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Assessment of sea-surface temperature at 42°N in the California Current over the last 30,000 years

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Abstract. Assessment of changes in surface ocean conditions, in particular, sea-surface temperature (SST), is essential to understand long-term changes in climate especially in regions where continental climate is strongly influenced by oceanographic processes. To evaluate changes in SST in the northeast Pacific, we have analyzed long-chain alkenones of prymnesiophyte origin at 38 depths in a piston and associated trigger core collected beneath the contemporary core of the California Current System at 42°N, ~270 km off the coast of Oregon/California. The samples span 30,000 years of deposition at this location. Unsaturation patterns ($U^{k'}_{37}$) in the alkenone series display a statistically significant difference ($p \ll 0.001$) between interglacial (0.44 ± 0.02, $n = 11$) and glacial (0.29 ± 0.04, $n = 20$) intervals of the cores. Detailed examination of other compositional features of the C_{37}, C_{38}, C_{39} alkenone series and a related C_{36} alkenoate series measured downcore suggests the published $U^{k'}_{37}$ – temperature calibration ($U^{k'}_{37} = 0.034 \times T + 0.039$), defined for cultures of a strain of *Emiliania huxleyi* isolated from the subarctic Pacific, provides best estimates of winter SST at our study site. This inference is purely statistical and does not imply, however, that the phytoplankton source of these biomarkers is most productive in winter or at the ocean surface. The temperature record for $U^{k'}_{37}$ implies (1) an ~4°C shift occurred in winter SST from ~ 7.5 ± 1.1°C at the last glacial maximum to ~ 11.7 ± 0.7°C in the present interglacial period, and (2) this warming trend was confined to the time frame 14–10 Ka within the glacial to interglacial transition period. These conclusions are corroborated entirely by results from an independent SST transformation of radiolarian species assemblage data obtained from the same core materials.

Introduction

The modern California Current is a well-studied hydrographic feature in the North Pacific Ocean [*Hickey*, 1979]. Temporal measurements of the physical and biological characteristics of this current system have been the focus of the California Cooperative Fisheries (CalCOFI) Program started in the early 1950s. CalCOFI data reveal variations in the character of the California Current on seasonal as well as interannual timescales. Detailed studies of the physics of this system and consequences of physics on regional patterns of primary productivity have evolved in more recent years through other programs [*Strub et al.*, 1990; *Hood et al.*, 1991].

The California Current derives from the West Wind Drift (Figure 1a). The West Wind Drift separates into northward and southward flowing components roughly coincident with the point where wind stress diverges [*Hickey*, 1979]. Wind stress divergence begins in the mid-ocean (~160°W) at ~40°N in summer and ~30°N in winter. Separation of the wind field continues to the east but at progressively higher latitudes as the North American continent is approached (50°N in summer; 40°N in winter). The northward and southward flowing currents separate in a broad transitional zone (Figure 1a). The northward component feeds the Alaskan Gyre, while that flowing southward becomes the core of the California Current. North of 40°N and nearshore, the California Current is largely Subarctic in type (low temperature and salinity, high dissolved O_2 and phosphate content). The percentage of Subtropical water (warmer and saltier, O_2 and phosphate-poorer) mixed into this system increases to the south and toward the west. The core of flow is located ~150–300 km off the coast from the Oregon/California border (Figure 1b). Flow intensity is always maintained southward but varies seasonally, being fully developed and situated most nearshore in late summer to early fall and diminished and situated most offshore in winter.

Changes in the structure of the California Current between the last glacial and the present interglacial pe-

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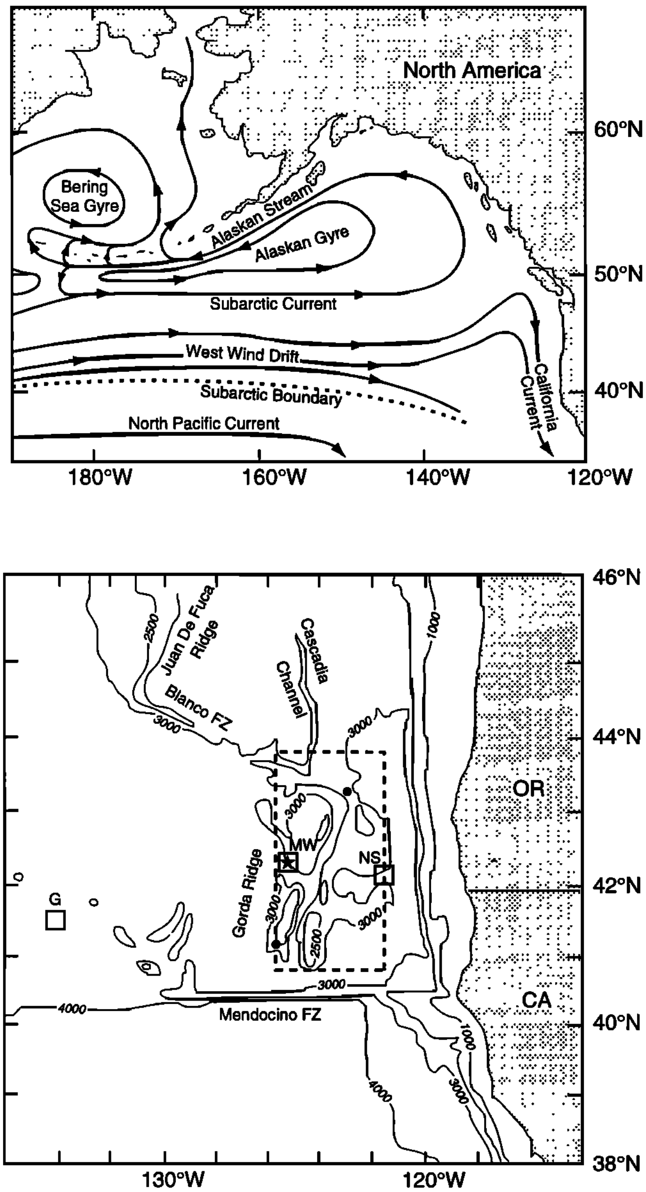

Figure 1. (a) Map identifying the major surface currents in the North Pacific and showing the relationship of the California Current system to the West Wind Drift (adapted from *Hickey* [1989]). (b) Expanded map indicating the coring site for W8709A-8TC and W8709A-8PC examined in this study (see star; 3111 m water depth, 42°32.5'N 127°40.7'W). The map relates the coring site to the longitudinal range of the contemporary California Current System off Oregon/northern California (see area enclosed by bold dashed lines). For reference purposes, three sediment trap sites for the MULTITRACERS project (NS, MW, and G [*Lyle et al.*, 1992]) and the collection site for two additional cores are also indicated (see solid circles; Y6604-10: 3002 m water depth, 43°16'N 126°24'W; Y6910-2: 2615 m water depth, 41°16'N 127°01'W). *Moore et al.* [1980] previously examined the microfossil records of the latter cores to reconstruct sea-surface temperatures at 18 Ka in this region of the northeast Pacific Ocean.

riod are known only vaguely at best. Some insight has been gleaned from paleoceanographic study of microfossil records in sediment cores from the region. The Subarctic boundary appears to have shifted northward (Figure 1a) since the last glacial period. *Moore* [1973a] showed the radiolarian assemblage now representative of the Alaskan Gyre withdrew from the region ~41° to 43°30'N and 126°25' to 127°W off Oregon/northern California and was replaced successively by a central Subarctic assemblage and finally a Transitional Zone assemblage. The same pattern of biotic change has been documented subsequently in a wider range of northeast Pacific cores spanning as far west as 132°W off Cape Blanco (~43°N) and as far south as 39°N off the Russian River [*Sabin*, 1995]. These observations argue that the contemporary positions of divergence for the West Wind Drift into northward and southward flowing currents [*Hickey*, 1989] and of coastal upwelling off the coast of the northwestern United States [*Huyer*, 1983] are significantly different today from those which prevailed during the last glacial period. In glacial times, either the intensity of coastal upwelling diminished markedly in this region by an increased influence of the Alaskan Low-Pressure System or the whole area of episodic coastal upwelling shifted southward [*Moore*, 1973a]. This oceanographic implication from the microfossil record in sediments is consistent with model predictions for large-scale changes in atmospheric circulation in the northeast Pacific resulting from deglaciation in North America [*Cooperative Holocene Mapping Project (COHMAP)*, 1988, and references therein].

In this paper, we examine sedimentary evidence for a glacial to interglacial change in sea-surface temperature (SST) within the California Current at a site off northern California. The site is located ~270 km offshore at ~42°N within the contemporary core of this current system (Figure 1b). *Moore et al.* [1980] analyzed microfossil species assemblages in a wide range of sediment cores and reconstructed a map of SST for the entire glacial Pacific Ocean. Their results suggested ≤2°C colder waters existed in this portion of the California Current during the last glacial period than at present, although SST estimates along the eastern limb of the North Pacific Current were not well constrained by sampling. We employ independent analyses of alkenone unsaturation patterns ($U^{k'}_{37}$) and radiolarian species assemblages on more recently collected core materials to reconfirm prior assessment of colder temperatures in the glacial California Current. Our results define winter SST in the northeast Pacific over the past 30,000 years and show (1) an ~4°C difference between glacial and interglacial estimates and (2) confinement of the shift from colder to warmer conditions to the time frame of 14–10 Ka during the glacial to interglacial transition.

Methods

Sample collection. A piston core (W8709A-8PC; 875 cm long, 10 cm diameter) and its associated trigger core (W8709A-8TC, 190 cm long) were collected in 1987 aboard RV *Wecoma* from 3111 m water depth at 42°32.5'N 127°40.7'W (Figure 1b). Both cores were sectioned immediately onboard ship into ~1.5-m lengths. Each length was capped, sealed, and returned to Corvallis under refrigeration (4°C) for storage in the Oregon State University (OSU) core repository. At OSU, the core sections were each split lengthwise to produce a working and archival half. One-centimeter-thick, quarter round subsamples were then taken as needed from the working half for purposes of organic geochemical and microfossil analysis.

Comparison of detailed magnetic susceptibility and calcium carbonate records for 8TC and 8PC indicated the piston core overpenetrated by 140 cm. So, all sampling depths for the 8PC are reported +140 cm to correct for overpenetration. A timescale for these cores was established using combined data for accelerator mass spectrometry (AMS) ^{14}C dates on bulk organic carbon and/or calcium carbonate and oxygen isotope ($\delta^{18}O$) stratigraphy on benthic foraminifera. Sedimentation rate varied from 10 to 12 cm/kyr over the 3.2 m of core examined in this study with lower values estimated at greater core depth. All data and the method used to establish chronostratigraphy for 8TC and 8PC are discussed elsewhere [*Lyle et al.*, 1992].

Alkenone analysis. Total extractable lipids (TEL) were recovered ultrasonically from 3 to 4 g of wet sediment using a 1:3 solvent mixture of toluene and methanol. Lipid fractions enriched in C_{37}, C_{38}, and C_{39} alkenones and structurally related C_{36} alkenoates of prymnesiophyte origin [*Marlowe et al.*, 1990] were isolated from TEL by column chromatography and analyzed by capillary gas chromatography (GC). Further details of the extraction and analysis procedure are discussed elsewhere [*Prahl et al.*, 1989, 1993].

Alkenone/alkenoate signatures were measured throughout the trigger core (8TC) and in all intervals examined from the top 1.8 m of the piston core (8PC). Various indices ($U^{k'}_{37}$, $K_{37:4}/K_{37}$, K_{37}/K_{38}, U^{me}_{36}, and ME/K_{37}; Table 1) are utilized to describe the overall prymnesiophyte biomarker composition identified by GC in each sample (Figure 2). $U^{k'}_{37}$, $K_{37:4}/K_{37}$, and U^{me}_{36} measure the degree of unsaturation in a given alkenone/alkenoate series. $U^{k'}_{37}$ is calculated from the abundance ratio of the diunsaturated C_{37} ketone to the combined diunsaturated and triunsaturated C_{37} ketone. The latter two unsaturation indices are new to the literature. $K_{37:4}/K_{37}$ is calculated from the abundance ratio of tetraunsaturated C_{37} ketone to the combined diunsaturated, triunsaturated, and tetraunsaturated C_{37} ketone. And U^{me}_{36} is calculated from the abundance ratio of diunsaturated C_{36} methyl alkenoate to the combined diunsaturated and triunsaturated C_{36} methyl alkenonate. K_{37}/K_{38} measures the overall chain length in a given alkenone series and is calculated from the abundance ratio of total C_{37} to C_{38} alkenones [*Prahl et al.*, 1988]. ME/K_{37} measures the relative abundance of alkenoates to alkenones in a given biomarker series and is calculated from the abundance ratio of total C_{36} methyl alkenoates to total C_{37} alkenones [*Prahl et al.*, 1988]. The reproducibility of measurements for each compositional ratio is better than ±5% in duplicate samples.

Radiolarian analysis. Radiolarian species census data (Table 2) were collected on these cores as part of a larger study of the northeast Pacific [*Sabin*, 1995]. Cores 8TC and 8PC were subsampled downcore every 10 cm yielding a total of 34 samples. Radiolarian microscope slides were prepared using the technique of *Moore* [1973b] as modified by *Roelofs and Pisias* [1986]. After chemical cleaning, samples were sieved with a 63-μm screen and radiolarian fossils were randomly settled onto microscope slides. Quantitative counts of radiolarian species were completed based on a total count of 800 radiolarian tests. The proportion of total radiolarian counted for 41 species was used in the estimation of mean annual SST.

Mean annual SST were estimated from radiolarian population studies by a paleoecological transfer function developed using the technique of *Imbrie and Kipp* [1971]. Radiolarian population data from 170 surface sediment samples from the Pacific basin were analyzed using Q mode factor analysis (N. Pisias and A. Mix, unpublished data, 1994). This approach identified seven radiolarian assemblages with discrete geographic distributions and thereby allowed statistical distinction between surface waters of specific oceanographic settings in the Pacific: Subtropical, Antarctic, Arctic, Transitional, Eastern Boundary Current, Gyre, and the Warm Western Basin. The relative abundance of these seven assemblages was used to develop a paleotemperature transfer function for mean annual SST.

The transfer function was developed using nonlinear multiple regression analysis where the assemblage data were the independent variable and mean annual SST at the location for each surface sediment sample was used as the dependent variable. Mean annual SST was estimated for each sample location using data in the atlas of *Levitus* [1982]. The standard error of the regression equation is ±1.5°C. Residuals of the regression fit for surface sediment samples from the northeast Pacific are less than ±1°C. Thus we feel that this paleotemperature transfer function provides estimates for past sea-surface conditions in the northeast Pacific accurate to within ±1.5°C.

Results and Discussion

Alkenone/alkenoate compositions. Figures 2a and 2b illustrate typical gas chromatograms of the alkenone/alkenoate series contained in sediment intervals of interglacial and glacial age, respectively. The most conspicuous compositional difference evident from this comparison is the virtual absence of a tetraunsat-

Table 1a. Compositional Properties of Alkenone and Alkenoate Series Analyzed With Depth in a Trigger Core (W8709A-8TC) and Piston Core (W8709A-8PC) From the Northeast Pacific Ocean

Core	Depth, cm	Age, Ka	$U^{k'}_{37}$	SST, °C	U^{me}_{36}	K_{37}/K_{38}	ME/K_{37}	$K_{37:4}/K_{37}$
TC8	2.5	0.2	0.438	11.7	0.77	1.06	0.24	0.02
TC8	4.5	0.4	0.435	11.6	0.80	1.09	0.24	0.00
TC8	23.5	2.1	0.484	13.1	0.87	1.02	0.22	0.02
TC8	26.0	2.3	0.414	11.0	0.72	1.11	0.27	0.01
TC8	47.5	4.5	0.421	11.2	0.75	1.18	0.24	0.00
TC8	65.5	6.4	0.427	11.4	0.74	1.05	0.27	0.00
TC8	67.5	6.6	0.427	11.4	0.76	1.11	0.23	0.02
TC8	88.5	8.9	0.428	11.4	0.80	1.14	0.21	0.00
TC8	89.5	9.0	0.477	12.9	0.83	1.07	0.23	0.01
TC8	97.5	9.9	0.448	12.0	0.77	1.21	0.22	0.02
TC8	107.5	10.9	0.417	11.1	0.74	1.18	0.24	0.03
TC8	117.5	12.0	0.364	9.6	0.64	1.19	0.24	0.06
TC8	127.5	13.1	0.391	10.4	0.69	1.15	0.30	0.03
TC8	128.5	13.2	0.369	9.7	0.67	1.17	0.26	0.06
TC8	134.5	13.9	0.308	7.9	0.63	1.13	0.23	0.08
TC8	137.5	14.2	0.309	7.9	0.68	1.16	0.22	0.08
TC8	140.5	14.6	0.317	8.2	0.64	1.04	0.24	0.08
TC8	141.5	14.7	0.331	8.6	0.62	0.97	0.26	0.09
TC8	144.5	15.0	0.339	8.8	0.61	0.95	0.28	0.09
TC8	146.5	15.2	0.328	8.5	0.61	0.90	0.28	0.10
TC8	149.5	15.5	0.326	8.4	0.62	0.86	0.25	0.10
TC8	152.5	15.8	0.337	8.8	0.61	0.88	0.28	0.10
TC8	157.0	16.3	0.308	7.9	0.59	1.00	0.28	0.11
TC8	163.5	17.0	0.323	8.4	0.62	0.90	0.26	0.10
TC8	166.5	17.4	0.333	8.6	0.62	0.96	0.26	0.10
TC8	175.0	18.1	0.315	8.1	0.61	0.87	0.24	0.10
TC8	183.5	19.0	0.319	8.2	0.61	1.02	0.23	0.11
TC8	185.5	19.2	0.301	7.7	0.63	0.99	0.24	0.11
PC8	159.5	16.6	0.271	6.8	0.61	0.79	0.28	0.09
PC8	178.5	18.5	0.323	8.4	0.70	0.92	0.20	0.11
PC8	199.5	20.5	0.249	6.2	0.66	0.89	0.21	0.10
PC8	219.5	22.2	0.265	6.6	0.60	0.82	0.30	0.13
PC8	239.5	23.7	0.226	5.5	0.54	0.82	0.26	0.13
PC8	259.5	25.1	0.227	5.5	0.56	0.89	0.28	0.14
PC8	259.5	25.1	0.235	5.8	0.57	0.89	0.29	0.13
PC8	279.5	26.5	0.294	7.5	0.74	0.88	0.20	0.04
PC8	299.5	28.0	0.249	6.2	0.56	0.76	0.29	0.15
PC8	319.5	29.4	0.311	8.0	0.53	0.97	0.21	0.08

See text for further details.

Table 1b. Average Alkenone Compositional Properties and $U^{k'}_{37}$-Based Sea-Surface Temperature Estimates Calculated for Interglacial and Glacial Sediment Intervals of Cores W8709A-8TC and 8PC From the Northeast Pacific Ocean

		$U^{k'}_{37}$		SST, °C		U^{me}_{36}		K_{37}/K_{38}		ME/K_{37}		$K_{37:4}/K_{37}$	
	n	Ave	Std	Ave	Std	Ave	Std	Ave	Std	Ave	Std	Ave	Std
Interglacial (0–10 Ka)	12	0.438	0.022	11.7	0.7	0.78	0.04	1.11	0.06	0.24	0.02	0.01	0.01
Glacial (15–30 Ka)	20	0.294	0.038	7.5	1.1	0.61	0.05	0.90	0.07	0.26	0.03	0.11	0.02
Overall (0–30 Ka)	34	0.344	0.070	9.0	2.1	0.67	0.08	1.00	0.13	0.25	0.03	0.07	0.05

Ave is average, Std is standard deviation, and n is the total number of samples in each age category.

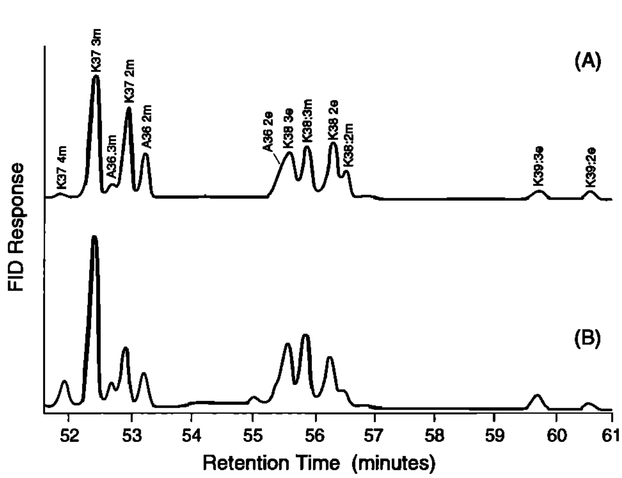

Figure 2. Partial capillary gas chromatograms of alkenone/alkenoate fractions isolated from (a) interglacial and (b) glacial intervals of W8709A-8TC and W8709A-8PC. The alkenones are depicted by the code K followed by 37, 38, or 39 indicating carbon chain length; :4, :3, or :2 indicating the number of double bonds; and m or e indicating methyl or ethyl ketone. The alkenoates are depicted by the code A followed by 36 indicating carbon chain length, :3 or :2 indicating number of double bonds, and m or e indicating methyl or ethyl ester. The observed chromatographic separation was accomplished using on-column injection, a 0.25-mm i.d. x 30-m-long DB-1 fused silica capillary column, hydrogen carrier gas maintained at constant head pressure (0.35 kg/cm^2) throughout the analysis, and temperature programming (5°C/min from 100-300°C then isothermal). As illustrated, a coelution problem existed between the ethyl alkenone K38:3e and the ethyl alkenoate A36:2e present in all samples. Quantitative measurement of the ME/K_{37} index in selected glacial and interglacial samples before and after transesterification with 14% boron trifluoride in methanol [*Prahl et al.,* 1989] showed the concentration of A36:2e was consistently 60–70% of the concentration for A36:2m. All reported values for K_{37}/K_{38} have been corrected for this coelution problem by mathematically subtracting away the A36:2e contribution to K38:3e using the following expression: K_{37}/K_{38} (corrected) = $[(K_{37}/K_{38})^{-1}$ (measured) $-\ 0.65 \times U_{36}^{me} \times ME/K_{37}]^{-1}$.

urated C_{37} ketone (K37:4m) in interglacial sediments and its clear occurrence in glacial sediments. Besides this feature, all analyzed sediment intervals contain the same set of alkenone/alkenoate components.

Table 1 displays complete data for the various attributes ($U_{37}^{k'}$, $K_{37:4}/K_{37}$, K_{37}/K_{38}, U_{36}^{me}, and ME/K_{37}) of the alkenone/alkenoate compositions measured at 38 depths in the cores. Comparison of data averaged for the interglacial (0–10 Ka, $n = 11$) and glacial (15–30 Ka, $n = 20$) sampling intervals shows significant differences (one-tailed Student-t test) for all three unsaturation indices ($p \ll 0.001$ for $U_{37}^{k'}$, $K_{37:4}/K_{37}$, and U_{36}^{me}). A difference of high statistical significance is also observed when the same time averages are compared for the alkenone chain length index (K_{37}/K_{38}, $p < 0.001$) but not for the index of alkenoate to alkenone abundance (ME/K_{37}, $p \sim 0.1$). Notably, all compositional changes occur during the period of glacial to interglacial transition (i.e., ~14–10 kyr B.P.).

Alkenone estimates of surface water temperature. The alkenone unsaturation index $U_{37}^{k'}$ varies with phytoplankton growth temperature [*Brassell et al.,* 1986]. For a single strain of *Emiliania huxleyi* (55a, Northeast Pacific Culture Collection), isolated from the subarctic Pacific Ocean, $U_{37}^{k'}$ changes quite linearly with growth temperature ($U_{37}^{k'} = 0.034 \times T + 0.039$, $r^2 = 0.994$ [*Prahl et al.,* 1988]). Prior field tests indicate the applicability of the $U_{37}^{k'}$ $-T$ calibration for strain 55a of *E. huxleyi* to Pacific waters ranging in

Table 2a. Sea-Surface Temperatures Predicted Using a Transform Function for Radiolarian Species Assemblage Data Obtained With Depth in a Trigger Core (W8709A-8TC) and Piston Core (W8709A-8PC) From the Northeast Pacific Ocean

Core	Depth, cm	Age, Ka	SST, °C
TC8	1	0.1	10.8
TC8	7	0.6	11.7
TC8	16	1.3	10.5
TC8	26	2.3	11.1
TC8	36	3.2	12.6
TC8	46	4.2	12.1
TC8	56	5.3	11.5
TC8	65	6.3	11.6
TC8	76	7.4	10.8
TC8	86	8.5	11.0
TC8	96	9.6	11.5
TC8	105	10.7	11.9
TC8	125	12.9	11.1
TC8	135	14.0	10.4
TC8	145	15.0	9.3
TC8	155	16.1	8.5
TC8	165	17.1	9.0
TC8	175	18.1	7.2
TC8	185	19.1	6.5
PC8	190	19.6	6.7
PC8	200	20.5	7.5
PC8	210	21.5	8.3
PC8	220	22.2	7.2
PC8	230	23.0	7.4
PC8	240	23.7	7.3
PC8	251	24.5	7.2
PC8	261	25.2	7.6
PC8	270	25.9	7.1
PC8	280	26.6	6.9
PC8	290	27.3	6.7
PC8	300	28.0	6.6
PC8	310	28.7	7.3
PC8	320	29.4	6.5
PC8	330	30.1	8.6

See text for further details.

Table 2b. Average Sea-Surface Temperature Estimates Based on a Transform Function for Radiolarian Species Assemblages Calculated for Interglacial and Glacial Sediment Intervals of Cores W8709A-8TC and 8PC From the Northeast Pacific Ocean

		SST, °C	
	n	Ave	Std
Interglacial (0–10 Ka)	12	11.4	0.6
Glacial (15–30 Ka)	20	7.5	0.8
Overall (0–30 Ka)	34	9.1	2.1

Ave is average, Std is standard deviation, and n is the total number of samples in each age category.

temperature from ~4 to ≥25°C [*Prahl and Wakeham*, 1987; *Sikes and Volkman*, 1993]. With this finding as precedent, the laboratory calibration equation was used to convert downcore measurements of $U^{k'}_{37}$ at our study site in the northeast Pacific into estimates of absolute surface water temperature (Table 1). Estimates average 11.7 ± 0.7°C and 7.5 ± 1.1°C for sediment intervals of interglacial and glacial age, respectively.

The steplike downcore decrease in $U^{k'}_{37}$ (Table 1) almost certainly depicts lower glacial relative to interglacial surface water temperatures. But we must now question the accuracy of the absolute water temperatures estimated above for two reasons. First, more recent culture studies show the specific $U^{k'}_{37} - T$ relationship defined for strain 55a of *E. huxleyi* is not applicable to all alkenone-producing prymnesiophytes potentially contributing to the marine sedimentary record [*Marlowe et al.*, 1990]. Most notably, significant deviations are evident between cultured strains of *E. huxleyi* isolated from various marine waters including off the coast of Bermuda ($U^{k'}_{37} = 0.053 \times T - 0.55$, calibration range: 15–25°C), the Gulf of Maine ($U^{k'}_{37} = 0.016 \times T - 0.028$, calibration range: 10–20°C), a Norwegian fjord ($U^{k'}_{37} = 0.033 \times T - 0.009$, calibration range: 10–20°C), and the Sargasso Sea ($U^{k'}_{37} = 0.013 \times T - 0.12$, calibration range: 15–25°C) (K. Amthor, unpublished results, 1994). Second, anomalous relationships between $U^{k'}_{37}$ and water temperature now seem apparent in the North Atlantic [*Conte et al.*, 1992], the Black Sea [*Freeman and Wakeham*, 1992], and in very cold (<4°C) waters from the Southern Ocean [*Sikes and Volkman*, 1993].

However, despite such concern, our alkenone-derived estimates of absolute water temperature are judged as reasonable by comparison of various compositional features of the alkenone/alkenoate signatures preserved in the cores with culture data for strain 55a of *E. huxleyi*. First, values of K_{37}/K_{38}, an index of carbon chain length in the alkenone series, decrease from interglacial to glacial intervals of the core (Table 1). This trend accompanies the ~4°C decrease in growth temperature inferred from the $U^{k'}_{37}$ data and follows consistently with the temperature response of K_{37}/K_{38} observed in cultures of strain 55a (Figure 3a). Second, values of the alkenone unsaturation parameter, $K_{37:4}/K_{37}$, increase from interglacial to glacial sediment intervals (Table 1).

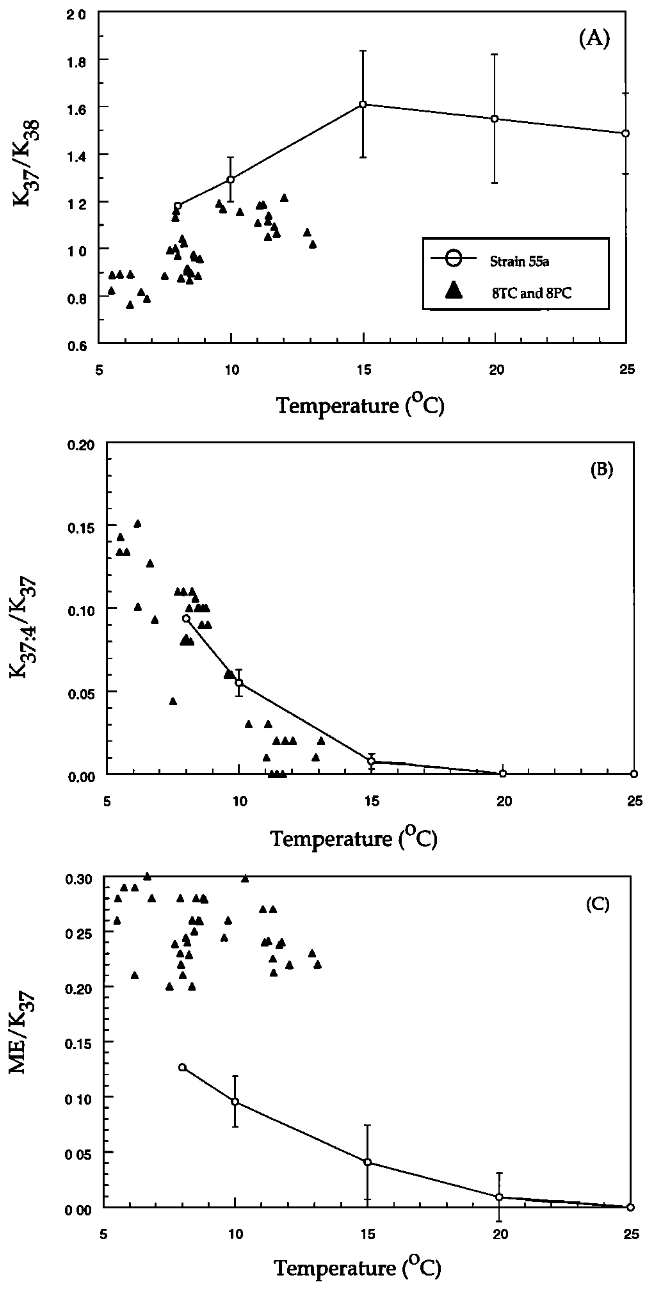

Figure 3. (a) K_{37}/K_{38}, an index of carbon chain length, (b) $K_{37:4}/K_{37}$, an index of alkenone unsaturation, and (c) ME/K_{37}, an index of the relative abundance of alkenoates to alkenones in a given biomarker series plotted versus temperature for strain 55a of *E. huxleyi* grown in culture [*Prahl et al.*, 1988]. For reference purposes, downcore data for each parameter are also plotted at growth temperatures predicted from $U^{k'}_{37}$ measurements using the calibration equation $U^{k'}_{37} = 0.034 \times T + 0.039$ [*Prahl et al.*, 1988].

In cultures of strain 55a, this precise trend is observed for $K_{37:4}/K_{37}$ as growth temperature decreases over the inferred range of 11.7° to 7.5°C (Figure 3b). So, a strain of *E. huxleyi* behaving like 55a is a probable, major alkenone contributor to sediments in this region of the northeast Pacific over the last 30,000 years of deposition and provides an appropriate temperature calibration for $U^{k'}_{37}$.

Evidence for selective degradation of prymnesiophyte biomarkers. Comparison of culture data for strain 55a of *E. huxleyi* with core data reveals one noteworthy compositional difference that warrants discussion. The alkenoate to alkenone composition (ME/K_{37}) of this strain displays considerable temperature dependence with values of 0.10–0.15 expected when growth occurs at $\leq 10°C$ (Figure 3c). But ME/K_{37} values show little significant difference ($p \sim 0.1$) between interglacial (0.24 ± 0.02) and glacial (0.26 ± 0.03) sediment intervals (Table 1) and are ~2-fold higher than expected if growth occurred in the inferred temperature range of 7.5–11.7°C (Figure 3c). Assuming a strain of *E. huxleyi* like 55a represents the major biomarker contributor to these sediments, selective degradation of alkenones relative to alkenoates would explain the disparity.

Alkenone/alkenoate data for sediment trap time series and surface sediments from this region of the northeast Pacific [*Prahl et al.*, 1993] support a selective degradation hypothesis. ME/K_{37} measured in three surface sediments between 120, 270, and 630 km offshore along 42°N (NS, MW, and G; Figure 1b) are uniform (0.25 ± 0.01), while average particulate materials settling through 1000 m water depth above each site are lower and vary widely (0.09, 0.06, and 0.02, respectively). Flux comparisons show only a small fraction of the alkenones transported through 1000 m water depth survives burial in sediment. If slight differences in the degree of degradation of alkenones relative to alkenoates occurred, the dissimilarity between ME/K_{37} values preserved in sediments and expected for the presumed algal source would be accountable.

The possibility of selective degradation of alkenones relative to alkenoates in the sedimentary process is relevant to recent work of *Conte et al.* [1992]. These investigators coined an index (AA36) to quantify the relative abundance of alkenoates to alkenones in a given sample and proposed its use either independently or in conjunction with $U^{k'}_{37}$ to assess surface water temperatures. If these two classes of biochemicals (esters of fatty acids and ketones) are derived from a common source [*Marlowe et al.*, 1990] but degraded selectively to any significant extent in the early stages of sedimentation as our data might suggest, the utility of AA36 as an unequivocal tool for paleotemperature reconstruction is compromised.

Similar concern for selective degradation of the more unsaturated alkenone isomers was raised in the early development of $U^{k'}_{37}$ as a paleotemperature index [*Prahl et al.*, 1988, and references therein]. A variety of field observations now bolster our view that $U^{k'}_{37}$ is insensitive to early diagenetic alteration [*Prahl et al.*, 1989; *McCaffrey et al.*, 1990]. Growth temperature remains the key factor recognized to affect alkenone unsaturation patterns recorded in sedimentary samples. But, as described above, determination of the absolute quantitative relationship between alkenone unsaturation patterns and growth temperature still requires a means of recognizing the specific algal source contributing the biomarker signal to a particular sedimentary setting. Current evidence for the resistance to diagenetic alteration of indices based on the abundance ratio of two biosynthetically related but chemically distinct compound classes (e.g., AA36, ME/K_{37}) is tenuous at best by comparison (see, for example, *Conte et al.* [1992]).

Both diunsaturated and triunsaturated C_{36} methyl alkenoates occur in all depth intervals of 8TC and 8PC examined in this study (Figure 2). U^{me}_{36}, an index analogous to $U^{k'}_{37}$, is now defined to quantify downcore variation in alkenoate unsaturation patterns (Table 1). U^{me}_{36} shows significant, positive correlation with $U^{k'}_{37}$ in the complete data set ($U^{me}_{36} = 1.00 \times U^{k'}_{37} + 0.33$, $r^2 = 0.74$). The correlation between these two unsaturation indices may, in fact, be higher if analytical conditions were optimized to allow baseline peak resolution of the minor triunsaturated C_{36} methyl ester (A36:3m) and the major diunsaturated C_{37} ketone (K37:2m) (Figure 2). Nonetheless, the observed degree of correlation supports our view that C_{36} alkenoates and C_{37}, C_{38}, and C_{39} alkenones derive from the same source and unsaturation patterns in these two biosynthetically related compound classes convey the same information about growth temperatures for *E. huxleyi* in the northeast Pacific. More significantly, however, if alkenones are degraded selectively over alkenoates in the sedimentary process, this correlation suggests that alkenoate degradation operates nonselectively on a compound specific basis, an inference completely consistent with our current view of alkenone geochemistry.

Relationship of biomarker estimates to sea-surface temperature. Using sediment traps deployed in time series, *Prahl et al.* [1993] examined the composition and flux of alkenones through 1000 m water depth at the coring site for the present study. Alkenone flux was evident in all sampling periods implying some level of prymnesiophyte productivity year round. Regardless of sampling period, $U^{k'}_{37}$ was remarkably uniform throughout the year (0.41 ± 0.04) and compared well with values recorded in underlying sediment (0.43). Again, average $U^{k'}_{37}$ values for sediment trap materials translated into growth temperatures of $10.9 \pm 1.2°C$ using the existing calibration for strain 55a of *E. huxleyi* [*Prahl et al.*, 1988]. This water temperature is observed at the sea surface along 42°N in the northeast Pacific throughout the winter and during summer periods of upwelling along the coast. But such cold water temperature occurs only within the upper thermocline at more offshore sites in the northeast Pacific during summer to fall periods of stratification [*Prahl et al.,* 1993]. Interestingly, the inferred subsurface depth of alkenone production invariably corresponds to a zone of chlorophyll maximum in these offshore regions [*Prahl et al.,* 1993]. Consequently, we surmise that the alkenone unsaturation patterns preserved in sediments from study regions such as ours beneath the core of the contemporary California Current provide a proxy of winter SST even though prymnesiophyte productivity is not constrained to or maximal in this season. And, on this basis, we conclude that winter SST in the glacial California Current situated at 42°N in the northeast Pacific was at least 4°C colder than at present.

Radiolarian species compositions. Figure 4 illustrates downcore changes in radiolarian assemblages observed in 8TC/8PC. Here we plot the four dominant factors found for modern and glacial sediments from the northeast Pacific, i.e., the Subtropical, Transitional, Eastern Boundary Current, and Arctic assemblages. The other three assemblages identified in the study of N. Pisias and A. Mix (unpublished data, 1994) are of minor importance in this region. A marked change in radiolarian assemblages preserved in these sediments is evident. The radiolarian population in glacial age sediments is dominated by a mixture of Arctic and Transitional assemblages. The species associated with the Arctic assemblage are not found in modern sediments of the northeast Pacific but are presently found in sediment from the far North Pacific and Bering Sea. At the glacial maximum (18 Ka), the Arctic assemblage prevails as the Transitional assemblage becomes much reduced in importance.

At the onset of the glacial to interglacial transition (18 to 14 Ka), the Arctic assemblage is replaced first by the return of the Transitional assemblage. Assemblages associated with the Subtropical Pacific and the Eastern Boundary Current subsequently increase in importance. The reduced importance of the Eastern Boundary Current assemblages, and associated reduction in the importance of upwelling related species, are consistent with inferred reduction of upwelling in the northeast Pacific during the last glacial episode [*Lyle et al.,* 1992]. This pattern suggests that the subpolar front of the northeast Pacific was located much farther south during the last glacial event. The observed changes in the radiolarian assemblages also suggest that deglaciation in the northeast Pacific is related to a northward migration of the subpolar front across the region. The pattern observed in 8TC/8PC is consistent with the overall regional response to deglaciation based on a north-south transect of cores from 55°N to 30°N [*Sabin,* 1995].

Radiolarian species assemblages and SST estimates. In Figure 5, we plot versus sediment age both the SST estimates based on $U^{k'}_{37}$ measurements (Table 1) and radiolarian paleotemperature transfer func-

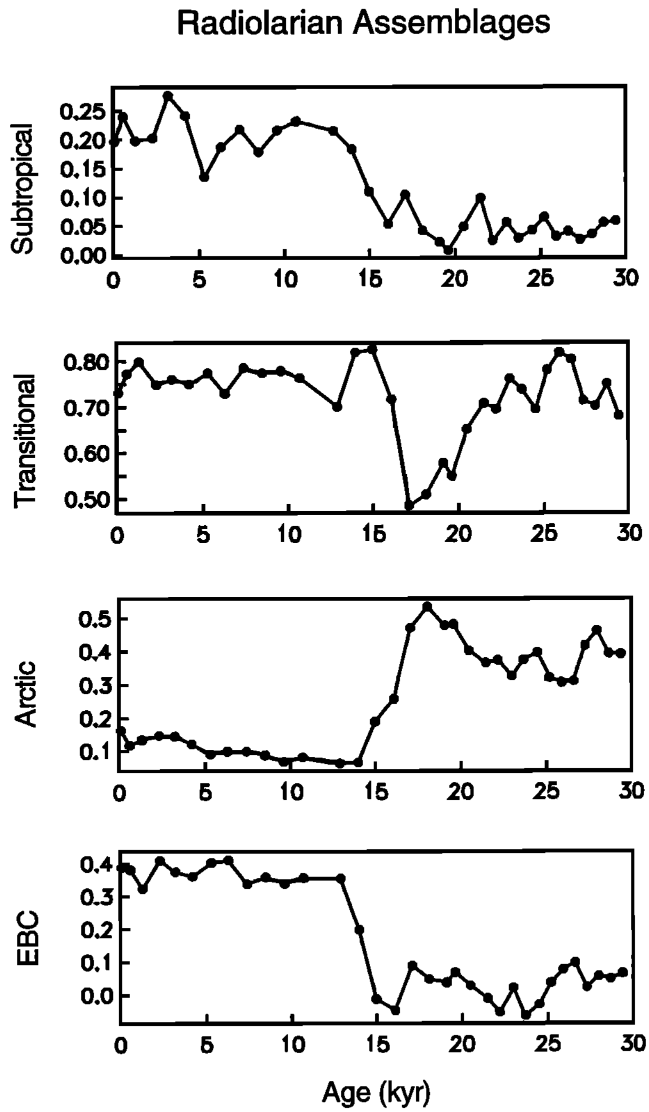

Figure 4. Downcore plots of radiolarian assemblages derived from a Q Mode factor analysis of radiolarian populations from 170 surface sediment samples spanning the Pacific Basin. Factors shown are the Subtropical, Transitional, Arctic and Eastern Boundary Current factors defined by N. Pisias and A. Mix (unpublished results, 1994).

tions (Table 2). The concordance of these two, independent estimates of past sea-surface conditions is striking. Thus the conclusion from alkenone analysis seems justified that SST was at least 4°C colder at this site in the northeast Pacific during the last glacial maximum than at present. But why should a paleotemperature equation, calibrated to mean annual SST, yield the same estimate as that provided by alkenone unsaturation patterns reflecting winter SST?

The radiolarian-based paleotemperature equation used in the present work was derived through study of basinwide sediments from the Pacific and has been applied to sediment records from the central and east-

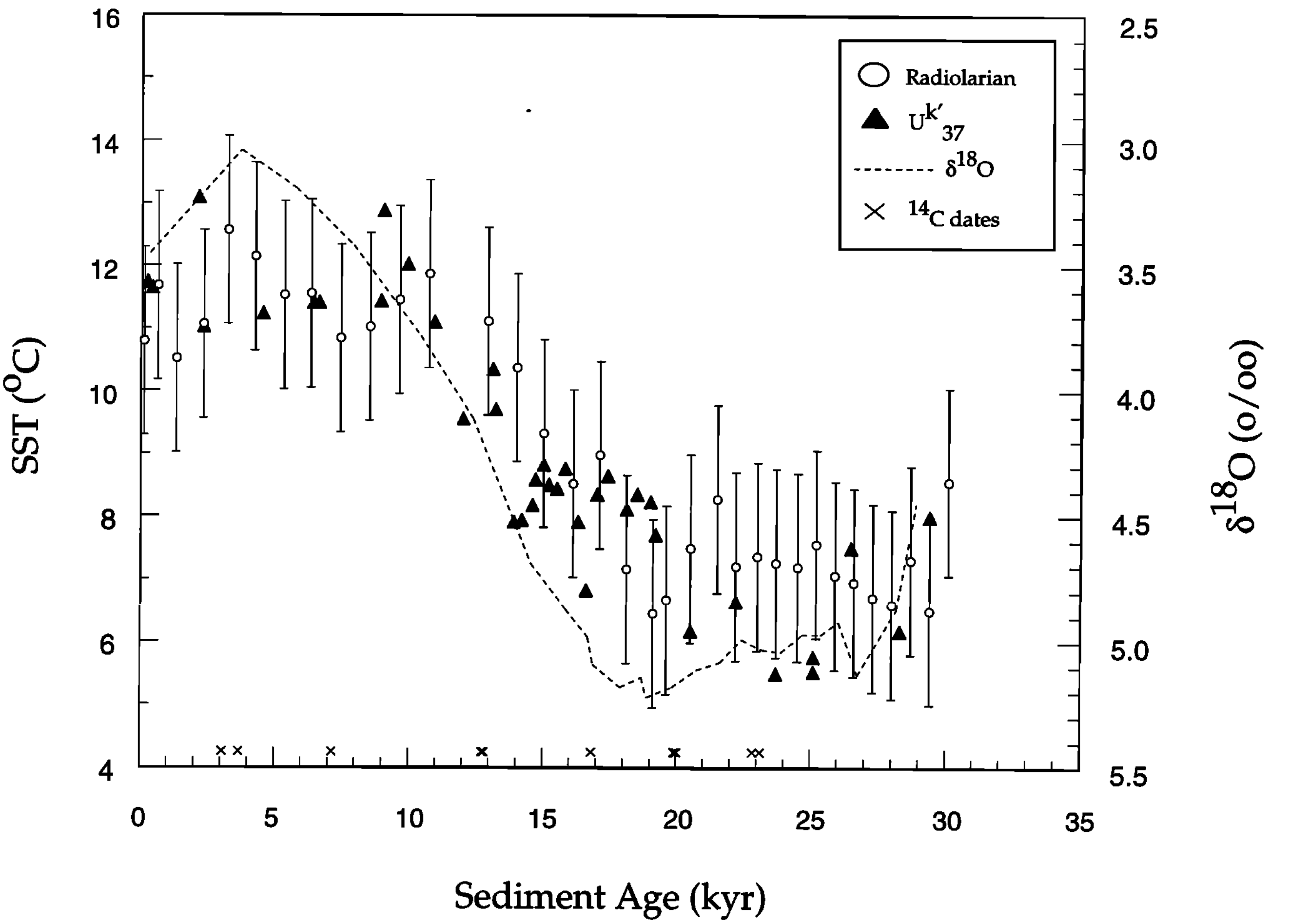

Figure 5. Comparison of downcore SST predictions based on $U^{k'}_{37}$ data with those estimated using a transform function for radiolarian species assemblages. For purposes of stratigraphic reference, a downcore profile is shown for $\delta^{18}O$ measured in tests of the benthic foraminifera *Uvigerina spp.*, and calendar ages calculated from AMS ^{14}C dates on bulk organic carbon and calcium carbonate samples are indicated (data from *Lyle et al.* [1992]). See text for further details.

ern equatorial Pacific as well as the northeast Pacific (N. Pisias and A. Mix, unpublished results, 1994). The strategy of developing paleoecological equations for both mean sea-surface temperature and seasonality was chosen for two reasons. First, prior approaches used paleotemperature equations to estimate a summer and winter SST. However, the correlation between SST during warm and cold seasons in the Pacific (data from *Levitus* [1982]) is very high ($r = 0.93$; N. Pisias and A. Mix, unpublished results, 1994) and thus independent regression equations cannot be developed, whereas the correlation between mean SST and seasonality (data from *Levitus* [1982]) is much reduced ($r = -0.44$) and thus independent equations can be developed. Second, the definition of winter and summer seasons near the equator becomes complicated because the thermal equator does not coincide necessarily with the geographic equator. If the position of the thermal equator also varies with past climate, then reconstructing past seasonal temperatures is much more complicated at low latitudes. So returning to the question of why mean SST estimates derived from radiolarian assemblage data should look similar to winter SST estimates derived from alkenone data, we compare the mean SST with water temperatures at the pycnocline in the summer season (Figure 6) where both parameters have been calculated from the hydrographic data set of *Levitus* [1982]. We assume that the temperature at the summer pycnocline provides an estimate of ocean temperatures at the base of the euphotic zone which seems to be the real physiological growth temperature reflected by the alkenones [*Prahl et al.,* 1993]. The correlation between these two temperature parameters is very high ($r = 0.90$; Figure 6), and the two parameters are equivalent over the temperature range of 0 to 15°C. The alkenone temperature estimates seem to reflect winter SST or subsurface temperatures in summer [*Prahl et al.,* 1993], and the radiolarian transfer function, while calibrated to annual mean sea-surface temperatures, also provides a reasonable estimate of subsurface temperatures in summer.

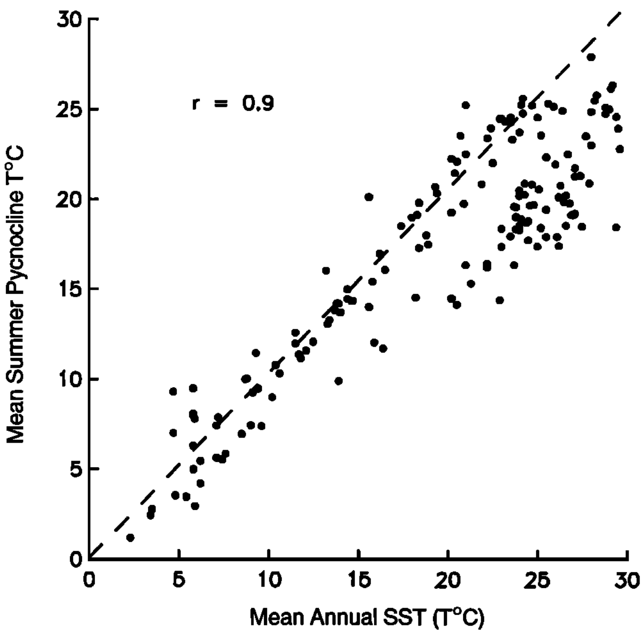

Figure 6. Observed mean sea-surface temperatures (estimated from average of winter, spring, summer, and fall data) compared to the mean temperature at the summer pycnocline as determined from data in the atlas of *Levitus* [1982]. Data are based on the geographic locations of the 170 surface sediments throughout the Pacific Basin used to develop the sea- surface temperature transfer function for radiolarian species assemblages (N. Pisias and A. Mix, unpublished data, 1994).

Thus it is not too surprising that our two independent estimates of glacial/interglacial difference in ocean temperature are of the same magnitude in this core from the northeast Pacific.

Our estimate of an ~4°C ocean temperature change since the last glacial maximum is higher than previous estimates [*Moore*, 1973a]. As in this study, *Moore* [1973a] used radiolarian-based transfer functions to estimate past sea-surface conditions and estimated a ≤2°C temperature change during the last deglaciation. There are two factors which should be considered in evaluating this difference: (1) the standard error of the transfer function analysis is of the order of 1.5–2°C and (2) the modern calibration data set used by *Moore* [1973a] and the Climate:Long-Range Investigation, Mapping, and Prediction (CLIMAP) project (1976) is biased and of the order of 1°C too cold compared to other more recently compiled modern calibration data sets (W. Prell, personal communication, 1995). Thus one possibility is that the ~2°C difference is only reflected in the standard error of the paleotemperature regression equations or that the range of *Moore* [1973a] is underestimated due to the bias in the modern temperature calibration data set.

Conclusions

1. Examination of various compositional properties of the alkenone/alkenoate series preserved in glacial/interglacial intervals of sediments from the northeast Pacific shows that the $U^{k'}_{37}$ – temperature calibration established for *E. huxleyi* strain 55a isolated from the subarctic Pacific ($U^{k'}_{37} = 0.034 \times T + 0.039$ [*Prahl et al.*, 1988]) provides realistic estimates of absolute water temperature.

2. Early diagenetic processes potentially alter the relative abundance of alkenones to alkenoates preserved in sediments even though values for $U^{k'}_{37}$ and other compositional indices (e.g., U^{a}_{36}, $K_{37:4}/K_{37}$, K_{37}/K_{38}) based on ratios of compounds within a given chemical class appear faithfully translated from algal source to sediments. Given this possible diagenetic effect, paleotemperature assessments based on indices such as AA36 [*Conte et al.*, 1992] should now be interpreted with caution.

3. $U^{k'}_{37}$-based paleotemperature estimates for the northeast Pacific correspond to winter SST. This correspondence is purely statistical and does not imply alkenone producers are most productive in the winter periods or at the ocean surface [*Prahl et al.*, 1993].

4. Ocean temperature estimates based on $U^{k'}_{37}$ and radiolaria transfer functions follow essentially identical patterns of change during the last deglaciation and show that the northeast Pacific warmed by ~4°C since the glacial maximum.

5. Convergence of the alkenone and transfer function-derived temperature estimates supports the hypothesis that the oceanographic parameter being reconstructed by these techniques in the northeast Pacific is a subsurface water temperature within the summer pycnocline.

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