19.87	-19.92	3409	0.35	0.47	1
V30-97	41.00	-33.93	3371		0.34	1

^aReferences: (1) *Boyle* [1992]; (2) *Bertram et al.* [1995]; (3) *Beveridge et al.* [1995]; (4) *Marchitto et al.* [2002]; (5) *Boyle and Keigwin* [1987]; (6) *Came et al.* [2003]; (7) *Willamowski and Zahn* [2000]; (8) *Zahn and Stüber* [2002]; (9) *Rickaby et al.* [2000]; (10) *Rickaby and Elderfield* [2005]; (11) *Marchitto et al.* [1998]; (12) *Rosenthal et al.* [1997]; (13) *Oppo and Rosenthal* [1996]; (14) *Lea* [1995]; (15) *Oppo and Horowitz* [2000]; and (16) *Martin and Lea* [1998].

^bSO₂-05 data not included in meridional sections because of very anomalous Holocene value.

[11] Finally, we cannot rule out analytical offsets between the various labs whose work is compiled here. At least three different cleaning protocols are represented: the original oxidative and reductive cleaning method developed for Cd/Ca [*Boyle and Keigwin*, 1985/1986]; a revised method that reverses the reductive and oxidative steps to better remove CdS overgrowths [*Boyle and Rosenthal*, 1996]; and a method developed for Ba/Ca that adds a DPTA step to dissolve sedimentary barite [*Lea and Boyle*, 1990]. We follow *Rosenthal et al.* [1997] in updating some early measurements [*Boyle*, 1992] that appear to be affected by CdS contamination. Published analyses were performed primarily by atomic absorption spectrophotometry (AAS) [*Boyle and Keigwin*, 1985/1986], but also by inductively coupled plasma mass spectrometry (ICP-MS) [*Lea and Martin*, 1996] and thermal ionization mass spectrometry (TIMS) [*Rickaby et al.*, 2000]. Inter-laboratory calibration for Cd/Ca has generally been informal, and there is currently no community-wide standard available for this purpose.

4. Methods

[12] We have compiled published benthic foraminiferal Cd/Ca data from all Atlantic sediment cores that include measurements from the Last Glacial Maximum (LGM, ~20 kyr BP) (Table 1). The

definition of LGM may vary slightly from study to study, but usually corresponds to near-maximum benthic $\delta^{18}\text{O}$ values [see, e.g., *Boyle*, 1992]. Some samples may span a few thousand years before and after 20 kyr BP. Combined with bioturbational mixing and the rather low sedimentation rates typical of the deep sea, this means that LGM values may incorporate foraminifera from more extreme intervals like Heinrich event 1, during which the formation of NADW/GNAIW may have ceased [*McManus et al.*, 2004]. Some high-resolution records show very elevated Cd/Ca during Heinrich event 1 [*Willamowski and Zahn*, 2000; *Zahn and Stüber*, 2002; *Rickaby and Elderfield*, 2005] and we avoid those measurements here. Some other cores may be so heavily bioturbated that LGM measurements include foraminifera from the Holocene and/or MIS 3.

[13] We also compile Holocene data, but only from the cores with LGM measurements. The definition of Holocene is even looser than that of the LGM. In some studies the reported Holocene values are only from core tops, which vary in age due to issues of core recovery and sedimentation. Other studies attempt to report late Holocene means, the true ages of which again vary with core quality.

[14] We include data from various benthic foraminiferal taxa as reported in the literature to allow for

Table 2. New Benthic Foraminiferal Cd_w Data

Core	Lat., deg	Long., deg	Depth, m	Hol. Cd _w , nmol/kg	LGM Cd _w , nmol/kg
OC205-2-97JPC	26.94	-77.85	1183	0.32	0.25
OC205-2-100GGC	26.06	-78.03	1057	0.36	0.28
RC8-19	-24.29	-14.70	3636		0.37
RC12-292	-39.68	-15.48	3541		0.54
RC13-188	1.82	-33.68	3451		0.57
RC24-10	-2.18	-11.25	3451		0.59
V22-26	8.72	-41.25	3720		0.70
V22-175	-8.77	-14.28	2950		0.51
V26-17	29.93	-45.08	3623		0.43



maximum spatial coverage. The dominant genera represented are *Cibicidoides*, *Uvigerina*, *Nutallides*, and *Hoeglundina*. In all cases we convert Cd/Ca to Cd_w (inferred paleo-seawater Cd concentration, in nmol kg⁻¹) using the depth-dependent calcitic partition coefficients from Boyle [1992] or the aragonitic *Hoeglundina* partition coefficient from Boyle *et al.* [1995]. Cd_w is therefore recalculated from studies that use “empirical” or “local” partition coefficients [Bertram *et al.*, 1995; Willamowski and Zahn, 2000]. The average error on individual Cd_w values, based only on Cd/Ca reproducibility, is estimated to be ±0.08 nmol kg⁻¹ (±1σ).

[15] In addition to published data, we report unpublished data from two Little Bahama Bank cores and new data from seven Mid-Atlantic Ridge cores (Table 2). The Little Bahama Bank measurements (cruise OC205-2) were made by AAS at the Woods Hole Oceanographic Institution following the methods of Marchitto *et al.* [1998] except that several different taxa were employed (*H. elegans*, *C. kullenbergi*, *C. wuellerstorfi*, and *U. peregrina*). The new Mid-Atlantic Ridge measurements were made at the University of Colorado on ~10–15 individuals of *C. wuellerstorfi* (>250 μm) each, oxidatively and reductively cleaned following the methods of Boyle and Keigwin [1985/6] as modified by Boyle and Rosenthal [1996]. LGM intervals were identified using a combination of unpublished radiocarbon dates and percent CaCO₃ stratigraphies. Multiple trace metals were measured on a Thermo-Finnigan Element2 sector field single-collector ICP-MS using methods adapted from Rosenthal *et al.* [1999] [Marchitto, 2006]. Long-term 1σ precision for Cd/Ca is 1.8% across a wide range of Cd/Ca values and sample sizes. Elemental measures of diagenetic (Mn/Ca) and sedimentary (Fe/Ca) contamination were low, ranging from 11 to 68 μmol mol⁻¹ and 4 to 51 μmol mol⁻¹, respectively.

[16] We have also compiled *Cibicidoides* δ¹³C data, where available, from the cores used for Cd/Ca (Table 3). We limit the compilation to *Cibicidoides* because this epifaunal genus is commonly considered to be the most reliable recorder of seawater δ¹³C [e.g., Duplessy *et al.*, 1984; Curry and Oppo, 2005]. We combine the δ¹³C data with Cd_w to calculate δ¹³C_{as} as described in section 5.2.

[17] We present meridional sections of Atlantic Cd_w and δ¹³C_{as} constructed using the program Ocean Data View (R. Schlitzer, Ocean Data View, 2005; <http://odv.awi-bremerhaven.de>). Our contour

Table 3. *Cibicidoides* δ¹³C With δ¹³C_{as} Calculated From Cd_w Data in Tables 1 and 2^a

Core	Hol. δ ¹³ C	LGM δ ¹³ C	Hol. δ ¹³ C _{as}	LGM δ ¹³ C _{as}
AII107-131	0.95	0.85		0.25
BOFS11K	1.43	1.40	0.51	0.49
BOFS14K	1.02	1.40	0.03	0.13
BOFS17K	1.03	1.61	0.51	0.61
BOFS28K	0.98	0.01	-0.05	-0.16
BOFS29K	0.82	0.00	-0.32	-0.17
BOFS31K	0.96	0.22	-0.11	-0.14
CHN82-4	1.11	0.48	-0.15	0.02
CHN82-11	1.17	0.66	-0.39	0.23
CHN82-15	0.96	1.21	-0.16	0.14
CHN82-20	1.30	0.76	0.00	0.15
EN66-10	0.82	0.19	-0.02	0.35
EN66-16	0.94	0.43	-0.04	0.68
EN66-32	0.86	-0.32	-0.21	-0.64
EN66-38	0.98	0.69	0.22	0.92
EN120-GGC1	0.33	-0.41	-1.05	-0.19
IOS82-PC-SO1	0.76	0.44	-0.44	0.10
KNR64-5	0.89	1.31	-0.48	-0.16
KNR110-82	1.11	0.21		-0.49
KNR159-5-36GGC	1.14	0.56	0.65	0.05
M12328	0.92	0.27	-0.29	-0.19
M12392	0.96	0.36		-0.39
M16004	1.03	1.10	-0.49	0.36
M23414	1.12	1.00	0.13	0.50
M35003	0.98	1.55	0.27	0.80
NEAP-4K	1.50	1.50	0.46	0.70
OC205-2-7JPC	1.30	1.37	0.32	0.19
OC205-2-33GGC	1.02	1.55	0.04	0.28
OC205-2-97JPC	1.23	1.53	0.12	0.62
OC205-2-100GGC	1.40	1.50	0.40	0.71
OC205-2-103GGC	1.27	1.56	0.23	0.24
OC205-2-106GGC	1.19	1.67	0.26	0.76
OC205-2-108GGC	1.14	1.71	0.21	0.57
OC205-2-149JPC	1.68	1.82	-0.12	0.46
ODP 980	1.04	0.82		-0.14
RC12-294	0.81	-0.23	0.02	-0.48
RC13-228	0.50	-0.31	-0.57	-0.92
RC13-229	0.39	-0.36	-0.27	-0.62
RC16-84	1.08	0.56	-0.51	0.22
RC16-119	1.10	0.99	0.23	0.22
SO75-26KL	1.02	1.60	0.01	0.43
SO82-05	1.35	1.60	1.20	0.96
V19-240		0.02		-0.11
V22-174	0.80	0.72	-0.27	0.12
V22-197	0.49	0.17	-0.44	-0.36
V23-100		0.00		-0.23
V24-253	1.10	0.48	-0.33	0.02
V25-59	1.03	0.07	-0.29	-0.32
V26-176		0.18		-0.52
V28-14	1.12	1.13		0.18
V28-73	1.17	1.16	0.74	0.41
V29-179	1.10	0.63	-0.05	0.05
V29-193	1.12	1.50	0.49	0.71
V29-202	1.06	0.45	-0.10	-0.11
V29-204	1.24	1.37	-0.32	0.23
V30-40		-0.11		-0.34
V30-49		0.21		0.07

^aReferences given in Table 1.

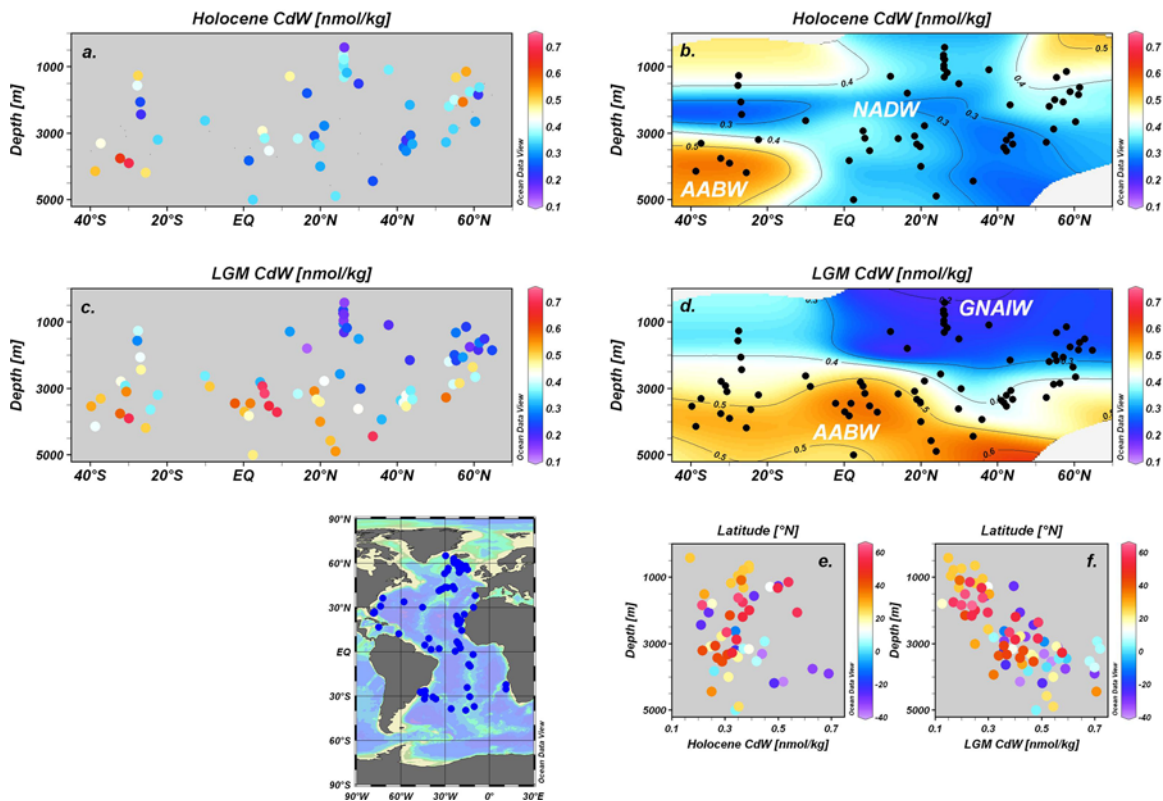


Figure 3. Meridional sections of inferred seawater dissolved Cd (Cd_W) for the (a and b) Holocene and (c and d) LGM Atlantic Ocean (see map for core distribution). Also shown are composite vertical profiles for the (e) Holocene and (f) LGM where colors indicate core latitude.

plots employ a relatively strong smoothing function (held constant between plots) to minimize the impact of anomalous cores. For Cd_W , individual values are also plotted for comparison with the smoothed plots. Only one core from the compilation (SO82-05) is not plotted due to its extremely

anomalous Holocene Cd/Ca value. We present Cd_W sections that include all Atlantic data (Figure 3) as well as comparisons of the western and eastern basins (Figure 4). The western and eastern sections each include several cores from the crest of the Mid-Atlantic Ridge and all cores

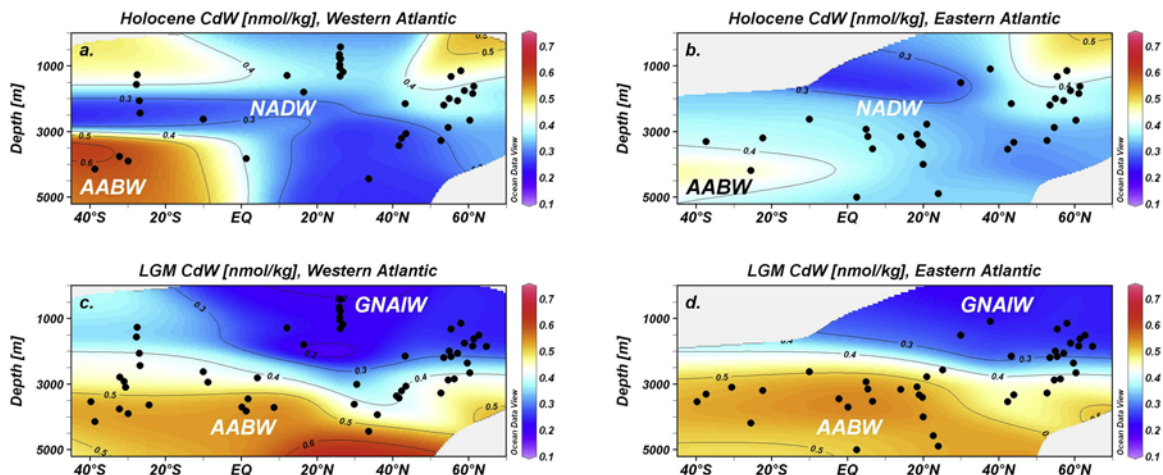


Figure 4. Meridional sections of Cd_W as in Figure 3 except separating (a and c) the western basins from (b and d) the eastern basins.



north of 50°N, most of which are from the eastern side of the Mid-Atlantic Ridge. No depth correction is made to the LGM data to account for lowered sea level.

5. LGM Atlantic Summary

5.1. Meridional Cd Sections

[18] Major syntheses of benthic foraminiferal Cd/Ca data for the LGM Atlantic have been performed by Boyle [1992], Rosenthal *et al.* [1997], and Oppo and Horowitz [2000]. Of these, only Rosenthal *et al.* [1997] presented a meridional section of glacial seawater Cd, following the approach that Duplessy *et al.* [1988] used for $\delta^{13}\text{C}$. We repeat that exercise here, incorporating new data that have appeared in the interim. Our LGM composite section contains data from 75 core locations, compared to Rosenthal *et al.*'s [1997] 19. Our main observations are broadly consistent with those of the earlier studies, with significant refinement afforded by the additional data.

[19] Before interpreting the LGM Cd_w sections, it is instructive to examine the Holocene sections to see how well Holocene foraminifera reproduce the modern Cd distribution. The nutrient pattern of the South Atlantic is captured reasonably well in the composite section (Figures 3a and 3b), with low-Cd NADW sandwiched between high-Cd AABW below and AAIW above. The volume of NADW expands to the north, as expected, with low-nutrient waters filling the entire water column by $\sim 30^\circ\text{N}$. However, intermediate to mid-depth cores in the high-latitude North Atlantic tend to exhibit anomalously high Cd/Ca values. This problem is locally pervasive but not ubiquitous, and its cause is not known. Bertram *et al.* [1995] chose to use elevated empirical partition coefficients in this region based on core top Cd/Ca values, but as discussed above (section 4) we use the global partition coefficients of Boyle [1992]. The western Holocene section (Figure 4a) is similar to the composite, but the eastern section (Figure 4b) shows a weaker north-south deep Cd_w gradient. Reconstructed low to midlatitude deep North Atlantic waters contain more Cd in the east than in the west, while the opposite is true in the deep South Atlantic. Although these observations may be biased by sparse coverage, the North Atlantic data are consistent with the modern distribution of nutrients. Concentrations are lower in the better-ventilated deep western boundary current of NADW and higher in the

northeastern basin, where deep recirculation is important for trapping nutrients [Broecker *et al.*, 1991].

[20] The composite LGM section is fundamentally different from the Holocene distribution, with NADW being replaced by low-Cd GNAIW lying above an expanded AABW (Figures 3c and 3d). This pattern is consistent with previous observations from Cd/Ca and $\delta^{13}\text{C}$ [e.g., Boyle and Keigwin, 1987; Oppo and Fairbanks, 1987; Duplessy *et al.*, 1988; Boyle, 1992; Oppo and Lehman, 1993; Curry and Oppo, 2005]. The boundary level between GNAIW and AABW appears to have been very sharp, occurring between ~ 2200 and 2500 m modern depth. The abruptness of this boundary and the dichotomy between the two water masses is well illustrated by the LGM depth profile (Figure 3f). The recent western Atlantic $\delta^{13}\text{C}$ compilation by Curry and Oppo [2005] also shows the sharpest vertical gradient between ~ 2000 and 2500 m. The relatively modest LGM Cd_w values found in the deepest Atlantic cores may suggest a slight depression of D_{Cd} by low- CO_3^{2-} AABW, but not by enough to obscure the accompanying rise in seawater Cd. The current lack of data poleward of 40°S prevents the accurate characterization of the AABW end-member, but we address this below using paired Cd and $\delta^{13}\text{C}$ (section 5.2). Data coverage in the intermediate depth South Atlantic is too sparse to infer the glacial presence or absence of AAIW. The deep (>3000 m) east-west Cd_w contrast during the LGM appears to have been weaker than during the Holocene, though there was perhaps a slightly deeper penetration of GNAIW in the west (Figures 4c and 4d). A reduced deep zonal contrast likely resulted from a combination of the loss of NADW and the spilling of AABW over the Walvis and Mid-Atlantic Ridges into the eastern basins [Beveridge *et al.*, 1995]. Comparison of western [Curry and Oppo, 2005] and eastern [Sarnthein *et al.*, 1994] sections of $\delta^{13}\text{C}$ at the LGM also suggest relatively little zonal contrast below ~ 3000 m.

5.2. Air-Sea $\delta^{13}\text{C}$

[21] The distributions of Cd and the $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC) are influenced by similar biological cycling, but $\delta^{13}\text{C}$ is also strongly impacted by air-sea exchange. If biological cycling were the only process acting on $\delta^{13}\text{C}$, it would decrease by about 1.1‰ for each $1 \mu\text{mol kg}^{-1}$ increase in dissolved phosphate, and a modern



oceanic range of $\sim 3.3\%$ would be possible [Broecker and Maier-Reimer, 1992]. However, air-sea exchange of CO_2 can isotopically enrich the DIC pool (increase $\delta^{13}\text{C}$), with greater enrichment in cases of (1) greater exchange due to long air-sea contact time or high winds; (2) exchange at colder temperatures; or (3) net CO_2 efflux out of the ocean into the atmosphere [Mook et al., 1974; Lynch-Stieglitz et al., 1995]. The net effect of the various air-sea exchange processes spans a modern surface ocean range of $\sim 2\%$.

[22] The air-sea component of $\delta^{13}\text{C}$ can be isolated by normalizing to zero phosphate, thus removing the biological component. Broecker and Maier-Reimer [1992] derived an equation for $\Delta\delta^{13}\text{C}$, later renamed $\delta^{13}\text{C}_{\text{as}}$ by Lynch-Stieglitz and Fairbanks [1994]:

$$\delta^{13}\text{C}_{\text{as}} = \delta^{13}\text{C} + 1.1\text{P} - 2.7 \quad (5)$$

where 2.7 is an arbitrary constant introduced to bring deep Pacific and Indian Ocean waters close to zero. $\delta^{13}\text{C}_{\text{as}}$ is a conservative tracer of deep waters because once a parcel of water leaves the surface ocean, its $\delta^{13}\text{C}_{\text{as}}$ signature is only altered by mixing [Lynch-Stieglitz and Fairbanks, 1994]. $\delta^{13}\text{C}_{\text{as}}$ can therefore be used to separate mixing and biogeochemical aging processes. Modern NADW is characterized by negative $\delta^{13}\text{C}_{\text{as}}$ values, while AABW and AAIW have positive signatures. AAIW is especially enriched in $\delta^{13}\text{C}_{\text{as}}$ due to formation from surface waters that are partially equilibrated with the atmosphere at cold temperatures [Charles and Fairbanks, 1990; Charles et al., 1993].

[23] Following the example of Oppo and Fairbanks [1989], Lynch-Stieglitz and Fairbanks [1994] proposed that paleo- $\delta^{13}\text{C}_{\text{as}}$ can be estimated by using phosphate estimates derived from Cd/Ca. They combined equation (5) with the global Cd:phosphate relationship of Boyle [1988] (for $\text{P} > 1.34 \mu\text{mol kg}^{-1}$; equation (3)) to give an equation for Holocene deep ocean $\delta^{13}\text{C}_{\text{as}}$:

$$\delta^{13}\text{C}_{\text{as}} = \delta^{13}\text{C} + 2.75\text{Cd} - 2.0 \quad (6)$$

Lynch-Stieglitz et al. [1996] noted that during the LGM, organic matter $\delta^{13}\text{C}$ was $\sim 2\%$ higher [Rau et al., 1991] and mean ocean $\delta^{13}\text{C}$ was $\sim 0.3\%$ lower [Duplessy et al., 1988], so the relationship between $\delta^{13}\text{C}$ and phosphate was slightly different. Taking this into account and assuming unchanged oceanic Cd and phosphate inventories, they derived

the following equation for $\delta^{13}\text{C}_{\text{as}}$ in the LGM deep ocean ($\text{P} > 1.34 \mu\text{mol kg}^{-1}$):

$$\delta^{13}\text{C}_{\text{as}} = \delta^{13}\text{C} + 2.375\text{Cd} - 1.46 \quad (7)$$

Two additional equations can be derived for waters with ($\text{P} < 1.34 \mu\text{mol kg}^{-1}$):

$$\delta^{13}\text{C}_{\text{as}} = \delta^{13}\text{C} + 5.29\text{Cd} - 2.7 \text{ (Holocene)} \quad (8)$$

$$\delta^{13}\text{C}_{\text{as}} = \delta^{13}\text{C} + 4.57\text{Cd} - 2.05 \text{ (LGM)} \quad (9)$$

[24] We use *Cibicidoides* $\delta^{13}\text{C}$ (where available) from our compiled Atlantic Cd/Ca sites to calculate $\delta^{13}\text{C}_{\text{as}}$ during the Holocene and LGM, using equations (6)–(9) (Table 3). It must be noted that the resulting Holocene meridional section of $\delta^{13}\text{C}_{\text{as}}$ bears relatively little resemblance to its modern distribution (Figure 5a). Although NADW below ~ 2000 m displays negative values and AAIW appears to be positive (both as expected), upper North Atlantic values are generally too positive and there is no sign of a positive AABW. The upper North Atlantic anomaly is related, at least in part, to the anomalously high Holocene Cd/Ca values found in this region, as noted above. The paucity of paired Cd: $\delta^{13}\text{C}$ data in the deep South Atlantic may hinder the proper reconstruction of AABW $\delta^{13}\text{C}_{\text{as}}$.

[25] Given the problems with the Holocene reconstruction, the LGM $\delta^{13}\text{C}_{\text{as}}$ section (Figure 5b) should be viewed with some caution. Nevertheless, some interesting patterns emerge. As in previous reconstructions [Lynch-Stieglitz and Fairbanks, 1994; Oppo and Horowitz, 2000] GNAIW is clearly characterized by positive $\delta^{13}\text{C}_{\text{as}}$ values, compared to ~ -0.4 to -0.6% for modern NADW [Charles et al., 1993; Lynch-Stieglitz et al., 1995]. The deep South Atlantic, in contrast, had a negative $\delta^{13}\text{C}_{\text{as}}$ signature instead of the slightly positive values of modern AABW. It has long been noted that South Atlantic Cd/Ca shows little to no glacial-interglacial change while $\delta^{13}\text{C}$ was much lower during the LGM, resulting in low $\delta^{13}\text{C}_{\text{as}}$ [Boyle, 1992; Boyle and Rosenthal, 1996; Rosenthal et al., 1997]. Although some very low Southern Ocean $\delta^{13}\text{C}$ values have been questioned because of microhabitat effects caused by high fluxes of algal detritus [Mackensen et al., 1993], the spatial uniformity of Southern Ocean $\delta^{13}\text{C}$ during the LGM argues for a real drop in deep water values [Ninnemann and Charles, 2002]. As noted above, deep South Atlantic Cd/Ca may hypothetically have been affected by decreased seawater CO_3^{2-}

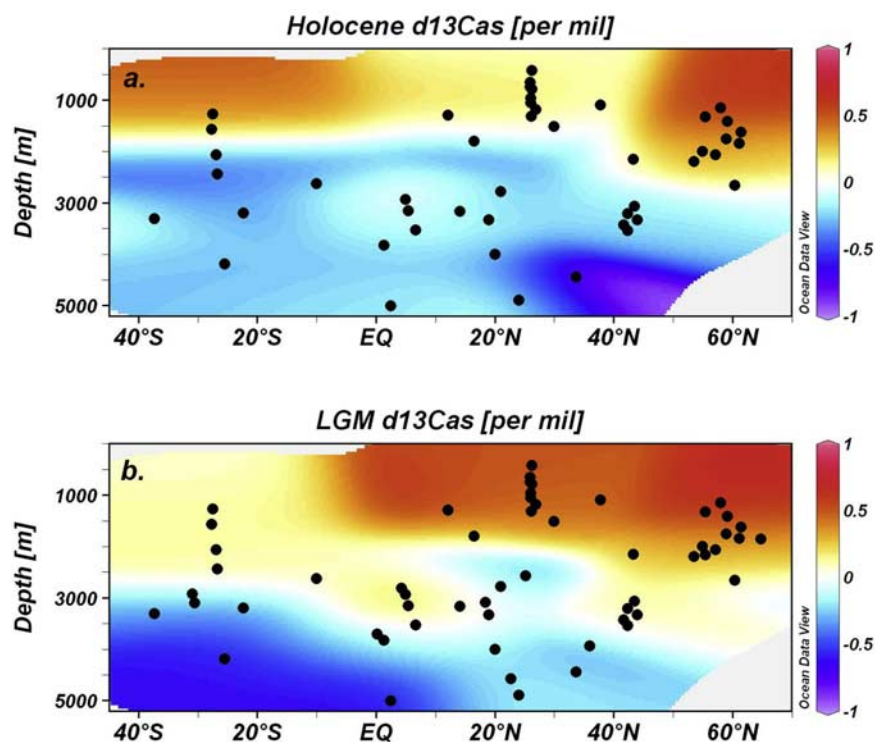


Figure 5. Meridional sections of $\delta^{13}\text{C}_{\text{as}}$ calculated from benthic foraminiferal Cd/Ca and $\delta^{13}\text{C}$ for the (a) Holocene and (b) LGM Atlantic Ocean.

during the LGM, but the magnitude of this effect is difficult to estimate.

[26] The glacial expansion of AABW allows for better $\delta^{13}\text{C}_{\text{as}}$ characterization of this water mass than in the Holocene section, yet we still have no data from the Southern Ocean poleward of 40°S . However, we can use a $\delta^{13}\text{C}:\text{Cd}_w$ cross-plot to extrapolate to an AABW end-member estimate for the LGM (Figure 6). The $\delta^{13}\text{C}:\text{Cd}_w$ plot allows for the separation of biogeochemical aging (along lines of constant $\delta^{13}\text{C}_{\text{as}}$) from mixing of water masses with different $\delta^{13}\text{C}_{\text{as}}$ signatures (across lines of constant $\delta^{13}\text{C}_{\text{as}}$). The LGM Atlantic data can largely be explained by mixing between high- $\delta^{13}\text{C}_{\text{as}}$ GNAIW and low- $\delta^{13}\text{C}_{\text{as}}$ AABW. Deep North Atlantic data fall between these two end-members, suggesting some mixing across the bathyal nutricline at ~ 2200 to 2500 m. *Ninnemann and Charles* [2002] reconstructed uniform LGM AABW values of $\sim -0.8\text{‰}$ in the Atlantic sector of the Southern Ocean. Extrapolating the mixing line to this value suggests that the AABW end-member had a Cd concentration of roughly 0.6 to 0.8 nmol kg^{-1} and a $\delta^{13}\text{C}_{\text{as}}$ signature of perhaps -0.5 to -1‰ . The implication of this analysis is that much of the $\delta^{13}\text{C}$ depletion in glacial AABW was due to

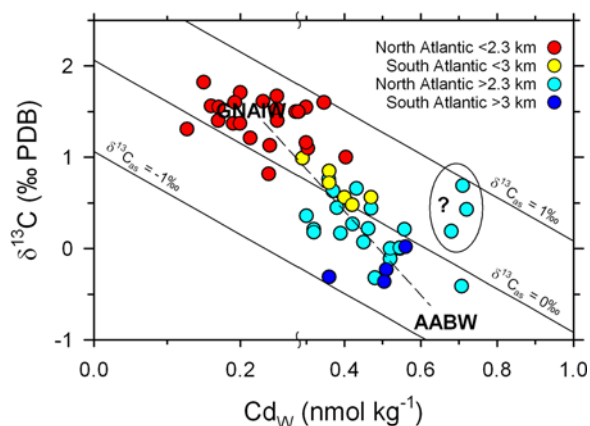


Figure 6. LGM $\delta^{13}\text{C}$ and Cd_w data from the Atlantic Ocean, with lines of constant $\delta^{13}\text{C}_{\text{as}}$. Note scale change on the Cd_w axis, which produces straight $\delta^{13}\text{C}_{\text{as}}$ isolines from two different $\delta^{13}\text{C}_{\text{as}}$ equations (equations (7) and (9)) and therefore better illustrates water mass mixing and biogeochemical aging. AABW placement is based on extending dashed mixing line to a $\delta^{13}\text{C}$ value of -0.8‰ [*Ninnemann and Charles*, 2002]. Three sites inside oval fall significantly off of the mixing line between high- $\delta^{13}\text{C}_{\text{as}}$ GNAIW and low- $\delta^{13}\text{C}_{\text{as}}$ AABW. These sites are from Sierra Leone Rise in the eastern tropical North Atlantic [*Boyle*, 1992] and are not easily explained by mixing or aging of other waters.



altered air-sea processes. Widespread microhabitat [Mackensen *et al.*, 1993] or CO₃²⁻ effects [McCorkle *et al.*, 1995] are not required to explain the distribution of $\delta^{13}\text{C}:\text{Cd}_w$ data in Figure 6.

[27] Although there are no LGM $\delta^{13}\text{C}_{\text{as}}$ data from the modern core region of AAIW, we note that upper South Atlantic values are generally lower than in GNAIW (Figures 5b and 6). This pattern could be explained by simple mixing between GNAIW and AABW, but we cannot rule out the existence of a negative- $\delta^{13}\text{C}_{\text{as}}$ AAIW during the LGM.

6. Discussion

[28] Most theories put forward to explain the deep water configuration of the LGM Atlantic have relied on changes in buoyancy forcing in the high latitude North Atlantic. That is, fresher and therefore less dense surface waters in the North Atlantic reduced the formation rate and/or penetration depth of NADW/GNAIW [e.g., Weyl, 1968; Broecker *et al.*, 1985; Boyle and Keigwin, 1987]. Ocean circulation models suggest that reduced sea surface salinities and greater sea ice cover in the glacial North Atlantic could cause not only a shallower mode of deep water production, but also a shift in its production site to south of the Nordic Seas [Rahmstorf, 1994, 2002; Ganopolski *et al.*, 1998]. Such a change in deep convection sites would reduce ocean heat transport to higher latitudes, even if the rate of NADW/GNAIW production was unchanged. Alternatively, reduced production rates in the north may have been balanced by increased rates of AABW production in the south [Broecker, 1998]. Although the question of rate cannot be addressed with paleonutrient data alone [LeGrand and Wunsch, 1995], the sharp mid-depth nutricline reconstructed here argues for a significantly altered mode of circulation during the LGM.

[29] It is also possible that surface processes in the Southern Ocean were mainly responsible for the LGM circulation pattern. Longstanding theories of the modern MOC require that deep waters return to the surface by vertical mixing through the thermocline [Stommel, 1958; Stommel and Arons, 1960]. The magnitude of this mixing, which derives its energy from winds and tides, may ultimately determine the global rate of deep water formation [Munk and Wunsch, 1998]. Toggweiler and Samuels [1995, 1998] argue that much of the modern mixing occurs not across the thermocline but in the Southern Ocean, where circumpolar

westerlies blowing over the latitude band of Drake Passage force northward Ekman drift that is balanced by deep upwelling. This upwelling, combined with adequately dense surface waters in the North Atlantic, may set the southward flux of NADW. Today net precipitation over the Southern Ocean allows for the buoyant conversion of NADW into AAIW. Keeling and Stephens [2001] hypothesized that during the LGM, deep water temperatures approached the freezing point, so exposure to the Southern Ocean surface resulted in extensive sea ice cover. This sea ice shielded deep waters from precipitation, retarding the buoyant conversion of NADW. Salt became concentrated in AABW and AAIW such that both theoretically became denser than NADW/GNAIW. The upper depth limit of AABW would then correspond to the lower limit of AAIW, which is set by the depth of the seafloor ridges crossing the latitudes of Drake Passage; below this depth topographic boundaries would cause southward geostrophic recirculation of AAIW. Warren [1990] estimated the relevant ridge depth to lie between ~1500 and 2500 m, which spans the GNAIW-AABW Cd nutricline (~2200–2500 m) reconstructed here.

[30] Glacial pore water $\delta^{18}\text{O}$ measurements, combined with benthic foraminiferal $\delta^{18}\text{O}$, suggest that the deep ocean was more homogeneously cold than today, very close to the freezing point of seawater [Adkins *et al.*, 2002; Schrag *et al.*, 2002]. Pore water chlorinity further suggests that glacial AABW within the Southern Ocean was much saltier and therefore much denser than deep waters in the North Atlantic [Adkins *et al.*, 2002]. Such a reversal of the meridional salinity gradient (modern AABW is fresher than NADW) could be explained by glacial AABW formation by brine rejection beneath extensive sea ice [Adkins *et al.*, 2002]. This scenario is broadly consistent with the Keeling and Stephens [2001] hypothesis of filling the deep Atlantic with dense Southern Ocean waters. However, it is not clear how well the pore water evidence for dense AABW coincides with the Cd and $\delta^{13}\text{C}$ reconstructions of widespread AABW: deep (4584 m) and mid-depth (2184 m) North Atlantic sites appear to have been equally less dense than AABW, with no clear evidence of a mixing gradient. Additional Atlantic pore water sites may be required to elucidate the glacial spreading of salty AABW.

[31] GNAIW likely acquired its high $\delta^{13}\text{C}_{\text{as}}$ signature through longer air-sea contact at cold temperatures [Lynch-Stieglitz and Fairbanks, 1994]. In



contrast, glacial AABW probably acquired its low $\delta^{13}\text{C}_{\text{as}}$ signature because of poor ventilation during its formation around Antarctica, with GNAIW not significantly contributing to its feed waters [Ninnemann and Charles, 2002; Sigman et al., 2003]. In particular, AABW formation beneath sea ice [Keeling and Stephens, 2001; Adkins et al., 2002] could have produced the observed negative $\delta^{13}\text{C}_{\text{as}}$ values. Reduced ventilation of the Southern Ocean is also an important mechanism in numerous models of glacial atmospheric CO_2 lowering [e.g., Francois et al., 1997; Toggweiler, 1999; Sigman and Boyle, 2000; Stephens and Keeling, 2000; Toggweiler et al., 2006].

7. Conclusions

[32] Benthic foraminiferal Cd/Ca and $\delta^{13}\text{C}$ both clearly support an LGM expansion of high-nutrient AABW and a replacement of low-nutrient NADW by the shallower GNAIW. Cd/Ca suggests that the main mixing boundary between AABW and GNAIW occurred abruptly between ~ 2200 and 2500 m modern water depth. Cd concentration differences between the western and eastern basins of the deep Atlantic may have been diminished during the LGM due to the spilling of AABW over mid-ocean ridges. Combined Cd and $\delta^{13}\text{C}$ data indicate that the entire glacial Atlantic can be characterized by mixing between high- $\delta^{13}\text{C}_{\text{as}}$ GNAIW and low- $\delta^{13}\text{C}_{\text{as}}$ AABW. Waters in the upper South Atlantic may alternately reflect mixing between GNAIW and a relatively low- $\delta^{13}\text{C}_{\text{as}}$ AAIW. Although we cannot determine whether conditions in the North Atlantic or Southern Ocean were more important for setting the LGM circulation pattern, it is apparent that both GNAIW and AABW formed under different conditions than their modern counterparts. In particular, low $\delta^{13}\text{C}_{\text{as}}$ suggests that AABW was more poorly ventilated than today, likely contributing to decreased atmospheric CO_2 .

[33] Cd/Ca data coverage is sparsest in the tropical South Atlantic and the Southern Ocean, with no LGM values poleward of 40°S . Glacial Cd/Ca data from the Southern Ocean are needed to better define the end-member composition of AABW and to determine the status of AAIW. Paired Cd and $\delta^{13}\text{C}$ data from the upper South Atlantic would be valuable for determining the air-sea conditions that AAIW may have formed under. Improved understanding of benthic foraminiferal trace metal incorporation and potential artifacts is also warranted,

especially in the high latitude North Atlantic where correspondence between core top Cd/Ca and modern seawater Cd is often poor. Laboratory culture work could be particularly valuable in this regard. Finally, numerical modeling of paleonutrient distributions is essential for exploring the dynamic and climatic implications of the data.

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