

28. QUANTITY, PROVENANCE, AND THERMAL MATURITY OF ORGANIC MATTER FROM THE NEW JERSEY CONTINENTAL MARGIN, DEEP SEA DRILLING PROJECT LEG 95¹

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ABSTRACT

Using methods of analysis from organic geochemistry and organic petrography, we investigated six Pliocene to Maestrichtian samples from DSDP Site 612 and five Pliocene to Eocene samples from DSDP Site 613 for the quantity, type, and thermal maturity of organic matter.

At both sites, organic carbon content is low in the Eocene samples (0.10 to 0.20%) and relatively high in the Pliocene/Miocene samples (0.87 to 1.15%). The Maestrichtian samples from Site 612 contain about 0.6% organic carbon. The organic matter is predominantly terrigenous, as indicated by low hydrogen index values from Rock-Eval pyrolysis and the dominance of long-chain wax alkanes in the extractable hydrocarbons. The organic matter is at a low level of thermal maturity; measured vitrinite reflectance values were between 0.27 and 0.44%.

INTRODUCTION

In order to complete a transect of the Baltimore Canyon Trough encompassing the continental slope and rise of New Jersey, two sites were drilled off the coast of New Jersey during DSDP Leg 95 (Sites 612 and 613; Fig. 1). The age and lithology of the sediments recovered at Sites 612 and 613 are summarized in Figure 2 (see also the site chapters, this volume).

The purpose of this study was to describe the amount, type, and composition of the organic matter in the sediments. The results are discussed in terms of origin, depositional environment, and thermal maturity. We investigated six samples of Pliocene to Maestrichtian age from Site 612 and five samples of Pliocene to Eocene age from Site 613 (Fig. 2).

ANALYTICAL PROCEDURES

The frozen samples were dried at 50°C for 12 hr. and ground. Total organic carbon was determined with a LECO IR-112 carbon analyzer after the sediments were treated with hydrochloric acid to remove the carbonate carbon. Extraction was performed using a modified flow-blending technique (Radke et al., 1978) and with dichloromethane as the extraction solvent. The total extracts were separated into monoaromatic hydrocarbons, aromatic hydrocarbons, and heterocomponents by automated medium-pressure liquid chromatography (Radke et al., 1980).

A Siemens L350 gas chromatograph equipped with a 23 m × 0.3 mm inner diameter (ID) glass capillary column coated with SE54 was used for gas chromatographic (GC) analysis of the nonaromatic hydrocarbon fractions. Helium was used as carrier gas. The temperature program was as follows: 80°C for 2 min.; 80 to 254°C at a rate of 3°C/min.; isothermal at 254°C for 25 min.

Gas chromatography/mass spectrometry (GC/MS) was carried out on a VG 7070E mass spectrometer linked directly to a Carlo Erba Fractovap model 4160 gas chromatograph via an open-split coupling. Samples were injected splitless onto a 25 m × 0.3 mm ID fused silica column coated with SE54. Helium was used as carrier gas, and the

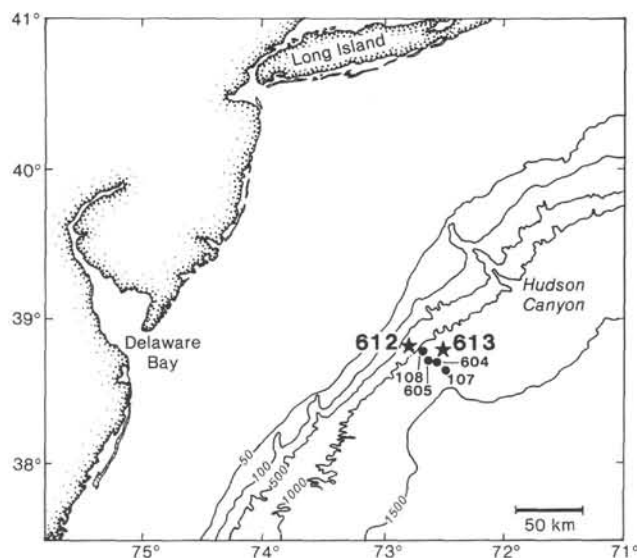


Figure 1. Locations of DSDP Sites 612 and 613 (Leg 95), Sites 604 and 605 (Leg 93), and Sites 107 and 108 (Leg 11). Bathymetry in m.

temperature was raised from 70 to 300°C at a rate of 4°C/min. The mass spectrometer was operated at an ionization energy of 80 eV. The source temperature was kept at 220°C, and the magnet scanned continuously at a rate of 3 s per scan. All data were stored and processed using a DS 55 on-line data system (Kratos AEI).

Rock-Eval pyrolysis was performed according to the method described by Espitalié et al. (1977). Hydrogen and oxygen contents of the rock samples, measured as hydrocarbon-type compound and carbon dioxide yields, respectively, were normalized to organic carbon and displayed as index values in a diagram adopted from Espitalié et al. (1977) and Roucaché et al. (1979).

The kerogen separation procedure included treatment with 7.5 N HCl and HF. The maceral types were analyzed using both transmitted and normal or fluorescence reflected light. Vitrinite reflectance (at 546 nm in oil) was measured on particles larger than 10 µm.

RESULTS

Organic Carbon

The total organic carbon (TOC) contents of the six samples from Site 612 vary between 0.17 and 1.11%

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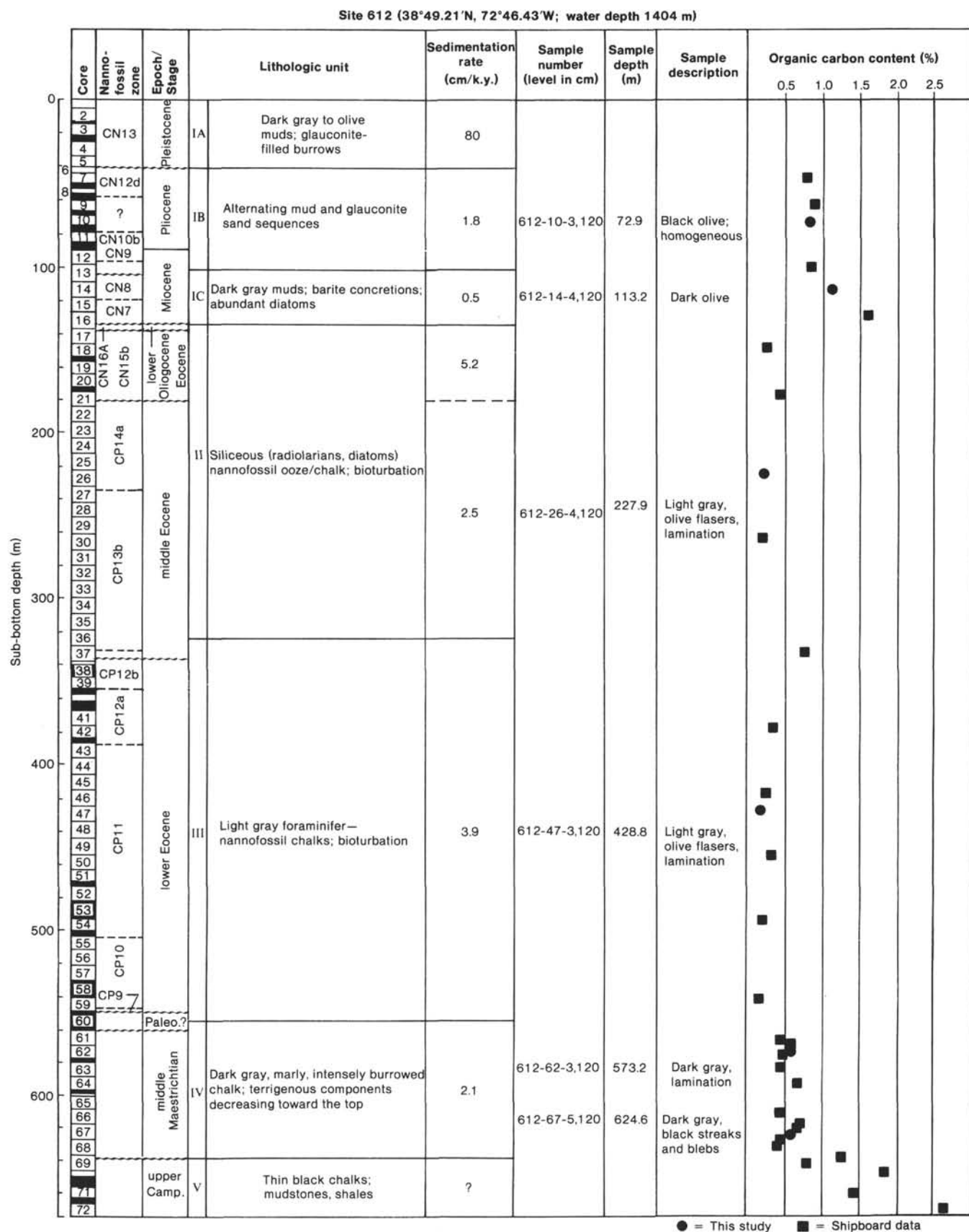


Figure 2. Summary of stratigraphy, lithology, and sedimentation rates for DSDP Sites 612 and 613. Samples investigated in this study are as described.

Site 613 (38°46.26'N, 72°30.43'W; water depth 2323 m)

Sub-bottom depth (m)	Core	Nanno-fossil zone	Epoch/Stage	Lithologic unit	Sedimentation rate (cm/10 ³ yr.)	Sample number (level in cm)	Sample sub-bottom depth (m)	Sample description	Organic carbon content (%)																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																								
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0	1x		middle to upper Pleistocene	IA Greenish gray to dark greenish gray muds, marly nannofossil oozes, nannofossil diatomaceous oozes, glauconitic sands, and silty sands	11.7																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																												

Figure 2 (continued).

(Fig. 2, Table 1). These values agree very well with the shipboard TOC data (Fig. 2). According to the TOC data, the sediment sequence of Site 612 can be divided into five intervals: (1) a Pleistocene/Pliocene interval (corresponding to lithologic Units IA and IB) with TOC values between 0.78 and 0.93% (mean 0.85%); (2) a Mio-

cene interval (corresponding to lithologic Unit IC) with TOC values of 1.11 and 1.58% (mean 1.34%); (3) an Eocene interval (corresponding to lithologic Units II and III) with very low TOC values of less than 0.50% (mean 0.30%); (4) a Maestrichtian interval (corresponding to lithologic Unit IV) with TOC values between 0.47 and

Table 1. Stratigraphy, organic carbon, pyrolysis, extract and liquid chromatography data for samples from DSDP Leg 95.

Sample (interval in cm)	Sub-bottom depth (m) of top of sample	Age	Organic carbon (wt. %)	Rock-Eval pyrolysis			Extract (mg/g C _{org})	Liquid chromatography fractions		
				Hydrogen index (mg HC/g C _{org})	Oxygen index (mg CO ₂ /g C _{org})	T _{max} (°C)		Aliph. HC (%)	Aromatic hydrocarbons (%)	Hetero- components (%)
612-10-3, 120-134	72.9	Pliocene	0.87	164	173	413	10.8	12.0	2.1	85.9
612-14-4, 120-135	113.2	late Miocene	1.11	243	170	421	16.1	9.9	3.5	86.6
612-26-4, 120-135	227.9	middle Eocene	0.20	137	a	412	15.2	26.7	13.3	60.0
612-47-3, 120-135	428.8	early Eocene	0.17	152	a	415	23.0	8.8	5.9	85.3
612-62-3, 120-133	573.2	Maestrichtian	0.59	42	348	412	4.4	6.7	3.3	90.0
612-67-5, 120-133	624.6	Maestrichtian	0.57	47	343	410	5.1	6.3	3.1	90.6
613-15-2, 120-134	224.2	Pliocene	1.15	138	259	417	7.4	8.8	1.0	90.2
613-27-2, 120-135	338.9	middle Eocene	0.17	82	a	369	8.0	12.5	6.3	81.2
613-36-3, 120-135	425.2	middle Eocene	0.14	109	a	410	52.4	64.9	7.4	27.7
613-39-4, 130-145	455.3	early Eocene	0.17	97	a	382	9.0	14.3	7.1	78.6
613-45-3, 135-150	510.1	early Eocene	0.10	103	a	393	19.8	31.6	26.3	42.1

^a All oxygen index values are greater than 900.

0.73% (mean 0.57%); and (5) an upper Campanian interval (corresponding to lithologic Unit V) with high TOC values between 0.80 and 2.68% (mean 1.62%) (Fig. 2).

For Site 613, no shipboard TOC data exist. The five samples we investigated have an organic carbon content of between 0.10 and 1.15% (Fig. 2, Table 1). The moderately high TOC value of 1.15% is from the Pliocene (lithologic Unit IC). As in the Eocene samples of Site 612, the TOC values of the Eocene samples of Site 613 range from 0.10 to 0.17%. The low organic carbon content at both sites during Eocene times is in agreement with the TOC determined at the neighboring Site 108, where the values for the Eocene sediments vary between 0.1 and 0.3% (Boyce, 1972).

Type and Maturity of Organic Matter

The results of the Rock-Eval pyrolysis (Espitalié et al., 1977) are shown in Figure 3 and Table 1. In Figure 3, we have only presented data derived from samples with TOC contents greater than 0.5%. The results for the six Eocene sediment samples that contain organic carbon below 0.2% (Table 1) were rejected because the extremely high oxygen indices determined for these organic-carbon-lean samples are questionable (Katz, 1983).

The hydrogen index values are low to moderate and range from 42 mg HC/g C_{org} in the Maestrichtian to 243 mg HC/g C_{org} in the Miocene (Fig. 3, Table 1). The oxygen index values vary between 170 and 348 mg CO₂/g C_{org}. According to Figure 3, the organic matter in the Pliocene and Maestrichtian samples investigated is characterized as kerogen type III, and the organic matter of the Miocene sample of Site 612 may represent a mixture of types II and III. In the Eocene samples of Sites 612 and 613, kerogen type III appears to be dominant, as implied by hydrogen index values of less than 150 mg HC/g C_{org} (Table 1).

The results of the kerogen microscopy are disappointing because the kerogen isolation yields were too low to allow quantitative estimates of the maceral composition of the organic matter. Some of the finely dispersed amorphous material may have been lost during the separation procedure. Qualitative results were obtained from only two samples (Table 2). The Miocene sample (612-14-4, 120-135 cm) contains debris of terrestrial plant tissue

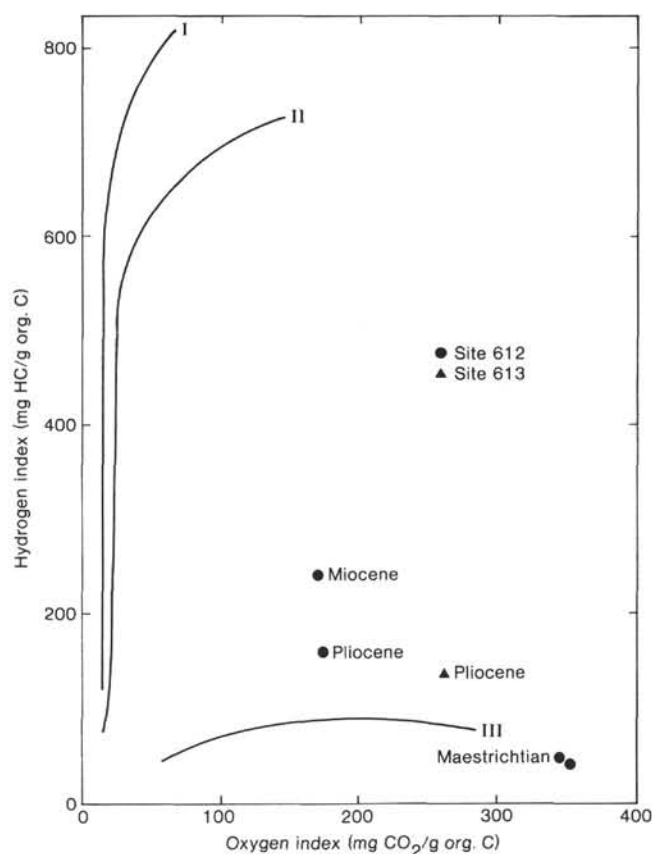


Figure 3. Results of Rock-Eval pyrolysis displayed as hydrogen index versus oxygen index (Espitalié et al., 1977) for sediment samples from DSDP Sites 612 and 613. I, II, III are simplified kerogen classifications (e.g., Tissot et al., 1980).

(textinite). In the Pliocene sample (613-15-2, 120-134 cm), some algal debris was observed. However, these observations are based on very limited counts of kerogen particles.

The temperatures of maximum pyrolysis yield (T_{max} ; Espitalié et al., 1977) range from 369 to 421°C (Table 1), indicating that the organic matter in all samples investigated was immature. This evaluation agrees well with the measured reflectance of primary vitrinite. The reflectance values are very low and range from 0.27 to

Table 2. Vitrinite reflectance data for samples from DSDP Leg 95.

Sample (interval in cm)	Sub-bottom depth (m) of top of sample	Primary vitrinite R_{random} (%)			Secondary vitrinite R_{random} (%)			Remarks
		\bar{X}	S	N	\bar{X}	S	N	
612-10-3, 120-134	72.90				0.66		2	Terrestrial plant tissue
612-14-4, 120-135	113.20	0.27	0.02	10	0.57		2	
612-62-3, 120-133	573.20				0.61	0.05	9	
612-67-5, 120-133	624.60	0.44	0.02	3	0.65	0.07	4	
613-15-2, 120-134	224.20	0.42	0.02	5	0.58	0.05	19	Algal debris

Note: \bar{X} = mean; S = standard deviation; N = number of measurements.

0.44% (Table 2). The occurrence of secondary vitrinites ($R_{\text{random}} = 0.57$ to 0.66%) indicates the presence of some redeposited material that is older and more mature.

Extractable Organic Matter

At Site 612, the amount of extractable organic matter is very low in the Maestrichtian samples (about 5 mg/g C_{org}) and moderate in the Eocene to Pliocene samples (10 to 23 mg/g C_{org}). The highest value determined for the most organic-carbon-lean sample may result partly from the difficulty of weighing a low amount of extract precisely. The same is probably true for the Eocene samples from Site 613, for which the normalized extract yields range up to 52.4 mg/g C_{org} . The early Pliocene sample, in contrast, has the expected low extract yield of 7.4 mg/g C_{org} (Table 1). The percentages of liquid chromatography fractions of the organic-carbon-lean samples should also not be over-interpreted.

Nonaromatic Hydrocarbon Composition

A Pliocene and a late Miocene sample from Site 612 (Fig. 4) and a Pliocene sample from Site 613 (Fig. 5) were analyzed for their nonaromatic hydrocarbon compositions by capillary gas chromatography. All samples show a dominance of long-chain wax alkanes derived from terrestrial higher plants which have inherited their strong odd-carbon-numbered predominance from the biological system (Eglinton and Hamilton, 1963). Low-molecular-weight *n*-alkanes and cyclic compounds are minor in each case. Gas chromatography/mass spectrometry of the samples revealed that most of the cyclic hydrocarbons identified (Appendix; Fig. 6) are either hopanoids or ferenes from bacterial sources (Eouris et al., 1979; Brassell and Eglinton, 1983) or terpenoids probably derived from terrestrial higher plants (Kulshreshtha et al., 1972). The mass spectrum of two unidentified C_{30} triterpanes are shown in Figures 7A and 7C. Two samples (612-14-4, 120-135 cm and 613-15-2, 120-134 cm) contain small amounts of tetracyclic terpanes probably derived from ring A degradation of 3-oxygenated triterpenoids of higher plants (Corbet, 1980; Corbet et al., 1980; Brassell and Eglinton, 1983).

Sterenes and steradienes were recognized only in Sample 613-15-2, 120-134 cm, but the concentrations were too small to identify most of them in the chromatogram (Fig. 5). Steroids are abundant in marine organisms (MacKenzie et al., 1982), and thus our observation is consistent with the microscopic observation of algal debris in

this sample. The structures of some C_{28} and C_{29} steradienes (two isomers each) with a key fragment of m/z 298 (Fig. 7B; Appendix) could not be identified with confidence, although the mass spectra (Fig. 7B) resemble those of the C_{28} ster-5,24- or ster-5,24(28)-dienes found in deep-sea sediments of the Gulf of California (Rullkötter et al., 1982).

The composition of the extractable nonaromatic hydrocarbons of the organic-carbon-lean samples was also screened by capillary gas chromatography, but it was found that most of these hydrocarbons were heavily contaminated with phthalate esters and hydrocarbons uncommon in immature deep-sea sediments (possibly from shipboard lubricants) and that the others were likely to be at least partly contaminated. Thus, these chromatograms are not reproduced here.

CONCLUSIONS

The organic matter in all of the sediment samples investigated from DSDP Sites 612 and 613 is predominantly terrigenous, as inferred from the low hydrogen index values, the visual kerogen description, and the dominance of long-chain wax alkanes from terrestrial higher plants in the extractable hydrocarbons. Unfortunately, the amounts of kerogen particles were too small to determine the proportions of terrestrial and marine organic matter quantitatively. The dominance of terrestrial organic matter may be the result of an increased supply of terrigenous matter, which in turn is due to the humid climatic conditions that have prevailed in North America since the Late Cretaceous (Hallam, 1984).

Although the high carbonate accumulation rates and high amounts of biogenic silica observed in the Eocene section of Sites 612 and 613 (Fig. 2; and site chapters, this volume) suggest high oceanic productivity, the content of organic matter is extremely low (less than 0.2%). Together with extensive bioturbation (Fig. 2; and site chapters, this volume), well oxygenated deep-water conditions may have prevented the preservation of significant amounts of marine organic matter in the sediments.

The temperatures of maximum pyrolysis yield, the low vitrinite reflectance values, and the presence of olefins among the extractable hydrocarbons indicate that the organic matter in all samples investigated is very immature.

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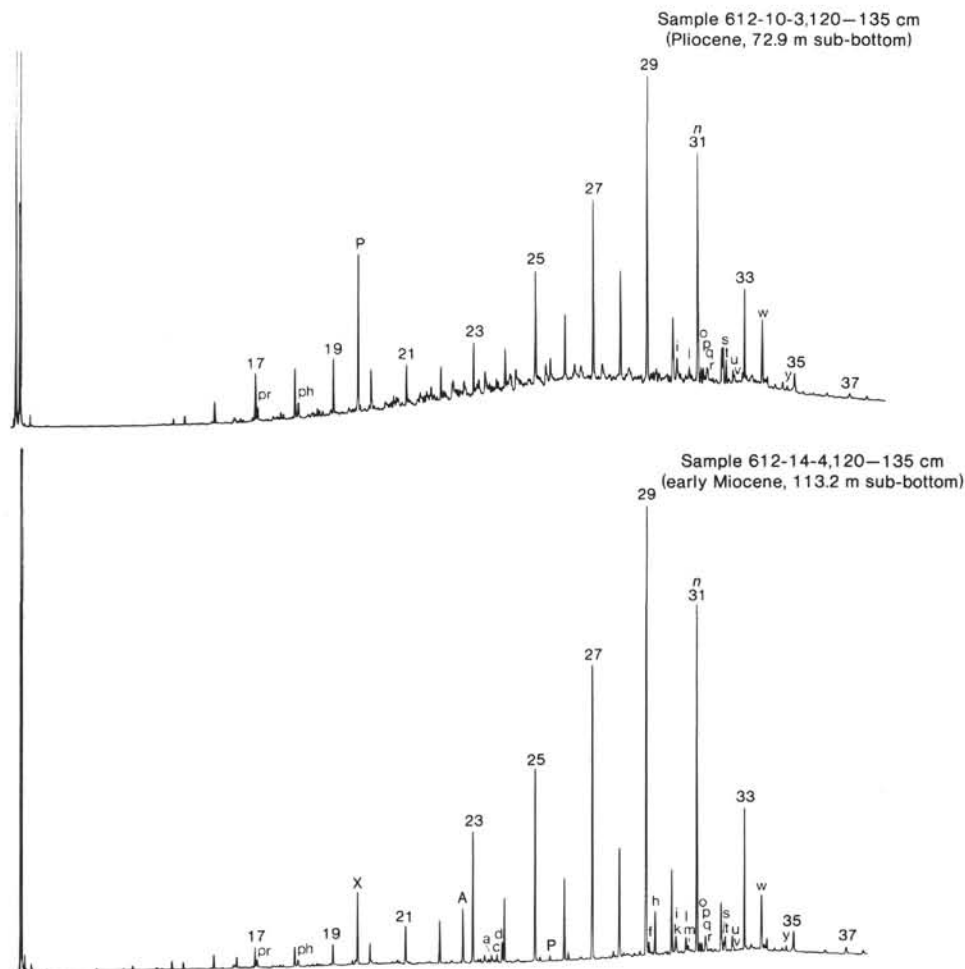


Figure 4. Capillary column gas chromatograms of the nonaromatic hydrocarbon fractions of two sediment samples from DSDP Site 612. Numbers indicate *n*-alkanes; lettered compounds were identified by GC/MS and are listed in the Appendix.

bon analyses and Rock-Eval pyrolysis, and gas chromatography, respectively. We thank W. Benders, U. Disko, F.-J. Keller, and K. Sellinghoff for technical assistance. Financial support by the Deutsche Forschungsgemeinschaft (Grant No. We 346-25) is gratefully acknowledged.

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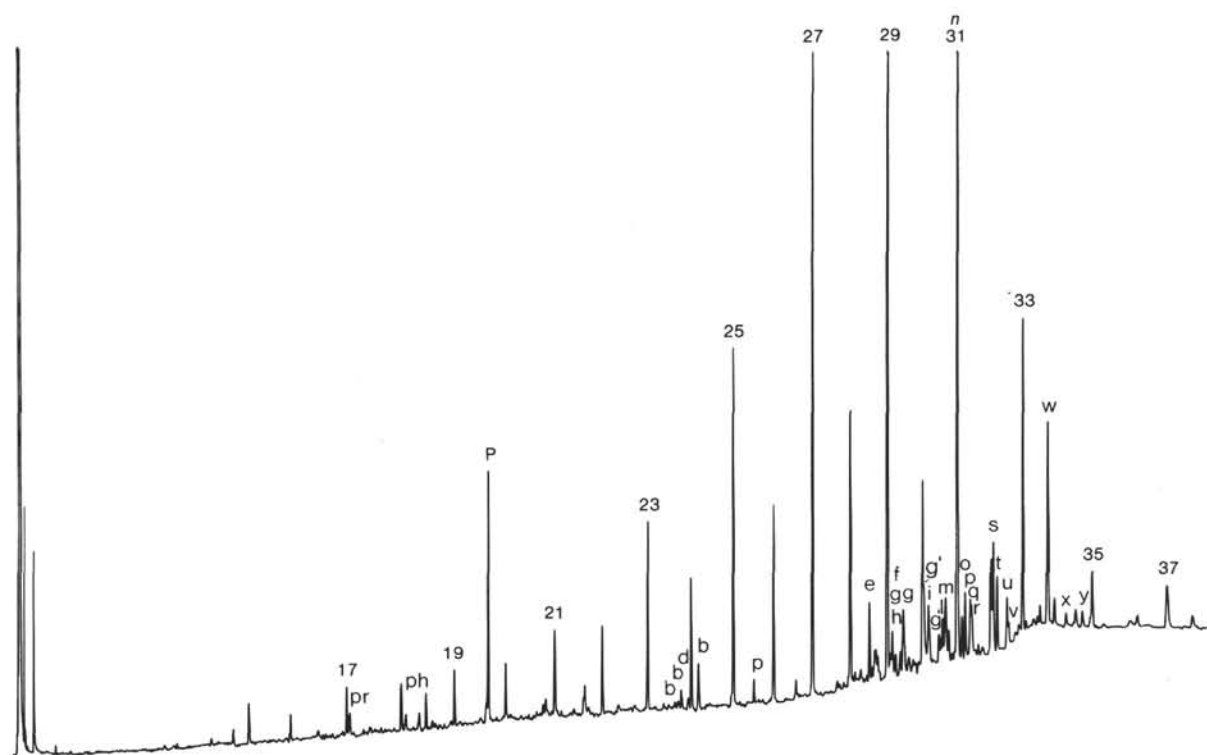


Figure 5. Capillary column gas chromatogram of the nonaromatic hydrocarbon fraction of Sample 613-15-2, 120–134 cm (early Pliocene, 224.2 m sub-bottom). Numbers indicate *n*-alkanes; lettered compounds were identified by GC/MS and are listed in the Appendix.

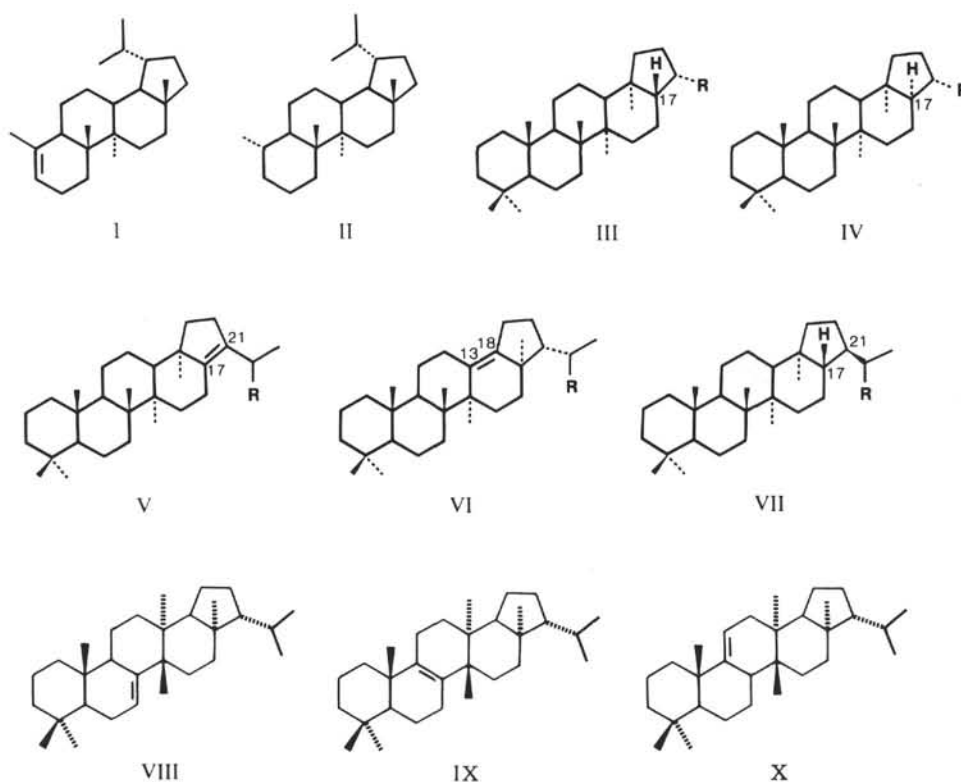


Figure 6. Structural formulae of compounds identified by GC/MS. For an explanation of the numbering see the Appendix.

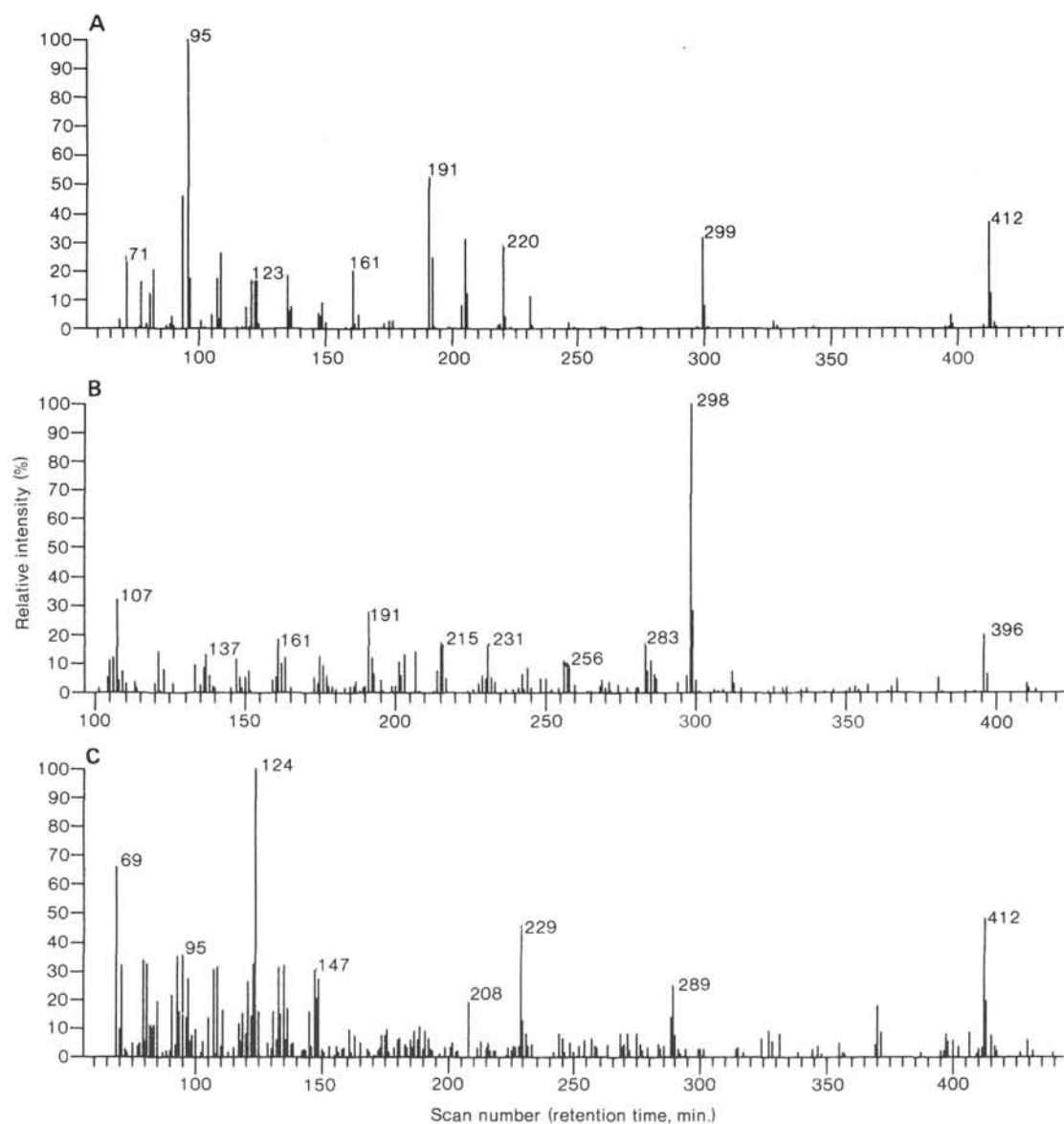


Figure 7. Mass spectra of unidentified components in the nonaromatic hydrocarbon fraction of Sample 613-15-2, 120–134 cm. A. C_{30} triterpane (e in Fig. 5). B. C_{29} steradiene (second-eluting g' in Fig. 5), possibly a ster-5,24-diene or ster-5,24(28)-diene. C. C_{30} -triterpane (x in Fig. 5). All spectra are background subtracted, and the quality of spectra B and C is fairly poor as a result of the low concentrations.

APPENDIX
Branched and Cyclic Hydrocarbons Detected in the Nonaromatic
Hydrocarbon Fractions of Sediments from DSDP Sites 612 and 613^a

Compound	Mass spectrometry data	Structure
pr pristane		
ph phytane		
a nor-de-A-lupane?	(M ⁺ 316,273,192,177,BP109)	
b tetracyclic terpenes	(M ⁺ 326,311,255,108,BP95)	
c de-A-lup-5(10)-ene		I
d de-A-10β(H)-lupane		II
e C ₃₀ triterpane	(M ⁺ 412,299,191)	
f 17β(H)-trisnorhopane		III, R = H
g C ₂₈ steradiene	(M ⁺ 382,298,255)	
g' C ₂₉ steradiene	(M ⁺ 396,298,255)	
h unknown	(M ⁺ 400)	
i 17 (H)-norhopane		IV, R = H
j norhop-17(21)-ene		V, R = H
k norneohop-13(18)-ene		VI, R = H
l hop-17(21)-ene		V, R = CH ₃
m normoretane		VII, R = H
n 17 (H)-hopane		IV, R = CH ₃
o fern-7-ene		VIII
p neohop-13(18)-ene		VI, R = CH ₃
q 17β(H)-norhopane		III, R = C ₂ H ₅
r fern-8-ene		IX
s fern-9(11)-ene		X
t 17 (H)-homohopane (22R)		IV, R = C ₂ H ₅
u 17β(H)-hopane		III, R = CH(CH ₃) ₂
v homomoretane		VII, R = C ₂ H ₅
w 17β(H)-homohopane		III, R = CH(CH ₃)C ₂ H ₅
x C ₃₀ triterpane	(M ⁺ 412)	
y 17β(H)-bishomohopane		III, R = CH(CH ₃)C ₃ H ₇
A aromatic hydrocarbon (incomplete separation)		
P phthalate		

^a Gas chromatograms are shown in Figs. 5 and 6. Structural formulae are given in Fig. 7. M⁺ = molecular ion, BP = base peak.