Thermal Structure of the Deep Pacific Ocean in the Early Pliocene

Abstract. *The thermal structure of the Pacific Ocean between water depths of about 1 and 4.5 kilometers is estimated from the oxygen isotopic ratio of benthonic foraminifera from deep-drilled and piston cores of early Pliocene age (about 3 to 5 million years ago). The ratio of oxygen-18 to oxygen-16 in the early Pliocene at each site varies by an average of only ± 0.12 per mil (1 standard deviation). A plot of the oxygen isotopic ratio against modern bottom-water temperature is adequately fit by a line having a slope of − 0.26 per mil per degree Celsius (the equilibrium temperature dependence of calcite-water fractionation), suggesting that the temperature gradient of the Pacific Ocean during the early Pliocene was similar to that of today.*

Determining the vertical temperature gradient of past oceans is a problem that has not been studied in detail. Previous workers were primarily concerned with studying the history of bottom-water temperature change throughout the Cretaceous and Tertiary rather than with reconstructing temperature gradients through deep and intermediate waters for a discrete interval of geologic time. These workers (*1-4*) measured the δ^{18}O (*5*) of benthonic foraminiferal calcite, which is temperature-dependent, as a deep-water temperature indicator. Their results showed that bottom-water temperatures have decreased throughout the Cenozoic (from 65 million years ago to the present). Savin *et al.* (*4*) used the oxygen isotopic composition of both planktonic and benthonic foraminifera to determine that surface and bottom-water temperature covaried until about the middle Miocene. Before the middle Miocene the surface-to-bottom temperature gradient was about 60 percent of that after the middle Miocene, implying that the thermocline was less clearly defined (*4*).

In this report we examine the thermal structure of the tropical and temperate Pacific Ocean during the early Pliocene (between about 3 and 5 million years ago). This period predates the cyclic Northern Hemisphere glaciation with its complicating effects and is a time of much less variable δ^{18}O in marine carbonates than the preceding or following period (*6-8*). Studies of water column structure and temperature at a time of variable bottom-water δ^{18}O and temperature would be complicated by the need to choose a precisely defined time slice for the reconstruction and by noise introduced by bioturbation.

For this reconstruction we used early Pliocene δ^{18}O data for samples of the benthonic foraminiferal genus *Uvigerina* (*6-8*), which is thought to deposit calcite in equilibrium with bottom water (*9*), and of other genera that do not fractionate ^{18}O relative to *Uvigerina* (*10*). These data, and data generated for this report by standard procedures (*8*), are presented in Table 1. Table 2 contains site locations and water temperatures at the depth of each site. Our δ^{18}O values are

Table 1. Isotopic results for all samples used in this study. The δ^{18}O values are relative to the B-1 standard. Data for sites 284 and 284A are from (*6*), data for site V28-179 from (*7*), and data for sites 158 and 310 from (*8*).

Sample*	Foram†	δ^{18}O (per mil)
	DSDP 284	
7-2, 40	U	2.15
7-5, 128	U	2.28
	DSDP 284A	
3-2, 40	U	2.26
3-6, 80	U	2.12
	DSDP 284	
9-1, 40	U	2.28
9-4, 40	U	2.04
10-1, 100	U	2.13
10-6, 30	U	2.09
11-1, 75	U	2.07
11-4, 10	U	2.25
13-2, 128	U	2.11
13-6, 40	U	1.98
14-1, 40	U	2.02
14-4, 128	U	2.04
15-1, 128	U	2.11
15-4, 140	U	2.23
	DSDP 207A	
2-1, 148	U	2.64
3-1, 75	U	2.55
3-1, 148	U	2.62
3-2, 75	U	2.41
3-3, 75	U	2.60
3-4, 75	U	2.60
3-5, 77	U	2.73
	DSDP 208	
9-2, 50	S	2.55
9-5, 148	S	3.08
10-2, 50	S	2.61
10-5, 125	S	2.65
11-2, 50	U	2.53
11-5, 125	S	2.51
	DSDP 158	
5-5, 100	U	2.46
6-1, 100	U	2.53
6-3, 100	U	2.77
6-5, 100	U	2.54
7-1, 101	U	2.68
7-3, 100	U	2.46
7-5, 100	U	2.69
8-1, 100	U	3.15
	U	3.07
8-3, 100	U	2.75
8-5, 100	U	2.49
9-1, 100	U	2.62
9-3, 100	U	2.54
9-5, 100	U	2.62
	DSDP 62.1	
9-3, 26	S	3.03
10-1, 100	S	3.20
10-2, 77	S	3.18
10-4, 97	S	3.23
10-5, 58	S	3.27
	U	2.99
10-6, 116	S	3.00
11-4, 10	S	3.13
11-4, 90	S	3.05
12-5, 71	S	2.99
12-5, 127	S	3.04
	DSDP 84	
17-1, 100	U	2.85
17-3, 100	S	2.66
18-1, 103	S	2.44
19-3, 100	U	3.03
19-5, 100	U	2.85
21-5, 52	U	2.92
	DSDP 206	
18-1, 90	U	2.70
18-5, 90	U	2.85
19-1, 90	U	3.03
19-2, 90	U	2.99
19-3, 90	U	2.88
19-5, 90	U	3.06
20-3, 90	U	3.01
20-5, 90	U	3.09
	DSDP 310	
6-3, 70	U	3.16
6-3, 140	U	3.16
6-4, 10	U	3.23
	U	3.28
6-4, 90	O	2.99
6-5, 18	O	2.84
6-5, 102	U	3.04
6-6, 10	U	3.16
6-6, 80	O	2.63
6cc	U	2.95
7-1, 138	O	3.03
7-2, 80	U	3.20
7-2, 140	U	3.01
7-3, 52	U	3.26
7-3, 120	U	2.98
	DSDP 83A	
7-1, 100	U	2.86
7-3, 100	U	2.89
7-5, 98	U	2.85
8-1, 100	U	3.01
8-3, 100	U	2.84
8-5, 100	U	2.88
9-1, 98	U	3.00
9-3, 99	U	2.94
9-5, 98	U	3.02
	DSDP 83A	
10-1, 100	U	2.86
10-2, 99	U	3.01
10-3, 100	U	2.95
10-5, 99	U	2.87
10-6, 102	U	2.76
	U	2.66
	V28-179	
1690	S	2.84
1700	S	2.21
1711	S	2.87
1721	S	2.90
1731	S	2.90
1741	S	3.08
1771	S	2.84
1780	S	3.14
1791	S	3.24
1800	S	2.85
1810	S	3.27
1820	S	2.90
1830	S	2.99
1840	S	3.01
1870	S	2.96
1890	S	2.91
1900	S	3.12
1911	S	3.00
1920	S	2.91
1940	S	2.95
1950	S	3.11
1961	S	3.07
1990	S	3.11
2030	S	3.01
2040	S	3.22
2051	S	3.16
2060	S	2.85

*The DSDP sample numbers give core, section, and interval in centimeters; for example, 9-5, 148 means core 9, section 5, 148 cm. The V28-179 sample numbers are all centimeters. †U, *Uvigerina* sp.; S, *Globocassidulina subglobosa*; O, *Oridorsalis* sp.

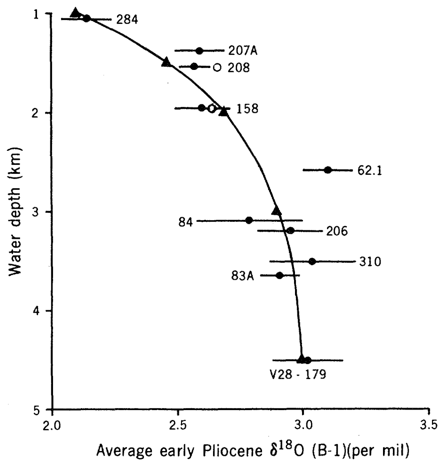

Fig. 1. Average early Pliocene $\delta^{18}O$ plotted against water depth (●). Error bars are ±1 standard deviation. The curved line is for $z^* = 1$ km, calculated (▲) for end points at 1 and 4.5 km (*23*). (○) Results at sites 158 and 208, including the two glacial samples (*13*). All data are presented in Table 1.

reported relative to the standard B-1 as our laboratory calibration to Pee Dee belemnite (PDB) is incomplete (*11*).

There is some evidence of early Pliocene glacial activity, although the standard deviation at each site discussed here is small (the average for all sites is about 0.12 per mil; Table 2). Mercer (*12*) presented evidence for significant glacial advances in southern South America at about 3.6 million years. At Deep Sea Drilling Project (DSDP) site 158, Keigwin (*8*) found evidence for a significant early Pliocene glaciation, or bottom-water temperature drop, based on one sample dated at about 4.2 or 4.3 million years. We report a similar isotopically heavy sample from DSDP site 208 (sample 9-5, 148 in Table 1), but our biostratigraphic precision is not sufficient to determine whether these samples are equivalent in time. At neither location is there evidence that foraminiferal specimens from these samples are displaced from later in the Neogene. These two isotopically heavy samples are excluded from further consideration in this report because we are attempting to reconstruct a preglacial ocean (*13*).

The average early Pliocene benthonic foraminiferal $\delta^{18}O$ values at all sites increase with increasing water depth (Fig. 1), as expected for equilibrium precipitation of calcite in waters of increasingly cold temperatures. The greatest enrichment in ^{18}O occurs between about 1 and 2 km. Below about 3 km $\delta^{18}O$ appears relatively stable throughout the tropical and temperate Pacific Ocean.

Several sources may contribute to the scatter of $\delta^{18}O$ values about a monotonic $\delta^{18}O$-depth curve (Fig. 1). These include possible violations of our assumption of nonequilibrium deposition of foraminiferal calcite due to vital effects, which we cannot test at this time, and different temperatures at the same depth in the ocean. For example, near sites 83A and 310, which lie at almost the same depth, modern temperatures differ by about 0.4°C (Table 2), corresponding to an isotopic difference of about 0.10 per mil. Site 84, at about 3100 m, is another example. It is located within the enclosed Panama Basin, which has a sill depth of 2920 m in the Equador trench (*14*). The next deepest sill is at 2330 m in a saddle on the Carnegie Ridge. Although modern hydrocasts indicate no spillover of water into the Panama Basin across the shallower sill (*14*), abyssal dunes of foraminiferal sand suggest that shallow spillover was a source of deep waters to the basin in the past (*15*). The data point for site 84 in Fig. 1 may thus represent equilibrium precipitation of calcite in water from a source as much as 700 m shallower and 0.07°C warmer.

A third source of scatter may be the sinking of oceanic crust into deeper water since the early Pliocene, which might cause some benthonic foraminifera to appear too light for the modern water depth (*16*). This could be significant where the oceanic crust is unusually shallow to begin with, as at site 158 (*17*), and where it is young and sinking most rapidly, and at sites 83A and 84 (*18*). We estimate, from the age-depth relationship of van Andel and Bukry (*19*) and the thickness of sediment accumulated in the past 4 million years, that early Pliocene benthonic foraminifera at sites 83A and 84 lived in water about 200 m shallower than the depth at which they live today. At these two locations today, such a depth difference does not correspond to an important temperature difference (*20*). At site 158, we estimate the net seafloor subsidence to be about 140 m, which equals a temperature decrease of 0.24°C and an isotopic difference of only −0.06 per mil.

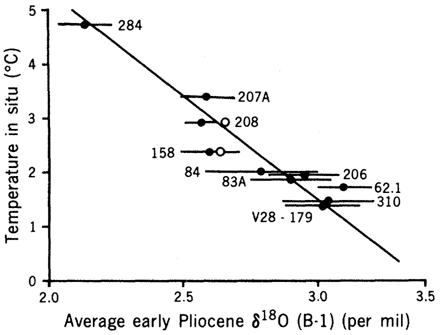

Fig. 2. Average early Pliocene $\delta^{18}O$ plotted against estimated present temperature at the depth of the sea floor at each site (●) (*21*). Error bars are ±1 standard deviation. (○) Results at sites 158 and 208, including the two glacial samples (*13*). A line of slope −0.26 per mil per degree Celsius (the equilibrium temperature dependence of calcite-water fractionation) (*22*) is fitted to the data by least squares.

The $\delta^{18}O$ data, when plotted against modern temperature at the depth and location of each site (*21*), give a line with a slope similar to that of the line for equilibrium precipitation of calcite, −0.26 per mil per degree Celsius (Fig. 2) (*22*). There are two ways to interpret this relationship. The first is that the early Pliocene benthonic foraminifera of this study deposited their calcite out of equilibrium with seawater, that the thermal structure of the Pacific Ocean was different from the modern thermal structure, and that the close fit of these data to the predicted slope is thus fortuitous. The second interpretation, which we favor, is that the early Pliocene Pacific Ocean temperatures changed with depth as they do today. Thus, the data in Fig. 1 suggest a temperature decrease of about 3.5°C between water depths of 1 and 4.5 km. We emphasize that this inferred temperature decrease is relative, and that absolute early Pliocene temperatures may have differed from those observed today.

Table 2. Site locations, present water temperature (*T*) at the depth of each site, and early Pliocene $\delta^{18}O$.

Site	Depth (m)	Latitude	Longitude	*T* in situ (°C)	Hydrocast location (*21*)	$\delta^{18}O$* (per mil)	*N*
DSDP 284	1068	40°30.48′S	167°40.81′E	4.73	61-0006-0022	2.14 ± 0.10	16
DSDP 207A	1389	36°57.75′S	165°26.06′E	3.40	09-0008-0022	2.59 ± 0.10	7
DSDP 208	1545	26°06.61′S	161°13.27′E	2.94	09-0014-0038	2.57 ± 0.06	5
DSDP 158	1953	06°37.36′N	85°14.16′W	2.37	31-1504-0014	2.60 ± 0.11	12
DSDP 62.1	2591	01°52.20′N	141°56.30′E	1.73	90-0863-0041	3.10 ± 0.10	11
DSDP 84	3096	05°44.92′N	82°53.29′W	2.03	31-1681-0012	2.79 ± 0.21	6
DSDP 206	3196	32°00.75′S	165°27.15′E	1.96	09-0005-0057	2.95 ± 0.13	8
DSDP 310	3516	36°52.11′N	176°54.09′E	1.48	31-8036-0090	3.04 ± 0.17	14
DSDP 83A	3645	04°02.80′N	95°44.25′W	1.86	(*21*)	2.90 ± 0.08	14
V28-179	4509	04°37.00′N	139°36.00′W	1.39	(*21*)	3.02 ± 0.14	27

*Values are means ± standard deviations. Glacial samples are excluded; see text and (*13*).

How temperature varies with depth in the deep ocean depends on the ratio, z^*, of the vertical eddy diffusivity to the upwelling rate (*23*, *24*), and temperature-depth relationships have been used to calculate z^*. The z^* value can, in fact, be calculated from the depth dependence of any conservative tracer in a region where only two water masses are mixing. The $\delta^{18}O$ of calcite precipitating in isotopic equilibrium with seawater is a function of temperature and of the seawater $\delta^{18}O$, and therefore is, to a first approximation, a suitable conservative tracer (*25*). The $\delta^{18}O$-depth trend in the early Pliocene (Fig. 1) is adequately fit by a curve having a z^* value equal to the present Pacific value of about 1 km (*23*, *24*). Today, the area of the Pacific studied here is marked by mixing of more than two water masses, and thus cannot be strictly treated by the diffusion-advection model. Furthermore, temperature-depth relationships may be influenced by lateral mixing as well as vertical advection and diffusion. The calculated z^* value must thus be considered with caution; we simply wish to point out that it is indistinguishable from the present-day value.

In summary, early Pliocene oxygen isotope data from Pacific Ocean benthonic foraminifera reflect a relative paleotemperature change of about 3.5°C between 1 and 4.5 km. The structure of the early Pliocene Pacific deep-water column is similar to the modern structure. This result is consistent with the fact that the early Pliocene has been compared with interglacial episodes during the Quaternary, when the most significant Northern Hemisphere continental ice was restricted to Greenland. The approach used in this study may be useful for other problems in deep-water paleoceanography.

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References and Notes

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5. The notation $\delta^{18}O$ is defined by

$$\delta^{18}O = \left[\frac{(^{18}O/^{16}O)_{\text{sample}}}{(^{18}O/^{16}O)_{\text{reference}}} - 1\right] \times 10^3$$

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9. N. J. Shackleton, *Colloq. Int. CNRS* **219**, 203 (1973).
10. *Globocassidulina subglobosa* (*7*, *8*) and *Oridorsalis* sp. (*8*) are thought to deposit their calcite close to equilibrium with the $\delta^{18}O$ of seawater.
11. The results of Shackleton and co-workers (*6*, *7*) are converted to B-1 from PDB by subtracting 0.29 per mil from the published values.
12. J. H. Mercer, *Quat. Res. (N.Y.)* **6**, 125 (1976).
13. Open circles in Figs. 1 and 2 show results at sites 158 and 208 including the two "glacial" samples. Including these two samples raises the average standard deviation for all sites from 0.12 to 0.14 per mil.
14. P. Lonsdale, *Deep-Sea Res.* **24**, 1065 (1977).
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16. We neglect horizontal plate motions because small changes in latitude and longitude since the early Pliocene are not likely to affect bottom-water temperatures within the study area.
17. Site 158 was drilled on the aseismic Cocos Ridge.
18. The remaining sites all lie on oceanic crust that is estimated to be at least 50 million years old.
19. T. H. van Andel and D. Bukry, *Geol. Soc. Am. Bull.* **84**, 2361 (1973).
20. Water about 212 m shallower in the vicinity of site 83A has the same temperature. Water about 240 m shallower in the vicinity of site 84 is warmer by 0.02°C.
21. We interpolated temperature from hydrocast stations typical of those within a 5° square of each site from the National Oceanographic Data Center (NODC) file. The reference number (Table 2) uniquely identified each hydrocast in the NODC file. Sea floor at sites 83A and V28-179 is deeper than stations listed by NODC. We estimated the temperature at these sites from results obtained by Scripps Institution of Oceanography cruises Step-1 (station 87) and Monsoon VIII-11, respectively.
22. J. R. O'Neil, R. N. Clayton, T. Mayeda, *J. Chem. Phys.* **51**, 5547 (1969). The value −0.26 per mil per degree Celsius is calculated from the carbonate-water isotopic temperature equation of O'Neil *et al.* for a temperature of 3°C.
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25. We ignore the very small effects of nonlinearity in $d\delta/dT$ for equilibrium calcite precipitation, and the difference between in situ and potential temperatures.
26. We thank the National Science Foundation for making samples available through the Deep Sea Drilling Project. This research was funded by NSF Cenozoic Paleoceanography (CENOP) grant OCE76-81489.

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Single Crystals of Linear Polyethylene Crystallized from the Glass

Abstract. *Isolated single crystals of polyethylene have been crystallized from the glassy state by annealing uniformly thick films of amorphous linear polyethylene just above their glass transition temperature. In agreement with previous results for polycarbonate, substantial molecular mobility at the glass transition temperature is implied.*

Recent reports from our laboratory described a reproducible method of quenching linear polyethylene (LPE) to the glassy state (*1*, *2*). Electron diffraction and differential scanning calorimetry showed that crystallization from the glass occurs on warming, at about 190 K. This is in agreement with the value reported previously by Hendra *et al.* (*3*) based on infrared measurements. More recently, we replaced the liquid nitrogen slurry quenchent with isopentane at its melting point and performed dynamic mechanical spectroscopy studies which indicate that the glass transition temperature (T_g) is ~ 190 K (*4*, *5*). A large peak in tan δ (loss angle) is observed at this temperature, as well as a rise in rigidity. This peak is not observed on cooling and reheating the sample or in normally crystallized samples. In agreement with Boyer (*6*) we define it as $T_g(L)$, the T_g of unconstrained amorphous LPE, whereas the large β peak (~ 260 K) observed in these samples would be $T_g(U)$, the T_g of molecules constrained by crystallites.

The effect of annealing the samples above and below $T_g(L)$ on the dynamic mechanical spectra and the morphology has been examined (*4*). We have shown that it is possible to grow isolated single crystals from uniformly thick, amorphous films of polycarbonate (PC) by annealing just above $T_g(L)$ (*7*). Here we report similar results for amorphous LPE. In addition to their intrinsic interest, the results have implications for the current controversy over the degree of molecular mobility during crystallization from the melt (*8*-*10*).

Thin-film samples of LPE (Dow HB-PE; melt index, 1.2; density, 0.955 g/cm³) mounted on electron microscope grids were prepared as previously described (*1*, *2*). These films are of essentially uniform thickness, displaying a nodular surface structure ~ 100 Å in diameter when shadowed cold. Rapid heating through T_g results in the development of a microcrystalline texture, the crystals being 100 Å or less in size and the surface resembling that observed in the amorphous state (*2*). The sample shown in Fig. 1 was annealed for 5 hours at ~ 200 K in a test tube immersed in an acetone-Dry Ice bath. It was then warmed rapidly to room temperature and shadowed with Pt/C before being placed in the microscope.

In various regions of the samples we observed numerous structures that were ~ 0.15 μm in diameter, frequently more or less hexagonal in outline, and interconnected with fibrils ~ 100 Å in diameter. No polymer remained between the fibrils, indicating that the molecules from at least these regions had moved dis-