AGE SCREENING OF DEEP-SEA CORALS AND THE RECORD OF DEEP NORTH ATLANTIC CIRCULATION CHANGE AT 15.4 KA

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ABSTRACT

Uranium rich, density banded deep-sea corals are a new archive of deep ocean behavior on decadal time scales. Large numbers of samples can be rapidly and inexpensively screened for their ages using an Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) technique. With this new method, 300 samples have been sorted into 5,000 year age bins and several dozen of these are useful for coupled precise uranium series and radiocarbon dating. Together with Cd/Ca data from a single coral's skeleton, these coupled ages show that there was a rapid and large shift in the deep circulation of the western north Atlantic at 15.4 ka and 1,800 m depth. This deep-sea coral signal, also found in sediment records from around the Atlantic, leads the Bolling/Allerod warming in the Greenland ice cores by 840 ± 340 years. Coupled ages from the two dating methods in the corals also constrain the southern source deep waters to be about 600 years older than their initial value just prior to 15.4 ka. This result is in contrast to the modern Atlantic where western basin deep waters are on average 100 years old or less.

1. INTRODUCTION

Studies of the stable isotope ratios and the trace metal content of benthic foraminifera which grew during the last glacial maximum (LGM) have revealed much about the past distribution and volumes of deep water masses. It is now widely accepted

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that the LGM deep western Atlantic was characterized by a shoaled form of modern North Atlantic deep water (NADW) and a larger invasion of southern source waters at abyssal depths (Boyle and Keigwin, 1987; Duplessy *et al.*, 1988). The nutrient gradient between these two water masses was a relatively sharp contact between 1,500 and 2,000 meters in the north Atlantic (Oppo and Lehman, 1993). In addition to this glacial to interglacial variation, studies of polar ice cores have shown that the pre-Holocene climate was characterized by very abrupt large amplitude shifts in atmospheric temperature (Dansgaard *et al.*, 1993; Grootes *et al.*, 1993). This same pattern of climate shifts has been found in a variety of archives distributed world wide (Bond *et al.*, 1993; Behl and Kennett, 1996; Hughen *et al.*, 1996). As the ocean contains most of the mass and much of the heat capacity of the climate system, changes in its deep circulation could have large global impacts on the climate. So, a key question is does the history of deep circulation contain evidence for rapid shifts associated with the observed sea surface and atmospheric signals?

To this end, some recent work in paleoceanography has focused on high accumulation rate deep-sea sediments sampled at high temporal resolution. Most, but not all, of these studies have focused on constraining water mass distributions in the Atlantic. Early work on Cd/Ca ratios and $\delta^{13}C$ values in benthic foraminifera found, with a relatively small amount of data, that there was some relation between deep circulation signals and sub-orbital shifts in surface proxies. Two cycles of % $CaCO_3$ changes in Stage 3 on the Feni Drift (in core KNR51 13GPC, 54°28.5′N, 15°17.9′W, 2,665 m) are directly correlated with benthic Cd/Ca cycles (Boyle and Rosener, 1990). In core CHN82-20 (43°30′N, 29°52′W, 3,020 m) on the Mid-Atlantic Ridge, Keigwin and Lehman (1994) found two light benthic $\delta^{13}C$ values, possibly indicative of a switch to more southern source waters, during Heinrich event 1. These early studies have been followed by a suite of more recent work on rapid changes in the deep ocean. A record of benthic $\delta^{13}C$ from 4,056 meters deep in the equatorial Atlantic correlates with planktonic $\delta^{18}O$ changes in the same core (Curry and Oppo, 1997). As the surface waters get colder/saltier, the normally strong signature of NADW shifts toward a stronger southern ocean influence. The largest of these shifts correlate with the longer duration interstadials. A stronger southern ocean influence in the deep Atlantic during rapid cold events is also seen in the eastern basin (Sarnthein *et al.*, 1994; Zahn *et al.*, 1997). In addition, Vidal *et al.* show that NADW formation sites are highly sensitive to surface water conditions and that the location of these sites varied for different climate events during the last glacial period on sub-orbital timescales (Vidal *et al.*, 1997). Recent work at the Bermuda Rise has documented rapid variability in both surface and deep proxies during stage 3 (Boyle and Keigwin, 1999).

This sedimentary evidence has established that deep circulation changes are involved in the rapid and high amplitude shifts in global climate that characterize the last glacial period. However, ice core records and certain varved sediment chronologies indicate that the shifts into and out of these interstadial conditions can happen in a few decades or less. This type of rapid variation is difficult to document precisely in bioturbated deep sea sediments. In addition, layer counting of ice cores provides this archive with absolute age control that is superior to that of current sediment age models. In this paper we present data from a new archive, deep-sea corals, that can overcome these limitations of sediment records and provide well dated, unbioturbated documentation of short intervals of deep-sea behavior during rapid climate events.

Deep-sea corals are especially useful in several ways. First, the coralline skeleton is enriched in uranium compared to other carbonate skeletons. This enrichment allows us to use Th/U Thermal Ionization Mass Spectrometry (TIMS) techniques to precisely and accurately date individual samples (Smith *et al.*, 1997; Cheng *et al.*, 1999). Coupled Th/U and Pa/U dates from Atlantic deep-sea corals have shown concordance between these two decay schemes (Mangini *et al.*, 1998). Second, preliminary work on growth rates of one aragonitic species of deep-sea coral, *Desmophyllum cristagalli*, constrains its vertical extension to be between 0.2 and 1.0 mm/yr (Adkins, 1998). This rate of deposition can potentially provide a continuous record of tracer behavior over a few hundred years at decadal or even sub-decadal resolution. Finally, the combination of uranium series ages and radiocarbon ages from the same deep-sea coral sample provide a new measurement of deep circulation rate. Because uranium series data constrain the absolute age of a sample, the radiocarbon age constrains the initial ^{14}C content of the coral at the time of growth. This initial value is directly related to the past water Δ^{14}C and is therefore a measure of the ^{14}C ventilation age of the water mass. These data add rate information to our current understanding of past deep circulation geometry. All three of these aspects of deep-sea corals are exploited in this paper to better constrain the climate's behavior and the deep Atlantic's circulation near 15.4 ka. In the first part of this paper, we describe a new method for screening large numbers of corals for their ages in a relatively inexpensive and fast procedure. The second half of the paper further elucidates a deep-sea coral record of rapid deep circulation change that has already appeared in the literature (Adkins *et al.*, 1998). Here we emphasize a conundrum in the relative timing of deep circulation and atmospheric temperature change at 15.4 ka and propose a way of viewing deep-sea coral data that graphically displays how ventilation ages can be calculated from this new archive.

2. AGE SCREENING METHOD

Precise and accurate ages for marine carbonates are generally obtained from one of two radiometric dating techniques. Accelerator Mass Spectrometry (AMS) is useful for sample sizes of several milligrams of $CaCO_3$. However, due to varying abundances of ^{14}C in the atmosphere over the past 35,000 years, these ages need to be "calibrated" with archives of known ages including tree rings (Kromer and Becker, 1993; Pearson *et al.*, 1993; Stuiver and Becker, 1993) and surface corals (Bard *et al.*, 1990; Bard *et al.*, 1993; Edwards *et al.*, 1993). TIMS dating of uranium series nuclides requires larger samples of phases that have appreciable uranium contents but can provide an absolute measurement of the samples calendar age without calibration. Advances in the analytical techniques for TIMS dating have shrunk the potential error bars for coral analyses to be routinely less than ±1% (Edwards *et al.*, 1998). Unfortunately, both AMS and TIMS methods are time consuming and expensive. With over 300 deep-sea corals from collections world wide, we required a method for rapid and inexpensive dating. Previous work on excess ^{230}Th in marine sediments demonstrated that Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) is faster than, and equally as precise as, α-counting methods for determining ^{230}Th concentrations (Shaw and Francois, 1991). Based on this study, we developed a ^{238}U and ^{230}Th ICP-MS technique to screen deep-sea corals for their ages. Though not as precise as TIMS or AMS dating, this screening process allows us to efficiently determine which specimens are suitable for further study by dividing them into ~5,000 year wide age "bins". Our new method, described below, is especially useful for deciding which corals grew during the 5–35,000 year old age window that is appropriate for ^{14}C paleo-ventilation rate studies of the deep ocean.

2.1. Analytical Procedures

In studies of surface corals, the ^{238}U-^{234}U-^{230}Th age equation is commonly used with the assumption that there is no initial ^{230}Th. Fossil deep-sea corals, on the other hand, may have unsupported ^{230}Th from either adsorption from the water column and incorporation into the aragonite lattice or from an Fe/Mn oxide crust formed after the coral grew. This crust traps aluminosilicate minerals and seawater detritus on the exterior of the coral that are very rich in ^{232}Th. With an understanding of the initial ^{230}Th/^{232}Th ratio of this contaminating Th and a measurement of the [^{232}Th], equation 1 can be used to calculate a sample's age:

$$\frac{A_{230}}{A_{238}} = 1 + \left(A_{232}^{meas} \left(\frac{A_{230}}{A_{232}} \right)^{0} \frac{1}{A_{238}} - 1 \right) e^{-\lambda_{230}{}^{t}} + \frac{\partial^{234}U(0)}{1{,}000} \left(\frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} \right) \left(1 - e^{(\lambda_{234} - \lambda_{230})^{t}} \right) \qquad (1)$$

However, many samples are so encrusted that a series of cleaning stages can greatly reduce the measured activity of the ^{232}Th term in equation 1 and therefore the age error due to uncertainty in the initial ^{230}Th/^{232}Th ratio (Adkins, 1998; Cheng *et al.*, 1999). Lattice bound sources of unsupported ^{230}Th are small, relative to both this crustal contribution and the relatively large error bars we are willing to accept in this screening method. Crusts appear to be bound to the coral skeleton by a reduced carbon phase akin to an "organic glue". We developed a series of oxidative leaches, which are described below, to dissolve this binding phase. The full cleaning procedure for trace metal analysis, precise U-series analysis and AMS radiocarbon dating are described elsewhere (Adkins, 1998).

A flow diagram of the entire age screening process is shown in Fig. 1. Approximately one gram samples are mechanically cleaned with a brush and distilled water to remove sediment trapped inside the coral and between the septa. Samples are then immersed in a 50/50 mixture of 30% H_2O_2/1N NaOH and ultrasonicated for 15 minutes. This process is repeated several times and occasionally, between oxidizing steps, samples are again scrubbed with a brush. Oxidizing steps are stopped once there is very little black crust left on the sample. However, this process often leaves a brownish-orange organic stain on the aragonite. Quick dips (30 seconds to 2 minutes) in a 50/50 mixture of 30% H_2O_2/1% $HClO_4$ efficiently remove this stain. The perchloric acid also dissolves about 5–10% of the sample. It is important to note that the solution's pH is always less than 2 during this step so that thorium released during cleaning is likely to remain in solution. Small siphons to remove spent cleaning solutions and plastic racks to hold samples aid in the mechanics of the cleaning process. After the dilute perchloric step, corals are rinsed thoroughly with clean distilled water.

To facilitate dissolution, samples are crushed into several smaller pieces with an agate mortar and pestle. Five milliliters of concentrated (16N) HNO_3 are added to the reservoir of a capillary, gravity drip coral dissolver, and the sample is placed underneath in a clean pre-weighed 16 ml polyethylene tube. Samples are left to dissolve overnight. Because the coral samples react vigorously with the addition of concentrated nitric acid, the dripping apparatus is necessary to allow for unattended spill-free dissolution. After dissolution, 20 μl of ^{229}Th spike (~10 nM) is added to the sample, the total weight of solution is measured and the sample is vortex mixed. A 25 μL aliquot is removed from the solution, spiked with 250 μL ^{235}U standard and then diluted with 1.5 ml of 0. 1N HNO_3. This solution is run directly on the ICP-MS to determine the ^{238}U abundance. After ^{230}Th analysis, the weight of the uranium aliquot is compared to the total weight

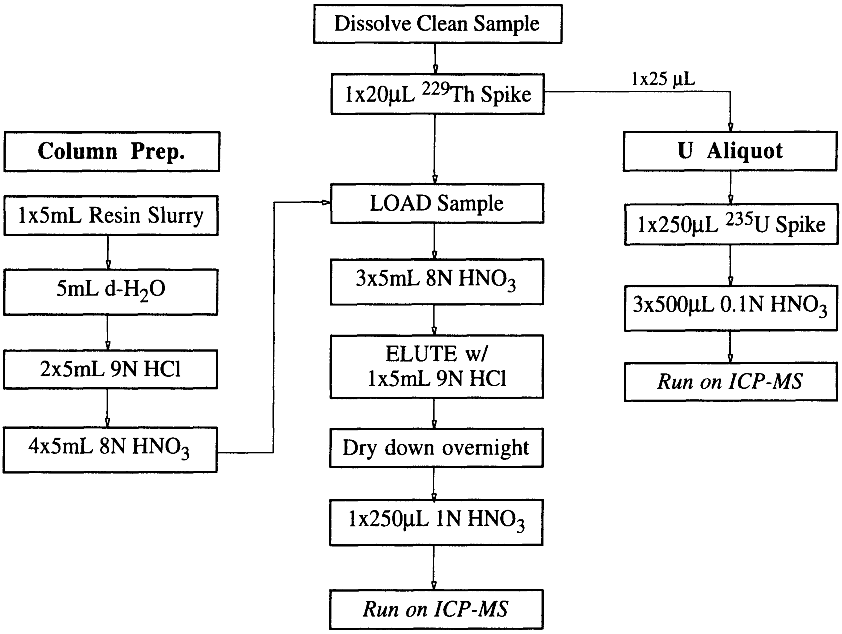

Figure 1. Flow diagram of the age screening technique. The center column outlines the analysis of ^{230}Th from dissolution to detection on the ICP-MS. After dissolution, a small uranium aliquot is taken off for ^{238}U and ^{232}Th measurements in order to preserve counting time on the bulk sample for ^{230}Th. The first column shows the column chemistry preparation. Samples are cleaned prior to entering the flow diagram at the dissolution step.

of the dissolved sample in order to calculate the original ^{230}Th/^{238}U ratio in the sample solution.

^{230}Th is purified and concentrated from the bulk solution with an anion exchange column. Five milliliters of a 50/50 mixture of wet Dowex AG1-X8 100–200 mesh resin and 8N HNO_3 are added to cleaned Kontes polyethylene columns. Distilled water is used to wash the resin into position. Approximately four column volumes of 9N HCl, the eluant for thorium, are added to eliminate any blank. Columns are pre-conditioned with 20 ml of 8N HNO_3 and the dissolved sample is loaded directly onto the resin. 15 ml of 8N HNO_3 are used to rinse the columns of major ions while still retaining the thorium. Without this rinse, calcium clogs the sample aperture of the mass spectrometer and dramatically decreases instrument sensitivity. The gain in ICP-MS sensitivity outweighs the small Th loss from the 15 ml of rinse solution.

Column concentration and purification are completed by eluting the sample with 5 ml of 9N HCl into a conical bottom acid-leached Teflon vial and drying down overnight. The residual is taken up in 250 μl of 0.1N HNO_3 and run on the ICP-MS (Fig. 1). By adding ^{232}Th to a synthetic coral solution, and spiking with ^{229}Th after elution, we determined the column efficiency to be between 40–50% (Adkins, 1998). Additional rinses with 9N HCl, after the 5 ml elution step, remove less than 10% of additional thorium. Replicate column blanks measured with each set of ten samples rarely showed ^{230}Th amounts above background on the ICP-MS.

Because a new ICP-MS was purchased during this study, measurements of uranium and thorium were made on two different machines. Mass 229/230 ratios are adjusted for

Table 1. Th SGS ICP-MS statistics

		Total counts		Daily Statistics		
Date	Machine	229	230	Average	Stdev	RSD
7/25/95	Old	3,990	2,744	1.466	0.051	3.51%
7/26/95	Old	4,001	2,761	1.477	0.041	2.78%
7/31/95	Old	3,586	2,457	1.476	0.041	2.81%
11/8/95	Old	3,605	2,468	1.453	0.060	4.12%
11/26/95	Old	3,510	2,533	1.479	0.034	2.31%
12/6/95	Old	4,485	2,806	1.475	0.026	1.76%
2/18/96	New	189,758	129,333	1.467	0.006	0.39%
3/11/96	New	196,706	133,206	1.479	0.006	0.41%
4/6/96	New	55,023	37,265	1.479	0.015	1.03%
4/7/96	New	78,206	52,868	1.481	0.018	1.19%
6/1/96	New	107,175	72,212	1.484	0.010	0.70%
7/7/96	New	74,017	50,047	1.478	0.012	0.81%

	Summary Statistics		
Machine	Average	Stdev	RSD
Old	1.470	0.044	2.96%
New	1.479	0.012	0.81%

instrumental bias by running a spiked gravimetric standard (SGS) of known 229/230 ratio several times during a run. Long term stability of the SGS ratio is very good (Table 1). As can be seen from Table 1, the ^{229}Th/^{230}Th ratio precision generally follows counting statistics. For the first 100 samples, a VG PQ 1 was used. All subsequent analyses were done on a 10–20x more sensitive VG PQ2+. This upgrade in machines allowed for two important changes; peak jumping, rather than scanning, was used for the 229 and 230 peaks, and the sample size was reduced to 0.5 grams. Switching to peak hopping also allowed for the measurement of ^{232}Th in the ^{238}U fraction. These detrital thorium measurements better constrain the extent of cleaning of individual samples and therefore give more accurate ages (see equation 1 and (Cheng *et al.*, 1999)).

2.2. Results

Reproducibility of the age screening method was examined by measuring six samples on two separate occasions. Figure 2 shows that within the age errors (this test was run on the less sensitive old ICP-MS) the two runs agree. There is a slight systematic bias to older ages for the first run over the second run that may be due to different cleaning intensities. Neither of these runs included ^{232}Th measurements which can account for variable cleaning. In addition, ICP-MS ages from the modified PQ2+ method were compared to TIMS ages for several samples. Figure 3 shows that the ICP-MS and TIMS ages agree and that the screening technique is accurate as well as precise. There is a tendency for older samples to fall off the 1 : 1 line in Fig. 3. However, there is good agreement in the crucial range of the radiocarbon age window, 5–35,000 years.

All of our age screened samples are shown as a histogram in Fig. 4A. About 60% of our samples fall in the modern, 0–5,000 year age window. There are over 50 samples that span the age range from the early Holocene to glacial stage 2. All of these are interesting for paleo-ventilation age work and several of the samples will be discussed in more detail in the second part of this paper. Nearly all of the samples in Fig. 4 are from the Atlantic Ocean with the majority of them coming from the subtropics and the northern

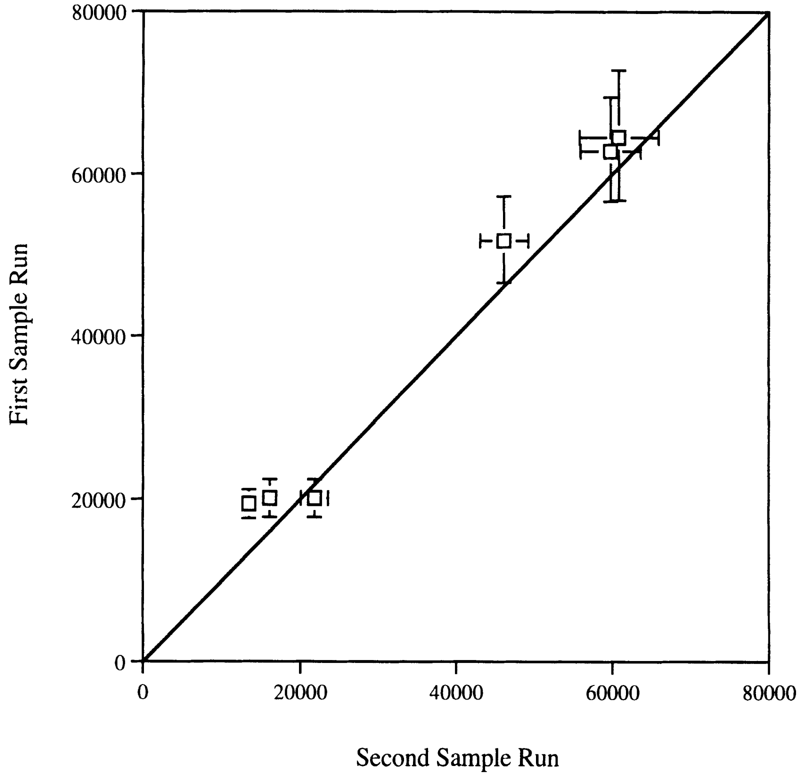

Figure 2. Replicate analysis of the same set of deep sea corals measured on separate days. The black line represents perfect 1:1 correlation. These data were collected on the old ICP-MS at MIT (see text).

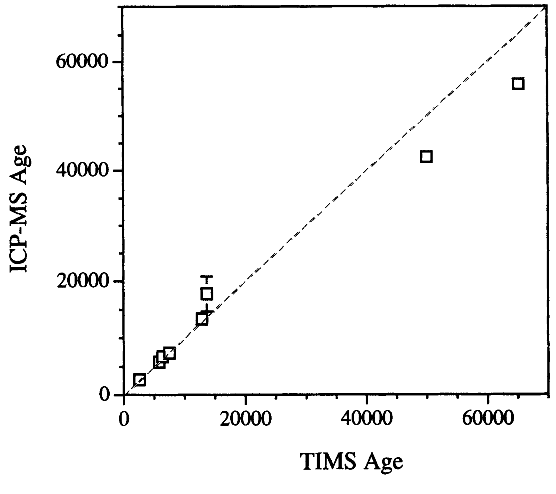

Figure 3. Comparison of TIMS and ICP-MS ages on the same sample. Data are from the same individual coral but from different pieces of this coral. Cleaning runs were also done separately.

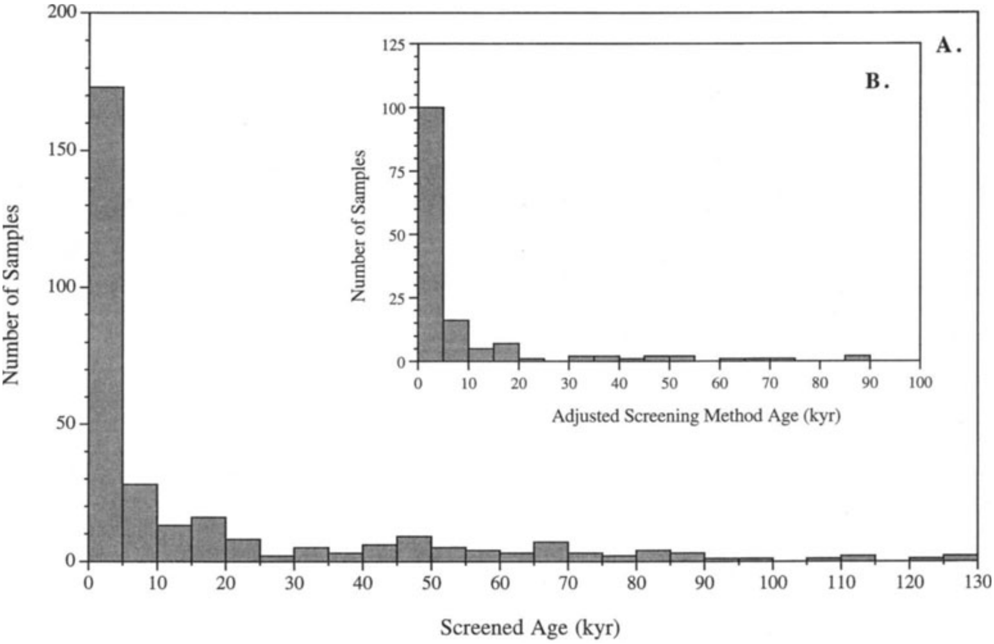

Figure 4. Histogram of screened ages for all our deep-sea corals run to date. Panel A has all of the samples plotted together. Panel B is that subset of samples from A that were run on the new ICP-MS at MIT and include the ^{232}Th correction. Panel B has a younger spread of ages which may indicate that the oldest samples in A. might be contaminated by unsupported ^{230}Th.

sub-polar regions. While there are considerable numbers of deep-sea corals from isotopic stages 3–5 in Fig. 4A, some of these may be biased by the screening method which did not include ^{232}Th corrections. The inset of Fig. 4B is a histogram of the sub set of samples from Fig. 4A that were run on the new ICP-MS with the ^{232}Th age corrections included. There are no samples older than about 90,000 years in this data and very few on the long tail beyond about 40,000 years. None of the oldest samples in Fig. 4A were run again with the new method, but we expect that some are compromised by unsupported ^{230}Th. Overall, this new ICP-MS age screening method offers a rapid and inexpensive alternative to AMS or TIMS dating for large numbers of samples where precise ages are not a priority.

3. 15,400 YEAR OLD CORALS

The screening technique described above identified several corals from the western basin of the North Atlantic that yielded interesting climatic information. These samples were measured for their coupled TIMS and AMS ages. Combined together, these two ages yield the Δ^{14}C of the water in which the coral grew (Adkins and Boyle, 1997):

$$\Delta^{14}C_{Deep\,Water} = \left(\frac{e^{-^{14}CAge/8033}}{e^{-Calendar\,Age/8266}} - 1 \right) \times 1{,}000 \tag{2}$$

The values 8,033 and 8,266 are the Libby and the true mean ages of ^{14}C respectively. The calculated $\Delta^{14}C$ is labeled as the deep water value because it has been established that there is a direct relationship between the $\Delta^{14}C$ of modern seawater and the radiocarbon age of coral skeletons grown in that water (Adkins, 1998). Today, $\Delta^{14}C$ values of Atlantic deep waters are a combination of mixing between waters of different initial radiocarbon contents and aging of the water mass. Measurements of Cd/Ca variations in a coral's skeleton record the variations in nutrient concentration in the deep water during the coral's growth and can therefore help to constrain the mixing portion of the $\Delta^{14}C$ signal in the past (Adkins, 1998). Both of these types of data were used in a previous paper to show that there was a rapid change in the deep circulation of the north Atlantic's western basin at 15.4 ka (Adkins *et al.*, 1998). Here, we briefly review those data in order to discuss two points about phasing in the climate system and deep water ventilation ages not fully developed in the previous work.

Two important changes have been made in the data table from our previous publication (Table 2). First, the calendar age error bars for some of the samples in Adkins *et al.* (1998) were underestimated. Our dating technique uses an assumed initial atomic $^{230}Th/^{232}Th$ ratio of $85 \pm 80 \times 10^{-6}$ and the measured [^{232}Th] to account for unsupported initial ^{230}Th. For some samples in Table 1 of the *Science* paper we incorrectly used an initial ratio of $80 \pm 40 \times 10^{-6}$. A new data table is presented here with the correct error estimates. In addition, recent work on secular equilibrium materials has shown that the ^{230}Th and ^{234}U half lives are slightly different than previously reported (Cheng *et al.*, 1999). Ages and $\delta^{234}U$ values in Table 2 of this paper also include the revised decay constants as well as the proper error estimates. Neither of these chages alter the conclutions of our previous publication.

Figure 5A shows deep-sea coral derived $\Delta^{14}C$ values for western North Atlantic intermediate waters during the last deglaciation. At 15.4 ka there are four corals from the New England sea mounts that have the same calendar age but a large range of calculated $\Delta^{14}C$ values. Measurements of the radiocarbon ages from the tops and bottoms of three of these corals show older ages at the tops than at the bottom. These age differences range from 120 to 670 radiocarbon years in different individuals. Because the growth pattern of this species is such that aragonite is precipitated first at the bottom and then extends upwards through time, the top to bottom age differences must represent switches in the coral's, and therefore the deep water's, initial $\Delta^{14}C$. The largest top/bottom age difference, 670 radiocarbon years from sample number JFA 24.8, corresponds to an ~80‰ change in the deep waters. Because the modern range of $\Delta^{14}C$ in the entire pre-bomb Atlantic ocean is only about 100‰ (Broecker *et al.*, 1991), this result implies a shift from nearly pure northern source waters to nearly pure southern source

Table 2. New Ages and Errors for Deep-Sea Coral Samples

Sample Number	^{238}U (ppb)	^{232}Th (ppt)	Measured $\delta^{234}U$	$^{230}Th/^{238}U$ (activity)	Calendar age (years)	Initial $\delta^{234}U$	$\Delta^{14}C$ (‰)
JFA 24.8	3,460 ± 3	1,813 ± 51	147.0 ± 1.4	0.15404 ± 0.00081	15,440 ± 260	153.6 ± 1.5	196 ± 40
JFA 24.19	3,623 ± 3	1,175 ± 44	145.9 ± 1.9	0.15294 ± 0.00056	15,440 ± 170	152.4 ± 2.0	96 ± 26
JFA 20.10	3,943 ± 3	2,754 ± 64	145.3 ± 1.2	0.15455 ± 0.00105	15,440 ± 350	151.8 ± 1.3	130 ± 50
JFA 24C	3,858 ± 1	3,255 ± 36	141.3 ± 1.3	0.15434 ± 0.00059	15,400 ± 400	147.6 ± 1.4	115 ± 55
JFA 2	3,752 ± 2	1,723 ± 26	141.3 ± 1.5	0.13731 ± 0.00068	13,740 ± 230	146.9 ± 1.6	166 ± 34
JFA 17	3,851 ± 1	877 ± 22	143.6 ± 1.3	0.12923 ± 0.00057	12,950 ± 120	149.0 ± 1.3	94 ± 18

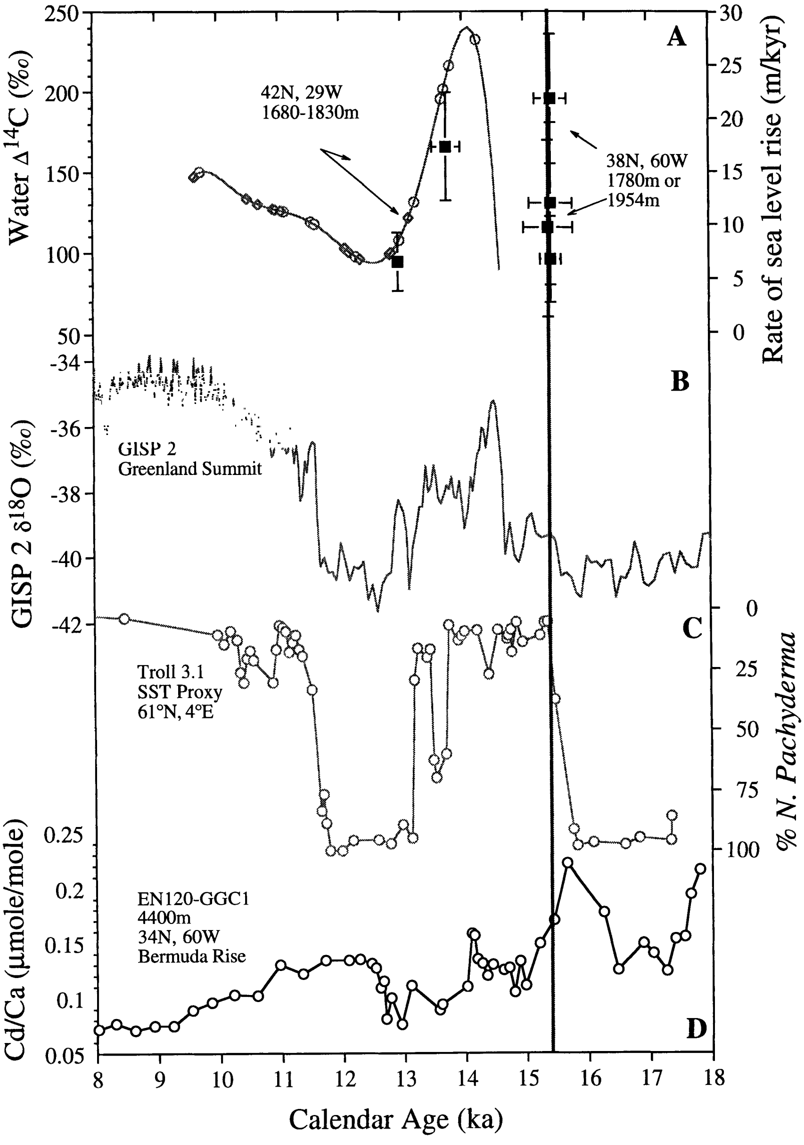

Figure 5. Records of climate change that span the deglaciation. **A**. Deep-sea coral derived $\Delta^{14}C$ measurements for intermediate waters of the North Atlantic (Adkins *et al.*, 1998). **B**. Oxygen isotope values of the ice at Greenland summit (Dansgaard *et al.*, 1993; Grootes *et al.*, 1993). This measurement largely reflects the temperature of the polar atmosphere at 3,000 meters over Greenland. **C**. Relative abundance of the cold dwelling planktonic foraminifera *N. pachyderma* in core Troll 3.1 from the Norwegian margin. **D**. Cd/Ca record of benthic foraminifera from core EN120-GGC1 on the Bermuda Rise.

waters during the coral's lifetime. JFA 24.8 also has a nearly factor of 2 increase in the Cd/Ca ratio from bottom to top, adding strength to the argument that all of these corals are recording a deep circulation change. From estimates of the growth rates in modern samples of this species, we estimate that the longest this individual could have lived is about 160 years. This rapid and large amplitude shift in deep circulation implies that there was a local water mass gradient in nutrients and $\Delta^{14}C$ that moved across the corals during their lifetime. Evidence for such a water mass boundary in the LGM north Atlantic has been well documented from $\delta^{13}C$ values in benthic foraminifera (Oppo and Lehman, 1993).

3.1. Deep Ocean/Atmosphere Phasing

Because we do not have corals from other depths and locations at 15.4 ka, it is not yet possible to determine the extent of this deep water reorganization from the coral data. However, there are several other climate records that show a significant contemporaneous event with the deep-sea corals. Figure 5C shows that in the high latitude north Atlantic the relative percentage of the left coiling planktonic foraminifera *N. pachyderma* dropped dramatically at 15.4 ka. This is probably an indication that the polar front migrated northward across the core site at this time. The age model used here accounts for a 440 year reservoir age of the surface waters at the site of Troll 3.1 (Lehmann and Keigwin, 1992). Recent work from the same site found an 800 year reservoir age during the Younger Dryas by using the Vedde Ash layer as an independent chronological marker (Haflidason *et al.*, 1995). These authors argue that the larger reservoir correction should be made at this site throughout the deglaciation in order to make the ice core and % *N. pachy.* records synchronous. However, this assumption actually requires an unreasonably large 1,100 year radiocarbon age, rather than 800 years, for the high latitude surface waters of the North Atlantic. In the absence of documented large reservoir ages outside of the Younger Dryas period, we adopt the 440 year modern day reservoir age, similar to the value found for the sub-topical feed waters to this site during the deglaciation (Bard *et al.*, 1993), that was used in the original age model (Lehmann and Keigwin, 1992). In addition to the Troll 3.1 evidence, Cd/Ca ratios from benthic foraminifera at 4,400 meters on the Bermuda Rise show a dramatic decrease at around 15.4 ka. This deep benthic signal is the inverse of the intermediate water signal seen in the deep-sea corals and supports the interpretation that deep waters of a northern origin, that previously were at shallower depths, densified and bathed the abyssal western Atlantic after 15.4 ka, leaving more nutrient rich, older southern source waters to bathe the corals at 1,800 meters (Adkins *et al.*, 1998). This type of "mirror image" between deep and intermediate nutrients in the western North Atlantic during the deglaciation has been conclusively documented by Cd/Ca measurements from benthics at 965 meters depth on the Bahamas banks (Marchitto *et al.*, 1998).

However, one record in Fig. 5 does not correlate at 15.4 ka. Neither the deep-sea coral evidence nor the surface and deep foraminiferal data at 15.4 ka correlate with the largest warming of the deglaciation, as recorded in the $\delta^{18}O$ of Greenland ice. Layer counting, dust data and electrical conductivity measurements all constrain the age of this warming to be 14,600 ± 300 years in the GISP2 core (Meese *et al.*, 1997). The most popular explanation for the cause of this rapid atmospheric warming at the Bolling/Alerod transition is a reinvigoration of NADW production (Broecker and Denton, 1989). However, we find the surface and deep oceanic expression of this deep circulation switch 840 ± 340 years before the atmospheric signal. Variations in surface reservoir age in Troll 3.1 and sparsely dated depth horizons in EN120-GGC1 can possibly explain why the sediment cores do not correlate with the ice core. But the U-series dated deep-sea coral record is constrained to 15,440 ± 170 years by the most precisely dated samples. Given the precise dating of the two archives, it is difficult to reconcile the ice core and deep-sea coral ages.

Other well dated benthic circulation records, not shown in Fig. 5, show a large event at around 13,000 radiocarbon years, which corresponds to a calendar age of 15.4 ka (Bard *et al.*, 1992) and supports the deep-sea coral chronology. From core RC 11–83 at 4,718 meters deep in the Atlantic sector of the Southern Ocean, Charles and Fairbanks find the largest $\delta^{13}C$ shift of the deglaciation to occur between 12.9 ± 0.1 and 13.2 ± 0.1 radiocarbon ka (Charles and Fairbanks, 1992). The sense of this shift, from southern source waters to northern source waters bathing the site, is the same as that found at the Bermuda Rise (Fig. 5D) and the eastern basin of the North Atlantic (Sarnthein *et al.*, 1994). Oppo and Lehman (1995) found that the benthic $\delta^{13}C$ switch characterizing the glacial to interglacial transition in core V29–202 (60°N, 21°W, 2,658 m) began before $13.05 \pm 0.8\,^{14}C$ka and continued until the early Holocene. These authors also document a drop, prior to $13.0\,^{14}C$ka, in the $\delta^{18}O$ and the percentage of *N. pachyderma*, indicating a warming of surface waters over the site. Using the $\delta^{18}O$ of both benthics and planktonics in core ENAM93-21 on the Iceland-Faroe Ridge, Rasmussen *et al.* (1996) and Vidal *et al.* (1998) find that the isotopically light meltwaters from Heinrich event 1 have mixed away from both the surface and 1,000 meters depth by $13.2 \pm 0.16\,^{14}C$ka. Therefore, just prior to the deep-sea coral circulation signal, the salinity cap that prevented dense NADW from filling the North Atlantic during Heinrich event 1 was removed. While we have no concrete explanation for the reason behind the 800 year phase difference between the deep ocean and atmosphere, we note that both chronologies are well constrained and this problem will be difficult to reconcile with dating uncertainties. One possible resolution is the observation that the smaller atmospheric warming that marks the beginning of the glacial to interglacial switch in the Greenland ice core does correlate, within error bars, with the 15.4 ka deep event. Why the large switch in deep circulation correlates with a relatively small temperature rise is also not clear.

3.2. Ventilation Ages

Oceanographers have traditionally used the radiocarbon clock as a measure of deep water ventilation age. Less affected by biological processes than $[O_2]$, the ^{14}C clock is reset at the surface by gas exchange with the atmosphere and decays with a half life similar to the mean ocean overturning rate. Globally distributed radiocarbon measurements of dissolved inorganic carbon (DIC) during the GEOSECS program in the 1970s showed that the oldest waters, found in the intermediate north Pacific, are about 2,200 ^{14}C years old (Ostlund *et al.*, 1987) and that the western Atlantic is on average less than 100 years old once mixing is accounted for (Broecker *et al.*, 1991). Surface corals that grew before nuclear testing show that the ^{14}C clock is not fully reset upon contact with the atmosphere because tropical surface waters were consistently 400 years old (Druffel and Linick, 1978; Druffel, 1981). Variability in this reservoir age (Bard *et al.*, 1994; Austin *et al.*, 1995) is a source of uncertainty in any method of calculating ^{14}C ventilation ages in the past.

With the advent of Accelerator Mass Spectrometry, several labs began to measure the ^{14}C ages of contemporaneous benthic and planktonic foraminifera (Shackleton *et al.*, 1988; Duplessy *et al.*, 1989; Broecker *et al.*, 1990). The difference between theses two ages, it was argued, is a measure of the surface to deep contrast of ^{14}C concentration in the past, and therefore a measure of ventilation age. However, a reanalysis of this data showed that in light of changing atmospheric $\Delta^{14}C$ values, this age difference is not strictly a ventilation age (Adkins and Boyle, 1997). Water masses bathing coeval benthics and planktonics have different initial $\Delta^{14}C$ values if the atmospheric inventory of ^{14}C was changing during the times the water masses reequilibrated at the surface. Given that the atmospheric $\Delta^{14}C$ has dropped by about 300‰ since the LGM, reanalysis of the benthic-planktonic data showed that the mean Pacific ocean was about 400 years older than today. These results are very preliminary and more ventilation age data are clearly needed for both the LGM and the deglaciation.

Here we try to show graphically how our deglacial $\Delta^{14}C$ data can be translated into a ventilation age by analogy with an analysis of modern GEOSECS $\Delta^{14}C$ data. Modern $\Delta^{14}C$ values from the deep Atlantic fall off a conservative mixing line. This non-conservative behavior is due to *in situ* decay of radiocarbon as the water masses age. The data for the modern Atlantic below the density of the Denmark Straits overflow water is plotted in Fig. 6 (after (Broecker and Peng, 1982)). Uncertainties in the end member values for $\Delta^{14}C$ arise from the contamination of surface and newly formed deep waters by bomb ^{14}C. However, other tracers not affected by bomb produced radionuclides can be used to estimate the end member values (Broecker *et al.*, 1991). The North Atlantic end member is slightly older than the 400 year surface reservoir age because of the influence of Gibbs Fracture Zone waters in the NADW mix. Southern Ocean surface waters are not reset at the surface because of their short residence times and the influence of Pacific Intermediate waters in the recirculation around Antarctica.

A similar plot to Fig. 6 can be made for past waters if we know the $\Delta^{14}C$ of the water, and can measure a conservative mixing tracer. We use the Cd/Ca ratios measured

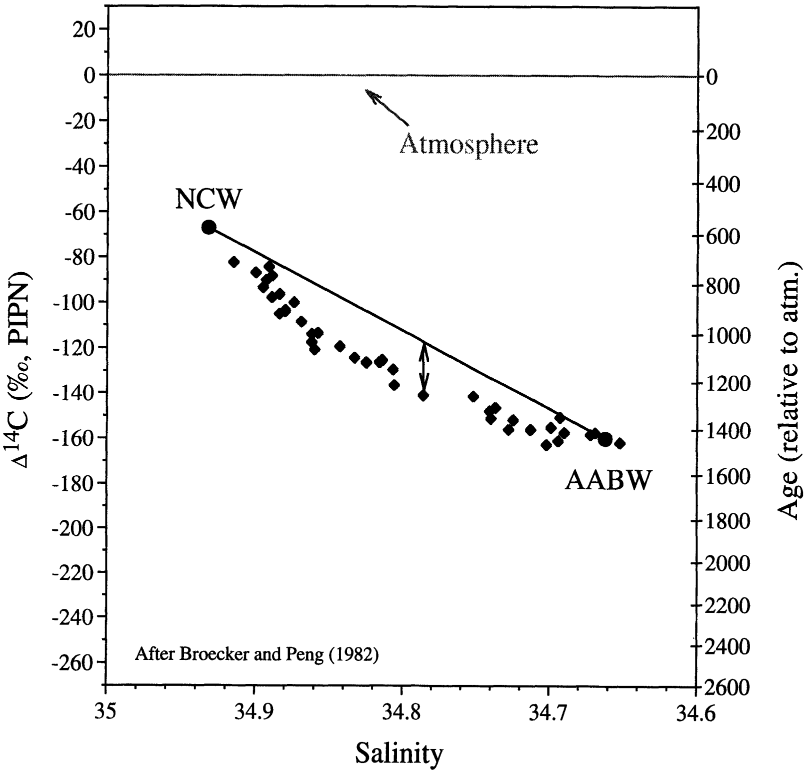

Figure 6. $\Delta^{14}C$ of dissolved inorganic carbon vs. salinity from the GEOSECS data set. Gray diamonds are all data from the Atlantic ocean that are deeper than the two degree discontinuity, roughly the density horizon of the Denmark Straits overflow. End members are chosen according to the criteria in (Broecker and Peng, 1982). The age scale on the right hand side is calculated using the true mean life, 8,266 years, of radiocarbon. The double headed arrow represents an age of 160 years, or about 20‰. An atmospheric value of 0‰ is used for the pre-industrial pre nuclear atmosphere.

in the same deep-sea coral for which we have $\Delta^{14}C$ data as this quasi-conservative mixing tracer. Due to the remineralization of organic matter, deep water masses accumulate Cd as they age. This process is the main reason for the separation of northern and southern end members in Fig. 7. This process is also a source of error in our analysis because relatively stagnant waters can collect cadmium without an influence due to mixing. However, this process would serve to make our conclusions about deep water ages even more extreme. If the southern source water mass had increased [Cd] over its preformed value, the point in Fig. 7 would have to be adjusted to the left, and lie even further from the conservative mixing line. End member values for $\Delta^{14}C$ were chosen by using the same offsets from atmospheric $\Delta^{14}C$ as observed in the modern. In other words, we assumed the same initial radiocarbon age for the end members as today. The $\Delta^{14}C$ value of the atmosphere is relatively uncertain for 15.4 ka and consequently, depending on the value chosen, the black mixing line in Fig. 7 can move up or down with the same slope. There are essentially no concrete constraints on the assumption of modern like initial ages for 15.4 ka. The value for the northern source could probably only be older than today given that the tropical reservoir age has been virtually constant through time. On the other hand, the southern source end member could be either younger or older.

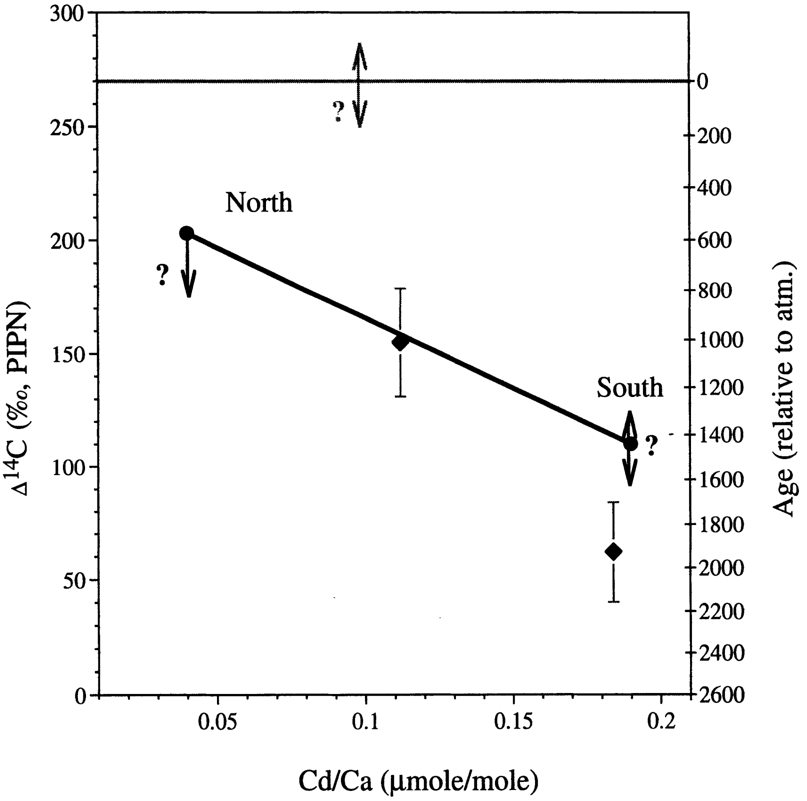

Figure 7. Graphical display of ventilation age for the deep-sea coral data at 15.4 ka. Deep water end members are calculated from the assumed atmospheric value of 270‰ and the modern initial ages for northern and southern components (see text). Gray diamonds are the top and bottom radiocarbon points for sample number JFA 24.8. Arrows represent the direction points could move given uncertainties in the assumption of modern offsets from the atmospheric value. Cd/Ca ratios for the end members were taken from benthic foraminifera records of Cd/Ca variability from the high latitudes.

Uncertainty in these values is the largest source of error in calculating ventilation ages at 15.4 ka.

The two deep-sea coral points from JFA 24.8 are plotted as diamonds in Fig. 7. Even with large error bars relative to the modern data, the slope between these two points is different than the mixing line's. Therefore, no matter what value is chosen for the atmospheric $\Delta^{14}C$, the pure southern source water point, from the top of JFA 24.8, is always older than the mixing line. Waters of a southern origin in the deep Atlantic just prior to 15.4 ka were much more stagnant than they are in the modern ocean, where on average waters are 100 years old or less (Broecker *et al.*, 1991). Only if the initial age difference between northern and southern source waters in the Atlantic at 15.4 ka were 600 years greater than today would the mixing line have the same slope as the coral data. There are at least two reasons why this age difference might be larger at the beginning of the deglaciation. First, according to the reanalysis of benthic-planktonic data, the Pacific ocean was older than it is today (Adkins and Boyle, 1997). Once mixed into the circumpolar current, these older waters could increase the initial age of southern source waters in the Atlantic. Second, a reinvigoration of NADW, after a prolonged shut down, could cause a transient drop in the apparent initial age of northern source waters. Due to both the formation of deep waters and the small mass of total carbon in the atmosphere and surface ocean, most of the ^{14}C produced in the atmosphere today decays in the deep-sea. Therefore, a shut down of NADW would quickly increase the $\Delta^{14}C$ of the atmosphere and surface waters. Reinitiation of deep water exchange with the surface would cause a transient of high $\Delta^{14}C$ values, and therefore younger looking waters, to propagate into the interior of the Atlantic. Because the southern ocean source does not fully equilibrate with the atmosphere even when deep waters are forming there, it is buffered against this type of transient build up in atmospheric $\Delta^{14}C$. One record from a varved Japanese lake appears to show that this process occurred in the past (Kitagawa and van der Plicht, 1998). However the calendar age control on this record is sufficiently poor that we can not conclusively say if the large (about 100‰) shift in atmospheric $\Delta^{14}C$ seen in the lake sediments happened before or after 15.4 ka. It is crucial to understand the order of events before we can use the lake data to further constrain our ventilation age calculation.

4. CONCLUSIONS

The combined advantages of no bioturbation and coupled uranium series and radiocarbon ages make deep-sea corals a useful new archive of deep ocean behavior on short time scales. Age screening using an ICP-MS can efficiently sort through large numbers of coral samples to find individuals that grew during times of rapid climate change. Of the 300 samples we have screened to date over 50 are both older than modern and lie within the ^{14}C age window. Several individuals from this subset show rapid variations in the $\Delta^{14}C$ of the intermediate Atlantic during the early deglaciation. At 15.4 ka there was a shift in both the $\Delta^{14}C$ value and the Cd/Ca ratio of the waters at around 1,800 meters in the western basin of the north Atlantic. This shift is ubiquitous in sediment records of deep circulation and leads the Bolling/Allerod warming by 840 ± 340 years. Coupled TIMS and AMS dates indicate that the southern source waters in the deep Atlantic just prior to 15.4 ka were about 600 years older than their initial value.

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