Pore fluid constraints on deep ocean temperature and salinity during the last glacial maximum

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Abstract. Pore water records of $\delta^{18}O$ and [Cl] from ODP Site 1063A on the Bermuda Rise constrain the change in seawater $\delta^{18}O$ and salinity from the Last Glacial Maximum (LGM) to the Holocene to be 0.75±0.05‰ and 2.5±0.1% respectively. Coupled with a measured benthic foraminiferal $\delta^{18}O$ change, this result means that bottom waters were 4.6±0.8°C cooler than the Holocene at the LGM and therefore at or near the seawater freezing point. Coupled $\delta^{18}O$ and chlorinity results give an extrapolated mean ocean LGM to Holocene change in $\delta^{18}O$ of 0.95±0.09‰. These data also constrain the past southern source deep-water salinity to be 35.76±0.04 psu, which is within error of the mean deep ocean value for this time.

1. Introduction

The oxygen isotopic composition ($\delta^{18}O$) [*Epstein et al.*, 1953] of benthic foraminiferal $CaCO_3$ is a function of both the temperature and the $\delta^{18}O$ of the water in which the foraminifera grows. The $\delta^{18}O$ of seawater ($\delta^{18}O_{sw}$) is related to the amount of isotopically-depleted ice that is stored on land during glaciations. This ambiguity in carbonate values has led to the interpretation of foraminiferal $\delta^{18}O$ records as mostly due to changes in temperature [*Emiliani*, 1955] and alternatively as mostly due to variations in ice volume [*Shackleton*, 1967].

Several approaches have been taken to determine how much each of the two factors, temperature and ice volume, contribute to the total change in foraminiferal $\delta^{18}O$. Fairbanks and Matthews [1978] measured the change in $\delta^{18}O$ of seawater per meter of sea level change in uplifted Barbados corals that grew during past sea level high stands. They calculated a maximum value of 0.011‰/meter which, when combined with the measured change in sea level since the LGM (121±5 m) [*Fairbanks*, 1989], yields an estimate of glacial-interglacial change in $\delta^{18}O_{sw}$ of 1.3‰. Chappell and Shackleton [1986] used a similar approach at the Huon Peninsula, obtaining a slightly lower value. Both these studies assume that temperature change is constant at their sites during the period when sea level is changing, an interpretation later contradicted by Guilderson et al. [1994]. Thus, their estimates are maximum values depending on the magnitude of tropical cooling during the LGM. An additional complication is that there is no requiremenmt that the

change in $\delta^{18}O_{sw}$ at a single location is representative of the global oceam. This is especially important in the surface ocean where evaporation and precipitation can lead to large local changes in $\delta^{18}O_{sw}$.

A direct approach to measuring LGM seawater $\delta^{18}O$ is based on the isotopic composition of deep-sea pore fluids. The isotopic history of the bottom water over glacial cycles provides an oscillating boundary condition on the sediment-pore fluid system yielding a record of past ocean composition attenuated by diffusion. This approach is similar to the method used to reconstruct surface temperatures from borehole temperature profiles in ice cores [*Cuffey et al.*, 1995]. McDuff [*McDuff*, 1985] first recognized the signal of Pleistocene glacial cycles in deep sea pore fluids from Deep Sea Drilling Project (DSDP) Site 576 in the central Pacific. Schrag and DePaolo [*Schrag and DePaolo*, 1993], using data from McDuff, showed that the pore fluid profile was primarily a measure of the change since the LGM, and that one could obtain an estimate for $\delta^{18}O_{sw}$ during the LGM by using a numerical model to calculate the effects of diffusion. They calculated a change of 1.0±0.25‰, although the error was limited by low sampling resolution and analytical precision. Schrag et al. [*Schrag et al.*, 1996] measured a pore fluid profile from a site at 3000m on the Ceara Rise with higher sampling resolution (every 1.5 m) and better precision (±0.03 ‰), obtaining a value for $\delta^{18}O_{sw}$ of 0.8±0.1‰, substantially lower than the previous estimates. This value is a combination of the global effect of sea-level change and a local effect due to changing deep-water masses at the site. The local circulation effect is most significant for the deep North Atlantic basin which experienced a change from relatively low-$\delta^{18}O$, southern source deep water during the LGM to relatively high-$\delta^{18}O$, northern source deep water in the Holocene. Given this complication, Schrag et al. [1996] suggested that the global average value (i.e., due to ice volume only) was 1.0±0.1‰, based on two different methods of extrapolation.

The pore water diffusion approach will work for any chemical or isotopic tracer that is not affected substantially by chemical reactions with sediments over the time scale of glacial cycles (i.e., conservative). Outside of methane clathrate chemistry (see Results), chlorinity is a conservative tracer (unlike salinity) and can be used to reconstruct the salinity of LGM seawater if precise measurements can be obtained. McDuff [*McDuff*, 1985] also identified a change in chlorinity in the pore fluids from DSDP Site 576, that correlated with the change in $\delta^{18}O$, although the data showed scatter due to low precision and sampling resolution. In this paper we present better measurements of chloride from deep-sea pore fluids from the Bermuda Rise, combined with high-precision $\delta^{18}O$ data. We

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show that by combining both data sets, we can determine the local change in seawater temperature and salinity, and better extrapolate the result from this site to a global average.

2. Methods

Pore water samples were collected for [Cl] and $\delta^{18}O$ analysis at high depth resolution from the ODP Bermuda Rise Leg 172 core 1063A (33° 41.204' N, 57° 36.898' W, 4584 meters). Chloride concentrations are measured by potentiometric titration of 0.5 ml samples against a $AgNO_3$ standard [McDuff, 1985]. Propagating weighing, titration volume, and standard concentration uncertainties through the calculation of [Cl] gives errors for individual measurements from 0.013-0.070% (2σ, Figure 1). Variability around the true value (independently determined by Autosal) of a daily consistency standard of Palau surface seawater is ±0.05%. Additionally, three of the four replicate down core analyses agree within their calculated 2σ errors. In general, we believe the titration method is good to ±0.05% (2σ). $\delta^{18}O$ values are determined by equilibration of a 2ml sample of pore fluid with CO_2 gas at 25°C, and subsequent measurement on a Micromass Optima gas-source mass spectrometer. Replicate analyses show that this method is good to better than ±0.03‰ (1σ).

Chloride and $\delta^{18}O$ profiles are modeled using a 1-D Eulerian finite difference diffusion code that includes the effects of compaction advection and changing bottom water concentration over the last 125,000 years. The model monitors the top 375 meters of sediment at 1.5 meter intervals and has a gradient bottom boundary condition. It must be passed values for the sedimentation rate, chiefly determined from orbital tuning of the

gray scale data [Keigwin et al., 1998], and bottom water concentration, the top boundary condition, at each time step. Assuming a known steady state porosity profile (from shipboard data), the compaction advection is calculated from the sedimentation rate and the porosity at which compaction stops [Berner, 1980]. This advection term is small relative to diffusion as the Peclet number varies between 0.02 and 0.06 for all time steps and all depths. Diffusion coefficients are determined by fitting the depth of the model pore water maximum to the measured profile. The change in the isotopic and chemical composition of seawater from 125 to 20 ka used in the model is based on the deep Equatorial Pacific benthic $\delta^{18}O$ record at site V19-30 [Shackleton et al., 1983]. For the last 20 kyr, we use the coral sea-level record [Cutler et al., 2000; Fairbanks, 1989]. The amplitude of this boundary condition is adjusted in multiple sensitivity calculations to obtain both the best fit to the data as well as an uncertainty in this fit. Initial conditions were chosen to match the deep portions of the profiles and do not influence the results within error.

3. Results

The upper 100 meters of chloride data (Figure 1) clearly show the expected last glacial maximum peak. We measure a modern to LGM range of 1.2% with peak values of 19.55-19.56 g/Kg between 21.0 and 31.3 meters. While the upper part of the profile is very consistent, below 100m the chloride data become scattered. At 60 meters, sulfate concentrations go to zero and methane first appears in the sediment pore waters [Keigwin et al., 1998]. Given the water depth, bottom temperature (2.34°C) and geothermal gradient (20°C/km) at Site 1063A, the whole
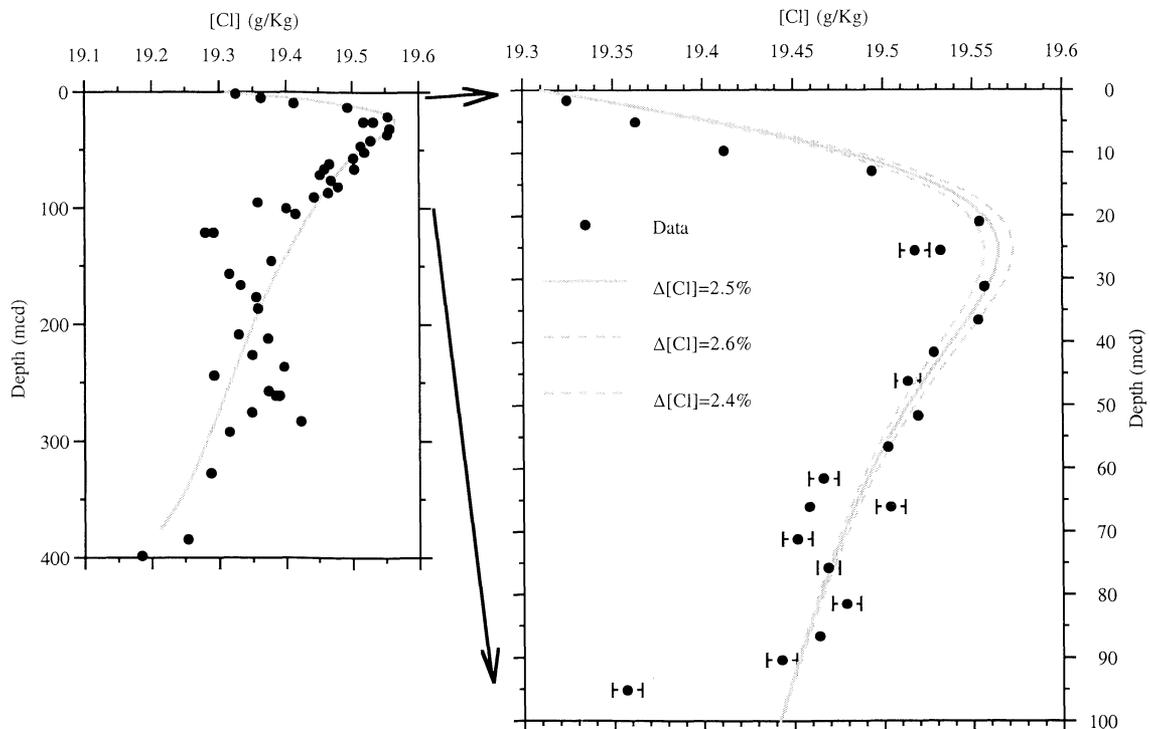

Figure 1. Plot of [Cl] vs. meters composite depth in ODP core 1063A. Error bars (2σ) are the propagated uncertainties from weighing, titration volume, and standard calibration. Replicate analyses generally agree within errors. The gray line is the best-fit result from a 1-D diffusion model that includes compaction advection and has a glacial to interglacial change of 2.5%. Dashed gray lines are two other fits that bracket the ideal result by 0.1%.

sediment column is in the methane hydrate stability zone [Dickens and Quinby-Hunt, 1994]. When raised to the surface, these clatherates are unstable and were observed on board ship to expand the sediment sections. We believe that diffusion of excess chloride away from in situ hydrates, and then rapid hydrate melting as the core is brought to the surface, cause our measured profile to vary around the diffusion line (Figure 1). The $\delta^{18}O$ profile (Figure 2) shows many of the same features as the chloride data but is much smoother at depth. As clatherate formation is not expected to alter the oxygen profile, these data are consistent with the methane hydrate hypothesis. Maximum $\delta^{18}O$ values of 0.34‰ are found between 21.0 and 35.6 meters. The profile then drops to lighter values faster than the chloride profile due to the different basalt/pore water boundary conditions for these two species. Model results yield glacial-interglacial changes for [Cl] of 2.5±0.1% and for $\delta^{18}O_{sw}$ of 0.75±0.05‰ at this deep North Atlantic site (Figures 1 and 2). A model with a slightly different numerical approach [Schrag and DePaolo, 1993] produced the same results for this data set.

4. Discussion

Given 121±5 meters of Glacial/Interglacial sea level change and a mean depth for the modern ocean of 3.8 km, the expected global salinity change is 3.16±0.13%. The change we measure at the Bermuda Rise is smaller than this number due to local circulation changes at this site. Benthic foraminiferal Cd/Ca and $\delta^{13}C$ evidence suggest that the LGM bottom waters at the Bermuda Rise were 100% of Southern Ocean origin [Boyle and Keigwin, 1987]. Today the waters bathing site 1063A consist almost exclusively of North Atlantic Deep Water. This hydrographic switch is reflected in the reconstructed Δ[Cl] and

$\Delta\delta^{18}O$ values as fresher and lighter values than the whole ocean average. Our measured freshness places an interesting constraint on the relative salinities of LGM deep waters. In practical salinity units, the modern salinities of the mean ocean and seawater at 4500 meters on the Bermuda Rise are 34.70 and 34.89±0.003 respectively. At the Last Glacial Maximum, when the core site is bathed by southern source water exclusively, these salinity values change to 35.80±0.05 for the mean and 35.76±0.04 for the Bermuda Rise. Within error, southern source waters are the same as the mean ocean.

To calculate a mean global ocean change in $\delta^{18}O$, we can account for local variations at our site by using the chloride data. Assuming a constant $\delta^{18}O$ vs. salinity relationship between the modern and LGM deep waters, we can write the following equation:

$$\frac{\Delta\delta^{18}O_{local}}{\Delta\delta^{18}O_{global}} = \frac{\Delta[Cl]_{local}}{\Delta[Cl]_{global}} \Rightarrow \frac{0.75 \pm 0.5}{\Delta\delta^{18}O_{global}} = \frac{2.5 \pm 0.1\%}{3.16 \pm 0.13\%}$$

Solving for the global $\Delta\delta^{18}O$ gives a value of 0.95±0.09‰.

This mean ocean $\Delta\delta^{18}O$ requires the $\delta^{18}O$ of the melting ice to be -29‰, in good agreement with other estimates [Dansgaard and Tauber, 1969; Hillaire-Marcel and Causse, 1989; Mix, 1987; Mix and Ruddiman, 1984]. However, the notion of ice melting with a constant $\delta^{18}O$ is probably too simple. With better global coverage of pore water sites we will be able to measure the $\delta^{18}O$ vs. salinity slope in deep waters and test our use of the modern relationship at the LGM. Our results also agree with Mg/Ca data, used as a temperature proxy, from glacial Southern Ocean planktonics [Mashiotta et al., 1999].
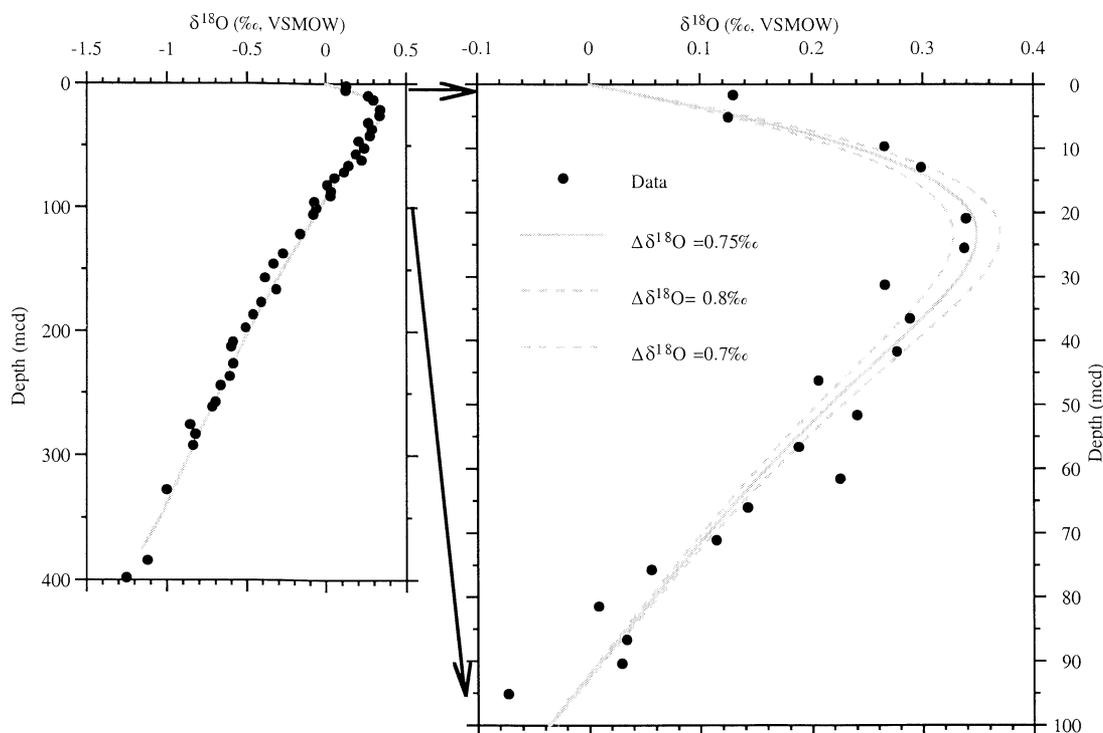

Figure 2. Plot of $\delta^{18}O$ vs. meters composite depth in ODP core 1063A. Error bars (1σ) are from replicate analyses of the same sample. The gray line is the best-fit model run using a glacial/interglacial change of 0.75‰. Dashed gray lines are the results of changing the 0.75‰ fit by ±0.05‰.

Reconstructed local $\Delta\delta^{18}O$ can also be used to estimate the magnitude of bottom water temperature changes at site 1063A. A continuous, single species, benthic isotope record from the Holocene to the LGM does not exist for the Bermuda Rise. Measurements of Holocene *cibicidoides sp.* in core GGC-1 give an average $\delta^{18}O$ value of 2.41±0.08‰ [*Keigwin and Boyle,* 1989]. LGM data for the same species show an average of 4.34±0.19‰ (L. Keigwin, personal communication). Together these data from two separate cores lead to a Glacial/Interglacial difference of 1.9±0.2‰. Subtracting off the water $\delta^{18}O$ value from the pore fluid data leaves a 1.15±0.21‰ residual that corresponds to a 4.6±0.8°C deep-water temperature cooling. This result implies that the LGM deep-water temperature at 4500 meters on the Bermuda Rise was at or near the freezing point. In contrast, the coupled pore water and benthic isotope study from 3000 meters on the Ceara Rise found a LGM temperature of −1.3°C [*Schrag et al.,* 1996]. This difference is expected as the Ceara Rise was bathed by a 40:60 ratio of northern and southern source waters at the LGM, indicating that glacial northern source was slightly warmer than glacial AABW.

An additional constraint from existing data can be joined with these deep-water temperature calculations to comment on LGM heat transports. Deep-sea coral radiocarbon data from 15,400 years ago and 1800 meters depth at 40°N in the Western Atlantic show a very stagnant deep-water mass [*Adkins and Boyle,* 2000; *Adkins et al.,* 1998]. Coupled $\Delta^{14}C$ and Cd/Ca measurements imply that waters of a southern origin were approximately 5 times less well ventilated in the northern Atlantic at this time than their modern counterparts. To the degree that 15.4 ka, which is inbetween Heinrich Event 1 and the deglaciation, can be taken as representative of the LGM hydrography, the coupled temperature and $\Delta^{14}C$ data imply a deep ocean that is transporting virtually no heat below about 2000 meters.

5. Conclusions

Pore fluid data from the deep Western North Atlantic show that the LGM to Holocene difference in seawater $\delta^{18}O$ was 0.75±0.05‰. Combined with benthic foraminifera data from the same site, this result means the LGM water was 4.8±0.8°C cooler, at or near the freezing point of seawater. Chloride data from the same core constrain the LGM salinity difference to be 2.5±0.1%. Normalizing the $\delta^{18}O$ data with the chloride data eliminates the contributions from local circulation changes and implies a mean ocean $\delta^{18}O$ change of 0.95±0.09‰ consistent with previous estimates. The reconstructed salinity for deep water during the LGM at the Bermuda Rise is equal to, within error, the salinity of the mean ocean during the LGM, consistent with a world ocean that had a large proportion of deep waters from a single southern source region.

References

Adkins, J.F., and E.A. Boyle, Age screening of deep-sea corals and the record of deep North Atlantic circulation change at 15.4 ka, in *Proceedings of the Sixth International Conference on Paleoceanography,* edited by F. Abrantes, and A. Mix, pp. in press, Elsiever, 2000.

Adkins, J.F., H. Cheng, E.A. Boyle, E.R.M. Druffel, and L. Edwards, Deep-sea coral evidence for rapid change in ventilation of the deep North Atlantic 15,400 years ago, *Science,280,* 725-728, 1998.

Berner, R.A., *Early Diagenesis: A theoretical approach,* 241 pp., Princeton University Press, Princeton, 1980.

Boyle, E.A., and L.D. Keigwin, North Atlantic thermohaline circulation during the last 20,000 years linked to high latitude surface temperature, *Nature, 330,* 35-40, 1987.

Chappell, J., and N.J. Shackleton, Oxygen isotopes and sea level, *Nature, 324,* 137-140, 1986.

Cuffey, K.M., G.D. Clow, R.B. Alley, M. Stuiver, E.D. Waddington, and R.W. Saltus, Large arctic temperature change at the Wisconsin-Holocen glacial transition, *Science, 270,* 455-458, 1995.

Cutler, K.B., R.L. Edwards, F.W. Taylor, H. Cheng, J. Adkins, C.D. Gallup, P.M. Cutler, G.S. Burr, J. Chappell, and A.L. Bloom, Rapid sea-level fall and deep ocean temperature change since the last interglacial, *in prep. Science,* 2000.

Dansgaard, W., and H. Tauber, Glacier oxygen-18 content and Pleistocene ocean temperatures 1, *Science, 166,* 499-502, 1969.

Dickens, G.R., and M.S. Quinby-Hunt, Methane hydrate stability in seawater, *Geophysical Research Letters, 21,* 2115-2118, 1994.

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

Epstein, S., R. Buchsbaum, H.A. Lowenstam, and H.C. Urey, Revised carbonate-water isotopic temperature scale, *Geol. Soc. Amer. Bull., 64,* 1315-1326, 1953.

Fairbanks, R.G., A 17,000-year glacio-eustatic sea level record: influence of glacial melting rates on the Younger Dryas event and deep-ocean circulation, *Nature, 342,* 637-642, 1989.

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

Guilderson, T.P., R.G. Fairbanks, and J.L. Rubenstone, Tropical temperature variations since 20,000 years ago: modulating interhemispheric climate change, *Science, 263,* 663-665, 1994.

Hillaire-Marcel, C., and C. Causse, The Late Pleistocene Laurentide glacier: Th/U dating of its major fluctuations and d18O range of the ice, *Quaternary Research, 32,* 125-138, 1989.

Keigwin, L.D., and E.A. Boyle, Late Quaternary paleochemistry of high-latitude surface waters, *Paleogeogr., Paleoclimatol., Paleoecol., 73,* 85-106, 1989.

Keigwin, L.D., D. Rio, G.D. Acton, and e. al., *Proc. ODP, Init. Repts., 172,* College Station, TX, 1998.

Mashiotta, T.A., D.W. Lea, and H.J. Spero, Glacial-interglacial changes in subantarctic sea surface temperature and delta 18O-water using foraminiferal Mg, *Earth and Planetary Science Letters, 170,* 417-432, 1999.

McDuff, R.E., The chemistry of interstitial waters, deep sea drilling project leg 86, *Init. Rept. of the DSDP, 86,* 675-687, 1985.

Mix, A.C., The oxygen-isotope record of glaciation, in *The Geology of North America, vo. K-3, North American and Adjacent Oceans During the Last Deglaciation,* edited by W.F.R.a.H.E.W. Jr., pp. 111-135, Geol. Soc. Am., 1987.

Mix, A.C., and W.F. Ruddiman, Oxygen-isotope analyses and Pleistocene ice volumes, *Quaternary Research, 21* (1), 1-20, 1984.

Schrag, D.P., and D.J. DePaolo, Determination of del18O of seawater in the deep ocean during the Last Glacial Maximum, *Paleoceanography, 8* (1), 1-6, 1993.

Schrag, D.P., G. Hampt, and D.W. Murry, Pore fluid constraints on the temperature and oxygen isotopic composition of the Glacial ocean, *Science, 272,* 1930-1932, 1996.

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

Shackleton, N.J., J. Imbrie, and M.A. Hall, Oxygen and carbon isotope record of East Pacific coreV19-30:implications for the formation of deep water in the late Pleistocene North Atlantic, *Earth Planet. Sci. Lett., 65,* 233-244, 1983.

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