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The oxygen isotopic composition of seawater during the Last Glacial Maximum

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Abstract

High-resolution oxygen and hydrogen isotope measurements were made on pore fluids from deep-sea sediments from sites in the North and South Atlantic. The data provide direct measurements of changes in the isotopic composition of bottom waters during the Last Glacial Maximum (LGM). Results from Ocean Drilling Program (ODP) Site 981 in the North Atlantic, currently bathed in North Atlantic Deep Water (NADW) reproduces previous results from the Ceara and Bermuda Rises, constraining the glacial–interglacial change in $\delta^{18}O$ of the deep Atlantic to be 0.7–0.8‰. Results from Site 984, which is located north of Site 981 and at a shallower water depth, yield a similar value (0.8‰), providing insight into the properties of Glacial North Atlantic Intermediate Water (GNAIW). Sites from ODP Leg 177 in the South Atlantic span the modern boundary between northern and southern sources of deep water. Data from the northern site (1088) yield a similar result to sites in the tropical and North Atlantic (0.7‰). At the southern site (1093), located south of the polar front, the change is substantially larger (1.1‰), representing the change in $\delta^{18}O$ of southern source waters since the LGM. These results confirm previous estimates that the global average change in $\delta^{18}O$ of seawater is 1.0 ± 0.1‰. Hydrogen isotopes measured on pore fluids from three sites are consistent with the oxygen isotopes from these locations, giving further support to these results. At all sites studied, the temperature of the deep ocean during the LGM, calculated by combining the pore fluid results with oxygen isotope data from benthic foraminifera, was within 1°C of the freezing point of seawater. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Since the 1950s, oxygen isotopic measurements of marine carbonates have been used to reconstruct past ocean temperatures. Such studies have contributed greatly to our understanding of Earth's climatic history, and yet they have been plagued by a fundamental ambiguity in the oxygen isotope paleothermometry technique. The oxygen isotopic composition of marine carbonate reflects both the temperature and the isotopic composition of the water in which it forms. This ambiguity is perhaps most evident in Pleistocene oxygen isotope records of glacial cycles. Cooling during glacial episodes increases the mass-dependent fractionation of oxygen isotopes between water and calcite, resulting in higher $\delta^{18}O$ values of carbonate microfossils. The growth of large ice sheets on continents enriches seawater in ^{18}O, also resulting in higher $\delta^{18}O$ values for carbonate microfossils. Determining how much each of these components contributes to the total change in $\delta^{18}O$ of foraminifera is an important step toward understanding Pleistocene climate change. In addition, knowing how much the $\delta^{18}O$ of seawater changed during the Last Glacial Maximum (LGM) is important to interpreting a variety of other geochemical and isotopic proxies such as the oxygen isotopic composition of O_2 in ice cores (Bender et al., 1994).

The ambiguity inherent in $\delta^{18}O$ records of marine carbonate has been a subject of controversy since Epstein et al. (1951) first introduced the oxygen isotope

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method for reconstructing past ocean temperatures. Over the next several decades, the argument was framed by two contrasting views. Emiliani (1955) argued that planktonic foraminiferal records from the Caribbean primarily reflected fluctuations in seawater temperature, estimating that the Caribbean was 6°C colder during the LGM. The opposite view was expressed by Shackleton (1967) in a paper that presented a benthic foraminiferal $\delta^{18}O$ record for the Pleistocene. Shackleton measured changes in the $\delta^{18}O$ of benthic foraminifera similar in magnitude to those Emiliani had observed in planktonics, concluding that the oxygen isotope records reflected primarily a change in seawater composition (i.e., the effect of ice volume). As additional foraminiferal $\delta^{18}O$ records were produced, it became clear that the change in $\delta^{18}O$ of benthic foraminifera since the LGM is relatively uniform. For example, in a compilation by Broecker (1986), data from 20 sites give an average glacial-interglacial change of 1.71‰ with relatively small variability ($\sigma = 0.08$‰). In contrast, the change in $\delta^{18}O$ of planktonic foraminifera is not as uniform, with higher values in the Atlantic (1.6–3.0‰) (McManus et al., 1999) and lower values in the Pacific (1.2–1.5‰).

Duplessy (1978) attempted to solve this controversy by pointing out that, because the deep ocean was not frozen during the LGM, the difference between modern deep ocean temperature and the freezing point of seawater is the maximum contribution that temperature can make to the $\delta^{18}O$ of foraminiferal carbonate, and hence sets a lower limit on the change in $\delta^{18}O_{sw}$. Duplessy applied this strategy to a southern Indian Ocean site with bottom-water temperature of 0.6°C and a glacial-interglacial change in the $\delta^{18}O$ of benthic foraminifera of 1.65‰, setting the minimum glacial-interglacial change in $\delta^{18}O_{sw}$ at 1.1‰. The problem with this approach is that neither the cooling nor the change in $\delta^{18}O_{sw}$ of the deep ocean during the LGM need be distributed uniformly. A site in the southern Indian Ocean, currently dominated by Antarctic Bottom Water (AABW), could experience minor cooling and have a larger change in $\delta^{18}O_{sw}$. A site in the central Atlantic could tolerate substantially more cooling through a change from North Atlantic Deep Water (NADW) to AABW but experience a smaller change in $\delta^{18}O_{sw}$. This contrast highlights the point that changes in $\delta^{18}O_{sw}$ at a single site are due to both the global ice volume variations and the local circulation switches. The relative uniformity in the $\delta^{18}O$ change in most sediment cores simply is a reflection of the dynamical constraint that deep ocean density be approximately uniform. This point emphasizes the need to obtain independent estimates for the temperature and $\delta^{18}O_{sw}$ change at different locations throughout the world ocean.

An influential argument was made by Fairbanks (1989), who suggested that the contribution of ice volume to the change in $\delta^{18}O$ of foraminiferal calcite is 1.3‰. The value of 1.3‰ grows out of the work of Fairbanks and Matthews (1978) who measured the $\delta^{18}O$ of fossil corals from Barbados that grew at different sea level heights. Because the corals grow only in the upper 5 m of the water column, they were able to calculate how the $\delta^{18}O$ of the coral changed with variations in sea level obtaining a value of 0.011 per mil per meter. If one assumes that that sea surface temperature was constant during this sea level change, then one can obtain the total contribution of ice volume to the change in $\delta^{18}O$ of foraminiferal carbonate simply by multiplying by the total sea level change since the LGM (121 ± 5 m) (Fairbanks, 1989), yielding the value of 1.3‰. This calculation yields a maximum value because of the assumption of constant sea surface temperature over the intervals analyzed by Fairbanks and Matthews (1978). Additional analysis of this result will be discussed below.

Over the last decade, a new approach was developed to measure the change in $\delta^{18}O_{sw}$ directly through the composition of deep sea pore fluids. McDuff (1984) recognized that for oxygen isotopes, chloride, and other relatively non-reactive species, the sediments on the ocean floor behave essentially as non-reactive, porous media with chemical transport in the pore fluid occurring primarily by diffusion. The changes in $\delta^{18}O_{sw}$ caused by glaciation and deglaciation represent a periodic boundary condition for the sediment-pore fluid system, leaving a profile of $\delta^{18}O$ or chloride versus depth in the pore fluid that is a record of the $\delta^{18}O$ history of the overlying seawater. Schrag and DePaolo (1993) showed that, for the sediment-pore fluid system, the attenuation factor is such that modern pore fluid preserves little record of the $\delta^{18}O$ history of the ocean at the frequency of glacial cycles except for the large $\delta^{18}O$ shift associated with the last deglaciation. If the depth and amplitude of the peak of higher $\delta^{18}O$ pore fluid can be measured precisely at a specific location, both the diffusivity of water in the sediments and the $\delta^{18}O_{sw}$ during the LGM can be determined. This approach is exactly analogous to that used to calculate the thermal diffusivity of soils from temperature variations at the Earth's surface (Kelvin, 1861), and to reconstruct past surface temperatures from borehole temperature measurements in ice cores (e.g. Cuffey et al., 1995). Because the existence of this peak of high $\delta^{18}O$ pore fluid depends only on the transport mechanisms in the sediment pore spaces, the presence of a pore fluid signal from the LGM is independent of sediment type and should exist everywhere on the ocean floor where diffusion is the dominant transport mechanism. Schrag and DePaolo (1993), using McDuff's data from DSDP Site 576 in the Pacific, calculated a glacial-interglacial change in $\delta^{18}O_{sw}$ of 1.0 ± 0.25‰. The precision of the calculation was limited by poor sampling resolution

(1 sample every ~10 m) and low analytical precision (±0.1‰).

Schrag et al. (1996) measured a pore fluid profile from Ocean Drilling Program (ODP) Site 925, located at a water depth of 3041 m on the Ceara Rise (4°12′N, 43°29′W) in the tropical Atlantic. Pore fluid was sampled from every section (1.5 m) in the first 50 m at Site 925 to substantially improve the resolution of the data. The model reconstructions for this site yield an estimate of glacial-interglacial change in $\delta^{18}O_{sw}$ of 0.8±0.1‰. The glacial-interglacial difference in $\delta^{18}O$ values of benthic foraminifera in the region of Site 925 is 1.8‰ (Curry and Lohmann, 1990). If the ice volume component of that difference is 0.8‰, then the temperature was 4°C colder during the LGM. As the modern temperature at 3 km water depth near Site 925 is 2.7°C, the water during the LGM cooled to within one degree of its freezing point. The result from Site 925 was surprising in that it is significantly lower than most previous estimates. This result emphasizes that spatial variability is an important component of the problem. As discussed above, previous studies have assumed a determination of the glacial-interglacial change in $\delta^{18}O_{sw}$ at a single location such as Barbados represents a global average (e.g. Fairbanks, 1989). In the modern ocean, the Atlantic at 3000 m depth is more than 1.5°C warmer than the Pacific and Indian oceans and could therefore tolerate substantially more cooling during the LGM. If AABW replaced NADW as the dominant source of deep water for the Atlantic during the LGM, the temperature (and salinity) contrast between the ocean basins would be greatly reduced if not eliminated. This switch in the dominant source of deep water for the Atlantic also helps to explain why we obtain a small change in $\delta^{18}O_{sw}$ for the deep Atlantic (today the $\delta^{18}O$ of AABW is approximately 0.5‰ lower than NADW, although one cannot assume this difference was constant through the LGM).

Schrag et al. (1996) used two different methods of extrapolation from a single site on the Ceara Rise to obtain an estimate of the global average change in $\delta^{18}O_{sw}$ of 1.0‰. Adkins and Schrag (2001) improved on this method of extrapolation by using reconstructions of local salinity changes from chloride measurements in pore fluids to relate the local change in $\delta^{18}O_{sw}$ to the global average value. Using pore fluid samples collected from the Bermuda Rise (ODP Leg 172, Hole 1063A, 33° 41′ N, 57° 36′ W, 4584 m water depth), they calculate a local change in $\delta^{18}O_{sw}$ of 0.75±0.05‰ and a global change of 0.95±0.09. This value is in good agreement with the result of Schrag et al. (1996). Adkins and Schrag (2001) also found that bottom water temperatures at Site 1063, like those from the Ceara Rise, were at or near the freezing point of seawater during the LGM.

In this paper, we present new oxygen isotope data on pore fluids from North and South Atlantic sites. Whereas in previous work we have been limited by a small number of sites, the data presented here allows us to test the reproducibility of previous results across the Atlantic basin. We also present the first high-precision deuterium data from pore fluids from several of these sites. The deuterium content of pore fluid, like oxygen isotopes, will record the change in seawater composition due to continental ice sheets as deuterium will not be affected by chemical reactions in the sediments over the time scale of glacial cycles.

2. Methods

2.1. Site descriptions

All site locations are shown in the map in Fig. 1. During ODP Leg 162 in the North Atlantic, pore fluids were collected at high resolution from two sites. Site 981 is located on the Feni Drift, east of the Rockall Bank, and was deposited along the northwestern flank of Rockall Trough under the influence of geostrophic currents formed by Norwegian Sea overflow waters flowing across the Iceland-Scotland Ridge. The sediment consists of nanofossil ooze and variable amounts of clay, with moderate sedimentation rates over the last million years (~5 cm kyr^{-1}). Site 981 is at 2184 m water depth, and today is predominantly bathed in NADW. However, carbon isotopes on benthic foraminifera suggest that southern source water was dominant during the LGM (Oppo and Lehman, 1993; McManus et al., 1999). In this sense, pore fluid data from 981 are similar to those from the Ceara Rise in the tropical Atlantic, and enable us to reproduce similar results at sites with slightly different boundary conditions (e.g., faster sedimentation rates). Site 984 is located on the Bjorn Drift at a water depth of 1660 m on the eastern flank of the Reykjanes Ridge. Pleistocene sedimentation rates are significantly faster than at Site 981 (10–13 cm kyr^{-1}), with more clay material and lower carbonate content. As this site is approximately 600 km to the northwest of Site 981 and is in much shallower water, pore fluid data from this site can be used to reconstruct waters closer to the core of Glacial North Atlantic Intermediate Water (GNAIW) during the LGM (Oppo and Lehman, 1993).

Pore fluids from several South Atlantic sites were collected during ODP Leg 177. The northernmost site (Site 1088) is located on the Agulhas Ridge north of the Subantarctic Front. This site was drilled at a relatively shallow depth (2080 m), and is bathed in NADW today. Samples were also taken from Site 1093, located at 49.5°S at a water depth of 3640, south of the polar front. Because it is so close to the southern source of deep water, we expected this site to record a substantially

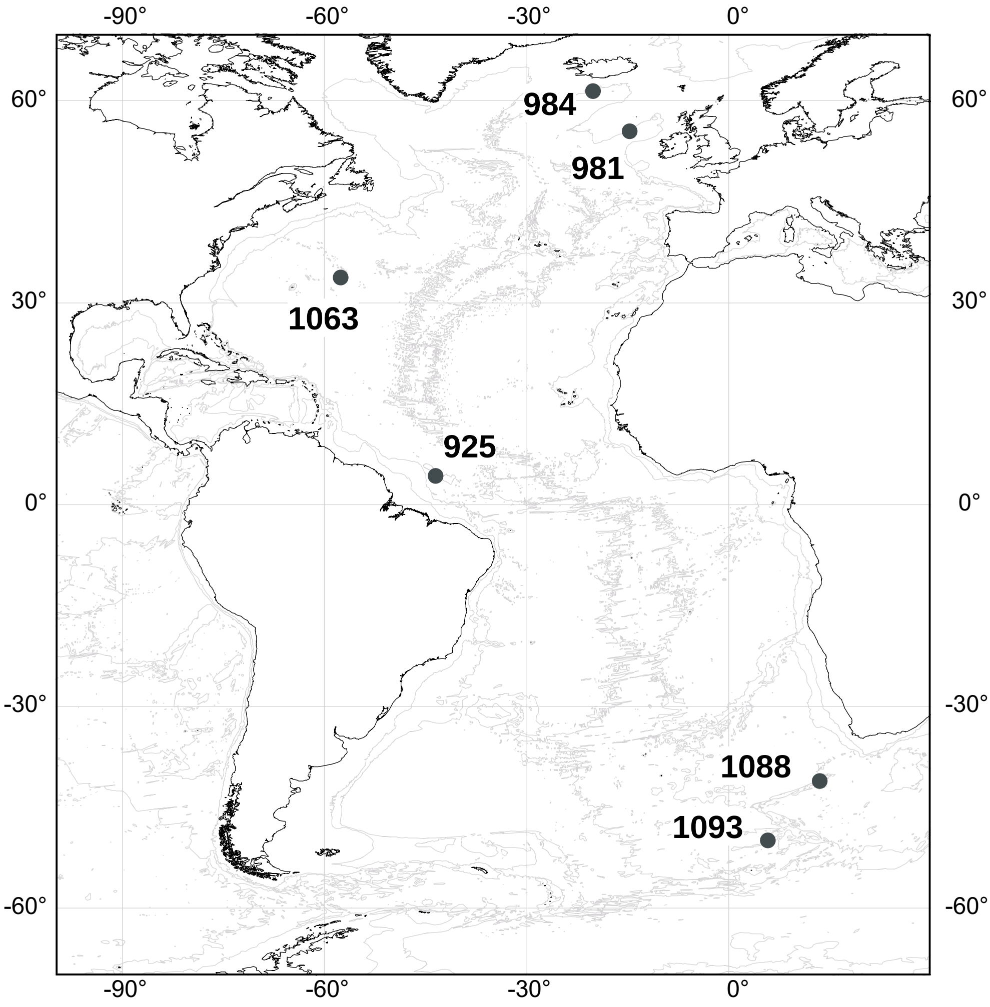

Fig. 1. Map of Atlantic Ocean showing location of ODP Sites discussed in this study.

larger change in $\delta^{18}O_{sw}$ than the other Atlantic sites. Samples were taken from additional sites during Leg 177 but at lower resolution (1 sample every 9 m), inadequate for precise determination of LGM composition.

2.2. Analytical techniques

Interstitial waters were squeezed from whole round samples from all sites following standard ODP procedures. 5 cm^3 of each sample was sealed in glass ampules and transported to Harvard University for analysis. Samples for oxygen isotope analysis were divided in two, and both splits were loaded into glass vessels for analysis using a modified VG Isoprep18 automated Shaker/Equilibrator. Samples were equilibrated with approximately 100 μmoles of CO_2 at 25°C for 24 hours before analysis on a VG Optima gas source mass spectrometer. Following analysis, samples were equilibrated with a fresh injection of CO_2 and re-analyzed. This method provides four replicate analyses for each sample from this hole. The overall precision is 0.03‰, calculated as the standard deviation (1σ) of several hundred replicate analyses of standard water analyzed at the same time as the interstitial water samples. For deuterium, pore fluids were analyzed by injecting them into a Finnigan MAT H/Device attached to a VG Elemental Prism gas source mass spectrometer. For each sample, 1.0 μl of water was injected through a septum using a gas tight syringe directly into a quartz furnace containing powdered chromium metal at 800°C. The reaction proceeds for 120 s, before allowing the H_2 gas to enter the inlet system of the mass spectrometer. An in-house standard (PSW) was calibrated using international standards. The PSW standard has a δD value of -12.09 ± 0.40‰ on the VSMOW-SLAP scale. Small linear drift in δD values during operation of the reduction furnace was corrected by running the PSW standard after every third sample. The average standard deviation of replicate samples measured during analysis of the pore waters is 0.45‰.

2.3. Numerical modeling

We simulate the transport of oxygen and hydrogen isotopes in deep sea pore fluids using a numerical model similar to that described by Schrag et al. (1996) and by Schrag and DePaolo (1993). The sediments are represented by a column of boxes 1 m thick, each with an isotopic composition and porosity. Boxes are added and compacted to simulate sediment accumulation at rates specific to each ODP site. Advection resulting from compaction is modeled by expelling excess fluid from one box into the overlying one. The effective diffusion coefficient (D_{eff}) varies with depth due to the changing tortuosity of the sediments, such that $D_{\text{eff}} = kD_0/\theta^2$ (where D_0 is the diffusion coefficient in water, θ is tortuosity, and k is a constant varied for each site to fit the pore fluid data). For many deep sea sediments $\theta = \phi^{-1}$, giving $D_{\text{eff}} = kD_0\phi^2$. However, the relationship between tortuosity and porosity depends on the sediment composition, and tortuosity is more accurately defined as $\theta = \sqrt{\phi F}$, where F is the formation factor ($F = R/R_0$), where R is the electrical resistivity of the sediment and R_0 is the resistivity of the pore fluid (Klinkenberg, 1951). This is a minor difference that affects how the diffusivity varies with depth, but it does not affect significantly any of the results presented here. The diffusion coefficient (D_0) used is that of the self-diffusion of water, $1.1 \times 10^{-5}\,\text{cm}^2\,\text{s}^{-1}$ (Simpson and Carr, 1958). The top box in the model represents the boundary between the sediment and the overlying ocean, and its isotopic composition is varied through time to simulate changes in seawater composition, reaching the modern bottom water composition at the end of the model simulation.

2.4. Uncertainty in model calculations

A critical feature of modeling the diffusion of the LGM signal in deep-sea pore fluids is that the shape and timing of the deglaciation are relatively well known. This means that the signal we measure in the pore fluid provides independent information about the effective diffusivity and the magnitude of the glacial–interglacial signal. We use a composite benthic foraminiferal δ^{18}O curve spliced with the coral record of sea level change to force the top boundary condition of the model through time. The effective diffusivity coefficient is constrained by the depth of the peak in δ^{18}O; lowering or raising the diffusion coefficient shallows or deepens the peak relative to the sediment–water interface. In this manner, we can determine the effective diffusivity for each site to within approximately 20%, as this difference in diffusivity moves the peak by approximately 4 m, which is well within the resolution of the measured profiles. Variations less than this magnitude result in uncertainties in the final reconstruction of significantly less than 0.1‰. After the optimal diffusivity is determined to match the depth of the peak, the amplitude of the glacial-interglacial δ^{18}O change is varied to yield a best fit to the measured pore fluid data. One of the largest uncertainties in our reconstruction is associated with error in the δ^{18}O of the bottom water at the top of the pore fluid profile. Small differences in this value will directly affect how we define the amplitude of the peak, and will affect the reconstructed change in $\delta^{18}O_{sw}$. Thus, the analytical precision in measuring the bottom water value (better than ±0.03‰) limits the precision of the reconstruction of the glacial–interglacial change in $\delta^{18}O_{sw}$ to no better than 0.05‰. An additional source of uncertainty is the magnitude of vertical advection (beyond that due to compaction, which is included in our calculation). This can distort and attenuate the signal, adding error to our determination of the diffusivity. However, additional pore fluid data (e.g., Ca^{2+}, Mg^{2+}, SO_4^{2-}) that are routinely measured by shipboard scientists on all cruises are sensitive to vertical advection, particularly in the upper 50 m most critical to our reconstruction. Magnitudes of vertical advection that would affect significantly the reconstructed glacial-interglacial change in $\delta^{18}O_{sw}$ cannot be reconciled with the shipboard data at the sites we have studied, in particular the large gradients in Ca^{2+}, Mg^{2+} and SO_4^{2-}. Smaller magnitudes of vertical advection leaving errors much less than 0.1‰ cannot be ruled out. However, we would not expect such errors to be systematic over many sites, and hence the reproducibility of our reconstructions at different sites remains an excellent test of the reliability of our method.

In previous work, we have shown that the model output is insensitive to changes in the shape of the glacial cycle prior to the LGM, as most of this information is lost to diffusive attenuation (Schrag and DePaolo, 1993). However, the timing of the deglaciation over the last 20,000 years is important to the result. For the calculations presented here, we use the Barbados sea-level curve from Fairbanks (1989) with U–Th dates provided by Bard et al. (1990). An uncertainty with this approach is that the exact shape and timing of the change in seawater composition may vary from place to place. We note that in most open-ocean locations in the deep ocean, this variation cannot be very large as ocean mixing is rapid enough to homogenize the extreme differences in salinity and δ^{18}O from the deglaciation over a few thousand years. However, we cannot rule out some significant variations within this time scale, especially in locations near boundaries between water masses of different isotopic compositions. A different approach from using the global sea level curve is to use the measured δ^{18}O record in benthic foraminifera as a proxy for the shape of the change in $\delta^{18}O_{sw}$. The problem with this approach is that the δ^{18}O record is a composite signal, and will only preserve the shape and timing of the change in seawater composition if temperature changes parallel the change in $\delta^{18}O_{sw}$. In addition, age models for such records are generally less well determined as they depend on radiocarbon ages corrected for reservoir effects, or on correlation to orbital variations. Nevertheless, such an approach will address the major concern of having spatially different time histories for the changes in seawater composition over the deglaciation, as the benthic record is a direct measure of local conditions. At Site 981 in the North Atlantic, we performed two different calculations for different $\delta^{18}O$ histories of seawater, one using the Barbados sea level curve (Fairbanks, 1989; Bard et al., 1990), and one using the measured benthic $\delta^{18}O$ record for this site (McManus et al., 1999). Although the exact shape and timing of the forcing functions are quite different, the resulting curves differ by less than 0.05‰. The reason for this surprising result is that the earlier deglaciation history results in more attenuation and deeper penetration into the sediment column. However, in order to fit the depth of the measured peak, the data demand a slower effective diffusivity, offsetting the attenuation. If the same benthic curve were used but with the age model shifted by 2000 years, the model would yield a result within 0.05‰. We have found that this result is also true at other sites, and that uncertainty in the forcing function is not the major source of error in our calculations, at least at the sites we have studied thus far. We also note that the problem of selecting the LGM in the sediment record at an individual site and correlating between sites does not affect any of our calculations. We define the glacial–interglacial change in $\delta^{18}O_{sw}$ to be the maximum amplitude of the forcing function. The precise depth of sediment deposited during the LGM in a particular core does not affect our results.

3. Results

The pore fluid profiles from all sites show the expected pattern of a peak of high $\delta^{18}O$ left from the LGM ocean. The $\delta^{18}O$ values increase over the first 25–40 m below sea floor, followed by a decrease. The exact shape of each profile varies between sites in the depth of the maximum $\delta^{18}O$ values, in the amplitude of the peak, and in the slope of $\delta^{18}O$ at greater depth in the hole. The model predicts these differences in shapes extremely well, adding additional confidence in the reliability of the reconstruction. The North Atlantic sites from Leg 162 demonstrate this feature of the profiles. The maximum $\delta^{18}O$ value at Site 981 is at approximately 25 m, and the amplitude of the peak (maximum value relative to modern seawater) is 0.25‰ (Fig. 2A). At Site 984, the maximum values occur at nearly 40 m below sea floor, and the amplitude is greater than 0.4‰ (Fig. 2B). These differences can be accounted for primarily by differences in the rate of decrease in $\delta^{18}O$ with greater depth in the hole and by the large difference in sedimentation rate between the sites. Site 981, with a relatively slow sedimentation rate ($5\,\mathrm{cm\,kyr^{-1}}$) displays a geometry very similar to Site 925 from the Ceara Rise, which had a sedimentation rate over the Pleistocene of $\sim 3\,\mathrm{cm\,kyr^{-1}}$. The sedimentation rate at Site 984 is two to three times higher than at Site 981, and the decrease in $\delta^{18}O$ towards the bottom of the profile is much more gradual. The more gradual decrease at the base of the profile means that the peak is less affected by diffusive attenuation from below, resulting in a larger peak at greater depth. Although the higher sedimentation rate results in only a small amount of new sediment since the LGM, there is also additional sediment deposited between 50 and 20 ka, during the peak of glaciation. This also reduces the diffusive attenuation of the glacial signal, resulting in a larger peak. Despite these substantial differences in the shape and magnitude of the profiles, both sites provide similar estimates of the glacial–interglacial difference. The best fit for Site 981 uses a glacial-interglacial change in $\delta^{18}O_{sw}$ of 0.7 ± 0.1‰, similar to the value obtained from the Ceara Rise and the Bermuda Rise. At Site 984, the pore fluid suggests a slightly larger change in $\delta^{18}O_{sw}$ (0.8 ± 0.1‰). The modern temperature at Site 981 is 3.0°C, and the measured glacial-interglacial change in benthic foraminifera is 1.9‰, yielding a bottom water temperature during the LGM of -2.0°C. This result reproduces the calculation by Schrag et al. (1996) and Adkins and Schrag (2001), suggesting that deep waters were at or near the freezing point during the LGM. The modern bottom water temperature at Site 984 is slightly higher than at 981 and the benthic change is 2.0‰, yielding an estimate for temperature of North Atlantic intermediate water during the LGM of -1.5°C. This value is slightly warmer than southern source water inferred from the Feni Drift and the Ceara Rise, but substantially cooler than NADW in the modern ocean. An important point is that the magnitude of the glacial interglacial change in $\delta^{18}O_{sw}$ calculated here is based on a smoothed benthic foraminiferal isotope record coupled with the sea level curve from Fairbanks (1989). For high-resolution benthic foraminiferal isotope records, different authors have defined the amplitude in different ways, some emphasizing extreme values while others using an average for the glacial interval from 25 to 20 ka. For the purposes of the diffusion calculations presented here, any high frequency variability during the LGM will not affect the results significantly. Therefore, the reported glacial-interglacial change should be understood as the difference between average LGM and modern bottom water values.

Data from Site 1088 (Fig. 3A) in the South Atlantic show considerable scatter relative to data from Leg 162.

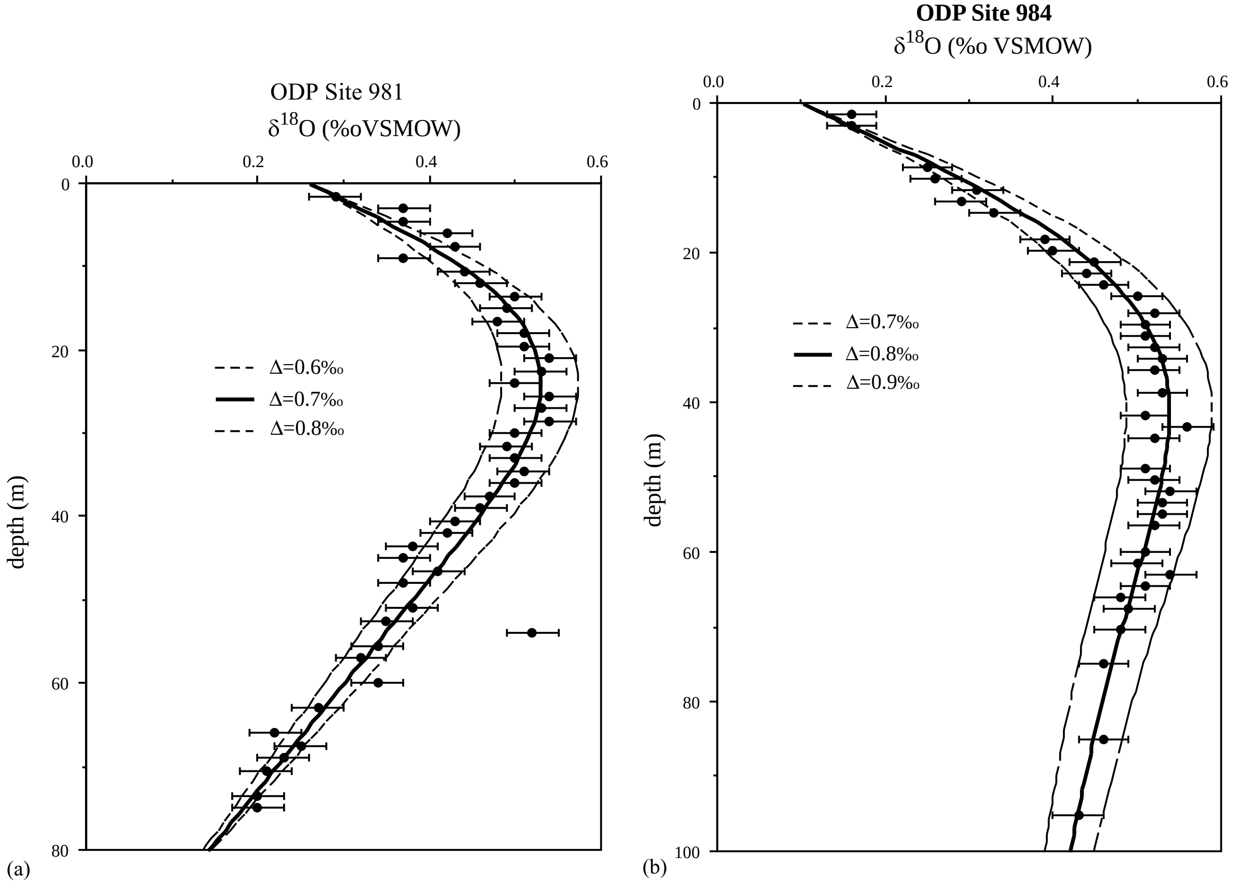

Fig. 2. Oxygen isotope data on pore fluids from ODP Leg 162, Sites 981 (A) and 984 (B). The lines indicate the model results for different changes in the $\delta^{18}O$ of seawater.

Even with the scatter, the peak of high-$\delta^{18}O$ pore fluid from the LGM is clearly visible at a depth of 28 m. The best fit of the model to the data yields a change in $\delta^{18}O_{sw}$ of 0.75‰. Because of the scatter, this determination is less precise than at other sites. This is consistent with the data from the Ceara Rise, and from the North Atlantic. Data from Site 1093 (Fig. 3B), at a greater depth and south of the polar front, tell a very different story. Because Site 1093 is so close to the southern source of deep water, we expected this site to record a substantially larger change in $\delta^{18}O_{sw}$ than the other Atlantic sites. As expected, the pore fluid data from this site yield a much larger value for the change in $\delta^{18}O_{sw}$. The best fit of the model to the data is obtained for $\delta^{18}O_{sw} = 1.2$‰. However, the model value for modern seawater is 0.1‰ higher than the observed value, due to a steepening of the profile in the upper 10 m. This is similar to a slight misfit in the profile at Site 925 on the Ceara Rise (Schrag et al., 1996). This misfit at the top lowers the estimate of the change in $\delta^{18}O_{sw}$ by approximately 0.1‰, yielding an overall estimate of 1.1‰. As we will discuss below, this problem of constant $\delta^{18}O$ values in the top few meters below the seafloor is seen at several other sites, and may be due to a switch in deep water circulation in the Holocene. However, even with the uncertainty of the fit at the top of the profile, the value of $\delta^{18}O_{sw}$ determined from Site 1093 is clearly higher than other sites we have measured thus far, and is consistent with the estimate of the $\delta^{18}O$ value of southern source water during the LGM based on extrapolation from Atlantic sites described above. There are not enough benthic foraminifera in this diatom-rich core to obtain a benthic isotope record. However, based on data from benthic foraminifera from the same region (Ninnemann et al., 1999), we calculate a deep-water temperature within 0.5° of the freezing point of seawater.

Deuterium profiles from the three sites measured are very similar to $\delta^{18}O$ profiles discussed above. For Site 984 in the North Atlantic (Fig. 4A), the best fit of the model curves with the data yield a glacial change in δD_{sw} of 6‰, 8 times larger than what was calculated for $\delta^{18}O_{sw}$. There is substantially more scatter in the profile due to the lower analytical precision relative to the magnitude of the signal, resulting in an overall error in the inversion of slightly greater than 1‰. For the South Atlantic sites, the deuterium profiles reproduce the contrast between Site 1088 and Site 1093 that we observe in the $\delta^{18}O$ data. The best fit of the model to

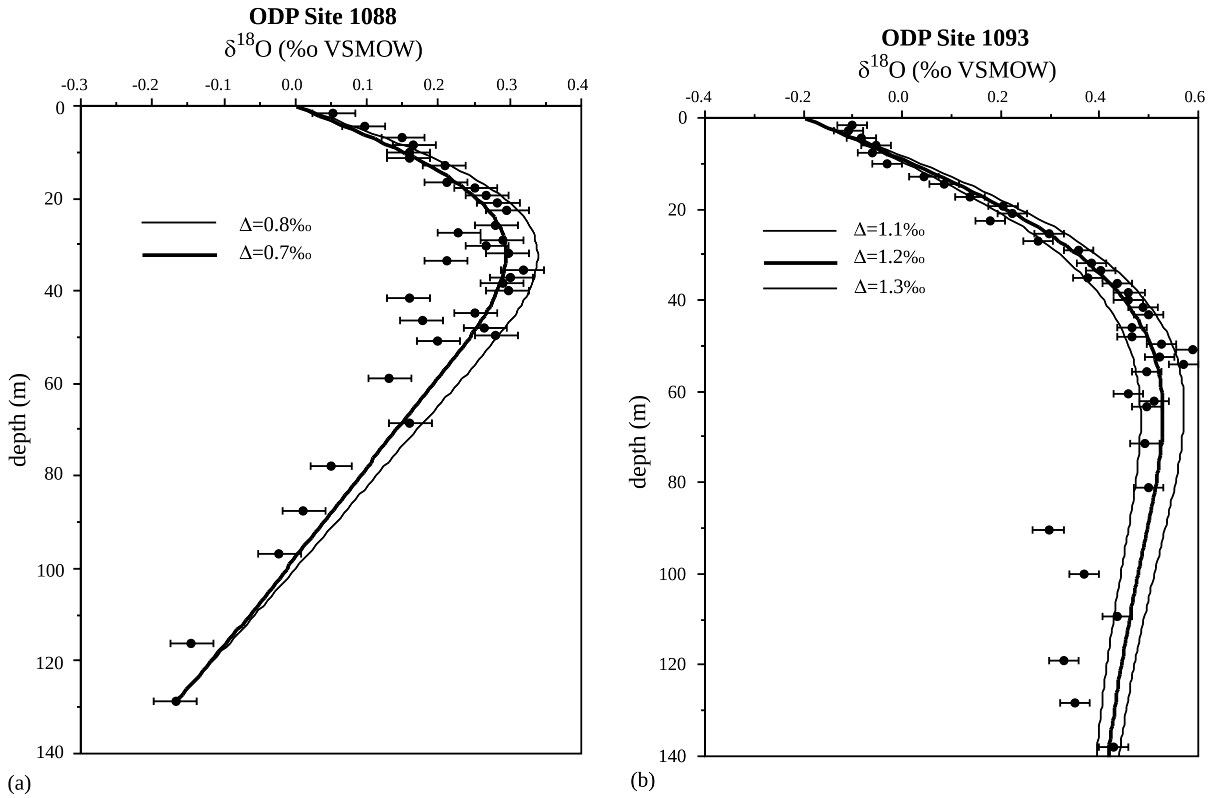

Fig. 3. Oxygen isotope data on pore fluids from ODP Leg 177, Sites 1088 (A) and 1093 (B). The lines indicate the model results for different changes in the $\delta^{18}O$ of seawater.

the data at Site 1088 is for a glacial-interglacial change of 6.5‰ (Fig. 4B), consistent with the $\delta^{18}O$ data. For the southernmost site (Fig. 4C), which showed the largest change in $\delta^{18}O_{sw}$, the model yields a best fit to the deuterium data of 9‰, substantially higher than the values from the other sites, and again consistent with the $\delta^{18}O$ data. At all other sites, the best fits to the deuterium profiles require diffusion coefficients identical to those required by the oxygen isotope profiles, demonstrating that diffusion of hydrogen in pore fields is controlled, like oxygen, by the self-diffusion of water.

4. Discussion

The data from the Atlantic sites from ODP Legs 162 and 177 confirm the conclusions from studies by Schrag et al. (1996) and Adkins and Schrag (2001) that the glacial-interglacial change in $\delta^{18}O_{sw}$ in most of the Atlantic basin was between 0.7‰ and 0.8‰ (Table 1). To extrapolate the Atlantic value to a global average change, one needs to consider the affects of changing water masses, specifically the shift from AABW which dominated the deep Atlantic during the LGM to NADW in the modern ocean. This is discussed in detail by Schrag et al. (1996) and by Adkins and Schrag (2001), who obtain a global average value of 1.0‰. From this extrapolation, we would expect the change in $\delta^{18}O$ of southern source deep water to be slightly larger than the global average. Our data from Site 1093 confirms this prediction, yielding a glacial-interglacial change of 1.1‰. Another interesting feature is the very cold temperatures we calculate for Site 984 in the North Atlantic, which was not dominated by southern source water in the LGM and instead represents GNAIW (McManus et al., 1999). The fact that the deep water formed in the North Atlantic was so cold during the LGM supports the idea that the process of deep-water formation was different during the LGM, perhaps due to brine rejection (Dokken and Jansen, 1999).

The glacial interglacial changes at all the sites are substantially lower than the 1.3‰ proposed by Fairbanks (1989), which is cited widely by paleoceanographers. Because of the large discrepancy, we examine the determination of Fairbanks (1989) here in more detail. The value of 1.3‰ derives from the results of Fairbanks and Matthews (1978), and there are several sources of uncertainty in the calculation that would allow for this approach to over-estimate the true ice volume component. The first problem is with the propagation of error in the original data from Fairbanks and Matthews (1978). The change in $\delta^{18}O_{sw}\,m^{-1}$ of sea level change of $0.011‰\,m^{-1}$ comes from averaging two pairs of coral terraces from Barbados. The first pair, Kendal Hill and

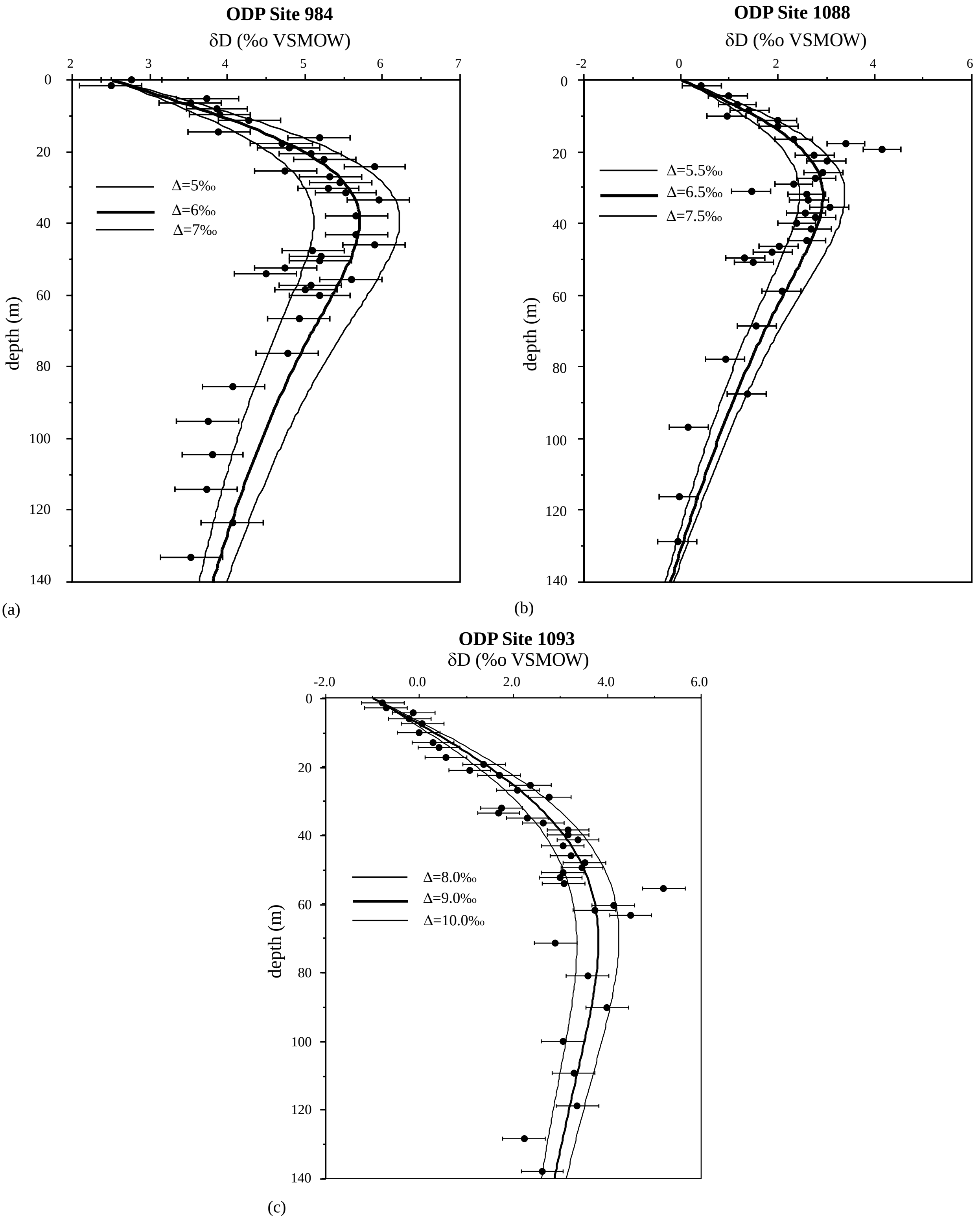

Fig. 4. Hydrogen isotope data from ODP Sites 984 (A), 1088 (B), and 1093 (C).

RKM23, represents a marine regression. The second pair, RKM20 and Rendezvous Hill, represents a marine transgression. For the first pair, the change in elevation between Kendal Hill and RKM23 is 54 m, while the difference in isotopic composition is 0.55‰ ± 0.17 (1σ), yielding a value of 0.010 ± 0.003‰ m^{-1}. For the second pair, the change in elevation between RKM20 and Rendezvous Hill is 51 m, while the difference in isotopic

Table 1
Glacial–interglacial changes in $\delta^{18}O$ and δD discussed in this study

Site	Latitude	Longitude	Depth (m)	$\Delta\delta^{18}O$ (‰)	$\Delta\delta D$ (‰)	Reference
925	4° 12′N	43° 29′W	3041	0.8 ± 0.1		Schrag et al. (1996)
981	55° 29′N	14° 39′W	2184	0.7 ± 0.1		This study
984	61° 26′N	20° 4′W	1660	0.8 ± 0.1	6 ± 1	This study
1063	33° 41′N	57° 37′W	4583	0.75 ± 0.05		Adkins and Schrag (2001)
1088	41° 8′S	13° 34′E	2082	0.8 ± 0.1	6.5 ± 1	This study
1093	49° 59′S	5° 52′E	3623	1.1 ± 0.1	9 ± 1	This study

composition is $0.63‰\pm0.21(1\sigma)$, yielding a value of $0.012\pm0.004‰\,m^{-1}$. Fairbanks and Matthews (1978) argue that tectonic uplift during the sea level changes would cause the former to be an underestimate of the true value and the latter to be an overestimate, resulting in the overall value of $0.011‰\,m^{-1}$. The error in the final value of $0.011‰\,m^{-1}$ (and also the value of 1.3‰) is approximately 30%.

A second uncertainty in the calculation of Fairbanks (1989) involves the assumption that tropical sea surface temperatures were constant during the sea level changes. Both Fairbanks (1989) and Fairbanks and Matthews (1978) were well aware of this assumption and made clear that the calculated value of 1.3‰ is a maximum one. However, most studies that use this value treat it as an exact one, not an upper bound (e.g., Clark and Mix, 2000). The problem is that this determination is very sensitive to even a small change in sea surface temperature. For example, if the sea surface temperature changed by 1°C over the sea level changes of ~50 m represented by the pairs of Stage 7 and Stage 5 coral samples, the value predicted for a full glacial-interglacial shift is reduced to 0.95‰, and the error (which remains the same in absolute value) is increased to 50%. We note that this is a small temperature change relative to the 5°C change proposed for Barbados over the full deglaciation by Guilderson et al. (1994). Another critical uncertainty in the Fairbanks (1989) determination is whether the value calculated from Barbados corals growing in the surface ocean reflects the global average change in $\delta^{18}O_{sw}$, i.e., the ice volume contribution. This is the same problem associated with the argument of Duplessy (1978), which neglected the possibility of substantial spatial variability.

A globally averaged glacial-interglacial change in $\delta^{18}O_{sw}$, of 1.0‰ implies a mean value for glacial ice of approximately −30‰. The chief source of uncertainty for this extrapolation is the uncertainty in the amount of water stored in ice sheets during the LGM (see Milne et al., 2001, for a more complete discussion). This value is consistent with independent estimates from models including Olausson (1965) and Dansgaard and Tauber (1969). A lower glacial-interglacial change in $\delta^{18}O_{sw}$ makes planktonic foraminiferal $\delta^{18}O$ records consistent with greater cooling of the tropics during the LGM. By assuming an ice-volume component of 1.3‰, $\delta^{18}O$ records of planktonic foraminifera yield tropical sea surface temperatures that are at most 2° colder during the LGM (Broecker, 1986), consistent with estimates from CLIMAP based on microfossil assemblages (CLIMAP Project Members, 1981). If the build-up of continental ice affects the carbonate oxygen isotope record for the LGM by only 1.0‰ as a global average, and by as little as 0.7‰ for deep water in the Atlantic Ocean, then $\delta^{18}O$ records of tropical planktonic foraminifera can yield from 3°C to 4°C of cooling since the LGM. Although it remains uncertain how the $\delta^{18}O$ of surface waters changed during the LGM due to changes in evaporation and precipitation, reducing the ice volume component helps to reconcile tropical planktonic foraminiferal $\delta^{18}O$ records with the coral $\delta^{18}O$ and Sr/Ca measurements (Guilderson et al., 1994), and with terrestrial climate proxies including snow-line elevations (Webster and Streten, 1978; Porter, 1979), noble gases in groundwater (Stute et al., 1992) and pollen records (Van der Hammen, 1974).

An interesting feature in some of the oxygen isotope profiles presented here and by previous workers (Paul et al., 2001) is the constant $\delta^{18}O$ over the first 5–10 m, rather than a steady decrease with depth as predicted by a diffusion model. The current method of sampling from ODP cores only allows one sample every 1.5 m, too low resolution to accurately determine whether this feature is robust. However, if this feature is not an artifact of drilling or sampling, the simplest explanation is that the oxygen isotopic composition of seawater during the mid-Holocene, at least locally, was lower than it is today. Either this reflects a change in the last few thousand years of the deep water $\delta^{18}O$ value from a mid-Holocene minimum, or it reflects a shift in location water masses through the Holocene. If the average $\delta^{18}O$ of the deep ocean were slightly lower in the Holocene, then the $\delta^{18}O$ of ice on Antarctica has decreased over this time interval. This change would not affect the salinity of the deep ocean as it does not require a change in ice volume, only the isotopic composition of the ice. If the pattern reflects a change in the location or composition of water masses, then salinity would be affected as well as was observed in pore fluids from the Mediterranean (Paul et al., 2001). Thus, the cause of this phenomenon may be tested with chloride measurements of pore fluids, following Adkins and Schrag (2001). The time scale for self-diffusion of water over the first 10 m of sediment is approximately 6000 years, consistent with either hypothesis. If such shifts in water masses have occurred over the Holocene, very high-resolution pore fluid samples over the first 10–20 m depth in the sediment should be able to resolve them.

5. Conclusions

Measurements of oxygen isotopes in pore fluids from deep sea sediments from sites in the North and South Atlantic provide direct measurements of changes in $\delta^{18}O$ of bottom waters. The results constrain the glacial-interglacial change in $\delta^{18}O$ of the deep Atlantic to be 0.7–0.8‰, consistent with previous estimates. At the southernmost site studied, the change is substantially larger (1.1‰), representing the change in $\delta^{18}O$ of southern source waters since the LGM. These results confirm previous estimates that the global average change in $\delta^{18}O$ of seawater is 1.0 ± 0.1‰. Hydrogen isotopes measured on pore fluids from three sites are consistent with the oxygen isotopes from these locations, giving further support to these results. At all sites studied, the temperature of the deep ocean during the LGM, calculated by combining the pore fluid results with oxygen isotope data from benthic foraminifera, was within 1°C of the freezing point of seawater.

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References

Adkins, J.F., Schrag, D.P., 2001. Pore fluid constraints on deep ocean temperature and salinity during the Last Glacial Maximum. Geophysical Research Letters 28, 771–775.

Bard, E., Hamelin, B., Fairbanks, R.G., Zindler, A., 1990. Calibration of the ^{14}C timescale over the past 30,000 years using mass spectrometric U–Th ages from Barbados corals. Nature 345, 405–410.

Bender, M., Sowers, T., Labeyrie, L., 1994. The Dole effect and its variations during the last 130,000 years as measured in the Vostok ice core. Global Biogeochemical Cycles 8, 363–376.

Broecker, W.S., 1986. Oxygen isotope constraints on surface ocean temperatures. Quaternary Research 26, 121–134.

Clark, P.U., Mix, A.C., 2000. Global change: Ice sheets by volume. Nature 406, 689–690.

CLIMAP Project Members, 1981. Seasonal reconstruction of the Earth's surface at the Last Glacial Maximum, G.S.A. Map and Chart Series, MC-36.

Cuffey, K.M., Clow, G.D., Alley, R.B., Stuiver, M., Waddington, E.D., Saltus, R.W., 1995. Science 270, 455–458.

Curry, W.B., Lohmann, G.P., 1990. Reconstructing past particle fluxes in the tropical Atlantic Ocean. Paleoceanography 5, 487–505.

Dansgaard, W., Tauber, H., 1969. Glacier oxygen 18 content and Pleistocene ocean temperatures. Science 166, 499–502.

Dokken, T., Jansen, E., 1999. Rapid changes in the mechanism of ocean convection during the last glacial period. Nature 401, 458–461.

Duplessy, J.-C., 1978. Isotope studies. In: Gribbin, J. (Ed.), Climatic Change. Cambridge University Press, New York, pp. 46–67.

Emiliani, C., 1955. Pleistocene temperatures. Journal of Geology 63, 538–578.

Epstein, S.B., Lowenstam, H.A., Urey, H.C., 1951. Carbonate-water isotopic temperature scale. Geological Society of America Bulletin 62, 417–425.

Fairbanks, R.G., 1989. 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.

Fairbanks, R.G., Matthews, R.K., 1978. The marine oxygen isotope record in Pleistocene coral, Barbados, West Indies. Quaternary Research 10, 181–196.

Guilderson, T.P., Fairbanks, R.G., Rubenstone, J.L., 1994. Tropical temperature variations since 20,000 years ago: Modulating inter-hemispheric climate change. Science 263, 663–665.

Kelvin, W.T., 1861. The reduction of observations of underground temperature. Transactions of the Royal Society of Edinburgh 22, 405.

Klinkenberg, L.J., 1951. Analogy between diffusion and electrical conductivity in porous rocks. Geological Society of America Bulletin 62, 559.

McDuff, R.E., 1984. The chemistry of interstitial waters, Deep Sea Drilling Project Leg 86. In: Heath, G.R., Burckle, L.H., et al. (Eds.), Initial Reports of the Deep Sea Drilling Project, 86. US Government Printing Office, Washington, pp. 675–687.

McManus, J.F., Oppo, D.W., Cullen, J.L., 1999. A 0.5-million-year record of millennial-scale climate variability in the North Atlantic. Science 283, 971–975.

Milne, G.A., Mitrovica, J.X., Schrag, D.P., 2002. Estimating past continental ice volume from sea-level data. Quaternary Science Review, 21(1–3), this issue.

Ninnemann, U.S., Charles, C.D., Hodell, D.A., 1999. Origin of global millennial scale climate events: constraints from the Southern Ocean deep sea sedimentary record. In: Clark, P.U., Webb, R.S., Keigwin, L.D. (Eds.), Mechanisms of Global Change at Millennial Time Scales. AGU Monograph Series 112, pp. 99–112.

Olausson, E., 1965. In: Sears, M. (Ed.), Progress in Oceanography 3. Oxford, Pergamon Press, pp. 221–252.

Oppo, D.W., Lehman, S.J., 1993. Mid-depth circulation of the subpolar North-Atlantic during the Last Glacial Maximum. Science 259, 1148–1152.

Paul, H.A., Bernasconi, S.M., Schmid, D.W., McKenzie, J.A., 2001. Oxygen isotopic composition of the mediterranean sea since the Last Glacial Maximum: constraints from pore water analyses. Earth and Planetary Science Letters 192, 1–14.

Porter, S.C., 1979. Hawaiian glacial ages. Quaternary Research 12, 161–187.

Schrag, D.P., DePaolo, D.J., 1993. Determination of $\delta^{18}O$ of seawater in the deep ocean during the Last Glacial Maximum. Paleoceanography 8, 1–6.

Schrag, D.P., Hampt, G., Murray, D.W., 1996. The temperature and oxygen isotopic composition of the glacial ocean. Science 272, 1930–1932.

Shackleton, N.J., 1967. Oxygen isotope analyses and Pleistocene temperatures re-assessed. Nature 215, 15–17.

Simpson, J.H., Carr, H.Y., 1958. Diffusion and nuclear spin relaxation in water. Physical Reviews 2nd Series 92, 1201–1208.

Stute, M., Schlosser, P., Clark, J.F., Broecker, W.S., 1992. Paleotemperatures in the Southwestern US derived from noble gases in groundwater. Science 256, 1000–1003.

Van der Hammen, T., 1974. The Pleistocene changes of vegetation and climate in tropical South America. Journal of Biogeography 1, 3–26.

Webster, P., Streten, N., 1978. Late Quaternary ice age climates of tropical Australasia, interpretation and reconstruction. Quaternary Research 10, 279–309.