# 20. ORGANIC CARBON AND BARIUM IN EOCENE SEDIMENTS: POSSIBLE CONTROLS ON NUTRIENT RECYCLING IN THE EOCENE EQUATORIAL PACIFIC OCEAN<sup>1</sup>

Annette Olivarez Lyle<sup>2</sup> and Mitchell Lyle<sup>2</sup>

# ABSTRACT

We present the first high-resolution organic carbon mass accumulation rate (MAR) data set for the Eocene equatorial Pacific upwelling region, from Sites 1218 and 1219 of the Ocean Drilling Program. A maximum C<sub>org</sub> MAR anomaly appears at 41 Ma and corresponds to a high carbonate accumulation event (CAE). Independent evidence suggests that this event (CAE-3) was a time of rapid cooling. Throughout the Eocene, organic carbon burial fluxes were an order of magnitude lower than fluxes recorded for the Holocene. In contrast, the expected organic carbon flux, calculated from the biogenic barium concentrations for these sites, is roughly equal to modern. A sedimentation anomaly appears at 41 Ma, when both the measured and the expected organic carbon MAR increases by a factor of two-three relative to the background Eocene fluxes. The rain of estimated Corg and barium from the euphotic zone to the sediments increased by factors of three and six, respectively. We suggest that the discrepancy between the expected and measured C<sub>org</sub> in the sediments is a direct consequence of the increased metabolic rates of all organisms throughout the Eocene oceans and sediments. This hypothesis is supported by recent work in ecology and biochemical kinetics that recognizes the fundamental basis of ecology as following from the laws of thermodynamics. This dependence is now elucidated as the Universal Temperature Dependence (UTD) "law" of

<sup>1</sup>Olivarez Lyle, A., and Lyle, M., 2005. Organic carbon and barium in Eocene sediments: possible controls on nutrient recycling in the Eocene equatorial Pacific Ocean. *In* Wilson, P.A., Lyle, M., and Firth, J.V. (Eds.), *Proc. ODP, Sci. Results*, 199, 1–33 [Online]. Available from World Wide Web: <http://www-odp.tamu.edu/ publications/199\_SR/VOLUME/ CHAPTERS/222.PDF>. [Cited YYYY-MM-DD]

<sup>2</sup>Center for Geophysical Investigations of the Shallow Subsurface, Boise State University, Boise ID 83725, USA. Correspondence author: **aml@cgiss.boisestate.edu** 

Initial receipt: 18 May 2004 Acceptance: 18 November 2004 Web publication: 9 May 2005 Ms 199SR-222

metabolism and can be applied to all organisms over their biologically relevant temperature range. The general pattern of organic carbon and barium deposition throughout the Eocene is consistent with the UTD theory. In particular, the anomaly at 41 Ma (CAE-3) is associated with rapid cooling, an event that triggered slower metabolic rates for all organisms, slower recycling of organic carbon in the water and sediment column, and, consequently, higher deposition of organic carbon in the sediments. This "metabolism-based" scenario is consistent with the sedimentation patterns we observe for both Sites 1218 and 1219.

# INTRODUCTION

Biological productivity in the equatorial Pacific Ocean is a significant part of the Holocene carbon cycle and likely was a major component of this cycle throughout the geologic past. Because the volume of the Pacific Ocean has shrunk from the early Cenozoic to modern conditions, the influence of the Pacific equatorial region on the carbon cycle was probably much greater in the Eocene than the present. Processes in the modern equatorial Pacific upwelling region are an important part of the global carbon cycle (e.g., Hammond et al., 1996) and this was probably true throughout the Cenozoic. This region is nearly equal in size to the Pacific continental margins (~ $1.1 \times 10^{13} \text{ m}^2$ ) for the area bounded by 5°N to 5°S latitude and 90°-180°W longitude (Chavez and Barber, 1987), and carbon respiration rates in the Pacific upwelling region are equal to ~25% of the Pacific margin area (shelf + slope). Two primary factors (sedimentation rates and oxygen exposure time) account for the fact that the continental margins are the location of 95% of the total oceanic C<sub>orq</sub> mass accumulation rate (MAR) (Gershanovich et al., 1974; Hedges and Kiel, 1995). The higher C<sub>org</sub> MAR is a consequence of much higher sedimentation rates and lower oxygen exposure times (Hartnett et al., 1998) for margin sediments relative to pelagic regimes.

The Pacific Ocean has been the largest ocean basin throughout the Cenozoic, and the Pacific equatorial upwelling region was increasingly larger further back in time. Therefore, it is reasonable to expect that throughout the Eocene, the Pacific equatorial upwelling region could have exerted a much greater influence on the global carbon cycle, nutrient cycling, and climate change than it does today.

This paper examines the organic carbon and biogenic barium (Bio-Ba) sedimentation history for the Eocene at two sites in the equatorial Pacific drilled during Ocean Drilling Program (ODP) Leg 199. During Leg 199, a transect was drilled across the Eocene equatorial region following 56-Ma crust, with one site located at the 40-Ma paleoequatorial position on 42-Ma crust (Lyle, Wilson, Janecek, et al., 2002) (Fig. F1). The primary objective of the cruise was to capture a latitudinal transect at the Paleocene/Eocene boundary, and the combination of sites on younger and older crust for the middle and late Eocene provided an opportunity to study the sedimentation history in detail after 42 Ma. Detailed site descriptions are in Shipboard Scientific Party (2002) and Lyle et al. (this volume). Paleoposition calculations, based on a fixed hotspot model, are reported in detail in Lyle et al. (this volume).

Organic carbon analyses from our laboratory focused on the Eocene and constitute a time series between 33.8 and 54.5 Ma. The behavior of barium and other elements (Shipboard Scientific Party, 2002) was examined to provide a perspective of the sedimentation history that spanned most of the Cenozoic. Together, Sites 1218 and 1219 span a paleo-





latitude and paleolongitude history for a large region of the equatorial Pacific—from 9°N to 5°S and 104°–135°W. This area, 1500 km<sup>2</sup>, represents one-third of the total modern upwelling region in the Pacific. Organic carbon data are reported at a resolution as small as 10 k.y. for the paleogeographic area bounded by 1°N to 5°S latitude and 104°–114°W longitude, an area representing ~7% of the modern Pacific upwelling region.

# METHODS

# **Calcium Carbonate and Organic Carbon**

Calcium carbonate and organic carbon were determined by coulometry at Boise State University (Boise, Idaho, USA) using a UIC, Inc., model CM-5012 CO<sub>2</sub> coulometer attached to our modified version of a CM-5120 combustion furnace. Approximately 30–70 mg of dried, homogenized sediment sample was combusted in an ultra-high-purity oxygen (>99.994% O<sub>2</sub>) atmosphere at 1000°C. The reported CaCO<sub>3</sub> data were calculated as the difference between two independent analyses of carbon from each sampled interval: total carbon and organic carbon. Inorganic carbon is calculated as the difference between the total carbon and the organic carbon fractions, and weight percent CaCO<sub>3</sub> is the product of inorganic carbon (wt%) and 8.33.

Organic carbon was measured after the sample was pretreated with acid to remove carbonates. Approximately 70 mg of dried sample was placed inside a fused quartz combustion boat and wetted with water and 10 drops of 10% (v/v) concentrated HCl. The slurry was stirred and heated at ~110°C until sufficient solution evaporated to accommodate a second treatment with the acid. After ~1 hr, samples were oven-dried and allowed to cool before analysis with the coulometer. We emphasize the importance of using fused quartz combustion boats. Previously, we had used a glazed porcelain boat (Coors #60032) but discovered that the glaze deteriorated after about a dozen sample runs. Absorption of the sample slurry into the porcelain produced erratic results and unacceptably high background readings.

Accuracy was estimated by including two independent standards in each sample run, and precision was estimated by repeating the analyses of a subset of the unknown samples. Standards included reagent-grade calcium carbonate, reagent-grade sucrose, and an in-house standard "Midway" marine sediment from the Pacific Ocean. Standards were run at the beginning, middle, and end of each sample set. Summary statistics for the Midway standard are given in Table T1 (average total carbon =  $2.64 \pm 0.02$  wt%, n = 523; average  $C_{org} = 0.85 \pm 0.01$  wt%, n = 570). Precision of the unknowns was estimated by repeating the analysis of every fourth sample in the sample run. The average difference between the repeated unknown samples is <0.01 wt% carbon. In general, samples were reanalyzed if the difference between the repeated analyses exceeded 0.02 wt% carbon. This level of precision was necessary because the average concentration of  $C_{org}$  at both Sites 1218 and 1219 was 0.03 wt%.

# **Limitations of Shipboard Organic Carbon Data**

Here we argue the importance of adopting our protocol for measuring organic carbon in pelagic sediments by elucidating the inadequacies **T1.** Summary statistics for inhouse sediment standards, p. 30.

of the *JOIDES Resolution* standard technique. Specifically, *JOIDES Resolution* C<sub>org</sub> measurements are inadequate for studies of carbonate sediments in pelagic environments when C<sub>org</sub> falls below ~0.3 wt%. C<sub>org</sub> values are calculated indirectly as the difference between total carbon and inorganic carbon. Note that we measure organic carbon directly, not as the difference between two parameters. Because both shipboard measurements are obtained by different analytical methods, negative C<sub>org</sub> values often result when carbonate content is high and C<sub>org</sub> is low, a situation that typifies marine sediments. The analytical precision (±0.2 wt% C<sub>org</sub>) is greater than the concentration in many samples, as demonstrated for duplicate analyses of samples from ODP Hole 847B (Shipboard Scientific Party, 1992).

To test the "general adequacy" of shipboard organic carbon measurements, Meyers and Silliman (1996) conducted a shore-based analysis of 95 samples for direct comparison with JOIDES Resolution shipboard values for identical sample intervals. They concluded "little error is introduced" using the shipboard procedure for measuring organic carbon "over a wide range of concentrations." For the range that Meyers and Silliman are interested in (>1 wt%), their conclusion is correct. Unfortunately, this result has been generally assumed (e.g., Shipboard Scientific Party, 1998) without closer examination of the data, especially for  $C_{org}$ values in the range typical of pelagic sediments (0.2 wt% Corg, based on the compilation of Deep Sea Drilling Project [DSDP] Legs 1-33 by McIver [1975]). Whereas direct Corg measurements of Meyers and Silliman (1996) are "positively correlated" to shipboard values, our examination of the two published data sets reveals a high degree of variability and unexplained deviations directly relevant to paleoceanographic studies. For example, we note that the sample-to-sample differences between the onshore direct C<sub>org</sub> measurements and the shipboard indirect  $C_{org}$  measurements range between -100% and 2,000\% for all 95 samples reported. (Corg content in the samples range between 0.06 and 3 wt%, using the Meyers and Silliman results). The median difference between the two analyses, or median deviation, is high: 34% for all 95 samples, which increases as the concentration range of Corg decreases. Specifically, the median deviation increases from 40% to 60% to 75% for samples containing 0.5 wt%  $C_{\text{org}},~0.4$  wt%  $C_{\text{org}},~and~0.3$  wt%  $C_{\text{org}},~re$ spectively. In contrast, our analytical protocol routinely produces direct Corg measurements with high precision (±0.01% Corg) at very low concentrations: <0.1 wt% Corg.

# Anomalous Corg Values

In our Eocene data set, all samples with  $C_{org}$  values of 0.10 wt% were repeatedly analyzed, yet the tests produced similarly high results. To further test the interpretation of the measurement results, we pursued two testable hypotheses that could explain the high values: (1) sample contamination and (2) inherent limitations of the analytical procedure.

#### **Sample Contamination Test**

We tested the anomalous samples for contamination by drilling muds and oils when drilling through chert horizons at both sites. Such horizons are typically difficult to drill, and contamination is possible through use of excess drilling muds and oils during subsequent retrieval and processing. Suspect samples were tested for contamination by comparing their proximity to identified chert horizons with their  $C_{org}$  con-

tent. Fifteen distinct chert horizons (occurring as fragments, nodules, or layers) at Site 1218 are relevant for comparison with our sampled intervals. Of the 15 horizons, nine samples coincide with the location of a chert horizon. If contamination is the cause, then these samples should exhibit high organic carbon values. In fact, these nine samples fall in the range of average values, between 0.01 and 0.06 wt% C<sub>org</sub>. Using a second approach, we tested this theory by measuring the distance between a sample with high organic carbon and its proximity to the closest chert horizon. We expected to find increasing organic carbon with decreasing proximity to the chert horizon if drilling resulted in sample contamination. As shown in Figure F2, no such relationship was found between these two variables. Based on these two tests, we find no evidence of sample organic carbon contamination from drilling through chert horizons.

### **Errors Associated with Analytical Procedure**

High organic carbon concentration could reflect the presence of dolomite, which is found in the basal sections of Leg 199 sites, or other dissolution-resistant phases. Because the organic carbon measurements are made after acidification to remove solid calcium carbonate, dissolution-resistant carbonates would artificially contribute to the Cora fraction when combusted at 1000°C. Our laboratory experiments have shown that dolomite-bearing samples respond well to a simple modification of the acid treatment (adding more acid and increasing the reaction time) to produce organic carbon values that are lower and consistent with the downcore trend. Because dolomite is found in Leg 199 samples, we were suspicious of all samples exhibiting spikes in the downcore trends of organic carbon; all were reanalyzed several times using this modified treatment (excepting the insufficient samples for six samples from Site 1218). All four samples from Hole 1219A responded to the modified treatment by falling to average levels for the site. These samples were taken from carbonate chalks (90 and 95 wt%) carbonate) at the base of Hole 1219A. Although dolomite was not noted in smear slide studies (see "Site 1219 Smear Slides" in Lyle, Wilson, Janecek, et al., 2002), the samples response to the modified treatment suggests the presence of a dissolution-resistant phase.

For Site 1218, only 3 of the 19 reanalyzed samples produced lower values which are in line with average levels (0.05 wt% Corg). Most samples remained high after the modified treatment. Ten of these samples remained in the anomalously high range (>0.10 wt%), and six samples resulted in lower values that were still in the elevated range between 0.06 and 0.09 wt% Corg. No common factor explains the results; there is no significant correlation with carbonate content, lithology, or location downcore. Furthermore, the "null hypothesis" was not confirmed (i.e., samples from sections known to contain dolomite did not necessarily exhibit high Corg values, even when the "weaker" acidification method was used). For example, dolomite contents between 15% and 20% are reported from smear slide analysis of sections at the base of Hole 1218A (Cores 199-1218A-29X and 30X; 266–274 meters below seafloor (mbsf); see "Site 1218 Smear Slides" in Lyle, Wilson, Janecek, et al. [2002]). These sections, described as nannofossil chalks, contain high carbonate contents (64-90 wt%). We analyzed 18 samples from this interval but only 2 produced moderately elevated Corq values using the standard method (0.09 and 0.11 wt%). These values fell to 0.02 and 0.06 wt%, respectively, after the harsher acidification treatment was used. More inF2. Distance between chert layers and samples with anomalously high  $C_{org}$  concentrations, p. 25.



triguing is the fact that the other 16 samples from the dolomite zones reflect the site average of 0.03 wt%  $C_{org}$ . Therefore, the presence of dolomite or chalk is *not* a predictor of the high  $C_{org}$  values we measured. With regard to data presentation and interpretation of the results, we included only the  $C_{org}$  values (Table T2) from the repeated analyses using the stronger acid treatment.

### **Biogenic Silica Analysis**

Biogenic silica was measured using a Hach model DR/4000 spectrophotometer after sediment samples were digested in a 2-M KOH solution. The method is described in Lyle et al. (this volume) and Olivarez Lyle and Lyle (2002), where we address the problems of measuring dissolution-resistant radiolarians in Eocene and Miocene marine sediments (Moore, 1969). The problems are twofold. First, the widely used Mortlock and Froelich (1989) method, which uses a 2-M sodium carbonate bath, is ineffective at dissolving Eocene radiolarians, which they acknowledge and which we demonstrated for sediments from the Leg 199 site survey (Olivarez Lyle and Lyle, 2002). The second problem is the pervasive assumption in the scientific community that a significant fraction of clay minerals dissolve during the alkaline bath and result in serious overestimations of the reported biogenic opal content of the sediments. The Olivarez Lyle and Lyle (2002) study shows that using the harsher KOH treatment can be successfully employed to dissolve radiolarians without compromising the analysis via clay dissolution. However, either solvent (KOH or Na<sub>2</sub>CO<sub>3</sub>) overestimates biogenic silica when the volcanic glass content is high, which is not the case for the Eocene samples from Sites 1218 and 1219.

We used two standards in the opal analysis: a reagent grade dissolved silica standard (Hach 1106-49) and one of two in-house dry sediment standards-the "1218C composite standard" or the "1219A composite standard." Composite sediment standards are mixtures of sediments from each interval we analyzed and therefore reflect the full range of variation in biogenic silica. matrix materials. and dissolution-resistant opal phases. In certain cases, a diatom ooze composite sediment standard was used from ODP Leg 178 Site 1098 because good reproducibility using our laboratory method previously had been established for this standard (Olivarez Lyle and Lyle, 2002). Summary statistics for the composite sediment standards are given in Table T1. Generally, every sample tube was analyzed twice and every fourth "unknown" sample was replicated as a separate unknown in the sample run. If the difference between the replicate analyses exceeded ~7 wt% SiO<sub>2</sub>, then the sample was reanalyzed during a subsequent run. Note that our reported biogenic silica data have not been corrected for structural water content, which is variable and may be as high as 15 wt% H<sub>2</sub>O for radiolarians. Hence, the biogenic SiO<sub>2</sub> content we report underestimates the true sediment fraction.

Table **T1** also includes the results of additional tests we conducted to gauge the efficiency of our standard method for dissolving Eocene biogenic opal and to gauge the contribution of dissolved silica from clays by using reagent-grade talc as the clay test sample. The former test involved collecting the sediment residue that remained in the centrifuge tube after a standard KOH digestion. All tubes contained the same 1218C composite sediment standard, a radiolarian ooze containing 32  $\pm$  2 wt% SiO<sub>2</sub> (n = 87). To achieve critical mass, the sediment residue from 24 tubes was combined to make nine samples and then dried, re-

T2. Data used in this study, p. 31.

weighed, and prepared for a second opal analysis using our standard procedure with the exception that samples were not subjected to a second hydrochloric acid and peroxide treatment. As shown in Table T1, 1.6 wt% SiO<sub>2</sub> was leached from the 1218C sediment residue during the second digestion. This value is  $\sim 5\%$  absolute of the average value from the first digestion and is consistent with our smear slide analyses of the KOH-digested residues of Leg 199 Eocene sediments showing trace amounts of radiolarian fragments; it suggests that very little silica is leached from the clay mineralogical matrix. In addition, we subjected 26 samples of reagent-grade talc to our digestion procedure to show that very little silica (1.5 wt% SiO<sub>2</sub>) is leached in a 2-M KOH solution subjected to our standard protocol (Table T1). We also repeated a KOH digestion of the recovered talc residue; this second digestion produced only 0.4 wt% SiO<sub>2</sub>. Hence, the silica released from the first leach could reflect contamination from the milling process used to refine the reagent-grade clay, implying that the lower value  $(0.4 \text{ wt}\% \text{ SiO}_2)$  from the second leach accurately reflects the amount of silica released from claydissolution using KOH. In either case, we are confident that our biogenic silica results are not compromised by clay dissolution, that our method efficiently dissolves thick-walled radiolarians, and that our biogenic silica data are the best available for Eocene marine sediments to date. Extremely low opal environments warrant caution when the 0.5-1 wt% SiO<sub>2</sub> that leaches from clays represents a higher proportion of the total biogenic silica present.

# Modern Bio-Ba/Corg Ratio in Surface Sediments

Here we estimate the biogenic barium to organic carbon ratio of modern surface sediments beneath upwelling regions. We used Leg 199 inductively coupled plasma-atomic emission spectrometer (ICP-AES) data for barium and other elements (Shipboard Scientific Party, 2002) to estimate the initial organic carbon content of surface sediments in the equatorial Pacific. We assumed that (1) the geologic processes and features that control biogenic barite precipitation in the water column today were also operative during the Eocene; (2) barium concentrations in the sediments are a valid proxy for barite, as demonstrated by Pfeifer et al. (2001) and specifically for Leg 199 sediments by Faul and Payton (this volume), who demonstrated a strong linear correlation ( $r^2 = 0.9$ ) between shipboard Ba and barite concentrations; (3) biogenic barite has been well preserved (see above); (4) our estimate of the Bio-Ba/Corg ratio of modern surface sediments for upwelling regions is valid for Eocene surface sediments beneath the equatorial upwelling region; and (5) seawater sulfate levels in the Eocene were the same. Note that recent work (Turchyn and Schrag, 2004) shows that seawater sulfate concentrations may vary by about  $\pm 10\%$  over short timescales of 2–3 m.y.

Barium concentrations in surface sediments can be used to predict the amount of primary productivity in surface waters when the Dymond et al. (1992) sediment trap model is employed (Pfeifer et al., 2001). We used two data sets to determine the Bio-Ba/C<sub>org</sub> ratio of equatorial surface sediments for this study. The first data set (Table T3) (SET-PAC data; Lyle, 1992) is directly related to our study because it represents the geochemistry of modern surface sediments from the eastern tropical Pacific Ocean. The second data set (Anderson, 2003) reflects surface sediments from a high-productivity region in the Southern Ocean. Together, these data provide a first-order characterization of the Bio-Ba/C<sub>org</sub> ratio of surface sediments from upwelling zones.

**T3.** Geochemistry of modern surface sediments in the eastern tropical Pacific, p. 32.

The SETPAC data set (Table T3) includes X-ray fluorescence measurements of barium, aluminum, and other elements for 153 surface sediments (upper 5 cm) and Corg measurements by acid-oxidizer methods (Weliky et al., 1983) from the eastern Pacific region. The Bio-Ba/Corg ratio varies significantly with proximity to the South American continent and ranges from 0.02 to 5.30 (average =  $0.59 \pm 0.66$ ; n = 158). To make valid comparisons between the modern and paleoupwelling region, we considered only samples located within 5° of the equator and west of 100°W longitude, thus eliminating samples likely to reflect a continental or hemipelagic signature. The average Bio-Ba/Corg ratio for the restricted data set, highlighted in Table T3, decreased slightly to 0.57 (± 0.15), but the range decreased significantly to 0.35 to 1.0 (n = 13). The restricted data set is bounded by ±5° latitude and 100°–130°W longitude and spans the paleolatitude and longitude coordinates of all Eocene samples from Sites 1218 and 1219. The Bio-Ba/Corg ratio is roughly correlated with water depth: the smallest ratio represents surface sediments at 3200 m; the largest ratio is from 4500 m water depth.

The Bio-Ba/C<sub>org</sub> ratios for the modern equatorial Pacific sediments are remarkably similar to the ratios for surface sediments beneath upwelling areas in the Southern Ocean. The Southern Ocean sediment data were obtained from Anderson (2003) and include a total of 29 samples from three cores (NBP98-02-05-2, NBP98-02-07-13, and NBP98-02-06-5). The study area is bounded by 60.24°-63.11°S latitude and 169.74°-170.19°W longitude—a high productivity region dominated by diatoms. Organic carbon contents range between 0.3 and 0.5 wt% and biogenic silica is generally high, between 30 and 80 wt%. Aluminum data, used to correct the total barium for terrigenous sources, are not reported. The amount of Bio-Ba was calculated by assuming that the nonbiogenic (terrigenous) fraction is an aluminosilicate with a SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> ratio of 3.5 and an average Ba/Al ratio of 0.0075 (Dymond et al., 1992). The terrigenous fraction was calculated as the difference between the total amount of sediment and the biogenic components (100% -[CaCO<sub>3</sub> wt% + Biogenic SiO<sub>2</sub>% wt%]). The Si:Al ratio we chose is robust because the proportion of biogenic components is very high (up to 80%); altering the SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> ratio of the terrigenous fraction between 3 and 4 made little difference in the ultimate Bio-Ba values. Applying this model to the 29 samples, we find that the Southern Ocean  $Bio-Ba/C_{org}$ ratios and those of the equatorial SETPAC data set closely agree. The median Bio-Ba/Corg value is 0.66 (wt%/wt%) and ranges between 0.36 and 1.4 (n = 29) for the Southern Ocean surface sediments vs. the equatorial Pacific (median = 0.54 [wt%/wt%]; range = 0.35-1.0; n= 13). This range applies to a depth within the sediment column of 2.6 m for Southern Ocean samples (the SETPAC data set is limited to the upper 5 cm of the cores). We found no substantive difference in the Bio-Ba/C<sub>org</sub> ratio based on sampling depth; for example, ratios for Southern Ocean samples located deeper than 0.5 m range between 0.33 and 0.87.

For both high-productivity regions we note the following similarities in the Bio-Ba/C<sub>org</sub> ratio of surface sediments: the median value at both sites is between 0.6 and 0.7 and ranges between 0.35 and 1.0 and the ratio increases with water depth in the restricted SETPAC data set but does not exceed the upper limit of 1. Processes which control this ratio, both within and between regions, are not explored in detail here but may reflect (1) differences in the initial ecology of the primary producers and their effects on new production (e.g., the diatom to coccolithophorid ratio would affect new production via more or less efficient recycling of nutrients), (2) differences in water depth and the impact on the burial

of organic matter, and (3) differences in the total sedimentation rate and its impact on the postdepositional exposure of organic carbon to oxygenated seawater.

# Method for Calculating Predicted C<sub>org</sub> and Bio-Ba

We estimated the "expected" organic carbon concentration in Leg 199 sediments by utilizing the surface sediment information above along with a Bio-Ba/ $C_{org}$  ratio that is representative of surface sediments and barium data for Leg 199 sediments from which we estimated the biogenic barium component. Using the data from modern upwelling regions, the maximum Bio-Ba/ $C_{org}$  ratio of 1.02 was chosen because it is the same for both upwelling regions and would tend to minimize the predicted  $C_{org}$  concentrations, consistent with the average measured content (0.03 wt%  $C_{org}$ ).

First, we corrected all shipboard ICP-AES barium data for terrigenous, authigenic, and clay sources. Dymond et al. (1992) used an average Ba/Al ratio of 0.0075 to adjust the total Ba content for terrigenous sources of barium. This correction alone left the measured barium content of Leg 199 sediments essentially unchanged, resulting in very high estimated  $C_{org}$  values uncharacteristic of pelagic sediments. We applied two additional corrections, for an authigenic and hydrothermal component, justified by compositional differences between sediment trap studies and Leg 199 sediments. Our estimated Bio-Ba concentration was calculated using Equation 1:

$$Bio-Ba = Total Ba - [(0.0075 Ba/Al) + (0.014 \times Ba/Mn) + (0.02 \times Ba/Fe)].$$
(1)

The ratio Ba/Al = 0.0075 is the correction used for the terrigenous component as explained above. Ba/Mn = 0.014 reflects the authigenic barium component (Burns and Burns, 1979), and the presence of this phase is suggested by the y = 1/x relationship between the Ba/Mn concentration ratio (y) vs. core depth (x) found for Site 1218, a profile that typifies authigenic enrichments. The Ba/Mn ratio is high at the surface in the slowly accumulating red clays and in the basal section above basement at Site 1218. The high ratio in the basal section may reflect Mn oxide precipitates from hydrothermal activity. Dymond (1981) reports that 20% of the total barium within 100 km of the East Pacific Rise (EPR) crest is of hydrothermal origin and falls to 5% of the total barium in the basins adjacent to the EPR crest. The bulk MAR of the upper sediment column of both Leg 199 sites is low, between 70 and 90  $mg/(cm^2 \times k.v.)$ , a condition favoring authigenic precipitation of Mn oxides. Barium has a high affinity for manganese oxides (e.g., todorokite) and forms as basal sediments near mid-ocean ridges; concentrations in todorokite and metalliferous sediments can exceed 3 wt% (Burns and Burns, 1979.) The ratio Ba/Fe = 0.02 represents the correction for barium contained in Fe-smectites and for nontronite, an Feenriched smectite, in particular (Corliss et al., 1978). This correction is necessary because smectites are enriched at both Leg 199 sites below 5 mbsf (Shipboard Scientific Party, 2002).

#### **Mass Accumulation Rates**

Differential compaction with depth and differences in average grain density of the cored intervals are accounted for by converting linear sedimentation rates (LSRs) to MARs. MAR is defined as the product of the LSR (length/time) and the dry bulk density (DBD; mass/volume) and has units of [mass/(unit area × unit time)]. DBD is related to wet bulk density (WBD) by the following equation:

$$DBD = [(1 - P)G],$$
 (2)

where P = porosity and G = average grain density of the sediment interval. Porosity is the fractional volume of a sediment sample filled with interstitial water before the sample is dried for analysis. Hence, WBD is the total mass of the original wet sample divided by the total volume of the wet sample. High-resolution DBD values were calculated every 2 cm from the shipboard "low-resolution" measurements of WBD and DBD. These two parameters are highly correlated and were used to define linear regression equations at each site. The appropriate linear equation was subsequently applied to the high-resolution gamma ray attenuation WBD data set (with a resolution at 2 cm) to predict the corresponding DBD value (Pälike et al., this volume). Linear correlation coefficients were very high (r = 0.997) for the "low-resolution" regression that utilized all of the site data (i.e., were based on all lithologic units). However, better correlation coefficients were obtained for regressions based on major lithologic units identified at each site. Ultimately, we used the appropriate equation based on lithology to predict the DBD values from WBD instead of using a single equation for each site because trial and error runs produced significant differences in the predicted DBD. For example, the calculated DBD values for intervals from a radiolarian ooze section are 8%–30% greater than calculated values from a nannofossil ooze at Site 1219. Calculated DBD values also diverged with increasing porosity, and porosity is strongly coupled to major lithology; hence, we decided to use regression equations generated for the major lithologic units in a given core.

# RESULTS

### **Organic Carbon**

The results of our analyses are presented in Table T2 along with additional geochemical data (Shipboard Scientific Party, 2002) for parameters discussed in this paper. Here we focus on three important results, which are briefly summarized. First, the measured  $C_{org}$  concentrations of Eocene sediments are an order of magnitude lower than modern marine pelagic sediments despite similar sedimentation rates. Second, anomalously high  $C_{org}$  concentrations relative to average values are evident for middle Eocene sections at Site 1218. Third, the downcore trends in organic carbon are not "flat" but display significant variations, both on a weight percentage and mass accumulation rate basis. This observation holds even when anomalously high values are excluded.

### **Result 1: Persistently Low Corg**

In contrast to modern surface sediments of the Pacific equatorial region, organic carbon concentrations throughout the Eocene sediments are lower by an order of magnitude. Corg values of modern sediments range between 0.2 and 0.4 wt% Corg (Lyle, 1988; Lyle, 1992; references in Hammond et al., 1996). Average values at Sites 1218 and 1219 equal 0.03 wt%  $C_{org}$ , with a standard deviation of ±0.03 and ±0.01 wt%, respectively, for each site. Values range between 0.01 and 0.08 wt% Corg for Site 1219 and 0.01 and 0.43 wt% Corg for Site 1218. The median value for both sites equals the mean value of 0.03 wt%  $C_{org}$ . More than 85% (584 of 668) of the samples from Site 1218 contain organic carbon values of 0.05 wt% or less. At Site 1219, 99% of all samples are in this range (n = 352). These average C<sub>org</sub> values typify all of the Paleogene samples we analyzed from Leg 199, including Sites 1220 and 1221, reported elsewhere in this volume, and are consistent with the generally low shipboard values reported in the Leg 199 Preliminary Report (Shipboard Scientific Party, 2002).

#### **Result 2: High Corg Intervals**

About 30 samples, or 3% of all samples, exhibit relatively high organic carbon values ranging between 0.10 and 0.28 wt%  $C_{org}$ . Values at the low end of this range (0.10 wt%  $C_{org}$ ) are more than three standard deviations greater than the average value for both sites. Values at the high end of the range (0.28 wt%  $C_{org}$ ) are an order of magnitude greater than the average value for both sites. Put into perspective, the  $C_{org}$  concentration of this "anomalous" subset of samples is typical modern pelagic sediments. We also observe a higher frequency of anomalies (0.10 wt%  $C_{org}$ ) at Site 1218 compared to Site 1219, both in terms of absolute numbers and proportionate to the number of samples from each site. At Site 1218, 25 of 668 samples were above this value vs. 4 of 355 samples at Site 1219. (Note: only 0.005% of all samples we analyzed [5 of 1020] would have been above the detection limit of 0.2% using the shipboard method or  $C_{org}$  analysis!)

# **Result 3: Trends in Total Organic Carbon**

#### **Biogenic-Free Plot of Data**

We note that the generally low  $C_{org}$  values at both sites still exhibit variability; downcore profiles are not flat, even when the anomalously high values are removed from consideration. For example, Figure F3 shows the changes in organic carbon, calcium carbonate, and biogenic opal on a weight percent basis. Note that  $C_{org}$  is not in phase with calcium carbonate or biogenic silica, and that it tends to lead calcium carbonate. This pattern persists when presented on a carbonate-free or opal-free basis (not shown). However, maxima and minima for all three parameters are coeval when presented on a mass accumulation ratebasis (i.e., the  $C_{org}$  "lead" disappears) (see below).

#### **Mass Accumulation Rates**

Positive correlations were found between bulk sedimentation rate and organic carbon weight percent, suggesting that organic carbon preservation is favored by "rapid" burial, hence its removal from the sediment/water interface. The  $C_{org}$  content is independent of bulk MAR at Site 1219 (not shown). In contrast, the inverse trend between these





parameters (bulk sediment MAR and wt% Corg) is found for Site 1218 as shown in Figure F4. The maximum Corq value at Site 1218 is 0.45 wt% (vs. 0.08 wt% at Site 1219) and the total MAR is three times greater than at Site 1219 (3.5 g/[ $cm^2 \times k.y.$ ]). At Site 1218, high organic carbon values (>0.1 wt%) are associated with low total mass accumulation rates (<0.5  $g/[cm^2 \times k.y]$ ). For MAR values greater than 0.5  $g/(cm^2 \times k.y)$ , samples display low  $C_{org}$  (<0.10 wt%), opposite the relationship observed in modern sediments. An important implication of this graph is that the processes which produced low Corg (0.1 wt%) were operative over the full range of modern mass accumulation rates (i.e., we cannot invoke low MAR to explain the low C<sub>org</sub>, especially because we find just the opposite relationship at Site 1218 [low MAR and high Corg]). In Figure F5, the component MARs of organic carbon, calcium carbonate, and biogenic opal are shown for the Eocene and suggest strong coherence between the two productivity signals and the burial flux of C<sub>org</sub>. Recent work by Francois et al. (2004) suggests that syndepositional redistribution of sediment by bottom currents (sediment focusing) can significantly affect the mass accumulation rates. Newer work by Lyle et al. (2005) suggests that "sediment focusing" has not obliterated the primary productivity signal in the eastern equatorial Pacific for sediments of the past 18 k.y. years. They demonstrate coherence for the sedimentation parameters both within and between the sediment columns at every scale (i.e., within the sediment column at the centimeter scale down to 500 m depth, and from tens of meters to 10,000 km at the horizontal scale). They also show that the maximum credible redistribution of sediments transported by the fastest deep currents is ~150 km, about 1.5 map degrees. Although sediment focusing may occur as a natural process, it is probably not relevant to our study.

As with the sedimentation rate, the surface area:mass ratio of host phases is recognized as an important factor that controls the organic carbon content of marine sediments (e.g., Weliky, 1983; Hedges and Keil, 1995). As the amount of clay, and clay-sized particles, increases in a sediment assemblage, so does the overall surface area:mass ratio and organic carbon content. To estimate the clay content, or nonbiogenic fraction, we used the simple relationship:

%nonbiogenic (clay) =  $(100 - [CaCO_3 wt\% + biogenic SiO_2 wt\%])$ . (3)

We report that no trend was found for either site between the organic carbon content and the fractional amount of the clay component.

# DISCUSSION

Two fundamental questions arise from the Leg 199 organic carbon records: the first is why the organic carbon values are so low for Eocene sediments at Sites 1218 and 1219, and the second is whether relevant geologic information can be extracted from the organic carbon variations, especially for the observed coherence between C<sub>org</sub> MAR and the MARs of the biogenic components (Fig. **F5**). The near absence of organic carbon in Eocene sediments could reflect one or more of the following mechanisms: (1) primary productivity, and therefore organic carbon production, was much lower than modern rates; (2) organic carbon production, sedimentation, and preservation were higher than measured, but diagenetic remineralization, perhaps long after deposition, recycled the organic carbon; and (3) organic carbon production

**F4.** Bulk MAR and C<sub>org</sub>, Site 1218 sediments, p. 27.



**F5.** MAR of biogenic components vs. age, p. 28.



was much higher than observed but some process "short-circuited" its sedimentation such that it was never preserved in the sediments. Our conclusions support the third of these three scenarios, and we present evidence which eliminates the first two.

The  $C_{org}$  content of Holocene surface sediments in the pelagic Pacific are low (range = 0.2–0.4 wt%  $C_{org}$ ) relative to continental margin sediments (range = 1–6 wt%  $C_{org}$ ), yet they are an order of magnitude higher than Eocene sediments at Sites 1218 and 1219. Only two possibilities can explain this discrepancy: (1) the initial  $C_{org}$  flux to surface sediments was higher when deposited (similar to modern?), and the low values we observe reflect  $C_{org}$  degradation over geologic time; or (2) the initial  $C_{org}$  flux to surface sediments was very low, resulting in the concentrations we observe. If the former case is true, then it follows that there has been postdepositional remineralization, and further studies of these sediments would provide insight into the many unresolved questions regarding organic matter degradation and preservation in marine sediments. If the latter scenario is true, then it implies that conditions in the equatorial Pacific Ocean that controlled the  $C_{org}$  rain to the seafloor were very different during the Eocene

Upper limits on the initial organic carbon content and subsequent diagenesis of the sediments can be inferred from the pore water chemistry (Shipboard Scientific Party, 2002). Diagenesis has been primarily oxic as evidenced by sulfate concentrations in the interstitial waters from both sites. Sulfate concentrations are similar to modern seawater (range =  $25-32 \text{ mM SO}_4$ ) and persists down to basement, suggesting that sulfate reduction was not a significant process that oxidized the labile fraction of organic matter. Assuming that the organic carbon rain and burial rate in the sediments remained below the sulfate reduction "threshold," the competing effects between  $C_{org}$  MAR and oxygen availability within the framework of oxic diagenesis provide boundary conditions. Indeed, it appears that throughout the Eocene, oxygen availability in equatorial Pacific sediments region was as high, if not higher than, modern sediments beneath deep waters in the equatorial Atlantic and Pacific Oceans.

The dissolved oxygen content of Eocene eastern equatorial Pacific seawater was estimated using the oxygen depletion history of North Atlantic surface-to-deep waters over an equivalent path length and modern temperature-oxygen saturation data of surface waters. Bottom water pathways are still debated (Corfield and Norris, 1996) but there was likely a North Atlantic source component to the equatorial Pacific (Bice et al., 2000; Huber and Sloan, 2001). Both the Drake Passage and South Australia pathways in the Southern Ocean were closed during the Eocene, and Atlantic-derived waters likely traveled through the Panama Gateway, which was still open to exchange (Frakes and Kemp, 1972).

We used the distance of the modern pathway from the North Atlantic to the South Atlantic to select an oxygen depletion value for the same distance to the equatorial Pacific via the Panama Gateway. For the modern case, the oxygen saturation value of high-latitude, North Atlantic surface waters is ~350 µmol/kg and is depleted to ~250 µmol/kg O<sub>2</sub> when it reaches the South Atlantic Deep Waters (Millero, 1996).

The oxygen concentration of surface waters depends upon temperature. We know that global Eocene deep-sea bottom waters were persistently warm, ranging between 12° and 5°C (Lear et al., 2000; Zachos et al., 2001). This epoch is characterized by a cooling trend from a high of 12°C at 52 Ma to 5°C during the latest Eocene. Warm bottom waters (10°–12°C) also characterize Leg 199 sites in the equatorial Pacific as ev-

idenced by the  $\delta^{18}$ O values of benthic foraminifers (Tripati et al., unpubl. data). Recent work by Thomas (2004) argues that the source of deep ocean waters to the equatorial Pacific during the early Cenozoic (prior to ~41 Ma) was the North Pacific, when bottom water temperatures were consistently above 7°C. After 41 Ma, temperatures cooled below 7°C and the source of deep water changed to the Atlantic Ocean. Differences in source latitude and path length for the source waters should then be reflected in the oxygen content of eastern equatorial Pacific deep water. The total path length from the North Pacific vs. the North Atlantic would have increased by ~20% after 41 Ma. Because other factors cannot be constrained at this time, we simplified our estimate by using the North Atlantic source (Millero, 1996).

We estimate that Eocene surface waters originating at 65°N and temperatures between 7° and 12°C would have contained between 250 and 300 µmol/kg O<sub>2</sub>, based on saturation data in Millero (1996). Deep waters formed from this mass would have contained between 175 and 200 µmol/kg O<sub>2</sub>, all other factors remaining equal, when they reached the eastern equatorial Pacific. This concentration is greater than deep waters in the modern Eastern equatorial Pacific (110 µmol/kg O<sub>2</sub>) (Emerson and Bender, 1981) between 3.1 and 3.5 km depth and North Pacific Deep Waters (~150 µmol/kg O<sub>2</sub>) between 3 and 5 km, the end-point of deepwater circulation. After 41 Ma, oxygen concentrations would have been lower than 175 µmol/kg O<sub>2</sub> if the source changed to the more distant Atlantic. Regardless of source, deep waters of the Eocene equatorial Pacific probably contained <175 µmol/kg given the longer path length but not <150 µmol/kg O<sub>2</sub>, the modern value for North Pacific deep waters between 2 and 3 km.

The estimated oxygen content of Eocene deep waters provides a framework for understanding organic carbon degradation during early sediment diagenesis. Two modern analogs of organic carbon burial relative to their respective oxygen exposure were considered for comparison with Leg 199 sediments. The modern examples record the organic carbon deposition and burial in both the Atlantic and Pacific equatorial upwelling regions (Lyle, 1988) over the past 300 k.y. Surprisingly, we found that the organic carbon profiles beneath these upwelling regions, in well-oxygenated waters, are identical to each other (Lyle, 1988) despite a fourfold difference in oxygen exposure time for Atlantic sediments vs. the Pacific. The Corg MAR in the equatorial Atlantic is lower by a factor of two, yet the deepwater oxygen saturation is higher by a factor of two (Levitus and Boyer, 1994) relative to the equatorial Pacific. Organic carbon sediment profiles are the same for both regions, ranging between 0.2 and 0.4 wt% Corg over the past 300 k.y. (Lyle, 1988). Bulk MARs at equatorial Pacific Sites 1218 and 1219 are 5 g/( $cm^2 \times k.y.$ ), equal to modern Atlantic equatorial sediments (Lyle, 1988). These data, combined with the estimated oxygen saturation in Pacific equatorial deep water (175 umol/kg O<sub>2</sub>) during the Eocene, predicts an oxygen exposure time that is lower than the modern equatorial Atlantic. The implication of this lower oxygen exposure time is that the order of magnitude lower organic carbon content in Leg 199 sediments does not result from diagenetic remobilization in the top few meters of the sediment column. To the contrary, it can be argued that lower oxygen exposure times should have produced higher than modern organic carbon contents in Leg 199 sediments. The question, then, is whether the low organic carbon content reflects significantly lower primary productivity, and here we turned to the barium content in Leg 199 sediments.

High pore water sulfate profiles suggest that barite was never undersaturated but was well preserved in the sediments (Shipboard Scientific Party, 2002) and can be used as a good proxy indicator of primary productivity in the overlying water column. A significant body of research suggests that barite is formed in the water column during the simultaneous decay of organic matter as it rains out of the euphotic zone (Dehairs et al., 1980; Bishop, 1988; Stroobants et al., 1991; Dymond et al., 1992; Gingele and Dahmke, 1994; Francois et al., 1995). Sulfate, released from the rain of decaying organic matter, likely forms sulfaterich microenvironments, which combine with barium in seawater to ultimately form dissolution-resistant barium sulfate crystals that are deposited in the sediments.

Dymond et al. (1992) quantitatively inferred surface water productivity from the particulate biogenic-barium rain collected in sediment traps near the ocean floor. Pfeifer et al. (2001) tested this against other models and compared the predicted primary productivity results to actual measurements in the South Atlantic Ocean. Their analysis of surface sediment barium concentrations shows that the model of Dymond et al. (1992) produced the best fit to independent measurements of modern primary productivity in the surface waters. Another important result of the Pfeifer et al. (2001) study is that the predicted level of productivity agreed more closely to measured values when the selected Bio-Ba/C<sub>orq</sub> ratio, a required model parameter, reflected the basin waters of the study area, rather than a "global average." Because barite crystals that form in the cells of xenophyophores, now commonly considered to be an unusual group of benthic foraminifera, are very similar to those formed in the water column (Hopwood et al., 1997), we cannot at this stage deconvolve our prediction of surface water productivity signal from this potential source of barium (K. Faul, pers. comm., 2004).

Leg 199 sedimentation fluxes and predicted rain fluxes of Bio-Ba and  $C_{org}$  for Eocene and younger ages are listed in Table T4 along with data for modern Pacific equatorial upwelling regions. Rain flux data in Table T4 were calculated from sediment flux measurements using the "recycled rates" from Dymond and Lyle (1994). They measured the "rain rate" ("export flux") and sediment "burial rate" (MAR) of the  $C_{org}$  component to calculate the  $C_{org}$  "recycled flux" for two equatorial Pacific sites: Site C (equatorial Pacific, 1°N) and Site S (11°N). The recycled flux is the difference between the rain rate and burial rate and represents the fraction of the rain not buried.

Figure F6 illustrates the measured Bio-Ba MAR in the sediments as a function of paleolatitude and age for both Leg 199 sites. The maximum flux occurs during the CAE-3 event between 41.4 and 41.1 Ma and also coincides geographically with the location of the paleoequator, consistent with our interpretation that Bio-Ba is a proxy for paleoproductivity. There is a general decrease in productivity away from the equator, as indicated by Bio-Ba, a pattern consistent with the modern regime. At both sites, the estimated Corg sediment MAR is in concert with the measured Bio-Ba MAR throughout the Eocene, except at 41 Ma, when the estimated Corg flux to the sediment roughly equals or exceeds modern fluxes at the equatorial Site C (Table T4; rows 1, 3, 7). At Site 1218, the measured Bio-Ba flux throughout the Eocene is 50% higher than modern (between 38 and 43 Ma) (Table T4; row 3). At Site 1219 between 36 and 49 Ma (Table T4; row 7) background Bio-Ba and Ba-estimated Corg sediment fluxes are approximately equal to modern. In general, the values are lower than those at Site 1218, which may be explained by the fact that Site 1219 was located off the equator, between 1° and 4°S. DurT4. Measured and estimated MARs and rain fluxes of Bio-Ba and  $C_{org}$ , p. 33.

**F6**. Bio-Ba MAR as a function of paleolatitude, p. 29.



ing the CAE-3 event that occurred between 41.1 and 41.5 Ma, a large flux in Ba-estimated  $C_{org}$  MAR occurred at both sites. At Site 1218 (Table **T4**; row 4), it is two-three times higher than modern Pacific equatorial Site C (Table **T4**; row 1), and Bio-Ba sediment MAR is four-six times greater than modern (Table **T4**; row 4). At Site 1219, the estimated  $C_{org}$ and Bio-Ba burial fluxes are two and three times modern, respectively (Table **T4**; row 8).

In the modern equatorial Pacific,  $C_{org}$  MAR is 2% of the rain flux and Bio-Ba MAR is 30% of the rain flux (Dymond and Lyle, 1994). We calculated rain fluxes from these results by assuming similar recycling rates during the 41-Ma CAE-3 event. As shown in Table T4 for Site 1218, the Bio-Ba rain flux was six times higher than modern, and the  $C_{org}$  rain flux estimated from Bio-Ba was three times higher than modern (Table T4; row 4: 28 and 400 mg/[cm<sup>2</sup> × k.y.], respectively). During this 41-Ma event at Site 1219, the estimated  $C_{org}$  rain flux is two times modern, and the Bio-Ba rain flux is three times modern. Again, the estimated rain fluxes are one-half that at Site 1218 but may also be explained by the differences in location relative to the paleoequator: Site 1219 was located 2°S of the equator, whereas Site 1218 was directly beneath the equator.

Collectively, our results suggest that throughout the Eocene there was higher productivity in surface waters as evidenced by the measured Bio-Ba sediment and predicted rain fluxes. The measured Corg MAR was lower than Holocene rates by a factor of 10. Because Corg and Bio-Ba fluxes covary, the Corg signal is probably robust. In contrast, the calculated Corg MAR (from the measured Bio-Ba) indicates fluxes that are roughly equal to modern sedimentation fluxes throughout the Eocene with the exception of the 41-Ma event, when calculated Corg fluxes triple. This 41 Ma event corresponds to CAE-3, the third carbonate accumulation event in a series of seven identified in the Eocene from Leg 199 sediments (Lyle et al., this volume; Tripati et al., unpubl. data). The calculated C<sub>org</sub> MAR increases by a factor of four at 41 Ma to a peak value of 7.8 mg/cm<sup>2</sup> × k.y. This calculated result is complementary to, and fits with, the interpretation of Tripati et al. (unpubl. data), who surmise that the large negative  $\delta^{13}$ C isotope excursion that also occurred at 41 Ma is a reflection of increased ocean productivity. Because the bulk sedimentation rates at both sites are the same as or higher than the modern analogs (Site C at 1°N and Site S at 11°N), organic carbon preservation during the Eocene should have been the same as, if not higher than, modern preservation.

Leg 199 organic carbon average concentrations (0.03 wt%) are an order of magnitude lower than modern pelagic sediments of equal or lower sedimentation rates in well-oxygenated seawater under Pacific and Atlantic upwelling regions (Lyle, 1988). Modern sediments exhibit near monotonous  $C_{org}$  concentration profiles ranging between 0.2 and 0.4 wt% over the past 300 k.y. However, a comparison of MARs for modern vs. Eocene sediments shows that the  $C_{org}$  fluxes are roughly equal in magnitude, between 2 and 10 mg/cm<sup>2</sup> × k.y. (Lyle, 1988). An increased flux occurs during the last glacial maximum at 18 Ka in the Atlantic, when  $C_{org}$  MARs doubled to 20 mg/cm<sup>2</sup> × k.y. relative to interglacial Stage 3. In the equatorial Pacific,  $C_{org}$  MARs increased by a factor of 3–10, with values ranging from 4 to 100 mg  $C_{org}/cm<sup>2</sup> × k.y$ . The coherency of the trends for Leg 199 Eocene and modern sites demonstrates that cooling events are associated with increasing  $C_{org}$  mass accumulation rates to the sediments and that some fundamental mech-

anism has operated throughout the Cenozoic to account for this association.

# Remineralization Hypothesis: C<sub>org</sub> Burial is Short-Circuited

We suggest that low  $C_{org}$  MARs in Eocene sediments reflect the fact that most of the organic carbon was remineralized in the water column or at the sediment/water interface, thus preempting burial. The notion that the fluxes reflect lower primary productivity is rejected because our evidence shows that the proxy indicator of productivity, Bio-Ba, which resists dissolution, has escaped recycling to become preserved in the sediments. A very simple model for carbon and nutrient utilization is based on the long-known biological "Q<sub>10</sub> rule" derived from the Arrhenius relationship for reaction rates as a function of temperature. The Q<sub>10</sub> model predicts a doubling to tripling of metabolic rates for ectothermic organisms with every 10°C increase in temperature. Faster recycling of organic carbon (and other nutrients) likely occurred in the very warm Eocene oceans for all organisms based on higher metabolic requirements alone.

The simple  $Q_{10}$  model of metabolism has been expanded and elucidated by Gillooly et al. (2001) to include many life forms such as microbes, ectotherms, endotherms, and plants. They show that the resting metabolism of all organisms is a function of both environmental temperature and body mass over the "biologically relevant" temperature range between 0° and 40°C (i.e., temperatures at which life is possible for these organisms). The lowest metabolic rates are associated exclusively with the smallest unicellular organisms, whereas metabolic rates are greatest for the largest organisms (endothermic vertebrates) by a factor of 20.

Gillooly et al. (2001) proposed a single equation, known as the Universal Temperature Dependence (UTD) of metabolism (Equation 4). The UTD equation predicts metabolic rate as a function of temperature and body mass and applies to all organisms over their biologically relevant temperature range. Specifically, the UTD equation is expressed as:

$$Q = b_0 M^{3/4} e^{-E/kT}$$
, (4),

where

- Q = metabolic rate,
- M = body mass,
- E = activation energy for the rate-limiting enzyme-catalyzed metabolic reactions,
- k = Boltzman constant,
- T = absolute temperature (K), and
- $b_0 = a \text{ constant independent of } M \text{ and } T.$

The UTD equation is more sophisticated than the  $Q_{10}$  rule because it accounts for the scaling of metabolism with the  $^{3}/_{4}$  power of body mass, yet preserves the temperature dependence term derived from classical statistical thermodynamics. In contrast, the  $Q_{10}$  relationship, although relevant, simply quantifies metabolic rate changes for 10°C jumps in temperature.

All cellular metabolic reactions are characterized by two features: (1) the requirement of water and (2) the production of adenosine triphosphate (ATP;  $C_{10}H_{16}N_5O_{13}P_3$ ), the primary energy currency for all cellular biochemical reactions. Because ATP production uses oxygen as the final electron acceptor for aerobic organisms, oxygen utilization rate is the traditional metric used to quantify metabolic rate.

Basal metabolism, or "maintenance metabolism," is defined as the sum of processes that require ATP. These processes are necessary for the cell to just remain alive, and for an individual organism, basal metabolism refers to the condition such that food intake results in neither an increase nor a decrease in body mass. For some ectotherms, the majority of their lifetime energy is spent on basal metabolism (i.e., it is not invested in growth or reproduction but used exclusively to maintain cellular function) (Clarke and Fraser, 2004). The function of basal metabolism involves protein synthesis, and most of the energy is spent on counteracting the passive leakage of protons across the inner mitochondrial membrane of eukaryotic cells (plants, animals, fungi, algae, and protozoa). This essential proton gradient, known as the proton motive force by Mitchell (1966), is the driving force for ATP synthesis and all subsequent biological functions. An intriguing consequence of our hypothesis is that the Cenozoic marine sedimentary record of organic carbon reflects this fundamental requirement of all living cells to maintain proton gradients across their cell membranes.

Nearly all studies of modern marine organisms show a positive, nonlinear relationship between temperature and resting metabolic rate (Clarke and Fraser, 2004, and references therein). Clarke and Fraser (2004) expanded upon these relationships and upon the simple UTD model proposed by Gilooly et al. (2001). They found that the basal metabolic function of an organism depends not only upon its ecology but also on the organism's evolutionary cost-benefit compromises. For example, in polar environments with severe food shortages, whether they are chronic or seasonal, selection has occurred for organisms with very low basal metabolic rates and efficient metabolisms. Within the polar environment, both benthic and planktonic organisms have evolved different strategies to meet their basal metabolic rates and "winter-over" strategies in the face of these food shortages. The two different strategies in turn reflect fundamentally different lifestyles. Immobile benthic organisms have very low basal metabolic rates and do not store energy reserves for winter food shortages. In contrast, planktonic organisms have much higher energy requirements for two reasons: first, they require energy for staying afloat in the water column, and second, these organisms synthesize lipid reserves for the purpose of using them during the over-wintering period.

Higher basal metabolic function during times of ocean warming also requires a concomitant supply of organic carbon and nutrients in surface waters in order to sustain a given unit of primary production. If the nutrient supply to the euphotic zone during the Eocene was lower than modern values, then it is reasonable to expect total primary productivity to have been lower than modern values, a result that is contradicted by Leg 199 Bio-Ba data. Indeed, both the measured Bio-Ba MAR and the calculated  $C_{org}$  MAR is two-three times higher than modern during the height of the CAE-3 "cooling" event at 41 Ma, despite the fact that ocean temperatures were warmer than modern and proportionately more  $C_{org}$  was required to maintain basal metabolism. This implies that large supplies of carbon and other nutrients to the euphotic zone were sustained.

Pleistocene marine sediments also support our proposal that the UTD theory is a fundamental mechanism controlling the global carbon cycle, at least since the beginning of the Phanerozoic. For example, during the Last Glacial Maximum (LGM) at 18 Ka, Corg MAR peaked in both the equatorial Atlantic and Pacific Oceans (Lyle, 1988). This history in core V19-28 is particularly relevant because of its location (2°S, 85°W) in the eastern equatorial Pacific. During the LGM, when global temperatures dropped, the C<sub>org</sub> MAR in core V19-28 peaked to 100 mg/cm<sup>2</sup> × k.y. This value is 10 times higher than those that preceded and followed this event. This peak MAR is 12 times greater than the value for the CAE-3 cold event at 41 Ma; at Site 1218, the maximum  $C_{\text{org}}\ \text{MAR}$  (calculated from Bio-Ba) is 8 mg/cm<sup>2</sup>  $\times$  k.y. Inasmuch as global ocean temperatures were colder during the LGM relative to the Eocene, the fivefold increase in organic carbon MAR is consistent with a fundamental temperature dependence on primary production and consequent nutrient supply affecting all organisms in the food web. Note also that the Lyle (1988) data set is itself internally consistent with our hypothesis: the LGM at 18 Ka represents a maxima in Corg MAR relative to warmer periods before and after this event.

In summary, carbon isotopic data, oxygen isotopic data, and the sedimentation patterns of the biogenic calcium carbonate and opal components (Tripati et al., unpubl. data; Lyle et al., this volume) point to a rapid cooling event at 41 Ma, which then rebounded to warm conditions by 40.2 Ma. This transition from relatively cold to warm conditions is reflected in changes in the organic carbon flux at Sites 1218 and 1219, supporting the geologic universality of the UTD theory: because basal metabolic rates and organic carbon recycling rates would have decreased at 41 Ma (colder), a higher proportion of Corg would be expected to reach the sediments and survive early diagenesis until burial. Slower basal metabolic rates during cold periods would not translate into lower export production of the biogenic proxies to the sediments. On the contrary, slower basal metabolism for all organisms would encourage higher overall productivity because the "excess carbon" could be used for reproduction instead of maintaining cell function. Indeed, at both Sites 1218 and 1219, the calculated rain of Bio-Ba and  $C_{orq}$  during the 41-Ma event is higher than modern rates; Bio-Ba was higher by factor of six and C<sub>orq</sub> was higher by a factor of three when Site 1218 was beneath the paleoequator.

# CONCLUSIONS

Our study shows that organic carbon burial during the Eocene was an order of magnitude lower than modern. In contrast, the measured Bio-Ba flux, a proxy for primary productivity and organic carbon rain and sedimentation, was greater than or equal to modern rates throughout the Eocene. This discrepancy between the observed and expected  $C_{org}$  flux suggests that a higher rate of organic carbon remineralization occurred in the upper water column or at the sediment/water interface during the Eocene. Higher utilization of  $C_{org}$  would be expected on the basis of thermodynamic considerations alone and is predicted by the UTD Theory by Gilooly et al. (2001) and new data from the field of ecology (e.g., Clarke and Fraser, 2004). Higher metabolic rates, and concomitant increased demand for carbon and all nutrients, would have resulted directly from the  $10^\circ$ – $12^\circ$ C increase in ocean temperatures for the Eocene equatorial Pacific Ocean relative to modern conditions. We

propose that organic carbon burial was "short-circuited" via remineralization and reutilization by all organisms. This proposed mechanism, combined with our data, is consistent with the evidence that the Calcite Compensation Depth was much shallower, and atmospheric CO<sub>2</sub> was much higher, during the Eocene.

Finally, our understanding of the global organic carbon cycle throughout geologic time requires a fundamental recognition that what we measure in the sediments (the component that is preserved) may not be modeled simply as the remainder that is left behind after the sum of processes has remineralized buried organic carbon. This shortcoming in our thinking is succinctly stated by Hedges and Keil (1995) and quoted here as we proceed to elucidate the geologic record of Earth's dynamic history: "it is useful to note that degradation of organic matter and its preservation in marine sediments are often treated equivalently, many times with the assumption that the selectivity and extents of early diagenesis will be informative of preservation potential. Degradation and preservation, however, are opposite processes and information on organic matter mineralization is not necessarily useful for understanding preservation."

# ACKNOWLEDGMENTS

First and foremost, the author A. Olivarez Lyle gratefully acknowledges the generous contributions of Robert M. Owen, who many years ago first conveyed to her the concept of the "Q<sub>10</sub> rule," a concept that was never forgotten and that now forms the basis of the conclusions presented in this paper. This manuscript was much improved by the thoughtful reviews and extensive comments by Ellen Thomas and Phillip Meyers. We also acknowledge the careful laboratory work of Linda Kenoyer, Brandi Murphy, and Christopher Paul. This research used samples and/or data provided by the Ocean Drilling Program (ODP). ODP is sponsored by the U.S. National Science Foundation (NSF) and participating countries under management of Joint Oceanographic Institutions (JOI), Inc. Funding for this research was provided by National Science Foundation OCE-024096, EPS-0132626, and JOI-U.S. Science Support Program.

# REFERENCES

- Anderson, R., 2003. Radionuclides from sediment cores, U.S. JGOFS Process Study Data 1989–1998, WHOI. Available from World Wide Web: <a href="http://www.pan-gaea.de/PangaVista">http://www.pan-gaea.de/PangaVista</a> (ID: 132771).
- Bice, K.L., Sloan, L.C., and Barron, E.J., 2000. Comparison of early Eocene isotopic paleotemperatures and the three-dimensional OGCM temperature field: the potential for use of model-derived surface water  $\delta^{18}$ O. *In* Huber, B.T., MacLeod, K.G., and Wing, S.L. (Eds.), *Warm Climates in Earth History:* Cambridge (Cambridge Univ. Press), 79–131.
- Bishop, J.K.B., 1988. The barite-opal-organic carbon association in oceanic particulate matter. *Nature*, 332:341–343.
- Burns, R.G., and Burns, V.M., 1979. Manganese oxides. *In Burns, R.G. (Ed.), Marine Minerals* (Vol. 6): Washington, D.C. (Mineralogical Soc. Am.).
- Chavez, F.P., and Barber, R.T., 1987. An estimate of new production in the equatorial Pacific. *Deep-Sea Res. Part A*, 34:1229–1243.
- Clarke, A., and Fraser, K.P.P., 2004. Why does metabolism scale with temperature? *Funct. Ecol.*, 18:243–251.
- Corfield, R.M., and Norris, R.D., 1996. Deep water circulation in the Paleogene Ocean. *In* Knox, R.W., Corfield, R.M., and Dunay, R.E., (Eds.), *Correlation of the Early Paleogene in Northwest Europe*. Geol. Soc. Spec. Publ., 443–456.
- Corliss, J.B., Lyle, M., Dymond, J., and Crane, K., 1978. The chemistry of hydrothermal mounds near the Galapagos rift. *Earth Planet. Sci. Lett.*, 40:12–24.
- Dehairs, F., Chesselet, R., and Jedwab, J., 1980. Discrete suspended particles of barite and the barium cycle in the open ocean. *Earth Planet. Sci. Lett.*, 49:528–550.
- Dymond, J., 1981. Geochemistry of Nazca plate surface sediments: an evaluation of hydrothermal, biogenic, detrital, and hydrogenous sources. *In* Kulm, L.D., Dymond, J., Dasch, E.J., Hussong, D.M., and Roderick, R. (Eds.), *Nazca Plate: Crustal Formation and Andean Convergence*. Mem.—Geol. Soc. Am., 154:133–173.
- Dymond, J., and Lyle, M., 1994. Particle fluxes in the ocean and implications for sources and preservation of ocean sediments. *In* Hay, W.W. (Ed.), *Material Fluxes on the Surface of the Earth:* Washington D.C. (National Academy of Science), 125–143.
- Dymond, J., Suess, E., and Lyle, M., 1992. Barium in deep-sea sediment: a geochemical proxy for paleoproductivity. *Paleoceanography*, 7:163–181.
- Emerson, S., and Bender, M., 1981. Carbon fluxes at the sediment-water interface of the deep-sea: calcium carbonate preservation. *J. Mar. Res.*, 39:139–162.
- Frakes, L.A., and Kemp, E.L., 1972. Influence of continental positions on early Tertiary climates. *Nature*, 240:97–100.
- Francois, R., Honjo, S., Manganini, S.J., and Ravizza, G.E., 1995. Biogenic barium fluxes to the deep sea: implications for paleoproductivity reconstruction. *Global Biogeochem. Cycles*, 9:289–303.
- Francois, R., Frank, M., Rutgers van der Loeff, M., 2004. <sup>230</sup>Th normalization: an essential tool for interpreting sedimentary fluxes during the late Quaternary. *Paleoceanography*, 19:1–16.
- Gershanovich, D.E., Gorshkova, T.I., and Koniukhov, A.I., 1974. Organic materials of modern marine sediments on continental margins. *In Vassoyevic*, N.B. (Ed.), *Organic Matter in Recent and Fossil Sediments and Methods of its Investigation:* Moscow (Izd. Nauka.), 63–80. (in Russian)
- Gillooly, J.F., Brown, J.H. West, G.B., Savage, V.M., and Charnov, E.L., 2001. Effects of size and temperature on metabolic rate. *Science*, 293:2248–2251.
- Gingele, F., and Dahmke, A., 1994. Discrete barite particle and barium as tracers of paleoproductivity in South Atlantic sediments. *Paleoceanography*, 9:151–168.
- Hammond, D.E., McManus, J., Berelson, W.M., Kilgore, T.E., and Pope, R., 1996. Early diagenesis of organic material in equatorial Pacific sediments: stoichiometry and kinetics. *Deep-Sea Res., Part II*, 43:1365–1412.

- Hartnett, H.E., Keil, R.G., Hedges, J.I., and Devol, A.H., 1998. Influence of oxygen exposure time on organic carbon preservation in continental margin sediments. *Nature*, 391:572–574.
- Hedges, J.I., and Keil, R.G., 1995. Sedimentary organic matter preservation: an assessment and speculative synthesis. *Mar. Chem.*, 49:81–115.
- Hopwood, J.D., Mann, S., and Gooday, A.J., 1997. The crystallography and possible origin of barium sulphate in deep sea rhizopod protists (*Xenophyophorea*). *J. Mar. Biol. Assoc. U. K.*, 77(4):969–987.
- Huber, M., and Sloan, L.C., 2001. Heat transport, deep waters, and thermal gradients: coupled simulation of an Eocene "greenhouse" climate. *Geophys. Res. Lett.*, 28(18):3481–3484.
- Lear, C.H., Elderfield, H., and Wilson, P.A., 2000. Cenozoic deep-sea temperatures and global ice volumes from Mg/Ca in benthic foraminiferal calcite. *Science*, 287:269–272.
- Levitus, S., and Boyer, T.P., 1994. World Ocean Atlas 1994 (Vol. 2): Oxygen. NOAA Atlas NESDIS 3.
- Lyle, M., 1988. Climatically forced organic carbon burial in the equatorial Atlantic and Pacific oceans. *Nature*, 335:529–532.
- Lyle, M., 1992. Composition maps of surface sediments of the eastern tropical Pacific Ocean. *In* Mayer, L., Pisias, N., Janecek, T., et al., *Proc. ODP, Init. Repts.*, 138 (Pt. 1): College Station, TX (Ocean Drilling Program), 101–115.
- Lyle, M., Mitchell, N., Pisias, N., Mix, A., Martinez, J.I., and Paytan, A., 2005. Do geochemical estimates of sediment focusing pass the sediment test in the equatorial Pacific? *Paleoceanography*, 20:10.1029/2004PA001019.
- Lyle, M., Wilson, A., Janecek, T.R., et al., 2002. *Proc. ODP, Init. Repts.*, 199 [CD-ROM]. Available from: Ocean Drilling Program, Texas A&M University, College Station TX 77845-9547, USA.
- McIver, R.D., 1975. Hydrocarbon occurrences from JOIDES Deep Sea Drilling Project. *Proc. Ninth Petrol. Congr.*, 269–280.
- Meyers, P.A., and Silliman, J.E., 1996. Organic matter in Pleistocene to Quaternary turbidites from Site 897, 898, 899, and 900, Iberia Abyssal Plain. *In* Whitmarsh, R.B., Sawyer, D.S., Klaus, A., and Masson, D.G. (Eds.), *Proc. ODP, Sci. Results*, 149: College Station, TX (Ocean Drilling Program), 305–313.
- Millero, F.J., 1996. *Chemical Oceanography* (2nd Ed.): Boca Raton, Florida (CRC Press LLC).
- Mitchell, P., 1966. Chemiosmotic coupling in oxidative and photosynthetic phosphorylation. *Biol. Rev.*, 41:445–502.
- Moore, T.C., 1969. Radiolaria: change in skeletal weight and resistance to solution. *Geol. Soc. Am. Bull.*, 80:2103–2108.
- Mortlock, R.A., and Froelich, P.N., 1989. A simple method for the rapid determination of biogenic opal in pelagic marine sediments. *Deep-Sea Res., Part A*, 36:1415– 1426.
- Olivarez Lyle, A., and Lyle, M.W., 2002. Determination of biogenic opal in pelagic marine sediments: a simple method revisited. *In* Lyle, M., Wilson, P.A., Janecek, T.R., et al., *Proc. ODP, Init. Repts.*, 199, 1–21 [CD-ROM]. Available from: Ocean Drilling Program, Texas A&M University, College Station TX 77845-9547, USA.
- Pfeifer, K., Kasten, S., Hensen, C., and Schulz, H., 2001. Reconstruction of primary productivity from the barium contents in surface sediments of the South Atlantic Ocean. *Mar. Geol.*, 177:13–24.
- Shipboard Scientific Party, 1998. Explanatory notes. *In* Wefer, G., Berger, W.H., and Richter, C., et al., *Proc. ODP, Init. Repts.*, 175: College Station, TX (Ocean Drilling Program), 27–46.
- Shipboard Scientific Party, 1992. Explanatory notes. *In* Mayer, L., Pisias, N., Janecek, T., et al., *Proc. ODP, Init. Repts.*, 138 (Pt. 1): College Station, TX (Ocean Drilling Program), 13–42.

- Shipboard Scientific Party, 2002. Leg 199 Preliminary Report. ODP Prelim. Rpt., 99 [Online]. Available from World Wide Web: <a href="http://www-odp.tamu.edu/publica-tions/prelim/199\_prel/199PREL.PDF">http://www-odp.tamu.edu/publica-tions/prelim/199\_prel/199PREL.PDF</a>>. [Cited 2004-05-10]
- Stroobants, N., Dehairs, F., Goeyens, L., Vanderheijeden, N., and Van Grieken, R., 1991. Barite formation in the Southern Ocean water column. *Mar. Chem.*, 35:411–421.
- Thomas, D.J., 2004. Evidence for deep-water production in the North Pacific Ocean during the early Cenozoic warm interval. *Nature*, 430:65–68.
- Turchyn, A.V., and Schrag, D.P., 2004. Oxygen isotope constraints on the sulfur cycle over the past 10 million years. *Science*, 303(5666):2004–2007.
- Weliky, K., 1983. Clay-organic associations in marine sediments: carbon, nitrogen, and amino acids in the fine grained fractions [M.S. thesis]. Oregon State Univ., Corvallis.
- Weliky, K., Suess, E., Ungerer, C.A., Müller, P.J., and Fischer, K., 1983. Problems with accurate carbon measurements in marine sediments and particulate matter in seawater: a new approach. *Limnol. Oceanogr.*, 28:1252–1259.
- Zachos, J., Pagani, M., Sloan, L., Thomas, E., and Billups, K., 2001. Trends, rhythms, and aberrations in global climate 65 Ma to present. *Science*, 292:686–693.

**Figure F1.** Map showing modern locations of Sites 1218 and 1219 (from Lyle, Wilson, Janecek, et al., 2002). DSDP = Deep Sea Drilling Project, F.Z. = fracture zone.



**Figure F2.** Distance between downcore locations of chert layers and those samples from Site 1218 with anomalously high  $C_{org}$  concentrations. The lack of an inverse trend suggests that our samples were not contaminated by drilling muds when drilling passed through the chert-bearing layers.



**Figure F3.** Concentrations of the biogenic components in samples from (A) Site 1218 and (B) Site 1219. CAE = carbonate accumulation event.



**Figure F4.** Relationship between bulk mass accumulation rate (MAR) and  $C_{org}$  concentration of Site 1218 sediments. Note that high  $C_{org}$  values are associated with low MARs, a relationship that is the opposite of that found in modern sediments.



**Figure F5.** Mass accumulation rates (MARs) of biogenic components vs. age for (A) Site 1218 and (B) Site 1219. CAE = carbonate accumulation event.



**Figure F6.** Bio-Ba mass accumulation rate as a function of paleolatitude for (A) Site 1218 and (B) Site 1219. Note the high Bio-Ba flux at the paleoequator and the anomalous accumulation at 40 Ma, corresponding to carbonate accumulation event 3 (CAE-3).



**Table T1.** Summary statistics of in-house sediment standards used for carbon and biogenic silica analyses. First digestions of talc and second digestions of residues (1218C Composite Standard and reagent grade talc) suggest that silica contamination from clay mineral dissolution is low.

Sediment standard	Description		Average (wt%)	Standard deviation (wt%)	N	Notes
			<u> </u>			
			Carbon			
Midway in-house	W8709A-5BC:5–20 cm	NE Pacific hemipelagic	2.64	±0.02	523	Total carbon
Midway in-house	W8709A-5BC:5-20 cm	NE Paific hemipelagic	0.85	±0.01	570	Organic carbon
			SiO <sub>2</sub>			
1218C composite	Cores 199-1218C-18X and 21X	Radiolarian ooze	32.2	±2	87	
1218C composite residue	Cores 199-1218C-18X and 21X	Residue from KOH digestion of radiolarian ooze	1.6	±0.69	9	Second digestion of sediment residue
1219A composite	Cores 199-1219A-19H through 27X	Radiolarian ooze	56.3	±1.7	52	
1098B composite	Section 178-1098B-3H-4	Diatom ooze	31.2	±1.4	14	This study
1098B composite	Section 178-1098B-3H-4	Diatom ooze	32	±2	41	Previous work
Reagent-grade talc		Phyllosilicate	1.5	±0.3	26	
Talc residue		Residue from KOH digestion of talc	0.4	±0.3	7	Second digestion of sediment residue

Note: N = number of analyses.

Core section	Top	Bottom	Offset	Top	Bottom	Average	Average	Average (rmcd)	1218 rmcd	Age	Paleolatitude	Paleolongitude	Bulk c (g/c	lensity :m³)	I SR	Bulk MAR
interval (cm)	(mbsf)	(mbsf)	(m)	(mcd)	(mcd)	(mbsf)	(mcd)	Pälike 02	equivalent depth	(Ma)	(°)	(°)	Wet	Dry	(m/m.y.)	$(g/cm^2 \times k.y.)$
199-1218A-																
26X-1, 10–11	234.4	234.41	26.07	260.47	260.48	234.405	260.475	261.03	261.03	38.060	0.32	-108.00	1.29	0.51	4.217	0.215
26X-1, 30–31	234.6	234.61	26.07	260.67	260.68	234.605	260.675	261.17	261.17	38.094	0.31	-107.98	1.32	0.55	4.252	0.235
26X-1, 50–51	234.8	234.81	26.07	260.87	260.88	234.805	260.875	261.31	261.31	38.128	0.31	-107.95	1.28	0.49	4.286	0.211
26X-1, 70–71	235.0	235.01	26.07	261.07	261.08	235.005	261.075	261.45	261.45	38.163	0.30	-107.93	1.24	0.43	4.255	0.183
26X-1, 90–91	235.2	235.21	26.07	261.27	261.28	235.205	261.275	261.59	261.59	38.196	0.30	-107.91	1.19	0.36	4.289	0.154
26X-1, 110–111	235.4	235.41	26.07	261.47	261.48	235.405	261.475	261.74	261.74	38.230	0.29	-107.89	1.19	0.36	4.322	0.153
26X-1, 130–131	235.6	235.61	26.07	261.67	261.68	235.605	261.675	261.88	261.88	38.263	0.29	-107.87	1.22	0.40	4.355	0.174
26X-2, 10–11	235.9	235.91	26.07	261.97	261.98	235.905	261.975	262.09	262.09	38.313	0.28	-107.83	1.27	0.48	4.406	0.211
26X-2, 30–31	236.1	236.11	26.07	262.17	262.18	236.105	262.175	262.23	262.23	38.346	0.28	-107.81	1.34	0.58	4.439	0.257
26X-2, 50–51	236.3	236.31	26.07	262.37	262.38	236.305	262.375	262.38	262.38	38.380	0.27	-107.79	1.54	0.87	4.472	0.389
26X-2, 70–71	236.5	236.51	26.07	262.57	262.58	236.505	262.575	262.58	262.58	38.427	0.26	-107.76	1.58	0.93	4.519	0.422
26X-2, 90–91	236.7	236.71	26.07	262.77	262.78	236.705	262.775	262.78	262.78	38.469	0.26	-107.73	1.43	0.72	7.341	0.526
26X-2, 110–111	236.9	236.91	26.07	262.97	262.98	236.905	262.975	262.98	262.98	38.495	0.25	-107.72	1.34	0.58	8.019	0.465
26X-2, 130–131	237.1	237.11	26.07	263.17	263.18	237.105	263.175	263.18	263.18	38.520	0.25	-107.70	1.37	0.62	8.044	0.501
26X-3, 10–11	237.4	237.41	26.07	263.47	263.48	237.405	263.475	263.48	263.48	38.558	0.24	-107.68	1.35	0.60	8.081	0.482
26X-3, 30–31	237.6	237.61	26.07	263.67	263.68	237.605	263.675	263.68	263.68	38.583	0.24	-107.66	1.34	0.58	8.106	0.467
26X-3, 50–51	237.8	237.81	26.07	263.87	263.88	237.805	263.875	263.88	263.88	38.608	0.24	-107.64	1.57	0.91	8.131	0.741

Core section	Total carbon	C average			Biogenic SiO <sub>2</sub>	1σ SiO2		Elements (wt%)						Element	Data	
interval (cm)	average (wt%)	(wt%)	(wt%)	Notes	average (wt%)	(wt%)	Si	Ti	Al	Fe	Mn	Mg	Ca	Sr	Ва	source
199-1218A-																
26X-1, 10–11	2.98	0.02	24.65		33.1	N/A										BSU
26X-1, 30–31	4.39	0.02	36.36		29.7	0.7										BSU
26X-1, 50–51	1.64	0.02	13.45		43.2	1.6										BSU
26X-1, 70–71	1.73	0.02	14.21		38.0	N/A										BSU
26X-1, 90–91	0.71	0.03	5.65		41.9	N/A										BSU
26X-1, 110–111	1.60	0.06	12.77		37.2	1.8										BSU
26X-1, 130–131	2.53	0.03	20.86		30.7	1.1										BSU
26X-2, 10–11	2.02	0.02	16.61		37.9	N/A										BSU
26X-2, 30–31	1.91	0.04	15.58		32.8	2.3										BSU
26X-2, 50–51	6.83	0.03	56.70		18.2	N/A										BSU
26X-2, 70–71	7.13	0.02	59.24		20.9	1.5										BSU
26X-2, 90–91	6.20	0.03	51.44		24.6	N/A										BSU
26X-2, 110–111	6.16	0.03	51.05		37.2	1.1										BSU
26X-2, 130–131	5.02	0.03	41.61		28.2	N/A										BSU
26X-3, 10–11	3.54	0.02	29.32		37.6	1.0										BSU
26X-3, 30–31	2.13	0.03	17.46		41.8	2.1										BSU
26X-3, 50–51	7.05	0.02	58.56		21.2	1.4										BSU

Notes: mcd = meters composite depth, rmcd = revised meters composite depth, LSR = linear sedimentation rate, MAR = mass accumulation rate, BSU = Boise State University, Pälike 02 = Pälike et al., this volume. Data after Olivarez Lyle and Lyle (2004). Only a portion of this table appears here. The complete table is available in ASCII.

		Core depth	Water depth	Latitude	Longitude					Eleme	nts (wt%	)				Ele	ements (pp	m)
Core	Sample ID	(cm)	(m)	(°)	(°W)	Na	Mg	Al	Si	Р	S	К	Ti	Mn	Fe	Rb	Sr	Ва
OC73-3-7	MP24043	3–5	4,247	-17.87	101.04	0.65	2.33	6.90	21.44	0.76	0.35	2.29	0.41	3.28	10.09	71	823	15,516
Y71-6-16	MP24025	6–8	6,761	-16.92	74.33	0.86	1.58	7.24	31.29	0.09	0.19	2.28	0.40	0.08	3.96	135	364	803
Y71-6-26	MP24026	7–9	4,813	-15.27	76.37	0.98	1.89	6.94	32.13	0.13	0.09	2.27	0.39	0.06	5.37	120	292	1,667
Y71-6-8	MP24024	3–5	5,273	-13.75	77.72	0.00	1.27	6.25	33.05	0.13	0.58	1.93	0.37	0.05	3.10	167	317	1,805
Y71-8-55	MP24033	5–7	6,309	-11.63	79.25	0.00	1.39	6.63	32.99	0.12	0.33	1.92	0.37	0.11	5.13	131	245	1,749
Y71-7-49	MP24031	3–5	3,116	-11.10	110.32	0.00	2.65	1.60	16.33	0.91	0.57	0.57	0.35	6.77	24.34	129	8,922	7,422
Y71-7-28	MP24027	3–5	4,491	-11.02	85.02	0.32	1.90	8.05	31.56	0.08	0.11	2.27	0.41	0.45	5.42	123	331	6,571
Y71-7-32	MP24030	3–5	3,850	-10.75	93.10	0.14	3.21	5.99	24.48	0.69	0.71	1.85	0.34	2.59	7.41	86	2,742	29,449
Y71-7-30	MP24028	10–12	4,237	-10.05	88.68	0.17	1.78	7.39	31.94	0.13	0.21	2.04	0.36	0.35	5.36	102	475	13,172
Y71-7-31	MP24029	3–5	4,114	-9.93	91.97	0.65	2.28	7.40	29.94	0.31	0.43	1.96	0.34	0.96	5.76	91	1,160	20,983
Y71-8-61	MP24034	3–5	5,843	-9.35	80.78	0.00	1.26	6.30	33.51	0.13	0.48	1.87	0.36	0.05	4.06	126	244	1,142
AMPH25GC	MP15096	2–5	3,660	-9.05	105.88	0.00	3.26	2.28	25.69	0.60	1.12	0.65	0.41	3.54	12.01	209	17,540	24,882
Y71-8-76	MP24035	7–9	5,122	-8.12	81.60	0.00	1.40	7.52	31.16	0.11	0.49	1.94	0.43	0.05	4.41	138	222	929
AMPH16GC	MP15087	0–5	3,240	-7.85	108.92	0.00	2.86	0.76	27.26	0.43	0.47	0.26	0.22	4.00	14.90	120	8,807	8,179
Y71-8-79	MP24036	3–5	6,165	-7.83	81.28	0.16	1.29	7.19	32.61	0.09	0.41	1.95	0.42	0.06	4.16	140	205	860
AMPH11PC	MP15082	0–4	3,728	-7.47	113.53	0.00	2.73	1.19	27.34	0.28	0.65	0.54	0.20	3.64	12.97	187	7,517	10,762
OC73-1-2	MP24044	3–5	3,160	-7.28	107.62	0.00	2.95	1.29	28.41	0.47	1.07	0.28	0.40	2.35	12.40	200	14,056	9,553

Table T3. Geochemistry of modern surface sediments in the eastern tropical Pacific (SETPAC) with Bio-Ba/C<sub>org</sub> ratios.

Core	Sample ID	Core depth (cm)	Water depth (m)	Normal biogenic SiO <sub>2</sub> (wt%)	Normal CaCO <sub>3</sub> from Ca (wt%)	Salt (wt%)	H <sub>2</sub> O based on Cl (%)	Sum of oxides	CaCO <sub>3</sub> (LECO) (wt%)	C <sub>org</sub> uncorrected (LECO) (wt%)	C <sub>org</sub> , salt and CC- free (wt%)	Bio-Ba* (ppm)	Bio-Ba/C <sub>org</sub> ratio
OC73-3-7	MP24043	3–5	4,247	10	17.2	9.5	75.4	91.2	16.3	0.292	0.362	14,999	4.15
Y71-6-16	MP24025	6–8	6,761	32.3	0.8	7.2	69.4	94.9	0.7	1.171	1.286	260	0.02
Y71-6-26	MP24026	7–9	4,813	33.9	1.8	7.2	69.6	98.9	1.5	1.165	1.259	1,147	0.09
Y71-6-8	MP24024	3–5	5,273	41.4	0.5	11.6	79.4	93.5	0.4	2.572	2.801	1,336	0.05
Y71-8-55	MP24033	5–7	6,309	39.3	0.3	11	78.4	97.3	0.7	1.608	1.785	1,252	0.07
Y71-7-49	MP24031	3–5	3,116	26.8	81.8	6.6	67.6	93.5	82.5	0.301	1.851	7,302	0.39
Y71-7-28	MP24027	3–5	4,491	27.7	0	10.9	78.2	99.9	0.8	0.464	0.506	5,968	1.18
Y71-7-32	MP24030	3–5	3,850	20.8	55.4	7.9	71.6	92.6	57.7	0.217	0.555	29,000	5.22
Y71-7-30	MP24028	10–12	4,237	32	0	13.5	82	99.4	0.5	0.466	0.510	12,618	2.48
Y71-7-31	MP24029	3–5	4,114	27	29.4	14	82.6	99.4	30.1	0.582	0.899	20,428	2.27
Y71-8-61	MP24034	3–5	5,843	42.2	0	8.3	72.6	95.8	0.4	2.147	2.401	669	0.03
AMPH25GC	MP15096	2–5	3,660	44.1	88	6	63.9	94.7	86.9	0.271	2.215	24,711	1.12
Y71-8-76	MP24035	7–9	5,122	31.5	0	9.5	75.5	93.9	0.8	2.403	2.686	365	0.01
AMPH16GC	MP15087	0–5	3,240	53.6	83.9	7.5	69.4	96	84.3	0.251	1.726	8,122	0.47
Y71-8-79	MP24036	3–5	6,165	36.4	0	7.5	70.3	95.9	0.6	1.917	2.063	321	0.02
AMPH11PC	MP15082	0–4	3,728	51.8	79.5	8.1	71	93.7	80.5	0.174	0.996	10,673	1.07
OC73-1-2	MP24044	3–5	3,160	54.2	86.7	6.9	68.5	94.3	86.1	0.353	2.912	9,456	0.32

Notes: Bio-Ba/C<sub>org</sub> ratios are from Lyle, 1992 (data table previously unpublished). \* = Ba – 0.0075 × Al. Elemental data are salt and calcium carbonate (CC) corrected unless noted. Samples highlighted in this study are located  $\pm 5^{\circ}$  latitude and >100°W longitude. Only a portion of this table appears here. The complete table is available in ASCII.

					Sediment MAR (g/cm <sup>2</sup> × k.y.)								
Sample	Age (Ma)	Latitude	Longitude (°W)	Water depth (m)	Bulk measured	Bio-Ba measured	C <sub>org</sub> measured	C <sub>org</sub> estimated from Ba model					
Site C (equator)	0	1.0°N	139	4445	848 (23% of rain)	1.4 (30% of rain)	2.6 (2% of rain)	_					
Site S	0	11.1°N	140.1	4620	32 (3% of rain)	0.6 (30% of rain)	0.15 (<1% of rain)	_					
Leg 199													
Site 1218 (equator)*	38–43	$0 \pm 0.4$	105–108		576 ± 330	2.1 ± 0.93	$0.30 \pm 0.30$	$2.0 \pm 0.88$					
Site 1218 (equator) <sup>†</sup>	41.1-41.4	0.15°S	106	3160	2000 ± 270	5.6 ± 1.6 (8.3 max)	0.26 ± 0.12 (0.63 max)	5.3 ± 1.6 (7.8 max)					
Site 1218	20-38	0.4°–3.5°N	108–120		1120 ± 490	1.65 ± 0.62	0.11 ± 0.11	1.6 ± 0.6					
Site 1218	0–18	4°–9°N	121–135		80 ± 50	0.51 ± 0.57	ND	$0.48 \pm 0.54$					
Hole 1219A	36–49	1.2°–3.6°S	109–116		213 ± 92	1.40 ± 0.52	$0.08 \pm 0.06$	$1.4 \pm 0.5$					
Hole 1219A (equator) <sup>†</sup>	41.2-41.5	2°S	112	3960	937 ± 190	4.60 ± 0.34	0.28 ± 0.06	$4.5 \pm 0.3$					
Hole 1219A (equator)*	25-34	0 ± 1°	117–123		1220 ± 500	1.88 ± 0.68	0.21 ± 0.25	1.84 ± 0.66					
Hole 1219A	1–18	2.5°–7°N	128–141		60 ± 24	$0.22 \pm 0.14$	ND	0.22 ± 0.14					

Table T4. Measured and estimated MARs and rain fluxes of Bio-Ba and Corg in Leg 199 sediments relative to modern fluxes in this region of t	the
eastern equatorial Pacific (Site C and Site S).	

	Rain flux (mg/cm <sup>2</sup> × k.y.)									
Sample	Bulk rain	Bio-Ba rain	C <sub>org</sub> rain via measured C <sub>org</sub>	C <sub>org</sub> rain via estimated C <sub>org</sub>						
Site C (equator)	3701	4.8	130							
Site S	1030	2.0	30							
Leg 199										
Site 1218 (equator)*	2500	7	15	100						
Site 1218 (equator) <sup>†</sup>	8700	28 max	32 max	400 max						
Site 1218	4900	6	6	80						
Site 1218	2700	2	ND	<48						
Hole 1219A	930	5	4	70						
Hole 1219A (equator) <sup>†</sup>	4000	15	14	225						
Hole 1219A (equator)*	5300	6	10	92						
Hole 1219A	2000	1	ND	22						

Notes: Data for Site S and Site C from Dymond and Lyle (1994) and Dymond et al. (1992). Their terminology for "rain" is "export flux." Estimated C<sub>org</sub> values calculated from measured Ba in Leg 199 sediments and Ba/C<sub>org</sub> ratios of modern surface sediments beneath upwelling regions (see text for full discussion). Rain flux estimated from sediment MARs except sites C and S (actual trap measurements). \* = data excludes maxima at 41 Ma. † = maxima at 41 Ma. MAR = mass accumulation rate.