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Pore Fluid Constraints on the Temperature and Oxygen Isotopic Composition of the Glacial Ocean

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Pore fluids from the upper 60 meters of sediment 3000 meters below the surface of the tropical Atlantic indicate that the oxygen isotopic composition ($\delta^{18}\text{O}$) of seawater at this site during the last glacial maximum was 0.8 ± 0.1 per mil higher than it is today. Combined with the $\delta^{18}\text{O}$ change in benthic foraminifera from this region, the elevated ratio indicates that the temperature of deep water in the tropical Atlantic Ocean was 4°C colder during the last glacial maximum. Extrapolation from this site to a global average suggests that the ice volume contribution to the change in $\delta^{18}\text{O}$ of foraminifera is 1.0 per mil, which partially reconciles the foraminiferal oxygen isotope record of tropical sea surface temperatures with estimates from Barbados corals and terrestrial climate proxies.

Pleistocene oxygen isotope records of foraminifera in deep sea sediments reflect changes in ocean temperature and in the oxygen isotopic composition of seawater ($\delta^{18}\text{O}_{\text{sw}}$) over glacial cycles. Cooling during glacial episodes increases the mass-dependent fractionation of oxygen isotopes between water and calcite, resulting in higher $\delta^{18}\text{O}$ values of carbonate microfossils. The growth of large ice sheets on continents increases the $^{18}\text{O}/^{16}\text{O}$ ratio of seawater, also resulting in higher $\delta^{18}\text{O}$ values for carbonate microfossils. Determining how much each of these components contributes to the total change in $\delta^{18}\text{O}$ of foraminifera since the last glacial maximum (LGM), which for benthic foraminifera averages 1.7

per mil (1), is an important step toward understanding Pleistocene climate change.

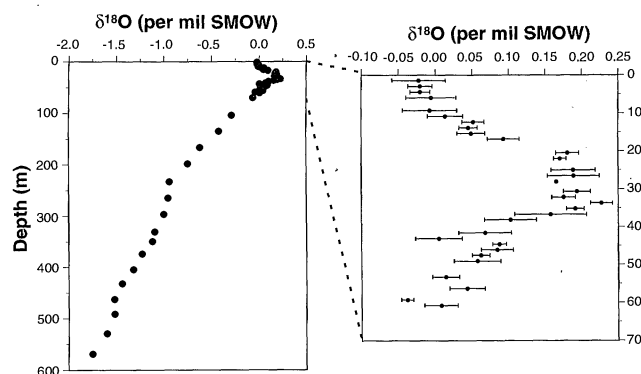
The generally accepted estimate for the contribution of ice volume to the change in $\delta^{18}\text{O}$ of foraminiferal calcite is 1.3 per mil (2, 3), which implies that the deep ocean was 2°C cooler during the LGM. We suggest a revision of this estimate based on measurements of deep sea pore fluids using a

method presented by Schrag and DePaolo (4). The change in $\delta^{18}\text{O}_{\text{sw}}$ caused by changes in continental ice volume through the Pleistocene represents a periodic boundary condition for the sediment-pore fluid system. This variation diffuses down from the sea floor, leaving a profile of $\delta^{18}\text{O}$ versus depth in the pore fluid that is a record of the $\delta^{18}\text{O}$ history of the overlying seawater. The $\delta^{18}\text{O}_{\text{sw}}$ during the LGM can be reconstructed with the use of a numerical model to calculate the attenuation of the signal as long as high-precision, high-resolution pore fluid data are available.

Pore fluids were sampled during Leg 154 of the Ocean Drilling Program (ODP) from Site 925, drilled at a water depth of 3041 m on the Ceara Rise ($4^\circ 12'\text{N}$, $43^\circ 29'\text{W}$) (5). The oxygen isotope data (6) identify a peak in $\delta^{18}\text{O}$ between 20 and 35 m below the sea floor (Fig. 1). The $\delta^{18}\text{O}$ values are constant at -0.02 per mil in the first 7 m. From 10 to 20 m, the $\delta^{18}\text{O}$ values increase to 0.18 per mil, followed by a plateau from 20 to 35 m. Below 35 m, the $\delta^{18}\text{O}$ values decrease to a minimum of -1.75 per mil at a depth of 569 m.

We modeled the data by using the periodic change in $\delta^{18}\text{O}_{\text{sw}}$ with time at the sediment-water interface given by benthic $\delta^{18}\text{O}$ records for ODP Site 677 (7) and Core V19-30 (8). We assumed that the relative contributions of temperature and $\delta^{18}\text{O}_{\text{sw}}$ to the benthic $\delta^{18}\text{O}$ records were constant with time and adjusted the amplitude of those records in multiple calculations with glacial-interglacial changes in $\delta^{18}\text{O}_{\text{sw}}$ of 0.7, 1.0, and 1.3 per mil. The decrease in $\delta^{18}\text{O}_{\text{sw}}$ over the last 20,000 years was calculated from the Barbados sea level curve (2, 9). The effects of sedimentation (~ 30 cm per 1000 years at Site 925) and chemical reaction were not considered because they are too slow over the time period to affect the calculations. We used diffusion coefficients from measured values of the self-diffusion of water (10) (adjusted for tortuosity using the square of the measured porosity) and a bottom-water temperature of 3°C (11). The diffusion coefficient

Fig. 1. Oxygen isotope data on pore fluids [relative to standard mean ocean water (SMOW)] from Site 925, plotted versus depth. Error bars for data in the upper 60 m represent one standard deviation of four replicate measurements.



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was corrected for down-hole temperature increases, although the effect of temperature on the diffusion coefficient is negligible in this setting. On the basis of measured values, the $\delta^{18}\text{O}$ of the pore fluid at the lower boundary of 200 m was fixed at -0.75 per mil; the reconstructed glacial-interglacial change in $\delta^{18}\text{O}_{\text{sw}}$ is not sensitive to slight changes in this lower boundary condition or to replacement with a constant-flux boundary. The best fit to the data, obtained by visual assessment, yields a glacial-interglacial change in $\delta^{18}\text{O}_{\text{sw}}$ between 0.7 and 0.8 per mil (Fig. 2). Changing the diffusivity does not improve the fit. A higher diffusivity shifts the peak deeper in the hole and increases the attenuation of the signal; a lower diffusivity reduces the attenuation of the glacial-interglacial signal and implies a glacial-interglacial change in $\delta^{18}\text{O}_{\text{sw}}$ even smaller than 0.7 per mil. If upward advection is added to the system, the peak in the pore fluid $\delta^{18}\text{O}$ -depth profile is shifted upward, and the amplitude of the peak is attenuated, allowing for larger changes in $\delta^{18}\text{O}_{\text{sw}}$ (Fig. 3). However, the $\delta^{18}\text{O}$ gradient down to 570 m implies that advection, if present, is below $0.05 \text{ mm year}^{-1}$. If we assume that the temperature of bottom water was constant from 115,000 to 20,000 years ago and that changes in the benthic $\delta^{18}\text{O}$ record reflect only changes in $\delta^{18}\text{O}_{\text{sw}}$, again of magnitude 0.7, 1.0, and 1.3 per mil, as suggested by Shackleton (12), then a glacial-interglacial change in $\delta^{18}\text{O}_{\text{sw}}$ of 0.9 per mil accounts for the data. The results are insensitive to changes in $\delta^{18}\text{O}_{\text{sw}}$ before 115,000 years ago. If the $\delta^{18}\text{O}_{\text{sw}}$ value is allowed to drop 0.1 per mil below the modern deep water value at 6000 years before present, followed by an increase to

the present value, then the model provides a better fit to the constant values in the upper 10 m, and a glacial-interglacial change in $\delta^{18}\text{O}_{\text{sw}}$ of 0.8 per mil accounts for the data.

Overall, we estimate that the data are consistent with a glacial-interglacial change in $\delta^{18}\text{O}_{\text{sw}}$ of 0.8 ± 0.1 per mil. The glacial-interglacial difference in $\delta^{18}\text{O}$ values of benthic foraminifera in the region of Site 925 is 1.8 per mil (13). If the ice volume component of that difference is 0.8 per mil, then the temperature in this region was 4°C colder during the LGM (14). As the modern potential temperature 3 km below the ocean surface is 3°C , the deep water in the tropical Atlantic cooled during the LGM to within 1°C of its freezing point. Our determination for the change in $\delta^{18}\text{O}_{\text{sw}}$ is significantly different from the value of 1.3 per mil based on Pleistocene corals from Barbados (2, 15). The likely source of error in that determination is the assumption that the change in sea surface temperature at Barbados was negligible during initial stages of deglaciation (15). Although this assumption is consistent with the findings of CLIMAP (16), a recent study reports that sea surface temperatures at Barbados, as recorded in coral skeletons, were 4.5° to 6°C colder during the LGM (3). If this conclusion is correct, even if it applies only to sea surface temperatures around Barbados, then it is likely that temperature contributes to the observed change in $\delta^{18}\text{O}$ of Barbados corals and that the maximum value of 1.3 per mil is higher than the true ice volume contribution to the Pleistocene oxygen isotope record.

These results, which make no assumptions about the relative importance of different water masses or about the global

mean value of $\delta^{18}\text{O}_{\text{sw}}$, emphasize that spatial variability is an important component of the problem. Previous studies have assumed that a determination of the glacial-interglacial change in $\delta^{18}\text{O}_{\text{sw}}$ at a single location such as Barbados represents a global average (2, 17). At present, the Atlantic is more than 1.5°C warmer at a depth of 3000 m than are the Pacific and Indian oceans (18) and therefore could have tolerated substantially more cooling during the LGM. If Antarctic Bottom Water (AABW) replaced North Atlantic Deep Water (NADW) as the Atlantic's dominant source of deep water during the LGM, as suggested by tracer studies (19), the temperature (and salinity) contrast between the ocean basins would be greatly reduced. This switch in the dominant source of deep water for the Atlantic also helps to explain why we obtain a small change in $\delta^{18}\text{O}_{\text{sw}}$ for the deep Atlantic [the $\delta^{18}\text{O}$ of AABW in the modern ocean is about 0.5 per mil lower than that of NADW (1), although one cannot assume this difference was constant through the LGM].

It is difficult to extrapolate from these results for a single site to a global mean estimate for the change in $\delta^{18}\text{O}_{\text{sw}}$ (that is, the global effect of ice volume on the oceans). However, because these results indicate that deep water in the Atlantic Ocean cooled to about -1°C , a conservative assumption would be that the Indian and Pacific oceans were at least as cold as the Atlantic during the LGM. The modern mean temperature for the Indian and Pacific oceans at a depth of 3 km is 1.5°C , so the basins were about 2.5°C cooler during the LGM. This cooling implies that 1.1 per mil of the 1.7 per mil change in benthic foraminifera in the Indian and Pacific oceans is

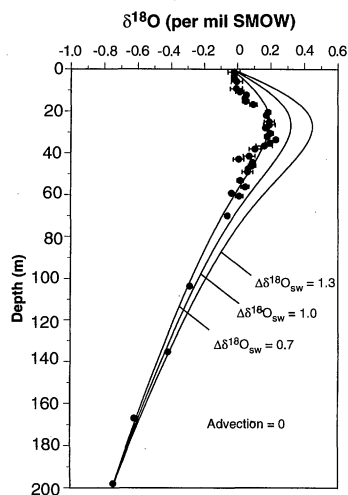


Fig. 2. Comparison of pore fluid data and model calculations for different glacial-interglacial changes in $\delta^{18}\text{O}_{\text{sw}}$ with no advection. The best fit to the data is obtained for a change in $\delta^{18}\text{O}_{\text{sw}}$ of 0.7 to 0.8 per mil.

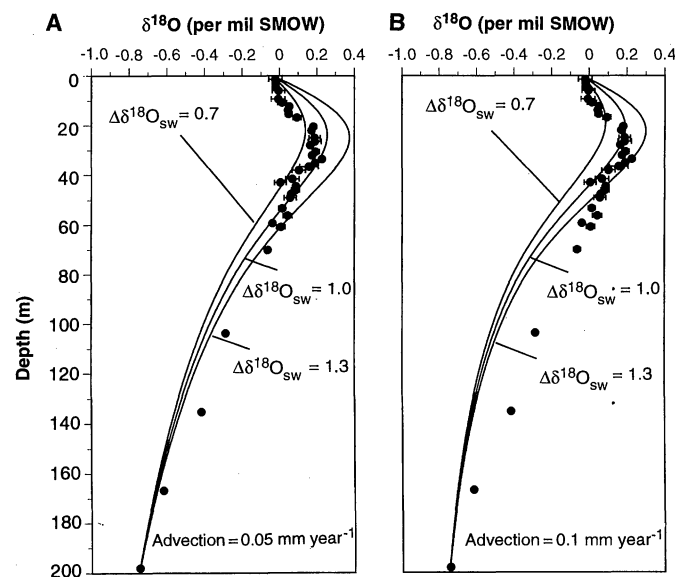


Fig. 3. Comparison of pore fluid data and model calculations for different glacial-interglacial changes in $\delta^{18}\text{O}_{\text{sw}}$ with two different advection velocities: (A) $0.05 \text{ mm year}^{-1}$ and (B) $0.10 \text{ mm year}^{-1}$. For advection greater than $0.05 \text{ mm year}^{-1}$, the model curves do not reproduce the $\delta^{18}\text{O}$ -depth gradient that persists to the base of the hole.

attributable to a change in $\delta^{18}\text{O}_{\text{sw}}$. This estimate yields a volume-weighted average for all oceans of 1.0 per mil, rather than 1.3 per mil, and requires the average $\delta^{18}\text{O}$ value of continental ice during the LGM to be -32 per mil rather than -42 per mil, consistent with estimates for the isotopic composition of continental ice during the LGM (20).

An alternative method for relating the 0.8 ± 0.1 per mil change in the tropical Atlantic to the global mean is to estimate how changes in the proportion of NADW and AABW would have affected the $\delta^{18}\text{O}_{\text{sw}}$ at Site 925 (21). On the basis of carbon isotopes in foraminifera from deep sea sediment (13) and the distribution of pre-formed phosphate in the modern ocean (22), the ratio of NADW to AABW in the region of Site 925 changed from 40:60 during the LGM to 90:10 today. If the difference between $\delta^{18}\text{O}$ values of AABW and NADW was the same during the LGM, the circulation changes at Site 925 during the LGM reduced the $\delta^{18}\text{O}_{\text{sw}}$ by 0.25 per mil. This reduction implies a mean ocean change of 1.05 per mil, in good agreement with the estimate based on deep water temperature changes.

A lower glacial-interglacial change in $\delta^{18}\text{O}_{\text{sw}}$ makes planktonic foraminiferal $\delta^{18}\text{O}$ records consistent with greater cooling of the tropics during the LGM. By assuming an ice-volume component of 1.3 per mil, $\delta^{18}\text{O}$ records of planktonic foraminifera yield tropical sea surface temperatures that are at most 2°C colder during the LGM (1), consistent with estimates from CLIMAP based on biodiversity (16). If the buildup of continental ice affects the carbonate oxygen isotope record for the LGM by only 1.0 per mil as a global average and by as little as 0.8 per mil for deep water in the Atlantic Ocean, then $\delta^{18}\text{O}$ records of tropical planktonic foraminifera can yield from 3° to 5°C of cooling since the LGM. Although it remains uncertain how the $\delta^{18}\text{O}$ of surface waters changed during the LGM as a result of changes in evaporation and precipitation, reducing the ice-volume component helps to reconcile tropical planktonic foraminiferal $\delta^{18}\text{O}$ records with the coral $\delta^{18}\text{O}$ and Sr/Ca measurements (3) and with terrestrial climate proxies, including snow-line elevations (23), noble gases in ground water (24), and pollen records (25).

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Nuclear Encoding of a Chloroplast RNA Polymerase Sigma Subunit in a Red Alga

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A chloroplast RNA polymerase sigma factor is encoded by a nuclear gene, *sigA*, in the red alga *Cyanidium caldarium* RK-1. The encoded protein functions as an RNA polymerase sigma factor in vitro and it is localized to the chloroplast in vivo. SigA shows high sequence similarity to the sigma factors of cyanobacteria, which is indicative of the ancestral endosymbiotic event and subsequent transfer of the *sigA* gene to the nuclear genome.

DNA sequence and phylogenetic analyses indicate that chloroplasts are close relatives of free-living cyanobacteria and are derived from an endosymbiotic event. Chloroplast RNA polymerase is closely related to that of cyanobacteria (1). Chloroplast genomes of

several plant species encode RNA polymerase subunits corresponding to α , β , and β' of the eubacterial core enzyme (2). However, although the σ subunit, a protein important for transcription initiation and promoter selectivity (3), has been found in chloroplasts (4), the corresponding gene has not been found in the chloroplast genome.

The unicellular red alga *Cyanidium caldarium* RK-1 is an acidophilic eukaryote with a small genome [13 mega-base pairs (Mbp)] (5). The cells contain a nucleus, a mitochondrion, and a chloroplast, each with its own genome. The chloroplast RNA polymerase and σ subunit of a related red alga,

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