

Interocean exchange of Glacial North Atlantic Intermediate Water: Evidence from Subantarctic Cd/Ca and carbon isotope measurements

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Abstract. New measurements of Cd/Ca ratios for glacial benthic foraminifera from the continental shelf and slope off Tasmania and South Australia are presented. When combined with glacial carbon isotope measurements [Lynch-Stieglitz *et al.*, 1994], these data from the glacial Subantarctic Zone suggest that a water mass with a high value of the conservative tracer $\delta^{13}\text{C}_{\text{as}}$ occupied not only the shallow (1-2 km) portions of the Atlantic and Pacific Oceans but was present in the glacial Subantarctic as well. The oceanic Cd concentrations, Cd_w , predicted for the glacial Subantarctic are intermediate between those from the glacial Atlantic and the glacial Pacific, supporting the idea that Glacial North Atlantic Intermediate Water may have reached the intermediate depth Pacific via the Antarctic Circumpolar Circulation [Lynch-Stieglitz and Fairbanks, 1994].

Introduction

The wind-driven Antarctic Circumpolar Current (ACC) has the largest transport of any current in the world's ocean, sweeping 110×10^6 to $140 \times 10^6 \text{ m}^3 \text{ s}^{-1}$ of water around the Southern Ocean and extending to the sea floor [Oceanography Course Team, 1989]. This circumpolar circulation involves waters cooler than about 15°C and provides an efficient means of communication for intermediate and deep waters between the three major ocean basins. The northern part of the ACC is located in the Subantarctic Zone, the region between the cold, fresh surface waters of the Antarctic and the warm, salty surface waters of the subtropics (Figure 1). A vertical profile through the Subantarctic water column will intersect most of the water masses that are involved in the circumpolar circulation, from intermediate (Subantarctic Mode Water, Antarctic Intermediate Water) to deep (North Atlantic Deep Water, Antarctic Bottom Water).

There is evidence that during the last glacial maximum, the dense variety of North Atlantic Deep Water (NADW) did not form or had a much reduced flux and that the deeper waters of the ACC (Circumpolar Deep Water, CDW) no longer reflected the presence of NADW [Charles and Fairbanks, 1992]. However, a less dense water mass did form in the glacial North Atlantic, Glacial North Atlantic Intermediate Water (GNAIW) [Boyle and Keigwin, 1987; Duplessy *et al.*, 1988]. This core of GNAIW appears to have been at 1- to 2-km depth in the

glacial North Atlantic. Cd/Ca and carbon isotope measurements on benthic foraminifera show that this water mass was depleted in nutrients [Boyle and Keigwin, 1987; Oppo and Fairbanks, 1987; Duplessy *et al.*, 1988; Bertram *et al.*, 1995]. It has been suggested that the very high $\delta^{13}\text{C}$ relative to only moderately lower Cd_w (nutrient) values of GNAIW was due to an increased tendency towards isotopic equilibration of this water mass with atmospheric carbon dioxide at cold temperatures [Oppo and Fairbanks, 1987; Broecker, 1993; Charles *et al.*, 1993].

The air-sea exchange signature (the deviation of $\delta^{13}\text{C}$ from the value predicted from biological cycling alone) can be calculated for these glacial water masses. Because biological cycling does not significantly change this air-sea exchange signature, $\delta^{13}\text{C}_{\text{as}}$, which is imprinted on the water mass at the surface, $\delta^{13}\text{C}_{\text{as}}$ can be used as a conservative tracer for subsurface water masses. An analysis of glacial Cd_w and $\delta^{13}\text{C}$ compiled by Boyle [1992] indicates that not only was the $\delta^{13}\text{C}_{\text{as}}$ of GNAIW high but also waters between 1- and 2-km depth in the glacial Pacific show high $\delta^{13}\text{C}_{\text{as}}$ values [Lynch-Stieglitz and Fairbanks, 1994]. However, the high $\delta^{13}\text{C}_{\text{as}}$ waters in the glacial Pacific had high nutrient (Cd_w) contents, indicating either a greater distance from the source region, or alternatively high preformed nutrient concentrations and a local source.

Lynch-Stieglitz and Fairbanks [1994] suggested that these high $\delta^{13}\text{C}_{\text{as}}$ waters in the glacial Pacific could have originated as GNAIW, making their way into the Pacific via the ACC, with their high nutrient content reflecting the regeneration of nutrients into this water mass as it aged. If this were the case, we should see high $\delta^{13}\text{C}_{\text{as}}$ waters of intermediate nutrient content in the upper/northward portions of the glacial ACC. On the basis of oxygen isotope measurements, Lynch-Stieglitz *et al.* [1994] concluded that a transect of sediment cores collected off Tasmania and South Australia (Figure 2) records a vertical profile of properties in the glacial

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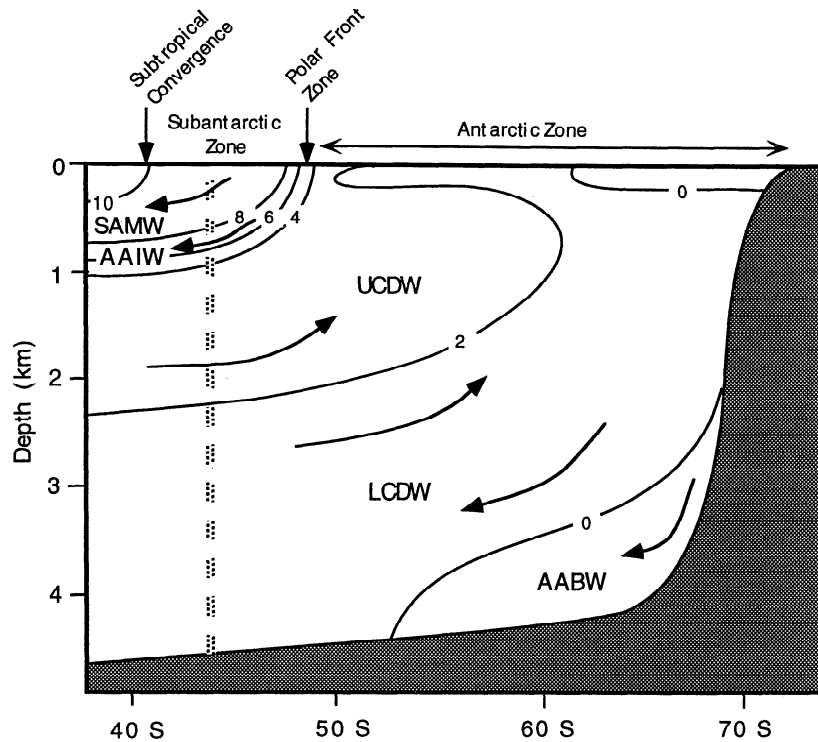


Figure 1. Schematic diagram showing the locations and meridional motions of water masses carried by the Antarctic Circumpolar Current. AABW is Antarctic Bottom Water, LCDW and UCDW are the lower and upper (North Atlantic Deep Water dominated) varieties of Circumpolar Deep Water, AAIW is Antarctic Intermediate Water, and SAMW is Subantarctic Mode Water. A vertical profile in the Subantarctic Zone (light dashed line) will intersect many of these water masses. Approximate temperature contours (in degrees Celcius) are also indicated.

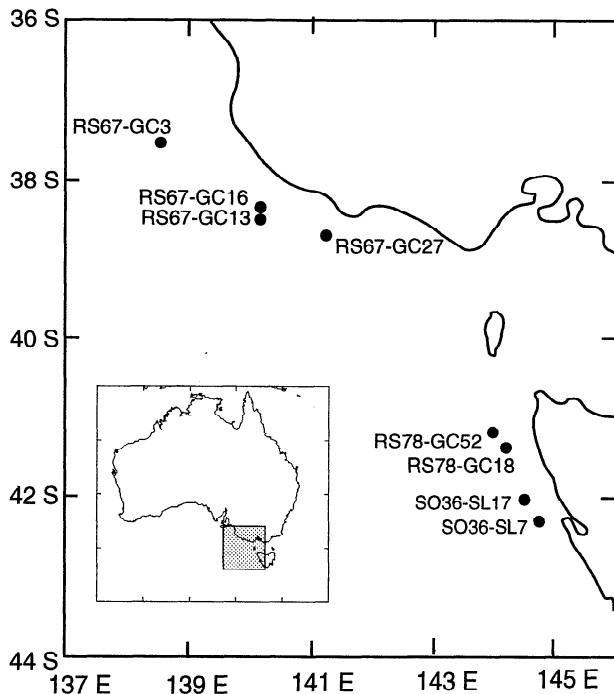


Figure 2. Core locations.

Subantarctic Zone. Here we present Cd/Ca measurements on benthic foraminifera from the glacial portions of these cores which, along with the previously published carbon isotope measurements, support the idea that GNAIW could have reached the Pacific via the glacial ACC.

Cd/Ca Determinations

Methods

The last glacial maximum was identified based on the oxygen isotope records presented by Lynch-Stieglitz *et al.* [1994]. Cd/Ca analyses were performed using 6-11 individual foraminifera for each analysis. No core top measurements were made due to an insufficient quantity of benthic foraminifera in the Holocene sections of the cores. The foraminifera cleaning procedure of Boyle and Keigwin [1985/1986] for Cd analysis by graphite-furnace atomic absorption was generally followed. Foram shells were subjected to a milder reducing step (15 μ L in each centrifuge tube of a solution containing 0.05 g citric acid, 75 μ L hydrazine in 2 mL NH_4OH), followed by a milder oxidation step (50 μ L per tube of a 0.1 N NaOH solution containing 10 μ L hydrogen peroxide), and ending with another mild reducing step (Cleaning Treatment "1" in Table 1). In addition, some samples (Treatment "2" in Table 1) were treated with one additional oxidation and reducing cleaning step before

Table 1. Cd/Ca Data

Depth in Core, cm	Foraminifera	Cleaning Treatment*	Cd/Ca, $\mu\text{mol/mol}$	Mn/Ca, $\mu\text{mol/mol}$	D	Cd _w , nmol/kg
			<i>RS67-GC27 506 m</i>			
180.5	<i>P. wuellerstorfi</i>	1	0.047		1.30	0.36
190.5	<i>P. wuellerstorfi</i>	1	0.023		1.30	0.18
220.5	<i>P. wuellerstorfi</i>	1	0.040		1.30	0.31
191	<i>P. wuellerstorfi</i>	1	0.115		1.30	0.88 [†]
191	<i>P. wuellerstorfi</i>	1	0.036		1.30	0.27
191	<i>P. wuellerstorfi</i>	1	0.023		1.30	0.17
197.5	<i>P. wuellerstorfi</i>	2	0.003	20	1.30	0.02
			<i>RS78-GC18 814 m</i>			
220.5	<i>Uvigerina</i>	1	0.075		1.30	0.58
220.5	<i>Uvigerina</i>	1	0.106		1.30	0.81
220.5	<i>P. wuellerstorfi</i>	2	0.038	10	1.30	0.29
			<i>SO36-SL17 1042 m</i>			
100	<i>Uvigerina</i>	1	0.250		1.30	1.92 [†]
100	<i>Uvigerina</i>	1	0.174		1.30	1.34 [†]
160	<i>Uvigerina</i>	1	0.101		1.30	0.78
160	<i>Uvigerina</i>	1	0.084		1.30	0.65
100	<i>Cibicides</i>	2	0.083	9	1.30	0.63
			<i>SO36-SL7 1085 m</i>			
65.5	<i>Uvigerina</i>	1	0.105		1.30	0.81
65.5	<i>Uvigerina</i>	1	0.122		1.30	0.94
			<i>RS67-GC3 1476 m</i>			
80.5	<i>Uvigerina</i>	1	0.105		1.58	0.66
62.5	<i>Cibicides</i>	2	0.170	5	1.58	1.08 [†]
62.5	<i>Uvigerina</i>	2	0.100	3	1.58	0.63
			<i>RS67-GC16 1650 m</i>			
104	<i>Uvigerina</i>	1	0.134		1.73	0.77
			<i>RS67-GC13 2525 m</i>			
99	<i>Uvigerina</i>	2	0.121	18	2.49	0.49
99	<i>Uvigerina</i>	2	0.120	28	2.49	0.48
110	<i>Uvigerina</i>	2	0.127	16	2.49	0.51
119	<i>Uvigerina</i>	2	0.107	23	2.49	0.43
119	<i>Uvigerina</i>	2	0.094	19	2.49	0.38
108	<i>Uvigerina</i>	2	0.118	40	2.49	0.47

D is the depth dependent distribution coefficient [Boyle, 1992] used to convert Cd/Ca to Cd_w.

* See "Methods" section for explanation of cleaning treatments.

[†] Not used in average

analysis. After cleaning, the shells were dissolved in 100 μL of 1% acetic acid. Samples were diluted to a constant Ca concentration following a preliminary Ca measurement by flame atomic absorption made on a 5- μL subsample. For each Cd determination, 5 μL of a matrix modifier containing 250 μL of acetic acid, 40 μL sulfuric acid, and 4 μL phosphoric acid added to 750 μL water was added to the graphite tube. Mn/Ca ratios were determined on some of the samples. Water column Cd concentrations (Cd_w) were determined using the depth-

dependent distribution coefficient of Boyle [1992]. Sediment cadmium concentrations were obtained by using atomic absorption spectrometry following the procedure described by van Geen *et al.* [1995].

Results

Cd/Ca ratios determined on glacial samples from within each sediment core show more variation than is typically obtained by this method (Table 1, Figure 3). Boyle and

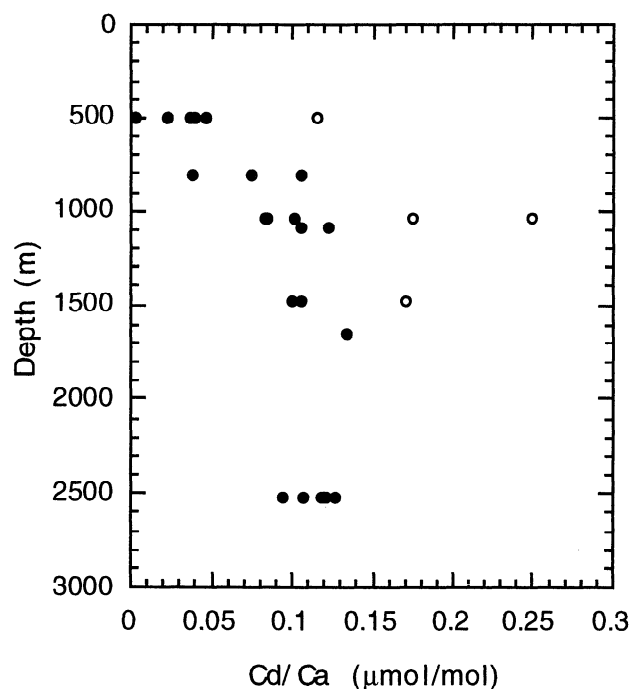


Figure 3. Measured Cd/Ca ratios for all analyses. Open circles represent data excluded from glacial averages for each core.

Keigwin [1985/1986] report that they typically reject only 5% of data points which have higher Cd/Ca ratios than would be expected based on the data trends. Presumably, the rejected samples were subject to contamination or insufficient cleaning before analysis. Samples which were subject to additional cleaning (Treatment "2" in Table 1) also had some high (rejected) Cd/Ca ratios. Mn/Ca ratios, where measured, are consistently low (less than 40 $\mu\text{mol/mol}$) and show no relation to the Cd/Ca values, suggesting no obvious problem due to incomplete cleaning of ferromanganese contaminants [Boyle, 1981]. In addition, a separate batch of foraminifera from the California Margin was cleaned using the same reagents and equipment and showed no signs of contamination or excessively high Cd/Ca ratios. Sediments from the glacial sections of the Australian margin cores were analyzed for Cd content (Table 2) and did not show anomalously high values relative to other measurements on oceanic sediments [Rosenthal *et al.*, 1995; van Geen *et al.*, 1995] or the mean crustal value of 0.1 $\mu\text{g/g}$ [Taylor and McLennan, 1985]. Although we have no satisfactory explanation for their presence, we discard the anomalously high Cd values shown in Figure 3 when we calculate average glacial Cd/Ca values for these cores (Table 3).

The Air-Sea Exchange Signature

The distribution of cadmium in the ocean is controlled by biological cycling and resembles that of the major nutrient phosphorus. Although the mechanism by which Cd becomes incorporated into organisms is not understood, the Cd_w is directly but not quite linearly related to PO_4 in the ocean [Boyle, 1988a]. The isotopic composition of carbon in

seawater also follows the nutrient distribution within the ocean, with low $\delta^{13}\text{C}$ values corresponding to nutrient-rich waters and high $\delta^{13}\text{C}$ to nutrient-depleted waters [Kroopnick, 1985]. Photosynthesis discriminates against the heavier carbon isotope, and as this isotopically light organic matter oxidizes in the deep sea, the deep water gains nutrients and the $\delta^{13}\text{C}$ of dissolved inorganic carbon decreases. However, seawater $\delta^{13}\text{C}$ can also be altered via exchange with atmospheric CO_2 without associated changes in nutrient concentrations. Isotopic equilibration of surface ocean waters with atmospheric CO_2 will cause higher $\delta^{13}\text{C}$ in cold surface waters and lower $\delta^{13}\text{C}$ in warm surface waters [Broecker and Maier-Reimer, 1992; Charles and Fairbanks, 1990].

The air-sea exchange signature, $\delta^{13}\text{C}_{\text{as}}$, can be isolated by subtracting the $\delta^{13}\text{C}$ predicted for an ocean with no air-sea carbon isotopic exchange [Broecker and Maier-Reimer, 1992] from the actual $\delta^{13}\text{C}$,

$$\delta^{13}\text{C}_{\text{as}} \equiv \delta^{13}\text{C} - \left[\delta^{13}\text{C}^{\text{M.O.}} + \frac{\Delta_{\text{org}}}{\Sigma\text{CO}_2^{\text{M.O.}}} \left(\frac{\text{C}}{\text{P}} \right)_{\text{org}} (\text{PO}_4 - \text{PO}_4^{\text{M.O.}}) \right]$$

where M.O. refers to mean ocean values, Δ_{org} is the photosynthetic fractionation factor for carbon isotopes, and $(\text{C}/\text{P})_{\text{org}}$ is the ratio of carbon to phosphate for oceanic organic material. Broecker and Maier-Reimer [1992] name this quantity $\Delta\delta^{13}\text{C}$, but we rename it $\delta^{13}\text{C}_{\text{as}}$ to avoid confusion with $\delta^{13}\text{C}$ gradients within the ocean, which are also referred to as $\Delta\delta^{13}\text{C}$. The oxidation of organic material within a parcel of water will change both the PO_4 and $\delta^{13}\text{C}$ but leave $\delta^{13}\text{C}_{\text{as}}$ unchanged. This means $\delta^{13}\text{C}_{\text{as}}$ approximates a conservative tracer within the deep sea, its distribution only reflecting the relative mixtures of water from different sources. As defined by Broecker and Maier-Reimer [1992] and as used here, $\delta^{13}\text{C}_{\text{as}}$ is actually not quite conserved, with small nonconservative behavior introduced by the assumption of constant dissolved inorganic carbon throughout the ocean and the assumption of constant $\delta^{13}\text{C}$ of organic material. However, in today's deep ocean the deviations in $\delta^{13}\text{C}_{\text{as}}$ from conservative behavior are expected to be negligible. The conservative behavior of $\delta^{13}\text{C}_{\text{as}}$ also requires the ratio of C/P in organic material to be constant upon regeneration of organic material, consistent with modern oceanographic measurements of these properties in the deep sea.

Because of the close relationship between Cd_w and PO_4 in the ocean, we can calculate $\delta^{13}\text{C}_{\text{as}}$ using $\delta^{13}\text{C}$ and Cd_w

Table 2. Sediment Cd Data

Core	Depth in Core, cm	Sediment Cd, $\mu\text{g/g}$
RS67-GC27	190-192	0.18
RS78-18	225	0.13
RS78-18	245	0.16
SO36-SL7	55	0.20
SO36-SL7	65	0.27
RS67-GC3	60-65	0.21
RS67-GC16	98-109	0.34
RS67-GC13	107-109	0.34

Table 3. Composite Subantarctic Profile

Core	Source*	Depth, m	Latitude	Longitude	Glacial Depth [†]	Glacial $\delta^{18}\text{O}$ (Cib Values)	Glacial $\delta^{13}\text{C}$	Glacial Cd_w Average	Glacial $\delta^{13}\text{C}_{\text{as}}$ [‡]
RS67-GC27	L	506	38° 38.9'S	141° 11.5'E	366	2.81	1.92	0.22	0.98
RS78-GC18	L	814	41° 23.1'S	144° 14.0'E	674	3.11	1.2	0.56	1.07
SO36-SL17	L	1042	42° 03.1'S	144° 35.1'E	902	3.39	0.7	0.69	0.87
SO36-SL7	L	1085	42° 18.5'S	144° 40.2'E	945	3.48	0.66	0.87	1.27
RS67-GC3	L	1476	37° 33.0'S	138° 35.0'E	1336	3.63	0.49	0.65	0.57
RS67-GC16	L	1650	38° 20.0'S	140° 10.9'E	1510	3.66	0.21	0.77	0.59
RS67-GC13	L	2525	38° 27.9'S	140° 10.0'E	2385	4.18	-0.22	0.46	-0.59
AII 107 65 GGC	B	2795	43° 31.2 'S	79° 52.2 'W	2675			0.44	
AII 107 131 GGC	B	2925	22° 19.8 'S	11° 12.0 'W	2805			0.36	
V19-240	B	3103	32° 3.6 'S	36° 11.4 'E	2983	4.35	0.02	0.56	-0.11
RC11-120	B	3135	30° 52.8 'S	38° 3 'E	3015	4.45	-0.42	0.51	-0.67
RC13-228	B	3204	30° 34.8 'S	13° 16.8 'E	3084	4.41	-0.31	0.40	-0.82
RC12-294	B	3308	37° 16.2 'S	10° 06.0 'E	3188	4.19	-0.23	0.56	-0.36
RC17-69	B	3308	31° 30.0 'S	32° 36.0 'W	3188			0.67	
RC15-61	B	3771	40° 37.2 'S	77° 12.0 'E	3651			0.55	
RC12-267	B	4144	38° 40.8 'S	25° 46.8 'E	4024			0.42	
RC13-229	B	4191	25° 30.0 'S	11° 19.8 'W	4071	4.26	-0.36	0.54	-0.54

* L, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ from Lynch-Stieglitz *et al.* [1994], Cd_w from this study. B, $\delta^{13}\text{C}$, Cd_w reported by Boyle [1992].

[†] Glacial Depth is Depth - 140 m for South Australian Cores [Lynch-Stieglitz *et al.*, 1994], and Depth - 120 m for other Southern Ocean Cores to reflect the global sea level drop.

[‡] Glacial $\delta^{13}\text{C}_{\text{as}} = \delta^{13}\text{C} + 2.375 \times \text{Cd}_w - 1.46$

estimates from benthic foraminifera. Modern $\delta^{13}\text{C}_{\text{as}}$ can be calculated using the above relationship between $\delta^{13}\text{C}_{\text{as}}$ and PO_4 , along with the $\text{Cd}_w\text{-PO}_4$ relationship for waters containing more than $1.3 \mu\text{mol kg}^{-1} \text{PO}_4$ [Boyle, 1988a], $\delta^{13}\text{C}_{\text{as}} = \delta^{13}\text{C} + 2.75 \times \text{Cd}_w - 2.0$. For glacial values, we modify the $\delta^{13}\text{C}_{\text{as}}$ equation to account for organic matter $\delta^{13}\text{C}$ which is 2 ‰ higher [Rau *et al.*, 1991], a mean ocean $\delta^{13}\text{C}$ which was .3 ‰ lower [Curry *et al.*, 1988; Boyle, 1992], and a corresponding increase in total inorganic carbon of 4% ($\delta^{13}\text{C}_{\text{as}} = \delta^{13}\text{C} + 2.375 \times \text{Cd}_w - 1.46$). The oceanic phosphate and cadmium inventories are assumed to be the same as today, and it is assumed that the relationship between PO_4 and Cd_w is the same as it is today. While Boyle [1992] calculates a 13% lower Cd inventory during the last glaciation, he finds this decrease is not significant within the uncertainty of the analysis. It is possible that the glacial Cd inventory could have decreased during the last glacial maximum if the area of suboxic sediments where Cd accumulates increased [van Geen *et al.*, 1995; Rosenthal *et al.*, 1995]. However, it is equally possible that the 13% decrease estimated by Boyle [1992] includes data which have been biased toward low values due to the dissolution related effects explored by McCorkle *et al.* [1995]. As the nature of the Cd_w/PO_4 link in the present-day ocean is poorly understood, it is difficult to evaluate how well this relationship will hold through time, adding another source of uncertainty to glacial $\delta^{13}\text{C}_{\text{as}}$ calculations.

The calculated values of glacial $\delta^{13}\text{C}_{\text{as}}$ values, and the subsequent utility of the reconstructions of this conservative tracer, are only as reliable as the reconstruction of ocean PO_4 from foraminiferal Cd/Ca and the reconstruction of the $\delta^{13}\text{C}$ of oceanic carbon from measurements on benthic foraminifera. Foraminifera incorporate varying amounts of Cd into their calcite tests, depending primarily on seawater concentrations, Cd_w , and the depth of calcification [Boyle, 1988a, 1992]. Core top calibrations show that foraminiferal Cd/Ca ratios can be used to estimate seawater Cd_w to an accuracy of about $\pm 0.1 \text{ nmol kg}^{-1}$ [Boyle, 1992]. However, measurements on benthic foraminifera from surface sediments in the deep Pacific suggest that the Cd/Ca ratio in benthic foraminifera may be reduced by dissolution of this calcite [McCorkle *et al.*, 1995]. McCorkle *et al.* [1995] show that this can result in systematic errors which lead to the underestimation of Cd_w by up to 0.4 nmol kg^{-1} , with consistently lower values in deep, nutrient-rich waters of today's deep Pacific which are corrosive to calcite. A 0.4 nmol kg^{-1} error in the estimate of Cd_w would translate into a 1 ‰ error in $\delta^{13}\text{C}_{\text{as}}$.

Deep water $\delta^{13}\text{C}$ is recorded by benthic foraminifera as oceanic carbon is incorporated into their calcite tests. *Planulina wuellerstorfi* has been shown to record seawater $\delta^{13}\text{C}$ to an accuracy of about ± 0.2 ‰ [Duplessy *et al.*, 1984]. However, it has been shown that foraminiferal $\delta^{13}\text{C}$ will be depleted relative to ambient bottom water by up to 0.5 ‰ in areas where there is a large flux of isotopically light organic material which is remineralized either in or near the surface of the sediment [Sarnthein *et al.*, 1988; Mackensen *et al.*, 1993]. This error will systematically bias deep water $\delta^{13}\text{C}$ estimates, and thus $\delta^{13}\text{C}_{\text{as}}$ estimates by the same amount, toward low values beneath areas of high productivity. In interpreting the distribution $\delta^{13}\text{C}_{\text{as}}$, we need to be aware of the possibility of potentially large systematic errors arising from

these flaws in the ability of foraminifera to accurately record seawater Cd and $\delta^{13}\text{C}$.

In a worst case scenario, where both systematic errors in Cd_w estimates due to dissolution effects and systematic errors in $\delta^{13}\text{C}$ due to productivity effects are present, the resulting estimate of $\delta^{13}\text{C}_{\text{as}}$ could be low by as much as 1.5‰. This sort of error is clearly unacceptable given that the range of $\delta^{13}\text{C}_{\text{as}}$ in today's ocean is only 2‰ [Lynch-Stieglitz *et al.*, 1995]. However, we still can gain useful information from measurements of foraminiferal Cd/Ca and $\delta^{13}\text{C}$ and thus estimates of $\delta^{13}\text{C}_{\text{as}}$ as long as we acknowledge and assess the possibilities of these sorts of systematic errors. Much, if not most, of the ocean floor will not be subject to the intense dissolution which takes place in the deep Pacific in the study area of McCorkle *et al.* [1995] and the large fluxes of organic material in the Southern Ocean which effected the data of Mackensen *et al.* [1993].

Glacial Subantarctic Profiles

We combine our last glacial maximum data with Cd_w and $\delta^{13}\text{C}$ estimates from deeper waters in the Southern Ocean [Boyle, 1992] in order to construct a composite vertical profile for the glacial Subantarctic (Figure 4). Although the deeper data are from all three sectors of the Southern Ocean, the relative homogeneity of these deep waters justifies their inclusion in the composite profiles. Relatively low glacial Cd_w values at 300-m depth increased to a maximum between 1- and 1.5-km depth. The Cd/Ca ratios we measured at 2.3 km are consistent with those measured elsewhere in the glacial Southern Ocean [Boyle, 1992], indicating slightly lower Cd_w values during the last glaciation relative to today.

Carbon isotope measurements for glacial Antarctic Intermediate Water (AAIW), situated at a depth of about 800 m in the Subantarctic Zone, suggest that glacial AAIW was composed exclusively of Antarctic Surface Waters [Lynch-Stieglitz *et al.*, 1994]. Measurements on glacial planktonic foraminifera from the Southern Ocean [Boyle, 1988b; Keigwin and Boyle, 1989] suggest that Cd_w of Southern Ocean Surface Water did not change from its present values 0.4 to 0.6 nmol kg^{-1} [Martin *et al.*, 1990; Nolting and de Baar, 1994] during the last glaciation. The Cd_w estimates directly above (0.6 nmol kg^{-1}) and below (0.7 nmol kg^{-1}) the depth of glacial AAIW from benthic foraminifera are consistent with these Southern Ocean Surface Water Cd_w estimates from planktonic foraminifera (Figure 4).

We use the glacial Cd_w and $\delta^{13}\text{C}$ data to calculate glacial values for the conservative tracer, $\delta^{13}\text{C}_{\text{as}}$. The deeper waters in the Subantarctic profile (below 2 km) show low values of this air-sea exchange signature, as do Glacial Deep Waters (GDW) in the Pacific [Lynch-Stieglitz and Fairbanks, 1994]. High $\delta^{13}\text{C}_{\text{as}}$ values for glacial Southern Ocean Surface Water suggest that the low $\delta^{13}\text{C}_{\text{as}}$ GDW originated elsewhere, perhaps in the Pacific. This analysis presumes any discrepancy between $\delta^{13}\text{C}$ and Cd_w estimates is due to air-sea exchange processes. However, new core top Cd/Ca measurements indicate that chemical dissolution of foraminiferal shells may be responsible for lower Cd/Ca measurements in glacial foraminifera in the deep ocean [McCorkle *et al.*, 1995]. McCorkle *et al.* [1995] show that Cd

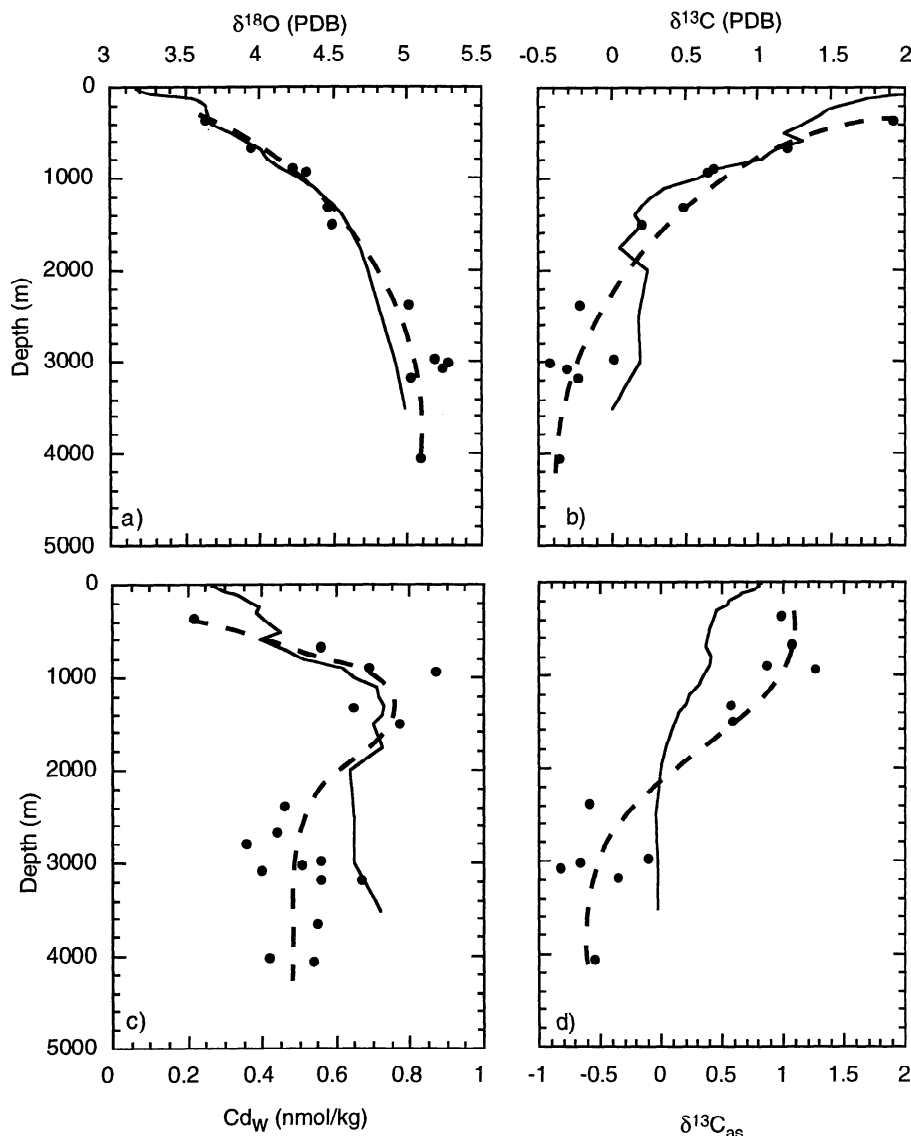


Figure 4. Vertical profiles from the glacial Subantarctic. See Table 3 for description of data. (a) The $\delta^{18}\text{O}$ of *Cibicidoides* spp. in the glacial subantarctic with 0.83 per mil added to the values [Herguera et al., 1992] to account for disequilibrium fractionation. The solid line is the $\delta^{18}\text{O}$ of calcite that would be precipitated in equilibrium with water in today's Subantarctic (51.5°S 144.5°E) about 10 degrees directly south of our core locations. We add 1.3‰ to the equilibrium $\delta^{18}\text{O}$ profile to compensate for heavier oceanic $\delta^{18}\text{O}$ due to the lower glacial sea level [Fairbanks, 1989]. The glacial $\delta^{18}\text{O}$ profile indicates that our core locations were bathed by water with thermal characteristics similar to today's Subantarctic, consistent with evidence for the northward shift of frontal boundaries in the Indian Ocean sector relative to their present-day conditions during the last glaciation [Howard and Prell, 1992]. (b) The $\delta^{13}\text{C}$ from *Cibicidoides* spp. for the glacial Subantarctic. The solid line is the $\delta^{13}\text{C}$ predicted for today's Subantarctic based on annual average salinity and PO_4 data at 51.5°S and 144.5°E [Levitus and Boyer, 1994] and correlations of these parameters with measured Geochemical Ocean Sections Study (GEOSECS) $\delta^{13}\text{C}$ data in this region. (c) Cd_w calculated for various species. Averages of several replicates are plotted. The solid line is the Cd_w predicted for today's Subantarctic based on annual average PO_4 data at 51.5°S and 144.5°E [Levitus and Boyer, 1994] and the global PO_4/Cd_w relationship of Boyle [1988a]. (d) The $\delta^{13}\text{C}_{\text{as}}$ calculated from the $\delta^{13}\text{C}$ and Cd_w shown in Figures 4b and 4c. The solid line is the predicted $\delta^{13}\text{C}_{\text{as}}$ for today's Subantarctic based on annual average salinity data at 51.5°S and 144.5°E [Levitus and Boyer, 1994] and the regional relationships between $\delta^{13}\text{C}_{\text{as}}$ and salinity [Lynch-Stieglitz et al., 1994]. For all panels, a dashed line is drawn which represents the authors' interpretation of the shape of the glacial profile. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are referenced to pee dee belemnite (PDB).

concentrations from core top foraminifera in today's Pacific Ocean decrease precipitously beneath the saturation horizon. This means that $\delta^{13}\text{C}_{\text{as}}$ as calculated from deep foraminiferal Cd/Ca measurements may not accurately reflect the actual glacial $\delta^{13}\text{C}_{\text{as}}$ in areas of the glacial ocean where foraminifera have been subjected to dissolution. Because the solubility of calcite increases with increasing pressure, dissolution alone could result in the appearance of a low $\delta^{13}\text{C}_{\text{as}}$ water mass in the deep ocean. In particular, there is evidence for increased carbonate dissolution in the South Atlantic and Indian Oceans [Howard and Prell, 1994] in the same locations as the paleochemical measurements which indicate low glacial Cd values. In this part of the ocean the saturation horizon is at about 3300 m, and was likely shallower by at least 600 m during the last glaciation [Howard and Prell, 1994]. This implies that the glacial Cd measurements from the South Indian and Atlantic Oceans, particularly those below 2500 m, could well be compromised by dissolution. High fluxes of organic matter could also have biased some of the glacial $\delta^{13}\text{C}$ and thus $\delta^{13}\text{C}_{\text{as}}$ estimates toward lower values. So it is indeed possible that the deep ocean was filled with a higher $\delta^{13}\text{C}_{\text{as}}$ water that left the surface in the Southern Ocean instead of a low $\delta^{13}\text{C}_{\text{as}}$ water mass which left the surface somewhere in the North Pacific. This problem will have to be resolved with more $\delta^{13}\text{C}$ and Cd/Ca measurements at sites where the changes in productivity above the site and the tendency for calcite dissolution are well documented.

The waters above 2-km depth show high $\delta^{13}\text{C}_{\text{as}}$ values, as do waters in the 1- to 2-km depth range throughout the Atlantic and Pacific Oceans [Lynch-Stieglitz and Fairbanks, 1994] (Figure 5). We have more confidence in $\delta^{13}\text{C}_{\text{as}}$ estimates for these upper water masses than we do for the deeper water masses discussed above for several reasons. Dissolution of calcite is unlikely to be a problem above 2 km in the ocean where seawater is oversaturated with respect to calcite. The tight clustering of high $\delta^{13}\text{C}_{\text{as}}$ estimates in these upper waters suggests that bias toward low $\delta^{13}\text{C}$ beneath areas of high productivity is not corrupting these estimates.

In the Atlantic, these high $\delta^{13}\text{C}_{\text{as}}$ waters have low Cd_w values and are identified as Glacial North Atlantic Intermediate Water (GNAIW). In the Pacific these high $\delta^{13}\text{C}_{\text{as}}$ waters have high Cd_w values. In our Subantarctic profile, the Cd_w values for this high $\delta^{13}\text{C}_{\text{as}}$ water mass are intermediate between the Atlantic and Pacific values. If we plot the individual measurements on foraminifera between 1 and 2 km for the glacial ocean (Figure 6), we see that measurements from the Atlantic, Subantarctic, and Pacific Oceans all fall along a line (constant $\delta^{13}\text{C}_{\text{as}}$) consistent with the regeneration of organic material in "Redfield" proportions. These Cd_w and $\delta^{13}\text{C}_{\text{as}}$ values are consistent with the idea that this high $\delta^{13}\text{C}_{\text{as}}$ water mass originates in the North Atlantic as GNAIW and makes its way into the Pacific via the Antarctic Circumpolar Current. The high Cd_w values in the Pacific would then reflect the low rates of renewal of this water mass from the Atlantic.

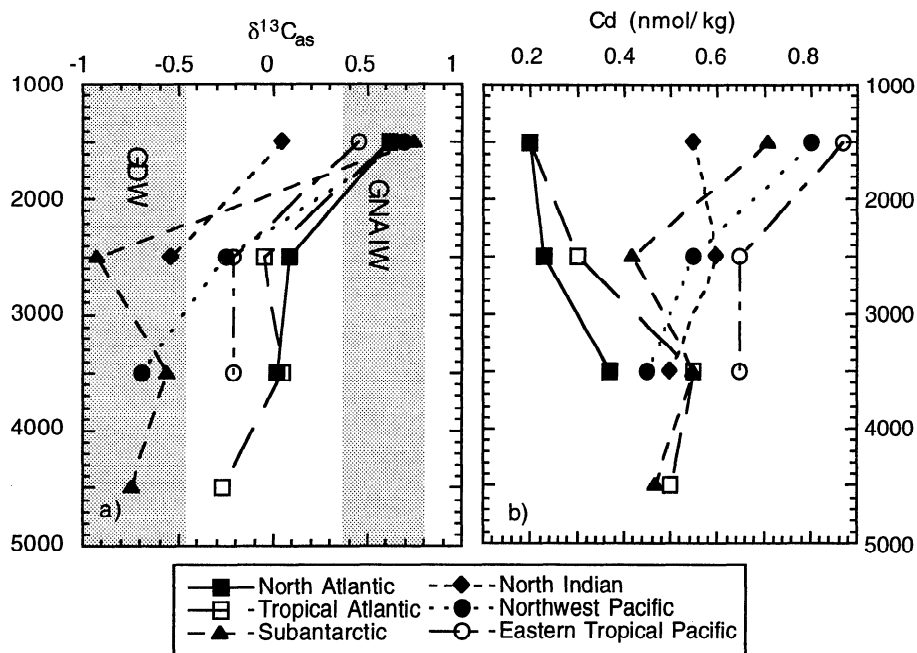


Figure 5. Glacial $\delta^{13}\text{C}_{\text{as}}$ and Cd_w averages for 1-km depth intervals [Boyle, 1992; Lynch-Stieglitz and Fairbanks, 1994] with a Subantarctic profile that now reflects the new Cd data presented in this paper. The shallow (1-2 km) portion of the Subantarctic profile shows the same high $\delta^{13}\text{C}_{\text{as}}$ measured in the shallow (1-2 km) portions of the glacial Atlantic and Pacific Oceans. The Cd_w values for the glacial Subantarctic at this depth are intermediate between those from the glacial Atlantic and the glacial Pacific, lending support to the idea that these shallower portions glacial Pacific were filled with aged Glacial North Atlantic Intermediate Water (GNAIW) which reached the Pacific via the Antarctic circumpolar circulation.

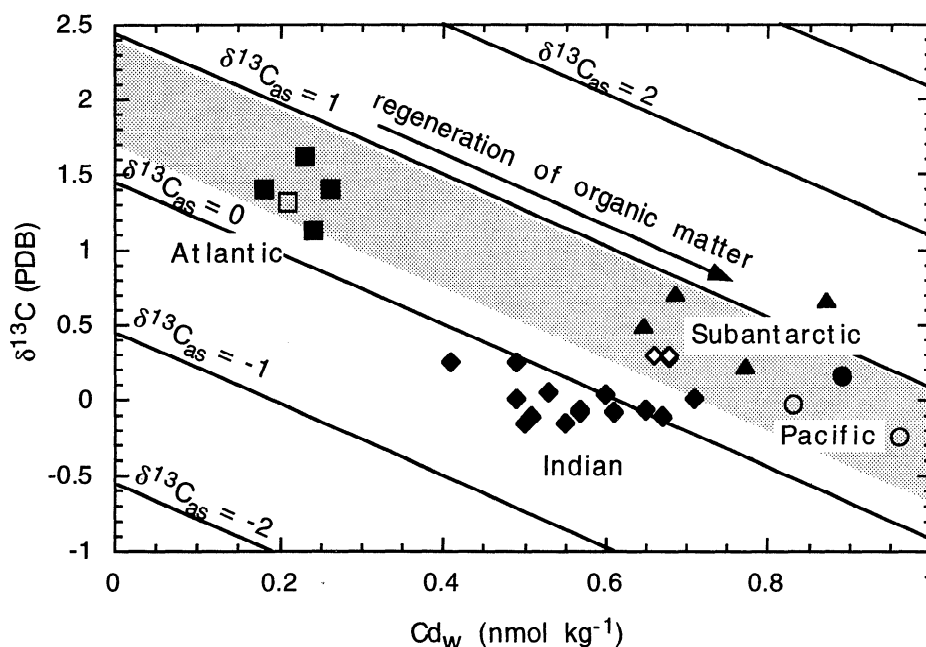


Figure 6. The $\delta^{13}\text{C}$ and Cd_w values [Boyle, 1992; Bertram *et al.*, 1995] from cores between 1 and 2 km in the Atlantic, Subantarctic, and Pacific Oceans (same symbols as in Figure 5). The values lie along a "Redfield" slope (line of constant $\delta^{13}\text{C}_{\text{as}}$). This means that the waters in the Subantarctic and Pacific could have originated in the North Atlantic, with their properties reflecting only : remineralization of organic material into the water mass as it aged. The $\delta^{13}\text{C}$ and Cd_w [Boyle *et al.*, 1995] values from cores between 1 and 2 km in the North Indian Ocean (solid diamonds) do not lie on the same slope, suggesting a separate contribution to the glacial Indian Ocean. The $\delta^{13}\text{C}$ and Cd_w from the South Indian Ocean (18° to 20°S , open diamonds) [Boyle *et al.*, 1995] do lie on the Atlantic, Subantarctic, Pacific slope suggesting a possible GNAIW source for these waters as well. The depth-dependent distribution coefficient of Boyle [1992] was used to convert data from all sources from Cd/Ca to Cd_w .

However, we cannot exclude the possibility of two separate high $\delta^{13}\text{C}_{\text{as}}$ water masses, one forming in the glacial Pacific or Antarctic (with higher preformed nutrient concentrations) and the other in the glacial Atlantic (with lower preformed nutrient concentrations). Note that the glacial North Indian Ocean does not share the same air-sea exchange signature and suggests at least one additional source of intermediate depth water to the glacial ocean (Figures 5 and 6).

Implications for Glacial Ocean Circulation

It is sometimes assumed that GNAIW formed a closed circulation within the Atlantic [e.g., Duplessy *et al.*, 1988], in contrast to today's NADW which spreads throughout the world ocean via the ACC. However, Yu *et al.* [1995] argue on the basis of the ratio of ^{231}Pa to ^{230}Th in glacial sediments that the export of water from the glacial Atlantic was at least as intense as that of NADW today. This study provides evidence that this water mass exported from the glacial Atlantic could have been GNAIW. If GNAIW also was exported from the Atlantic, we must reevaluate our thoughts on how a switch from NADW to GNAIW production influenced the transport of heat and salt within the glacial ocean and how these transports may have influenced glacial climate. It has been postulated that the absence of NADW formation during the last glaciation was accompanied by a lessened transport of heat to high

northern latitudes by northward moving warm surface waters. Whether or not it left the Atlantic Ocean basin, as long as GNAIW formed far enough south and the production rate was sufficiently modest, this "boreal heat pump" [Lehmann and Keigwin, 1992; Imbrie *et al.*, 1992] could not have supplied as much heat to high northern latitudes as today's NADW (the "Nordic heat pump"). It has also been postulated that the reduction in NADW formation during glacial conditions resulted in a reduced export of salt from the Atlantic. This salt buildup could have been responsible for switches back to periods of NADW formation during marine oxygen isotope Stage 3, resulting in the warm intervals observed in high northern latitudes [Broecker *et al.*, 1990; Birchfield and Broecker, 1990]. A NADW shutdown may not lead to as efficient salt buildup if GNAIW is being exported from the Atlantic during these NADW shutdown events. But as long as flux of GNAIW is sufficiently smaller than today's NADW and/or this water mass is sufficiently fresh, reduced salt export is still possible during the NADW shutdown. High nutrient content in the Pacific points to low renewal rates for these Intermediate waters, indicating that a relatively low flux of GNAIW out of the Atlantic is reasonable.

Conclusions

Cd/Ca measurements on benthic foraminifera from the glacial Subantarctic Zone suggest that a high $\delta^{13}\text{C}_{\text{as}}$ water

mass occupied not only the shallow (1-2 km) portions of the Atlantic and Pacific Oceans but was present in the glacial Subantarctic as well. The Cd_w values predicted for the glacial Subantarctic are intermediate between those from the glacial Atlantic and the glacial Pacific. This supports the idea that GNAIW was transported around Antarctica and to the rest of the world ocean by the Antarctic Circumpolar Current.

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References

- Bertram, C.J., H. Elderfield, N.J. Shackleton, and J.A. MacDonald, Cadmium/calcium and carbon isotope reconstructions of the glacial northeast Atlantic Ocean, *Paleoceanography*, 10, 563-578, 1995.
- Birchfield, G.E. and W.S. Broecker, A salt oscillator in the glacial Atlantic?, 2, A "scale analysis" model, *Paleoceanography*, 5, 835-843, 1990.
- Boyle, E.A., Cadmium, zinc, copper, and barium in foraminifera tests, *Earth Planet. Sci. Lett.*, 53, 11-35, 1981.
- Boyle, E.A., Cadmium: Chemical tracer of deepwater paleoceanography, *Paleoceanography*, 3, 471-489, 1988a.
- Boyle, E. A., The role of vertical chemical fractionation in controlling Late Quaternary atmospheric carbon dioxide, *J. Geophys. Res.*, 93, 15,701-15,714, 1988b.
- Boyle, E. A., Cadmium and $\delta^{13}C$ paleochemical ocean distributions during the stage 2 glacial maximum, *Annu. Rev. Earth Planet. Sci.*, 20, 245-287, 1992.
- Boyle, E.A., and L.D. Keigwin, Comparison of Atlantic and Pacific paleochemical records for the last 215,000 years: Changes in deep ocean circulation and chemical inventories, *Earth Planet. Sci. Lett.*, 76, 135-150, 1985/1986.
- Boyle, E.A., and L.D. Keigwin, North Atlantic thermohaline circulation during the last 20,000 years linked to high latitude surface temperature, *Nature*, 330, 35-40, 1987.
- Boyle, E.A., L. Labeyrie, and J.-C. Duplessy, Calcitic foraminiferal data confirmed by cadmium in aragonitic *Hoeglundina*: Application to the last glacial maximum in the northern Indian Ocean, *Paleoceanography*, 10, 881-900, 1995.
- Broecker, W.S., An oceanographic explanation for the apparent carbon isotope-cadmium discordancy in the Glacial Antarctic?, *Paleoceanography*, 8, 137-140, 1993.
- Broecker, W.S., and E. Maier-Reimer, The influence of air and sea exchange on the carbon isotope distribution in the sea, *Global Biogeochem. Cycles*, 6, 315-320, 1992.
- Broecker, W.S., G. Bond, M. Klas, G. Bonani, and W. Wolfi, A salt oscillator in the glacial Atlantic?, 1., The concept, *Paleoceanography*, 5, 469-478, 1990.
- Charles, C.D., and R.G. Fairbanks, Glacial to interglacial changes in the isotopic gradients of Southern Ocean surface water, in *Geological History of the Polar Oceans: Arctic Versus Antarctic*, edited by U. Bleil and J. Thiede, pp. 519-538, Kluwer Acad., Norwell, Mass., 1990.
- Charles, C.D., and R.G. Fairbanks, Evidence from Southern Ocean sediments for the effect of North Atlantic deep-water flux on climate, *Nature*, 355, 416-419, 1992.
- Charles, C.D., J.D. Wright, and R.G. Fairbanks, Thermodynamic influences on the marine carbon isotope record, *Paleoceanography*, 8, 691-697, 1993.
- Curry, W.B., J.C. Duplessy, L.D. Labeyrie and N.J. Shackleton, Changes in the distribution of $\delta^{13}C$ of deep water ΣCO_2 between the last glaciation and the Holocene, *Paleoceanography*, 3, 317-341, 1988.
- Duplessy, J.-C., N.J. Shackleton, R.K. Matthews, W. Prell, W.F. Ruddiman, M. Caralp, and C.H. Hendy, ^{13}C record of benthic foraminifera in the last interglacial ocean: Implications for the carbon cycle and the global deep water circulation, *Quat. Res.*, 21, 225-243, 1984.
- Duplessy, J.C., N.J. Shackleton, R.G. Fairbanks, L. Labeyrie, D. Oppo, and N. Kallel, Deepwater source variations during the last climatic cycle and their impact on the global deepwater circulation, *Paleoceanography*, 3, 343-360, 1988.
- Fairbanks, R.G., A 17,000 year glacio-eustatic sea level record: Influence of glacial melting rates on the Younger Dryas event and deep-ocean circulation, *Nature*, 342, 637-642, 1989.
- Herguera, J.C., E. Jansen, and W.H. Berger, Evidence for a bathyl front at 2000-m depth in the glacial Pacific, based on a depth transect on Ontong Java Plateau, *Paleoceanography*, 7, 273-288, 1992.
- Howard, W.R., and W.L. Prell, Late Quaternary surface circulation in the southern Indian Ocean and its relationship to orbital variations, *Paleoceanography*, 7, 79-117, 1992.
- Howard, W.R., and W.L. Prell, Late Quaternary $CaCO_3$ production and preservation in the Southern Ocean: Implications for oceanic and atmospheric carbon cycling, *Paleoceanography*, 9, 453-482, 1994.
- Imbrie, J., et al., On the structure and origin of major glaciation cycles, 1., Linear responses to Milankovitch forcing, *Paleoceanography*, 7, 701-738, 1992.
- Keigwin, L.D., and E. A. Boyle, Late Quaternary paleochemistry of high-latitude surface waters, *Paleogeogr. Paleoclimatol. Paleoecol.*, 73, 85-106, 1989.
- Kroopnick, P.M., The distribution of ^{13}C of ΣCO_2 in the world oceans, *Deep Sea Res. Part A*, 32, 57-84, 1985.
- Lehmann, S.J., and L.D. Keigwin, Sudden changes in North Atlantic circulation during the last glaciation, *Nature*, 356, 757-762, 1992.
- Levitus, S., and T.P. Boyer, *World Ocean Atlas 1994, NOAA Atlas NESDIS*, Nat. Oceanic and Atmos. Admin., Silver Spring, Md., 1994.
- Lynch-Stieglitz, J., and R.G. Fairbanks, A conservative tracer for glacial ocean circulation from carbon isotope and paleo-nutrient measurements in benthic foraminifera, *Nature*, 369, 308-310, 1994.
- Lynch-Stieglitz, J., R.G. Fairbanks, and C.D. Charles, Glacial-interglacial history of Antarctic Intermediate Water: Relative strengths of Antarctic versus Indian Ocean sources, *Paleoceanography*, 9, 7-29, 1994.
- Lynch-Stieglitz, J., T.F. Stocker, W.S. Broecker and R.G. Fairbanks, The influence of air-sea exchange on the isotopic composition of oceanic carbon: Observations and modeling, *Global Biogeochem. Cycles*, 9, 653-665, 1995.
- Mackensen, A., H.-W. Hubberton, T. Bickert, G. Fischer, and D.K. Futterer, $\delta^{13}C$ in benthic foraminiferal tests of *Fontbotia wuellerstorfi* (Schwager) relative to $\delta^{13}C$ of dissolved inorganic carbon in Southern Ocean deep water: Implications for Glacial ocean circulation models, *Paleoceanography*, 8, 587-610, 1993.
- Martin, J.H., R.M. Gordon, and S.E. Fitzwater, Iron in the Antarctic waters, *Nature*, 345, 156-158, 1990.
- McCorkle, D.C., P.A. Martin, D.W. Lea, and G.P. Klinkhammer, Evidence of a dissolution effect on benthic foraminiferal shell chemistry: $\delta^{13}C$, Cd/Ca, Ba/Ca and Sr/Ca results from the Ontong Java Plateau, *Paleoceanography*, 10, 699-714, 1995.
- Nolting, R.F., and H.J.W. de Baar, Behavior of nickel, copper, zinc and cadmium in the upper 300 m of a transect in the Southern Ocean (57° - 62°S, 49°W), *Mar. Chem.*, 45, 225-242, 1994.
- Oceanography Course Team, *Ocean Circulation*, Open Univ., Milton Keynes, England, 1989.
- Oppo, D.W., and R.G. Fairbanks, Variability in the deep and intermediate water circulation of the Atlantic during the past 25,000 years: Northern hemisphere modulation of the Southern Ocean, *Earth Planet. Sci. Lett.*, 86, 1-15, 1987.
- Rau, G.H., P.N. Froelich, T. Takahashi, and D.J. Des Marais, Does sedimentary organic $\delta^{13}C$ record variations in Quaternary ocean $[CO_2(aq)]$?, *Paleoceanography*, 6, 335-347, 1991.
- Rosenthal, Y., E.A. Boyle, L. Labeyrie, and D. Oppo, Productivity induced enrichment of authigenic Cd and U in glacial Subantarctic sediments: A climate control on the elements' oceanic budget?, *Paleoceanography*, 10, 395-414, 1995.
- Sarnthein, M., K. Winn, J.-C. Duplessy, and M.R. Fontugne, Global variations of surface ocean productivity in low and mid latitudes: Influence on CO_2 reservoirs of the deep ocean and atmosphere during the last 21,000 years, *Paleoceanography*, 3, 361-399, 1988.

- Taylor, S. R., and S. M. McLennan, *The Continental Crust: Its Composition and Evolution*, Blackwell, Cambridge, Mass., 1985.
- van Geen, A., D. McCorkle, and G. Klinkhammer, Sensitivity of the phosphate-cadmium-carbon isotope relation in the ocean to cadmium removal by suboxic sediments, *Paleoceanography*, 10, 159-169, 1995.
- Yu, E.-F., M.P. Bacon, and R. Francois, Sediment $^{231}\text{Pa}/^{230}\text{Th}$ ratios as a constraint on ocean circulation during the Last Glacial Maximum (LGM), paper presented at 5th International Conference on Paleocyanography, Scientific Committee on Ocean Research, Halifax, Canada, Oct. 10-14, 1995.

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