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25. DATA REPORT: RECONNAISSANCE OF ORGANIC BIOMARKERS IN LEG 199 SEDIMENTS[1]

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ABSTRACT

Six samples from Sites 1219 and 1221 ranging in age from early Eocene to early Oligocene were analyzed for freely extractable lipids to determine whether the low organic carbon (C_{org}) sediments of the Eocene equatorial Pacific (C_{org} content typically 0.03%) are appropriate for biomarker studies. Only one sample from the Oligocene equatorial Pacific (Sample 199-1219A-13H-3, 50–54 cm) contained any biomarkers of interest to paleoceanography. The only lipids identified in the remaining samples appear to be contaminants from drilling or subsequent handling. Sample 199-1219A-13H-3, 50–54 cm, contained alkenone biomarkers specific to haptophyte algae that are used for estimating past mean annual sea-surface temperature (maSST). If the Holocene calibration of maSST is appropriate for the Oligocene, the estimated equatorial temperature is ≥28.3°C, or at least 3°C warmer than modern equatorial maSST at a similar longitude.

INTRODUCTION

One important challenge in paleoceanographic research is to estimate sea-surface temperature (SST) because surface ocean temperature is a primary factor needed to model climate. Properly estimating SST in the Paleogene is more difficult than in the Neogene because long-term changes in ocean chemistry affect the baseline of certain geochemical estimates (e.g., Mg/Ca and oxygen isotopes), whereas evolutionary processes may invalidate biomarker estimates or plankton community

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analysis. It is important to estimate SST redundantly, that is, with multiple proxies, to determine to what extent these problems exist. Typical ways of estimating Pleistocene SST include the use of plankton censuses and plankton water preferences, oxygen isotopes, Mg/Ca, and biomarkers. SST within the Paleogene equatorial region has been a matter of controversy lately. SST estimates based on oxygen isotopes (Zachos et al., 1994) identified an equatorial region that was the same temperature or cooler than modern conditions. Cool equatorial temperatures imply a much larger transfer of heat out of the tropics than those that occur under modern conditions. However, Pearson et al. (2001) suggested that these cool tropical SST measurements represented partial overgrowth of calcite during early diagenesis and that the equatorial region was warmer than modern. A warmer-than-modern equatorial region better fits with Eocene reconstructions with high atmospheric pCO_2 (Pearson and Palmer, 2000; Shellito et al., 2003). Other SST information from the Paleogene would be extremely useful.

A second great challenge in paleoceanography is to understand the feedbacks between climate and the biosphere under different climate regimes and at different times in the past. Typical needs are to estimate paleoproductivity, biogeochemical cycling, and structure of ecosystems. These types of analyses require information about the members of the plankton community. For the test-forming plankton, a first-order approach to study the community is to examine the tests preserved in the sediments. Plankton assemblages in sediment are not pristine, however, and suffer from dissolution prior to burial. Another approach that has proved useful in Pleistocene sediments is to study the distribution of biomarkers, molecular fossils that remain in the organic fraction of the sediment.

For these reasons, we decided to analyze a reconnaissance suite of samples from the early Eocene to the early Oligocene from Ocean Drilling Program (ODP) Leg 199 Sites 1219 and 1221 to determine whether biomarkers could be measured in these sediments and whether important paleoceanographic information was preserved in the organic sedimentary fraction. One of our concerns was the extremely low levels of C_{org} found in the Eocene sections of Leg 199 sediments (see **Olivarez Lyle and Lyle,** this volume). For example, the average C_{org} measured by **Olivarez Lyle and Lyle** (this volume) for the Eocene section of Site 1219 was 0.03 wt%, over an order of magnitude less than Holocene and late Pleistocene C_{org} percentages at equivalent longitudinal positions (Lyle et al., 1988; Lyle, 1992). We did not know prior to the reconnaissance reported here whether useful biomarker data would be preserved in sediments with such low C_{org}.

One important biomarker we specifically looked for is the alkenones produced by *Emiliania huxleyi* and other haptophyte algae (Conte et al., 1994). They are known to provide SST information in Neogene sediments (Brassell et al., 1986; Prahl and Wakeham, 1987), as well as information about the abundance of the carbonate-producing coccolithophorids. In addition, it is known that these biomarkers are found throughout the Cenozoic (Marlowe et al., 1990). If we can find these biomarkers in Leg 199 sediments, we can independently estimate Paleogene SST without the ice volume correction needed for oxygen isotopes.

METHODS

A total of six samples from Leg 199 (Table T1) were analyzed for freely extractable lipids using commonly established techniques (Prahl et al., 1989). In brief, after exhaustive ultrasonic extraction using methanol:dichloromethane (3:1), total lipid extracts from each sample were separated into four discrete fractions via silica gel column chromatography. These four fractions comprised aliphatic hydrocarbons (L1), polycyclic aromatic hydrocarbons (PAH) (L2), alkenones/fatty acid methyl esters (L3/4) and sterols/fatty alcohols (L5). Each fraction was concentrated and then analyzed after appropriate derivatization, if necessary, by capillary gas chromatography with flame ionization detection (GC-FID). Two standards (nonadecan-10-one and ethyltriacontanoate) were added prior to ultrasonic extraction to monitor recovery of compounds in the L3/4 fraction through the procedure.

T1. Sample information, p. 9.

RESULTS

The results from each fraction are summarized in Table T2. Effectively, only one sample (199-1219A-13H-3, 50–54 cm) contained any biomarkers of specific interest: three long-chain (C_{37}, C_{38}), diunsaturated (:2) methyl (m)/ethyl (e) ketones (K) (alkenones) (see K37:2m, K38:2e, and K38:2m; Fig. F1) specific to the unicellular algae *E. huxleyi* but also found in other haptophytes (Conte et al., 1994). Given the measured $U^{k'}_{37}$ of unity and the established calibration for this unsaturation index ($U^{k'}_{37} = 0.034T + 0.039$; Prahl and Wakeham, 1987), a mean annual sea-surface temperature (maSST) of ≥28.3°C is estimated. None of the other samples showed any trace of alkenones.

T2. Sample summary data table, p. 10.

F1. Gas chromatograph trace, p. 7.

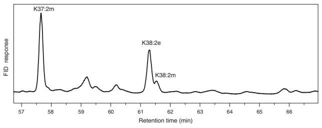
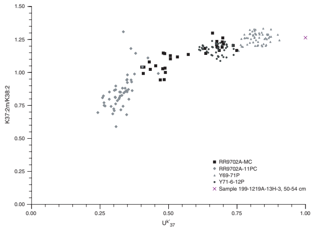


Table T3 shows the quantified amounts of detected alkenones and the percentage recovery of the standards added, ranging from 70% to 83%. The minimum detectable amount of alkenones was also calculated for each sample based on the grams of sediment extracted. Calculations show the amounts detected in the one Leg 199 sample ranged from 5 to 35 times the detection limit. K37:2m concentration (per gram of dry weight) in this sample was compared to that measured in Holocene to late Pleistocene age sediments collected by coring off the west coast of South America (Table T4). Clearly, the concentration measured in sample 3 is at the lowest end of that measured in these other sediment samples, emphasizing the paucity of organic matter in the Leg 199 samples. Data for the ratio of K37:2m to the sum of K38:2m and K38:2e (or K37:2m/SK38) measured in the one Leg 199 sample is also reported in Table T4, along with values measured in these other sediments. This comparison shows that the ODP sample is at the higher end of values for this ratio but falls consistently along the temperature-dependent trend for this compositional property (Fig. F2).

T3. Ketone recovery, p. 11.

T4. Comparison of alkenone recovery and properties, p. 12.

F2. Alkenone property-property plot, p. 8.



All of the samples show the presence of a homologous long chain n-alkane series in the aliphatic hydrocarbon fraction (L1). In all cases, the series showed no odd-to-even carbon number predominance. This feature is characteristic of fossil organic matter. The concentration of the dominant *n*-C_{27} alkane in each sample ranged from 19 to 753 ng/g dry sediment. Because a procedural blank lacked any appreciable level of n-alkanes, this feature was either present in these samples naturally or, more likely, introduced as a contaminant at some stage of the sediment collection and handling procedure.

PAH fractions (L2) showed nothing detectable above the blank, whereas the alcohol/sterol fraction (L5) showed several nonblank compounds. These compounds were identified by GC-mass spectrometry as a homologous series of α,ω-diacid esters (e.g., hexanedioic acid and dibutyl ester). Such compounds are commonly used as plasticizers and motor oil additives. As such, we speculate that they are probably contaminants introduced at some stage of the sample collection and handling procedure and are not authentic to the sample.

DISCUSSION

It is clear from the results of this reconnaissance work that organic geochemical analysis of pelagic samples with these low levels of C_{org} should be approached with caution. The levels of contamination under typical shipboard sediment handling conditions are too large and the preserved biomarker concentrations are too low to get any definitive information out of all the samples from the Eocene sections of Sites 1219 and 1221.

Nevertheless, the one sample from the early Oligocene equatorial sediments (Sample 199-1219A-13H-3, 50–54 cm) contained detectable alkenones of haptophyte origin. As shown in Table T4, the levels of alkenone present were extremely low, as would be expected with the low C_{org} measured in the sample (Table T2). If a Holocene maSST calibration is applied to estimate Oligocene maSST, we find that the maSST is ≥28.3°C. The sample has no 37:3 alkenones, and therefore the warming may be larger than 28.3°C but undetectable by the alkenone method. At the time Sample 199-1219A-13H-3, 50–54 cm, was deposited, Site 1219 was at the equator at ~119°–120°W. A search of the National Oceanic & Atmospheric Administration National Oceanographic Data Center World Ocean Atlas (1998; **www.nodc.noaa.gov/OC5/pr_wodv2.html**) yields a modern maSST of 24.6°C at that location. Assuming the alkenone calibration is correct, we find >3°C of cooling of the equatorial region since 30 Ma.

The alkenone maSST conflicts with the regional oxygen isotope SST estimate of 18°C for the early Oligocene from Zachos et al (1994). Alkenones provide evidence that the equatorial region was warmer in the Paleogene than under modern conditions. Resolution of the cause for this conflict will require further investigation.

CONCLUSIONS

Low levels of sedimentary C_{org} in the Eocene sedimentary sections of Leg 199 relative to typical contamination caused by drilling and handling rule out biomarker studies of these sediments without extreme precautions. In only one out of six trials were we able to detect biomarkers that were not contaminants. Nevertheless, that early Oligocene sample suggests the equatorial Pacific was warm during the Paleogene, perhaps >3°C warmer than modern conditions.

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Figure F1. Gas chromatograph trace of early Oligocene Sample 199-1219A-13H-3, 50–54 cm, showing the presence of three long-chain (C_{37}, C_{38}), diunsaturated (:2) methyl (m)/ethyl (e) ketones (K) (alkenones) labeled K37:2m, K38:2e, and K38:2m. These biomarkers are specific to the unicellular algae *Emiliania huxleyi* but are also found in other haptophytes (Conte et al., 1994). FID = flame ionization detection.

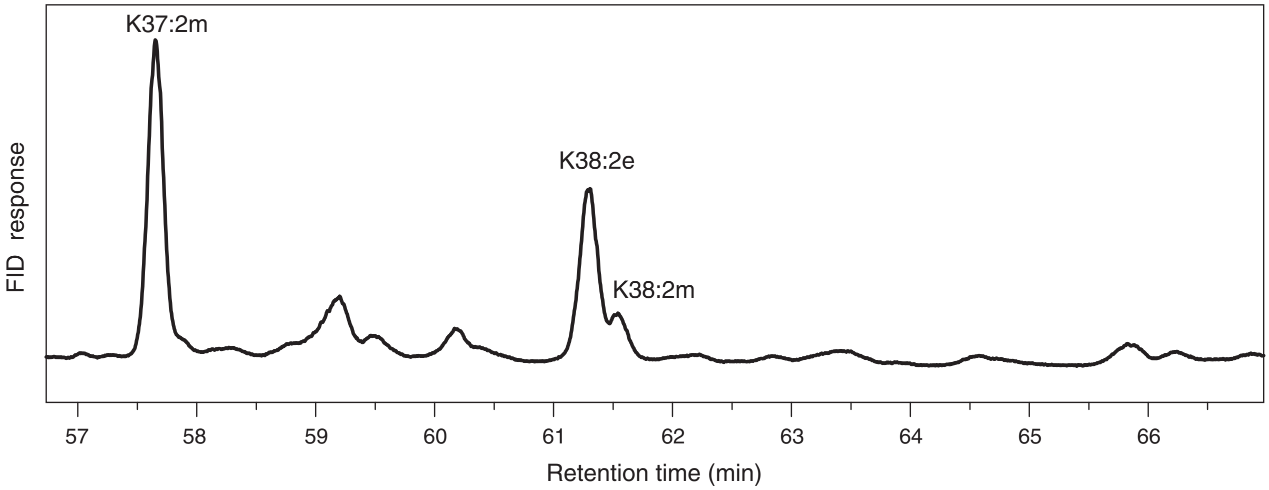

Figure F2. Sample 199-1219A-13H3, 50–54 cm (sample 3 from Table T1, p. 9), shown on an alkenone property-property plot for southeast Pacific surface sediments and cores from the Peru-Chile margin. RR9702A-MC = collection of surface multicore samples from the 1997 *Roger Revelle* site survey cruise for ODP Leg 202. RR9702A-11PC = piston core from the southern Chile margin taken on the same cruise. Y71-6-12P = piston core collected from the Nazca Ridge by the *Yaquina* in 1971. Y69-71P = piston core from the eastern equatorial Pacific collected by the *Yaquina* in 1969.

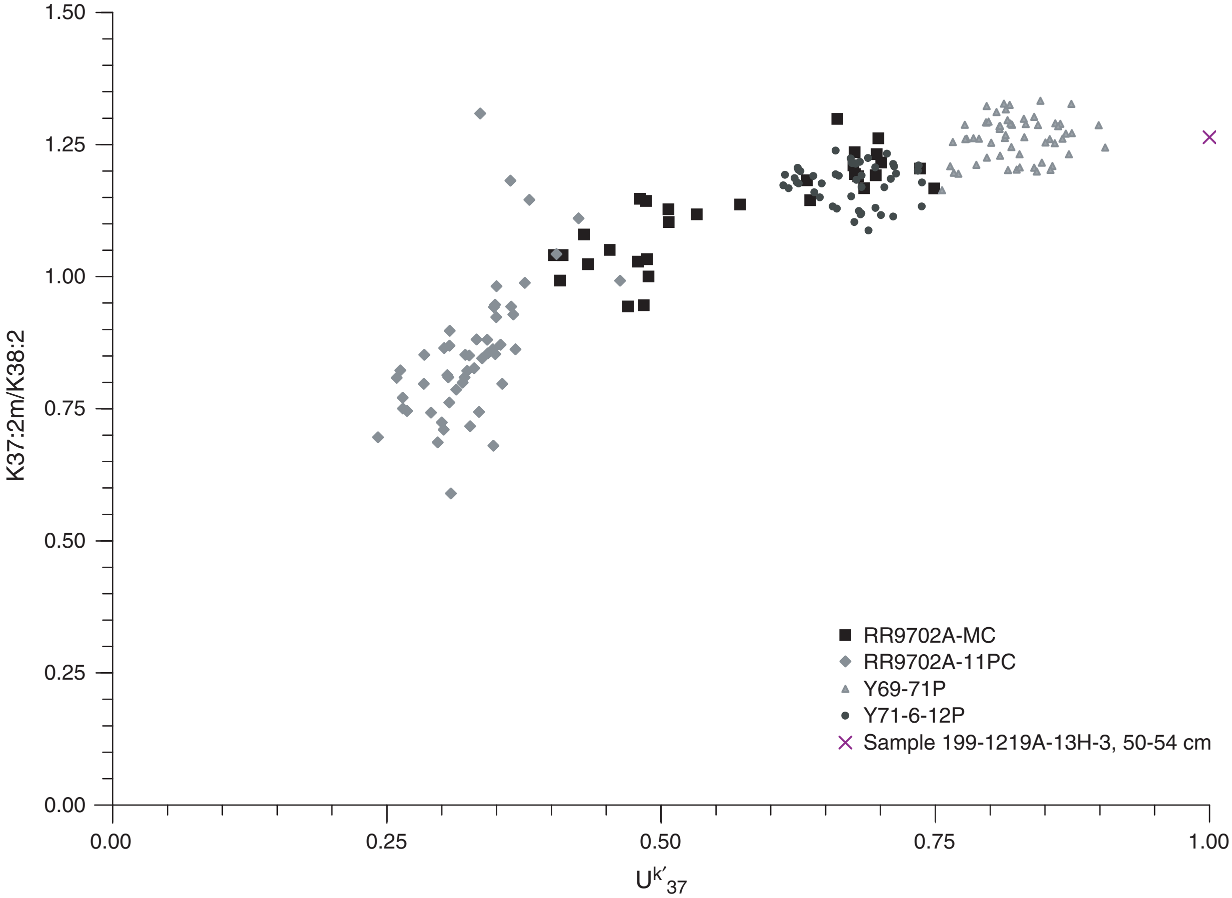

Table T1. Sample information.

Sample ID number	Core, section, interval (cm)	Depth (mbsf)	Depth (mcd)	Age (Ma)	Paleolatitude	Paleolongitude
	199-1219A-					
3	13H-3, 50–54	130.33	149.92	29.72	–0.1°N	119.80°W
1	16H-6, 50–54	147.13	171.46	33.04	–0.72°N	117.65°W
2	17H-6, 50–54	155.37	180.70	34.37	–0.96°N	116.78°W
4	23H-2, 50–54	207.52	238.85	43.63	–2.53°N	110.74°W
	199-1221C-					
5	11X-2, 10–12	152.01	152.01	53.50	–0.65°N	110.43°W
6	11X-2, 10–12	152.22	152.22	53.60	–0.67°N	110.40°W

Notes: Site 1219 ages are from Palike et al., this volume. Site 1221 ages are estimated based on data from Lyle, Wilson, Janecek, et al., 2002.

Table T2. Sample summary data table.

Sample ID number	Core, section, interval (cm)	Extracted dry weight (g)	Total organic carbon (wt%)	Hydrocarbon fraction	PAH fraction	Alkenone fraction	Sterol/ Alcohol fraction
	199-1219A-						
3	13H-3, 50–54	38.38	0.03	A	—	B	—
1	16H-6, 50–54	28.48	0.01	A	—	—	—
2	17H-6, 50–54	16.26	0.02	A	—	—	—
4	23H-2, 50–54	20.57	0.02	A	—	—	—
	199-1221C-						
5	11X-2, 10–12	10.35	0.66	A	—	C	D
6	11X-2, 30–34	33.03	0.03	A	—	C	D
Bulk	Sample blank						

Notes: A = hydrocarbon series (contaminants) present with no odd/even predominance (C_{27} = 56, 29, 71, 753, 46, and 19 ng/gm, respectively). B = K37:2m, K38:2e, and K38:2m alkenones present (10.5, 6.8, and 1.5 ng/g, respectively). C = fatty acid methyl ester series present (contaminants). D = dioic acid series present (contaminants). PAH = polycyclic aromatic hydrocarbons.

Table T3. Ketone recovery from Leg 199 samples.

Sample ID number	Core, section, interval (cm)	C19–10one recovery (%)	EtTriacon recovery (%)	Extracted dry weight (g)	Dry/Wet	Ketones (µg/g dry) K37:2m	Ketones (µg/g dry) K38:2e	Ketones (µg/g dry) K38:2m	Minimum µg/g detectable
	199-1219A-								
1	16H-6, 50–54	75.4	82.3	28.48	0.55	<0.0004			0.0004
2	17H-6, 50–54	83.1	78.4	16.26	0.33	<0.0008			0.0008
3	13H-3, 50–54	79.4	70.5	38.38	0.66	0.0105	0.0068	0.0015	0.0003
4	23H-2, 50–54	80.3	77.9	20.57	0.42	<0.0005			0.0005
	199-1221C-								
5	11X-2, 10–12	Contaminated	75.2	10.35	0.56	<0.0010			0.0010
6	11X-2, 30–34	Contaminated	70.9	33.03	0.68	<0.0003			0.0003
Bulk	Sample blank	82	78						

Notes: C19–10one = nonadecan-10-one. EtTriacon = ethyl triacontanoate.

Table T4. Comparison of alkenone recovery and properties.

Core		K37:2m (μg/g dry)	K37:2/ K38's
ODP 199-1219A-13H-3, 50–54		0.0105	1.26
RR9702A MC (modern core tops)			
	max:	35.35	1.30
	min:	0.04	0.83
	n:	32	32
RR9702A-11PC (0–150 ka)			
	max:	0.58	1.31
	min:	0.01	0.59
	n:	52	52
Y69–71P (0–150 ka)			
	max:	7.40	1.24
	min:	1.50	1.09
	n:	61	46
Y71-6-12P (0–150 ka)			
	max:	3.42	1.33
	min:	0.70	1.16
	n:	46	60

Notes: RR9702A-11PC cored at 46.3°S, 76.5°W in 2825 m water. Y69-71 cored at 0.1°N, 86.5°W in 2740 m water. Y71-6-12 cored at 16.4°S, 77.6°W in 2734 m water.