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DETERMINATION OF $\delta^{18}O$ OF SEAWATER IN THE DEEP OCEAN DURING THE LAST GLACIAL MAXIMUM

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Abstract. We present a method for determining the $\delta^{18}O$ of seawater in the deep ocean during the last glacial maximum from the measured $\delta^{18}O$ values of deep sea pore fluids. Using data from Deep Sea Drilling Project (DSDP) site 576 in the Western Pacific, this method yields a glacial to interglacial change in $\delta^{18}O_{sw}$ of 1.0±0.25‰. This value for $\Delta\delta^{18}O_{sw}$ is the first direct measurement of deep ocean $\delta^{18}O$ for the last glacial maximum and avoids the problems of spatial and temporal variability of the $\delta^{18}O$ of surface water implicit in previous determinations. More precise, higher-resolution pore fluid measurements are required to improve this determination.

INTRODUCTION

The $\delta^{18}O$ values of foraminifera tests in deep sea sediments record episodes of glaciation over at least the last 35 million years of Earth history. The $\delta^{18}O$ of foraminiferal carbonate ($\delta^{18}O_{fc}$) reflects a combination of the temperature and the $\delta^{18}O$ of seawater ($\delta^{18}O_{sw}$); the latter changes with the volume of low-$\delta^{18}O$ continental ice sheets. To understand global climatic changes between glacial and interglacial periods, it is necessary to determine how much of the measured change in foraminiferal $\delta^{18}O$ from glacial to interglacial ($\Delta\delta^{18}O_{fc}$) is produced by changing seawater temperature and how much by changing $\delta^{18}O_{sw}$. Previous studies have established that the average $\Delta\delta^{18}O_{fc}$ for the deep ocean is 1.7‰ [Broecker, 1989]. The maximum contribution from change in seawater temperature, calculated from the freezing point of seawater, gives a minimum change in $\delta^{18}O_{sw}$ of 1.1‰ [Duplessy,1981], although this determination was for a southern ocean site and may not apply to sites in other oceans that have more potential for cooling during glacial periods. A maximum value of 1.3‰ for the change in $\delta^{18}O_{sw}$ is obtained by combining the observations of Fairbanks and Mathews [1978], who measured the dependence of $\delta^{18}O$ of coral aragonite on sea level change, and the observations of Fairbanks [1989], who measured the total sea level change since the last glacial maximum (LGM). Shemesh et al. [1992] obtained a similar result for the change in $\delta^{18}O_{sw}$ by measuring the $\delta^{18}O$ of silica in diatoms and of foraminiferal carbonate at the same location.

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RECORD OF $\delta^{18}O_{sw}$ IN DEEP SEA PORE FLUIDS

We present here an alternative method for determining $\delta^{18}O_{sw}$ in the deep ocean during the LGM, using isotopic analyses of pore fluids combined with modeling of the diffusive transport of oxygen through the sediment column. Because oceanic deep water is isotopically less variable than surface water, this method eliminates the uncertainties associated with previous determinations which measured surface water $\delta^{18}O$ variations [Fairbanks and Mathews, 1978; Shemesh et al., 1992].

Our method is based on the observation that over the relatively short time interval since the LGM, most sediments on the ocean floor behave as porous media with chemical transport in the pore fluids occurring primarily by diffusion. Over this time interval, the sediments can be considered essentially nonreactive with respect to oxygen because of the slow rate of diagenetic reactions and the fact that oxygen is a major component of both fluids and solids. The changes in $\delta^{18}O_{sw}$ caused by glaciation and deglaciation represent a periodic boundary condition for the sediment-pore fluid system. These changes diffuse down from the seafloor, leaving a profile of $\delta^{18}O$ versus depth in the pore fluid that is a record (albeit degraded) of the $\delta^{18}O$ history of the overlying seawater. If there is no advection, the relationship between the $\delta^{18}O$-depth record in pore fluid and the $\delta^{18}O$-time history of the ocean is determined only by the rate of self-diffusion of water in the sediment. In mathematical terms, if $\delta^{18}O_{sw}$ oscillates with time t as some linear combination of sine functions,

$$\delta^{18}O_{sw}(t) = \sum_n A_n \sin(n\omega t) \tag{1}$$

then the $\delta^{18}O$ of the pore fluid will vary with depth z and time as

$$\delta^{18}O(z,t) = \sum_n A_n e^{-kz\sqrt{n}} \sin(n\omega t - kz\sqrt{n}) \tag{2}$$

where $k=(\omega/2D_{eff})^{1/2}$ and D_{eff} is the diffusion coefficient of water in the pore fluid [Carslaw and Jaeger, 1959]. For the sediment-pore fluid system, the attenuation factor is such that modern pore fluid preserves little 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, which should appear as a high-$\delta^{18}O$ peak in the pore fluid $\delta^{18}O$-depth profile at a depth of 25 to 50 m (depending on the diffusivity). Thus, if the depth and amplitude of the pulse of higher $\delta^{18}O$ pore fluid can be measured accurately 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 analogous to that used to calculate the thermal diffusivity of soils from temperature variations at the Earth's surface [Kelvin, 1861].

If chemical transport in the sediment occurs by advection as well as diffusion, both the depth and the amplitude of the positive $\delta^{18}O$ anomaly in the pore fluid can be affected. Advective transport in deep sea sediments is driven either by temperature gradients forming a convection cell or by compaction of sediment. In this context, we consider only upward advection, most likely due to compaction of sediment. If there is upward advection, it is still possible to use the pore fluid $\delta^{18}O$-depth profile to obtain a value for $\Delta\delta^{18}O_{sw}$ as long as the rate of advection or the effective diffusivity can be determined independently.

The pulse of high-$\delta^{18}O$ pore fluid from the LGM should exist everywhere on the ocean floor where diffusion is the dominant transport mechanism, regardless of lithology. A survey of data from 37 Deep Sea Drilling Project (DSDP) sites identifies several sites with positive deviations of $\delta^{18}O$ relative to the normal decrease with depth [Lawrence and Gieskes, 1981]. Sampling intervals on these and most other DSDP and Ocean Drilling Program (ODP) cores are too large to measure accurately the amplitude of the signal. One exception is site 576 from DSDP leg 86 in the western Pacific Ocean where seven samples were taken in the top 60 m of core. McDuff [1984] recognized that a positive deviation in $\delta^{18}O$ values at a depth of approximately 30 m, correlated with a peak in chloride concentration, had implications for past seawater composition at this site. McDuff [1984, p. 677] attributed these profiles to glacial-interglacial cycles in seawater controlled by "a diffusive process acting over ~1m.y." In this paper, we show that it is possible to invert such pore fluid data to calculate what the isotopic composition of seawater was during the LGM, and that the time scale is not 1 m.y. but just the 20 kyr since the LGM. As McDuff's measurements are the best data available, our approach is to use a model of oxygen isotope transport in pore fluids with parameters appropriate to site 576 to obtain values of $\delta^{18}O_{sw}$ that reproduce the measured pore fluid values. When higher resolution measurements are available from future ODP drilling legs (which will require closely spaced pore fluid samples to a depth of circa 100 m), a more precise determination of $\Delta\delta^{18}O_{sw}$ should be possible.

We note that there are previous studies where inferences about the isotopic composition of paleoseawater have been made from the isotopic characteristics of pore fluids [Bath and Shackleton, 1984; Friedman and Hardcastle, 1988]. However, in both of the cited papers, the authors have made the incorrect interpretation that paleoseawater is preserved unaltered in sediments, and therefore that pore fluid coexisting with sediments at a particular depth is a sample of ocean water of the same age as the sediment at that depth. Numerous studies of pore fluid chemistry [McDuff and Gieskes, 1976; McDuff, 1981; Lawrence and Gieskes, 1981] as well as studies of the diffusive properties of pore fluids [Klinkenberg, 1951], show conclusively that diffusion significantly modifies the chemical properties of pore fluids. While information about past seawater chemistry is indeed recorded in the composition of modern pore fluids, the time scale of that record is determined by the rates of transport processes in the pore fluid, not by the age of the coexisting sediment.

MODEL

To account for the depth dependence of the diffusion coefficient and the sediment porosity, as well as to evaluate the effects of advection in the system, we use a numerical model to describe the transport of oxygen in the pore fluids rather than the analytical solution given above. The sediment is treated as a fluid-saturated, non-reactive porous medium with porosity decreasing from 0.8 at the seawater-sediment interface to 0.6 at 200 meters below sea floor (based on measured porosity at site 576 from Schultheiss [1984]). The transport of oxygen by diffusion and advection of $H_2{}^{16}O$ and $H_2{}^{18}O$ in the pore fluid is described in $\delta^{18}O$ notation by the following equation of mass conservation:

$$\frac{\partial(\delta^{18}O_f)}{\partial t} = \frac{\partial\left(\phi D_{eff} \frac{\partial(\delta^{18}O_f)}{\partial z}\right)}{\phi \partial z} - \frac{\partial(\phi U_f \delta^{18}O_f)}{\phi \partial z} \qquad (3)$$

where ϕ is porosity, D_{eff} is effective diffusion coefficient, and U_f is advective velocity. This equation neglects the small (5%) difference between the diffusion coefficients for $H_2{}^{16}O$ and $H_2{}^{18}O$. These equations are solved by finite difference methods; oxygen isotopic composition of the fluid is monitored at 1-m intervals. The change in effective diffusivity with depth because of changes in temperature and tortuosity is accounted for by allowing D_{eff} to vary as $D_0(T)\phi^2$. The results are not sensitive to this porosity dependence of the diffusion coefficient because we are interested in only the top 50 m of sediment. We use values of $D_0(T)$ from measured values of the self-diffusion of water [Simpson and Carr, 1958], assuming a bottom temperature of 2°C and a temperature gradient in the sediment of $0.03°m^{-1}$ (although the effect of the temperature change on the diffusion coefficient is small). We then adjust D_{eff} based on the fit of the model to the data from site 576 [McDuff, 1984] by adding a multiplier k so that the final expression is $D_{eff}=kD_0(T)\phi^2$. Two approaches are taken to fitting the data. First, we assume no advection ($U_f=0$) and determine the value of k and the magnitude of $\Delta\delta^{18}O_{sw}$ that produce the best fit. Next, we assume that k=1, and determine the value of U_f and the magnitude of $\Delta\delta^{18}O_{sw}$ that produce the best fit. Sedimentation and chemical reaction are not considered because they are too slow over the time period of interest (~20 kyr) to affect the calculations. We fix the $\delta^{18}O$ of the pore fluid at -0.6‰ at a depth of 200 m to account for the effects of basalt alteration below the sediments [Lawrence and Gieskes, 1981; Schrag et al., 1992].

The optimal approach is to invert the $\delta^{18}O$-depth data to obtain a $\delta^{18}O_{sw}$-time curve. However, the amplitudes of all but the circa 100 kyr period glacial variations are too greatly attenuated for this to be useful. Instead, we assume that the $\delta^{18}O_{sw}$-time record is identical to the $\delta^{18}O_{fc}$-time record in all respects except amplitude, and use the data to constrain the amplitude. This is equivalent to assuming that the fractional contribution to the $\delta^{18}O_{fc}$ variation from the $\delta^{18}O_{sw}$ variation is constant. We start the model one million years in the past. For the first 500,000 years of simulated time, we hold the $\delta^{18}O_{sw}$ at the upper boundary (seafloor) constant at -0.1‰ (the measured value at site 576) to allow the profile to reach steady state. From 500,000 years to 980,000 years, we use the benthic $\delta^{18}O_{fc}$ record for ODP site 677 to simulate the $\delta^{18}O_{sw}$ [Shackleton and Hall, 1989]. The details of the record prior to 20,000 years before present have little effect on the calculations because the glacial-interglacial signals are rapidly attenuated. For the last 20,000 years of simulated time, we calculate the decrease in $\delta^{18}O_{sw}$ from the Fairbanks sea level curve [Fairbanks, 1989] using coral ages measured by U-Th disequilibria [Bard et al., 1990] and using a range of $\delta^{18}O_{sw}$-sea level proportionality factors from 0.0058 ‰m^{-1} ($\Delta\delta^{18}O_{sw}=0.7$‰) to 0.011 ‰$m^{-1}$ ($\Delta\delta^{18}O_{sw}=1.3$‰). At the end of the calculation (t=1,000,000 years which is equivalent to the present) $\delta^{18}O_{sw}$ =-0.1‰. The use of the sea level curve for the critical last 20,000 years of simulated time largely removes the uncertainty associated with the assumption of proportionality between the $\delta^{18}O_{fc}$ and $\delta^{18}O_{sw}$ records used for the 500,000-980,000 year time range.

RESULTS

The oxygen isotope measurements of pore fluids from site 576 define a positive anomaly in $\delta^{18}O$ with depth with the peak occurring between 20 and 35 meters below seafloor. Assuming that diffusion dominates chemical transport in the pore fluid ($U_f=0$), we obtain a best fit to the data when k=0.55 ($D_{eff}=3.6\times10^{-6}$ cm^2s^{-1} at the top of the sediment) and $\Delta\delta^{18}O_{sw}=1.0$‰ (Figure 1). On the basis of results of calculations using other values of $\Delta\delta^{18}O_{sw}$ (Figure 1), we estimate the error on this calculation to be ±0.25‰. This error could be reduced with higher resolution sampling as the present fit is strongly dependent on the single measurement of seawater at the top of the sediment.

If we assume that k=1 ($D_{eff}=6.6\times10^{-6}$ cm^2s^{-1} at the top of the sediment), some upward advection is required to fit the model results to the data. As discussed by McDuff [1984], there is an upper limit to upward advection of approximately 0.5

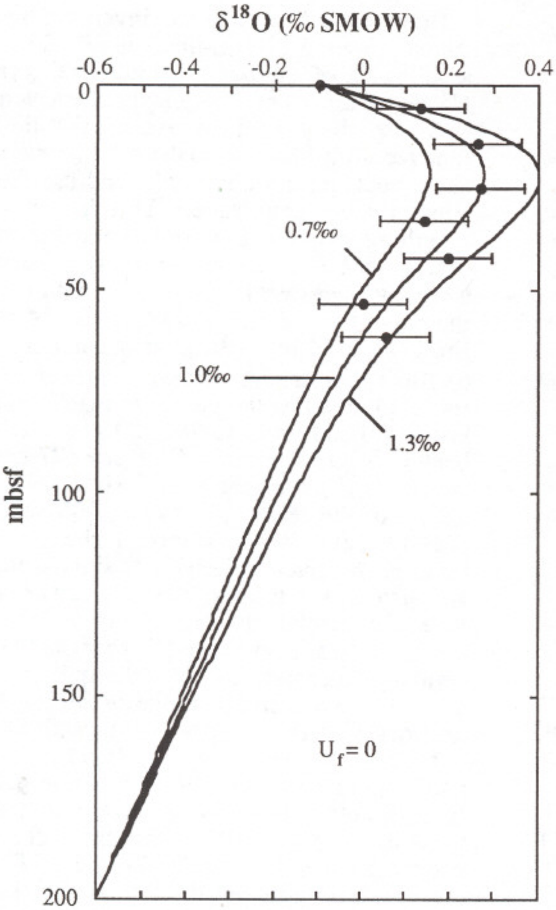

Fig. 1. Model results (lines) and pore fluid data (dots) for DSDP site 576. The model lines are labeled with the value used for $\Delta\delta^{18}O_{sw}$, the change in $\delta^{18}O$ of seawater from the last glacial maximum to the present. In this model, there is no advection (U_f=0). A best fit to the data is obtained for k=0.55 ($D_{eff}=3.6\times10^{-6}$ cm^2s^{-1} at the top of the sediment) and $\Delta\delta^{18}O_{sw}$=1.0‰. The error on this calculation, which we estimate to be ±0.25‰, is illustrated by the lines generated for $\Delta\delta^{18}O_{sw}$=0.7 and 1.3‰.

mm yr^{-1} beyond which the $\delta^{18}O$ anomaly would vanish completely and no other chemical gradients in the pore fluid could be sustained. Lower rates of upward advection on the order of 0.1 mm yr^{-1} would decrease the depth of the glacial-interglacial signal below the sea floor and lower the amplitude of the signal beyond that caused by diffusion (Figure 2). The best fit to the pore fluid data from site 576 is obtained when U_f=0:12 mm yr^{-1} and $\Delta\delta^{18}O_{sw}$=1.3‰ (Figure 3). Although it is impossible to rule out advection of this magnitude, flow from compaction would be no more than ten times smaller because of the low sedimentation rate at site 576 (<0.01 mm yr^{-1}), and upward hydrothermal flow of this magnitude is unlikely given the relatively old age of the oceanic crust and the existence of impermeable cherts deeper in the section. Therefore we suggest that a value of 1.0±0.25‰ obtained from the diffusion-dominated solution is the most reasonable interpretation of the data. A value of 1.0±0.25‰ is consistent with that obtained by Shemesh et al. [1992] for surface $\Delta\delta^{18}O_{sw}$ but is lower than the value of 1.3‰ from Fairbanks [1989]. This difference may be due to variability of $\delta^{18}O_{sw}$ between oceans, as neither value may represent the global average $\Delta\delta^{18}O_{sw}$. The difference is significant because if the average $\delta^{18}O_{sw}$ during the LGM were 1.0‰ higher than today instead of 1.3‰, it would require the $\delta^{18}O$

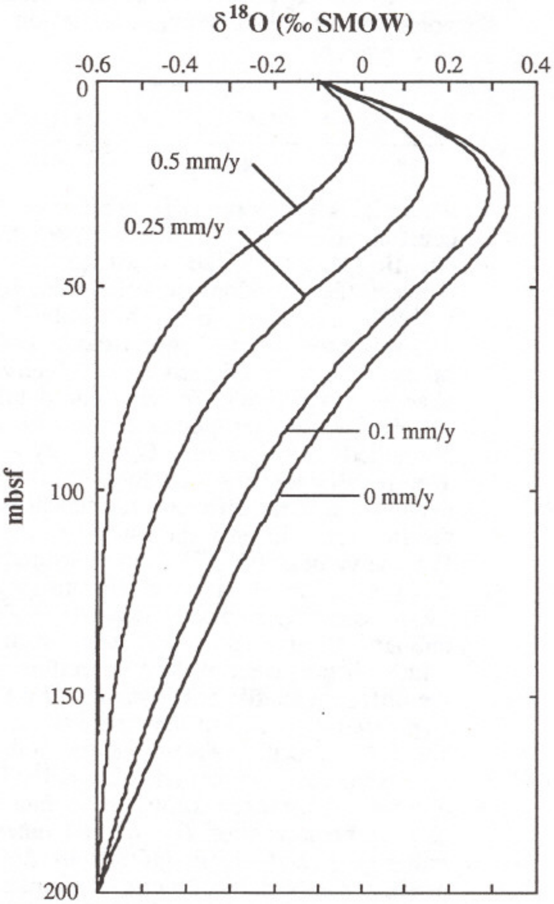

Fig. 2. Model results for different rates of advection assuming k=1 ($D_{eff}=3.6\times10^{-6}$ cm^2s^{-1} at the top of the sediment) and $\Delta\delta^{18}O_{sw}$=1.3‰. Upward advection decreases the depth of the glacial-interglacial $\delta^{18}O$ peak below the seafloor and changes the shape of the profile. If advection is faster than 0.5 mm yr^{-1}, the $\delta^{18}O$ anomaly will be almost completely removed.

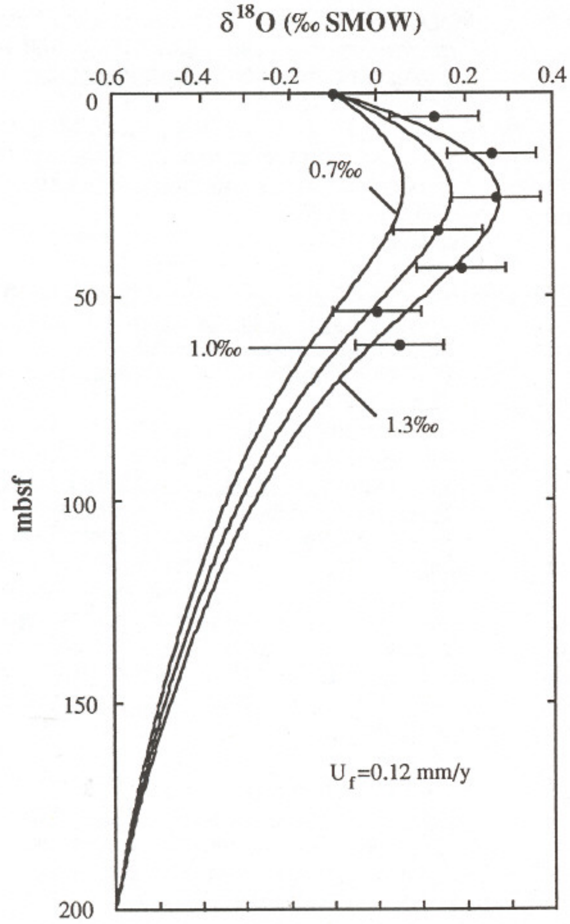

Fig. 3. Model results (lines) and pore fluid data (dots) for DSDP site 576. In this calculation, we assume that k=1 ($D_{eff}=6.6\times10^{-6}$ cm^2s^{-1} at the top of the sediment). The best fit to the pore fluid data is obtained when $U_f=0.12$ mm yr^{-1} and $\Delta\delta^{18}O_{sw}=1.3$‰. Also shown are model results for $\Delta\delta^{18}O_{sw}=0.7$ and 1.0‰. Advection velocities as high as 0.12 mm yr^{-1} are unlikely to have occurred over the last 20,000 years at site 576.

value of average LGM ice to be -32‰ instead of -42‰ [Fairbanks, 1989]. This change would imply a higher average temperature at the sites of ice accumulation, reducing estimates of glacial-to-interglacial temperature change in high latitude continental interiors and facilitating moisture transport to the sites of ice accumulation. A change in the average value of LGM $\delta^{18}O_{sw}$ would also alter the LGM sea surface temperatures and salinities calculated from the $\delta^{18}O$ values of planktonic foraminifera [Broecker, 1989].

The results obtained here could be significantly refined by sampling pore fluids at higher resolution and removing uncertainty about the rate of advection, perhaps by determining the diffusion coefficient from electrical conductivity data on fresh cores [Klinkenberg, 1951; McDuff and Gieskes, 1976]. A new sampling method tested on ODP leg 119 yields high resolution samples for chemical analysis, but as the extraction process involves dilution of pore water with deionized water, the samples are unsuitable for precise isotopic analysis [Cranston, 1991]. Nevertheless, both of our requirements could easily be accomplished on future ODP drilling legs using existing technology. Because sediment of any age and any composition could be used for such a study, most locations would be appropriate except for those sites where pore water transport is likely to be dominated by advection (i.e., young crust, convergent margins, and places with extremely rapid sedimentation). Ultimately, with higher-resolution sampling and more precise analyses, the error could be reduced to as little as ±0.1‰, which is at least as good as that achievable with other approaches. At that resolution, this method could be used to study spatial variability in deep ocean $\delta^{18}O_{sw}$ during the LGM. In addition, this method could be applied to other chemical species, such as chloride, that are not affected by reactions with the sediment over glacial time scales.

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