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39. ACCUMULATION RATES AND COMPOSITION OF ORGANIC MATTER IN LATE CENOZOIC SEDIMENTS UNDERLYING THE ACTIVE UPWELLING AREA OFF PERU[1]

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ABSTRACT

Deep-sea sediment samples from three Ocean Drilling Program (ODP) Leg 112 sites on the Peru continental margin were investigated, using a number of organic geochemical and organic petrographic techniques, for amounts and compositions of the organic matter preserved. Preliminary results include mass accumulation rates of organic carbon at Site 679 and characteristics of the organic facies for sediments from Sites 679, 681, and 684.

Organic-carbon contents are high, with few exceptions. Particularly high values were determined in the Pliocene interval at Site 684 (4%–7.5%) and in the early Pliocene to Quaternary section of Hole 679D (2%–9%). Older sediments at this site have distinctively lower organic-carbon contents (0.2%–2.5%). Mass accumulation rates of organic matter at Site 679 are 0.02 to 0.07 g carbon/cm^2/k.y. for late Miocene to early Pliocene sediments and higher by a factor of 5 to 10 in the Quaternary sediments. The organic matter in all samples has a predominantly marine planktonic and bacterial origin, with minor terrigenous contribution. Organic particle sizes are strikingly small, so that only a minor portion is covered by visual maceral analysis.

Molecular organic-geochemical data were obtained for nonaromatic hydrocarbons, aromatic hydrocarbons (including sulfur compounds), alcohols, ketones, esters, and carboxylic acids. Among the total extractable lipids, long-chain unsaturated ketones from Prymnesiophyte algae strongly predominate among the gas chromatography (GC) amenable components. Steroids are major constituents of the ketone and free- and bound-alcohol fractions. Perylene is the most abundant aromatic hydrocarbon, whereas in the nonaromatic hydrocarbon fractions, long-chain n-alkanes from higher land plants predominate, although the total terrigenous organic matter proportion in the sediments is small.

INTRODUCTION

During Leg 112 10 sites were occupied on the continental margin of western South America between 9° and 14°S. Two primary objectives of this leg were to unravel the tectonic history of the continental margin and to study the evolution of the coastal upwelling system (Suess, von Huene, et al., 1988). The sediments deposited in the forearc basins off Peru not only contain the relic effects of vertical movements of the basement foundation of the Andes margin, but also the sedimentary expression of the oceanographic history of one of the major upwelling regimes in the world. Several of these forearc basins, such as the Salaverry, Trujillo, and Lima basins, have contrasting tectonic histories, especially since the late Miocene (e.g., Suess et al., 1987). For instance, this is expressed by a landward migration of upwelling centers in the Lima Basin between upper Miocene and Quaternary time, as revealed by benthic foraminifer assemblages (Suess, von Huene, et al., 1988). The Peru upwelling system is a classical example of coastal upwelling (e.g., Parrish, 1982; Thiede and Suess, 1983). These upwelling areas are characterized by high fertility of the surface-water masses, resulting in an enhanced primary productivity. Thus, sediments deposited under such an active upwelling area often have elevated (marine) organic-matter contents and can, therefore, become potential petroleum source rocks in the course of geologic evolution (Demaison and Moore, 1980).

PREVIOUS ORGANIC-GEOCHEMICAL STUDIES IN THE PERU UPWELLING AREA

A wealth of organic geochemical data are available from studies of sediment trap and core samples, especially from the Chemistry Department of the Woods Hole Oceanographic Institution (e.g., Farrington et al., 1988; Gagosian et al., 1983a, 1983b; Repeta, 1989; Repeta and Gagosian, 1983, 1984, 1987; Volkman et al., 1983, 1987; Wakeham, 1985; Wakeham et al., 1983, 1984). All these data refer to samples collected around 15°S. In addition, a detailed study of an interfacial sediment from 12°S was conducted by the Organic Geochemistry Group of the University of Bristol (Smith, 1984; Smith et al., 1982, 1983a, 1983b).

Repeta (1989) and Repeta and Gagosian (1983, 1984, 1987) reported the identification and distribution of carotenoids and their degradation products in suspended matter, sediment trap material, zooplankton fecal pellets, and surface sediments. Carotenoids, like chlorophyll a, function as photosynthetic pigments in all species of marine phytoplankton. Studies have shown that, in addition to unknown sources, zooplanktonic crustaceans, diatoms, dinoflagellates, cryptomonads, and purple nonsulfur photosynthetic bacteria contribute to organic matter. However, the distribution of carotenoids in surface sediments has also been shown as totally different from their distribution in sediment trap material. Typical carotenoid biomarkers for diatoms and dinoflagellates were nearly absent in surface sediments, an observation that the authors attributed to rapid degradation because of the presence of labile 5,6-epoxides in these carotenoids. In this respect, note that Klok et al. (1984) estimated that the concentration of loliolide, one of the principal degradation products (Repeta, 1989), was ~2% of the total organic matter of a diatomaceous ooze from the Walvis Bay upwelling area.

The studies of Wakeham and his coworkers (Wakeham, 1985; Wakeham et al., 1983, 1984) emphasized the distribution

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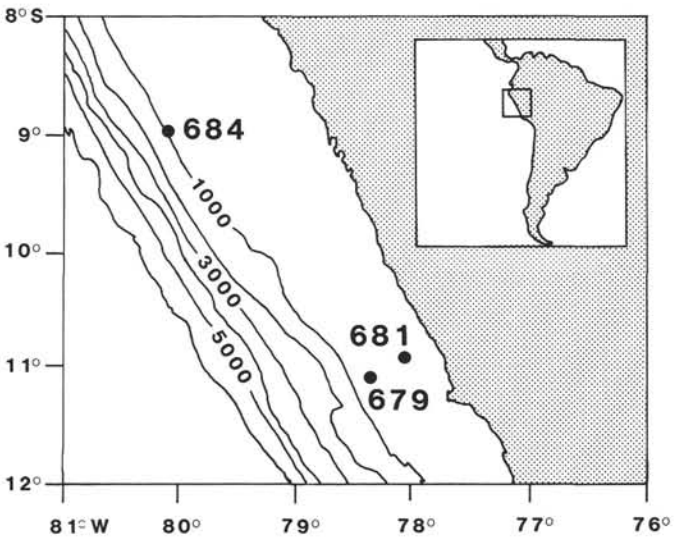

Figure 1. Location map of Sites 679, 681, and 684 of Leg 112 off the Peruvian coast.

of lipids, e.g., fatty acids, wax esters, and triacylglycerols, in particulate matter having a different size and from different depths and different geographic locations. Changes in the standing crop of primary producers were already noted during sampling: within a period of 4 days, a diatom bloom was replaced by a dinoflagellate bloom. The results indicate that the flux and composition of lipids is variable, even between daytime and nighttime.

The distribution of other classes of lipids, such as aliphatic hydrocarbons, sterols, long-chain ketones, and triterpenoid alcohols, was the focus of the research by Gagosian et al. (1983a, 1983b), Volkman et al. (1983, 1987), and Farrington et al. (1988). These studies included surface sediments. Typical hydrocarbons observed include *n*-alkanes, $C_{37:3}$ and $C_{38:3}$ alkenes,[4] sterenes, and highly branched alkenes. Sterols from a variety of marine sources and long-chain unsaturated ketones were present in abundance (see also Cooper et al., 1986). The incorporation of many of these labile compounds into fast-sinking anchovy fecal pellets was proposed as a major mechanism of transport to the seafloor (cf. Staresinic et al., 1983). Triterpenoid alcohols of terrigenous and bacterial origin also were found.

In addition to several classes of lipids described above, Smith and his coworkers (Smith 1984; Smith et al., 1982, 1983a, 1983b) reported the presence of highly labile polyunsaturated fatty acids in a saponified extract from a surface sediment, indicating that little degradation or reworking of the lipids had occurred at that stage. They did not detect long-chain alkandiols and alkan-15-on-1-ols (Smith et al., 1983c), although these compounds were found by Volkman et al. (1987; see also Farrimond et al., this volume).

This brief overview gives one an impression of the complexity of lipid sources and molecular sedimentary constituents in the Peru upwelling area.

SAMPLES AND BACKGROUND INFORMATION

This study detailing the amounts and compositions of organic matter deposited at Sites 679, 681 and 684 (Fig. 1) is based on core samples from Holes 679C, 681C, and 684C dedicated to organic geochemistry (Table 1); all the recovered cores from these holes were deep-frozen on board the *JOIDES Resolution* immediately after collection. In addition, we analyzed a large number of samples from Hole 679D (Table 2) to monitor changes in organic- and carbonate-carbon accumulation during late Neogene and Quaternary time. The background information summarized next was taken from the respective site chapters of the *Initial Reports of the Proceedings of the Ocean Drilling Program,* Volume 112 (Suess, von Huene, et al., 1988).

Site 679 (Hole 679C; 11°03.81′S, 76°16.33′W, water depth of 461 m) is located on the seaward flank of the structural ridge separating the Lima Basin from the Salaverry Basin. Sediments of middle Miocene to Holocene age extending to a maximum depth of 359.3 meters below seafloor (mbsf) were recovered at this site. The sequence has been divided into five lithologic units. The upper two units, which we studied, are classified on the basis of diatom and carbonate contents. Lithologic Unit I consists of diatomaceous foraminiferal mud, which is olive, olive gray, dark olive, dark gray or black, while Unit II is a diatomaceous mud having the same color gradation. Horizons containing phosphate nodules are common in all units. At the bottom of Hole 679E (350 mbsf), a dramatic increase in the concentration of thermogenic gas (ethane) was observed, and when combined with the petroliferous odor of the sediment, prompted Leg 112 scientists to abandon this site. However, a drilling-induced, artificial formation of the gas cannot be totally ruled out (see Suess, von Huene, et al., 1988, Site 679 chapter).

Site 681, located in the Salaverry Basin (Hole 681C; 10°58.60′S, 77°57.46′W, water depth of 161 m), is the most landward site and nearest to today's coastal upwelling centers. The water depth at this site nearly coincides with the top of the oxygen-minimum zone. The Quaternary sediment sequence that was penetrated to a maximum depth of 187 mbsf, has been divided into four lithologic units. Our sample suite is from the upper two units. Unit I primarily consists of dark olive-gray diatomaceous mud, with thin laminae of yellow-brown diatomaceous ooze. The distinctive laminated character is interrupted by an interval of bioturbated sediment between 12 and 15 mbsf. Unit II has a lower diatom content and a greater degree of bioturbation. Frequent sandy and silty beds represent a high proportion of this sequence.

Site 684 (Hole 684C; 8°59.49′S, 79°54.35′W, water depth of 437 m) is located in the Trujillo Basin approximately 2° north of Sites 679 and 681. The penetrated sediment sequence of Miocene to Quaternary age (maximum depth 136.1 mbsf) was divided into five lithologic units. We received samples from the upper three units. Two hiatuses separate time-stratigraphic sections of late Quaternary, Pliocene, and Miocene age, respectively. Unit I was subdivided into two subunits, IA and IB; the former consists of dark olive diatomaceous mud and the latter of two sand beds separated by laminated diatomaceous mud. Unit II consists of black, silty or sandy, homogeneous to mottled, bioturbated mud almost devoid of diatoms. Unit III is characterized by dark olive-gray to black, homogeneous to mottled, bioturbated diatomaceous mud.

EXPERIMENTAL METHODS

Sediment samples were dried at 40°C, and aliquots were impregnated with a resin for microscopic analyses. The surface of the block was ground and polished. Maceral composition was determined using a two-step counting procedure, both in reflected white light and in a fluorescence mode. Details of the analytical procedure are described elsewhere (Littke et al., 1988). Kerogen concentrates were prepared by treating samples with concentrated hydrochloric acid for 2 hr.

[4] $C_{37:3}$ denotes organic compounds with 37 carbon atoms and 3° of unsaturation (double bonds or rings).

Table 1. Depth intervals and bulk characteristics of the organic geochemistry samples.

Core, section, interval (cm)	Depth (mbsf)	Lithol. unit	Age	$CaCO_3$ (%)	C_{org} (%)	HI (mg HC/g C_{org})
112-679C-1H-1, 30–37	0.35	I	Quaternary	7.75	7.90	438
679C-1H-6, 133–140	8.85	I	Quaternary	51.15	2.09	272
679C-2H-4, 30–37	13.85	I	Quaternary	14.66	3.72	381
679C-3H-4, 30–37	23.85	I	Quaternary	25.41	8.95	471
679C-4H-4, 30–37	32.85	I	Quaternary	11.24	3.21	443
679C-5H-4, 30–37	42.35	I	Quaternary	9.00	3.05	462
679C-6H-4, 30–37	51.85	II	Quaternary	37.40	2.57	463
679C-7H-4, 30–37	61.35	II	Quat./Plio.	23.82	2.68	713
679C-8H-2, 30–37	67.85	II	l. Pliocene	n.d.	7.52	446
679C-8H-6, 30–37	73.85	II	l. Pliocene	0.01	5.31	424
681C-1H-1, 30–37	0.35	I	Quaternary	1.92	4.65	343
681C-2H-1, 30–37	6.25	I	Quaternary	5.91	4.47	356
681C-2H-6, 5–12	13.50	I	Quaternary	0.08	1.32	401
681C-3H-4, 30–36	20.25	I	Quaternary	10.33	3.13	377
681C-4H-4, 30–36	29.75	I	Quaternary	3.25	6.51	422
681C-5H-4, 32–38	39.25	II	Quaternary	13.83	2.71	463
681C-7H-4, 30–37	58.25	II	Quaternary	10.08	0.20	355
681C-8H-4, 30–37	67.75	II	Quaternary	3.33	1.16	286
681C-9H-4, 30–37	77.25	II	Quaternary	6.58	0.53	140
681C-10H-4, 30–37	86.75	II	Quaternary	4.33	3.09	389
684C-1H-1, 30–37	0.35	IA	Quaternary	8.91	3.56	339
684C-1H-4, 30–37	4.85	IA	Quaternary	7.08	2.57	385
684C-2H-4, 30–37	12.65	IB	Quaternary	50.40	0.86	240
684C-3H-1, 30–37	17.65	II/III	l. Pliocene	n.d.	6.21	269
684C-3H-6, 30–37	25.15	III	Pliocene	0.01	5.89	380
684C-4H-3, 30–37	30.15	III	Pliocene	11.33	7.46	395
684C-4H-7, 30–37	36.15	III	Pliocene	4.91	4.09	387

n.d. = not determined.

After careful washing and neutralization, residues were stirred with concentrated hydrofluoric acid for 16 hr and subsequently washed neutral with distilled water (cf. Durand, 1980). The resulting powder was then prepared for maceral counting, as described above.

From a large set of kerogen concentrates of sediments from Hole 679D, the hydrogen and carbon contents were determined with a CHN analyzer to calculate atomic hydrogen/carbon (H/C) ratios.

Sample-preparation techniques for organic geochemical studies, including carbon measurements, lipid extraction, compound class separation, derivatization, as well as instrumental conditions used for Rock-Eval analyses, gas chromatography (GC), and gas chromatography-mass spectrometry (GC-MS) were identical to those described in earlier studies of ODP samples (ten Haven and Rullkötter, 1988; ten Haven et al., 1989). However, in this study the esterification of acids was performed with diazomethane.

Compound identifications are based on comparison of relative GC retention times and mass spectra with those reported in the literature. The distribution of organic compounds is discussed in qualitative, rather than quantitative terms. Structures of selected compounds are given in the Appendix, and in the text these structures are referred to with Roman numerals.

RESULTS AND DISCUSSION

Depth, stratigraphic age, and bulk characteristics of the samples investigated are given in Tables 1 and 2. Results of carbonate, organic-carbon and Rock-Eval measurements show similar variations as data collected on board the ship (Suess, von Huene, et al., 1988). Carbonate values fluctuate from 0% to 66.2% (Tables 1 and 2; Fig. 2). The carbonate content may be primarily controlled by the presence or absence of calcareous plankton in discrete layers (Suess, von Huene, et al., 1988). Indeed, in the two samples having carbonate contents of more than 50% (Table 1) numerous foraminiferal tests were microscopically observed. Organic-carbon contents are high, with the exception of Sample 112-681C-7H-4, 30–37 cm (Table 1). The more detailed organic-carbon record of Hole 679D can be divided into two parts (Fig. 2). The late Miocene and earliest Pliocene (lithologic Unit III) records are characterized by organic-carbon contents of 0.25% to 2.83%, whereas the early Pliocene and Quaternary (lithologic Units I and II) records show distinctively higher values, ranging from 1.46% to 7.81%. Note the high organic-carbon values of the Pliocene section of Site 684

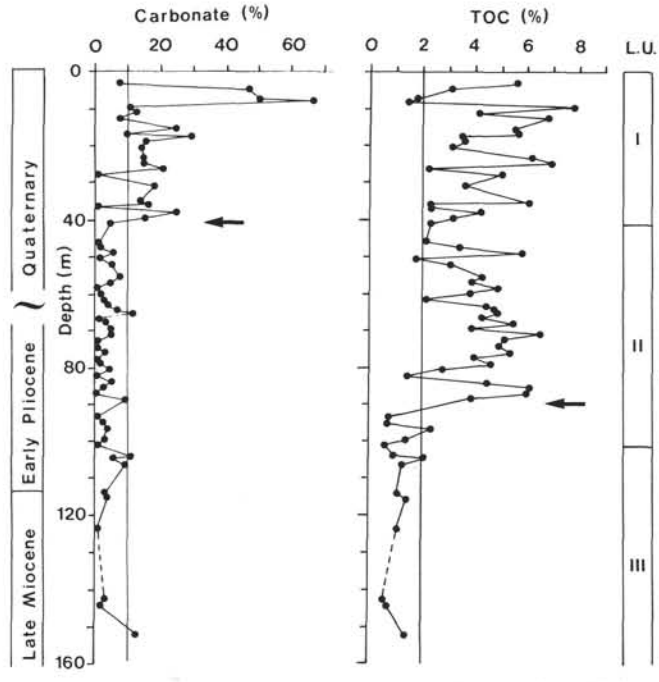

Figure 2. Organic and carbonate carbon records at Hole 679D (see Table 2). Arrows indicate the depth where major changes occur.

Table 2. Carbon contents of sediments and organic carbon and hydrogen data for kerogen concentrates of samples from Hole 679D.

Core, section, interval (cm)	Depth (mbsf)	$CaCO_3$ (%)	C-tot (%)	C-org (%)	Kerogen concentrates		
					C (%)	H (%)	H/C (at)
112-679D-1H-1, 19	0.20		11.50		55.26	6.76	1.47
679D-1H-2, 19	1.70		11.25				
679D-1H-3, 19	3.20	7.2	6.52	5.65	40.78	5.28	1.55
679D-1H-4, 19	4.70	46.9	8.73	3.10	55.10	6.56	1.43
679D-1H-5, 19	6.20				47.48	6.05	1.53
679D-1H-6, 10	7.61	50.2	7.78	1.76	45.57	5.57	1.59
679D-2H-1, 21	8.12	66.2	9.40	1.46	49.79	6.23	1.50
679D-2H-2, 20	9.61	10.5	9.07	7.81	44.51	5.31	1.43
679D-2H-3, 20	11.11	12.3	5.64	4.16			
679D-2H-4, 21	12.62	7.5	7.71	6.81	47.88	6.07	1.52
679D-2H-5, 20	14.11		4.83		52.68	6.99	1.59
679D-2H-6, 20	15.61	24.7	8.52	5.55	56.15	6.34	1.35
679D-2H-7, 18	17.09	9.6	6.81	5.66	55.41	6.82	1.48
679D-3H-1, 19	17.60	29.4	7.08	3.55	54.65	6.83	1.50
679D-3H-2, 19	19.10	15.3	5.48	3.64	55.24	6.70	1.46
679D-3H-3, 20	20.61	14.3	4.86	3.15	55.77	6.67	1.43
679D-3H-4, 20	22.11		8.25				
679D-3H-5, 19	23.60	14.6	7.92	6.16	57.31	7.14	1.50
679D-3H-6, 19	25.10	14.8	8.70	6.93	53.83	6.43	1.43
679D-3H-7, 19	26.60	20.6	4.70	2.23	38.53		
679D-4H-1, 118	28.09	0.0	5.05	5.05	56.93	7.22	1.52
679D-4H-2, 118	29.59		10.96		57.83	6.98	1.45
679D-4H-3, 118	31.09	18.2	5.80	3.62	54.19	6.53	1.45
679D-4H-6, 118	35.59	13.6	7.72	6.09			
679D-4H-7, 00	35.91	16.1	4.21	2.28	45.62	5.93	1.56
679D-5H-1, 20	36.61	0.5	2.38	2.32			
679D-5H-2, 20	38.11	24.6	7.20	4.25	55.69	7.07	1.52
679D-5H-3, 20	39.61	15.2	5.04	3.21	42.89	5.57	1.59
679D-5H-4, 20	41.11	4.6	2.90	2.34	48.30	6.00	1.49
679D-5H-5, 20	42.61			2.13			
679D-6H-1, 22	46.13	0.9	2.27	2.16	51.21	6.51	1.52
679D-6H-2, 22	47.63	1.4	3.61	3.44			
679D-6H-3, 22	49.13	5.4	6.48	5.83	47.00	5.93	1.49
679D-6H-4, 22	50.63	1.5	1.96	1.78	23.79	3.43	1.73
679D-6H-5, 24	52.15	4.8	3.64	3.07	45.31	5.83	1.54
679D-7H-1, 12	55.53	7.5	5.19	4.29	41.39	5.21	1.51
679D-7H-2, 12	57.03	4.5	4.45	3.91	44.79	5.95	1.59
679D-7H-3, 12	58.53	0.0	4.91	4.91	50.63	6.75	1.60
679D-7H-4, 12	60.03	1.6	4.07	3.88	50.05	6.14	1.47
679D-7H-5, 12	61.53	2.5	2.50	2.20	40.45	5.30	1.57
679D-7H-6, 12	63.03	3.5	4.88	4.46	45.88	5.84	1.53
679D-7H-7, 12	64.53	6.6	5.57	4.78			
679D-8H-1, 22	65.13	11.7	6.34	4.93	49.42	6.77	1.64
679D-8H-2, 22	66.63	0.6	4.42	4.35	53.31	6.52	1.47
679D-8H-3, 22	68.13	3.1	5.90	5.53	48.91	6.73	1.65
679D-8H-4, 22	69.63	4.8	4.49	3.92			
679D-8H-5, 22	71.13	4.7	7.11	6.54	51.51	6.65	1.55
679D-8H-6, 22	72.63	0.9	5.32	5.22	40.83	5.19	1.52
679D-9H-1, 12	74.53	0.0	4.95	4.95	51.63	6.72	1.56
679D-9H-2, 12	76.03	3.1	5.77	5.39	48.62	6.03	1.49
679D-9H-3, 12	77.53	0.5	4.06	4.00	53.75	6.40	1.43
679D-9H-4, 12	79.03	1.3	4.81	4.66			
679D-9H-5, 12	80.53	4.4	3.36	2.84			
679D-9H-6, 12	82.03	0.4	1.53	1.49	41.59	4.86	1.40
679D-10H-1, 23	84.14	5.3	5.15	4.52	49.10	5.43	1.33
679D-10H-2, 23	85.64	2.9	6.50	6.15			
679D-10H-3, 23	87.14	0.0	6.02	6.01	42.54	5.32	1.50
679D-10H-4, 23	88.64	9.4	5.06	3.94	40.05	5.02	1.50
679D-11H-1, 20	93.61	0.0	0.78	0.78			
679D-11H-2, 20	95.11	2.5	1.00	0.70			
679D-11H-3, 20	96.61	3.7	2.83	2.39	37.11	4.67	1.51
679D-11H-4, 20	98.11		2.75		43.54	5.32	1.47
679D-11H-5, 20	99.61	2.6	1.71	1.40			
679D-11H-6, 20	101.11	0.9	0.76	0.65			
679D-12H-1, 20	103.11			0.25			
679D-12H-2, 20	104.20	11.1	2.24	0.91	35.12	4.74	1.62
679D-13X-1, 18	104.59	5.5	2.78	2.11	36.45	4.81	1.58
679D-13X-2, 18	106.09	9.7	2.45	1.29			
679D-14X-1, 18	114.09	3.2	1.50	1.12			
679D-14X-2, 18	115.59	3.7	1.90	1.46			
679D-15X-1, 20	123.61	0.0	1.08	1.08			
679D-17X-1, 38	142.79	3.1	0.95	0.58			
679D-17X-2, 38	144.29	1.7	0.91	0.71			
679D-18X-1, 15	152.06	12.5	2.90	1.40			
679D-18X-2, 15	153.56		1.98				
679D-18X-3, 15	155.06		1.62				

Table 3. Mean organic-carbon values and mass accumulation rates of total organic carbon at Hole 679D.

Cores	Depth (mbsf)	Age*	SR*	WBD*	PO*	TOC		MARTOC	
						Range	Mean	Range	Mean
1. 1H–7H	0–64.9	Quaternary	14	1.3	82	1.5–7.8	4.0	0.10–0.50	0.26
2. 8H–10H	64.9–93.4	e. Pliocene	1.5	1.3	80	1.5–6.5	4.7	0.01–0.05	0.03
3. 11H–13X	93.4–113.9	e. Pliocene	1.5	1.6	68	0.3–2.4	1.2	0.004–0.03	0.02
4. 14X–18X	113.9–161.4	l. Miocene	8	1.5	73	0.6–1.5	1.1	0.04–0.09	0.07

SR = Mean sedimentation rate (cm/k.y.); WBD = Wet bulk density (g/cm^3); PO = Porosity (%); TOC = Total organic carbon (%); MARTOC = Mass accumulation rates of total organic carbon (gC/cm^2/k.y.).
*From Suess, von Huene, et al. (1988).

(Table 1); however, this phenomenon cannot be attributed simply to an intensification of upwelling because diagnostic diatom and coccolith upwelling assemblages are rare in lithologic Unit III (Suess, von Huene, et al., 1988, Site 684 chapter).

Mass Accumulation Rates of Organic Carbon

Changes in the percentages of organic carbon can result from changes in the supply of both mineral components and organic carbon. Hence, it is difficult to interpret an organic-carbon record, as shown in Figure 2 for Hole 679D. Therefore, the values were converted into mass accumulation rates (Table 3), following the equation developed by van Andel et al. (1975); MARTOC = TOC/100 * SR * (WBD—1.025 PO/100), where MARTOC = mass accumulation rate of total organic carbon (g/cm^2/k.y.), TOC = total organic carbon (%), SR = mean sedimentation rate (cm/k.y.), WBD = wet bulk density (g/cm^3), and PO = porosity (%). Using mass accumulation rates, dilution effects by inorganic components can be excluded, and the carbon data can be interpreted in terms of changes in supply or preservation of organic matter.

The mass accumulation rates of organic carbon were calculated for four time intervals at Hole 679D (Table 3). The late Miocene and early Pliocene intervals are characterized by low mean accumulation rates of 0.02 to 0.07 gC/cm^2/k.y. During Quaternary time, accumulation rates increased to an average value of 0.26 gC/cm^2/k.y. (range between 0.1 and 0.5). These latter rates are higher than the late Miocene and the early Pliocene values by factors of about 3 and 10, respectively. Quaternary values are similar to those calculated for the same time interval in sediments from the Northwest African upwelling area (Site 658; Stein et al., in press). However, a comparison with the organic-carbon accumulation rates determined by Reimers and Suess (1983) for Holocene sediments from the Peru upper slope (0.5 to 6.3 gC/cm^2/k.y.) shows that the Quaternary values at Hole 679D are relatively low. In the study of Reimers and Suess (1983), Holocene sedimentation rates could be determined much more accurately than was possible at Site 679, due to the availability of ^{210}Pb activity profiles. These sedimentation rates are as high as 30 to 1200 cm/k.y., resulting in the very high organic-carbon accumulation rates. Recalculation of the accumulation rates of organic carbon for the youngest interval of Site 679 may eventually lead to higher values, when better estimates of the sedimentation rates are available for this sequence.

The atomic H/C ratios are about 1.5 (range 1.33 to 1.73) throughout the sediment sequence (Fig. 3; Table 2) and can be interpreted to indicate a dominantly marine origin of the organic matter. Such an origin is corroborated by high hydrogen-index (HI) values (Table 1) and the composition of the extractable lipids. Thus, the accumulation rates of total organic carbon represent the accumulation of marine organic carbon. In general, high amounts of marine organic carbon

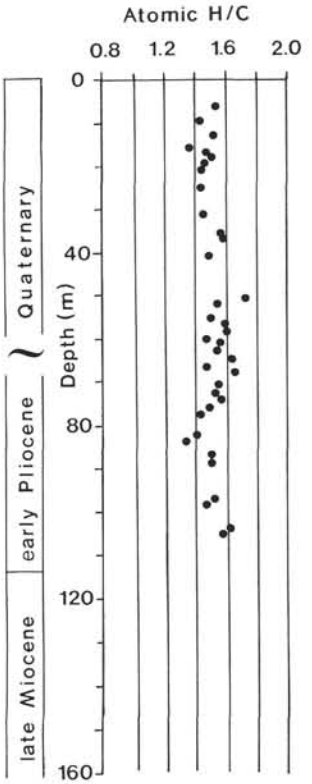

Figure 3. Atomic H/C ratios of kerogen concentrates from sediments of Hole 679D (see Table 2).

can be accumulated in high-productivity (e.g., upwelling) areas and/or in oxygen-deficient environments, characterized by a high preservation rate of organic matter. According to the organic carbon/sedimentation rate diagram (Fig. 4), we suggest a distinct increase in paleoproductivity during Quaternary time as the major cause of the high content of marine organic carbon. Furthermore, high-amplitude variations in accumulation of organic carbon may imply short-term fluctuations in the magnitude of productivity, probably caused by changes in coastal upwelling intensity during Quaternary time (for a detailed study of these short-term, climate-induced changes in paleoproductivity, see Wefer and Suess, this volume).

The upper part of the early Pliocene at Hole 679D (interval 2 in Table 3) is characterized by high values of (marine) organic carbon and very low sedimentation rates (also low accumulation rates; Fig. 4). This may indicate special conditions leading to an enhanced preservation of organic matter, e.g., oxygen depletion in the water column from restricted circulation (cf. Stein, 1986). Thus, a large amount of marine organic matter could be preserved, although the sedimentation rate was very low.

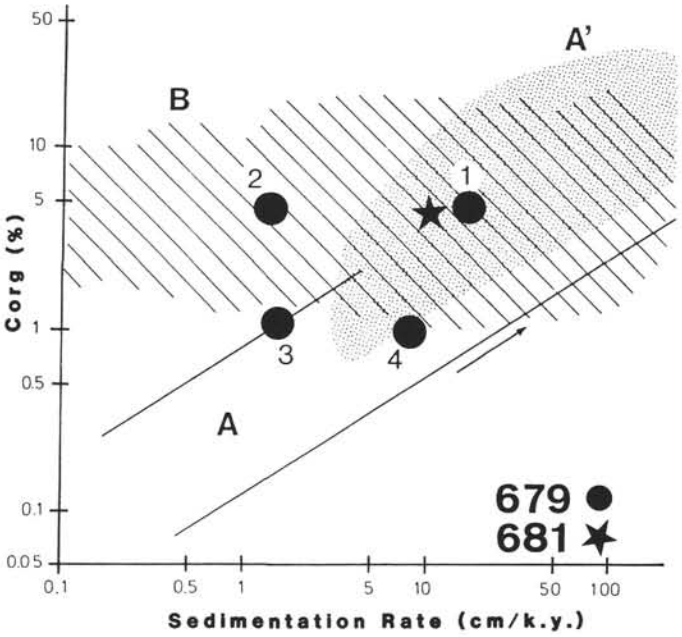

Figure 4. Organic carbon/sedimentation rate relationship (adapted from Stein, 1986). A = Open-marine oxic environment. A'= High productivity field. B = Anoxic environment. Numbers 1 to 4 refer to Table 3.

Organic Petrography

Particles visible with a microscope (macerals in the organic-matter fraction of the sediments) include vitrinite, inertinite, and sporinite, all probably derived from higher land plants, as well as alginite, liptodetrinite, and large unstructured liptinite of marine origin. Alginites are defined here as brightly fluorescing, discoid particles that appear as long stripes in sections perpendicular to bedding. Liptodetrinites are defined as small fluorescing particles of irregular shape; most of these particles are probably related to alginite. Unstructured liptinites are large, brightly fluorescing particles sometimes occurring within fossil shells, e.g., in foraminifers. The bulk of the unstructured liptinites appear as ring-shaped particles having a diameter of less than 10 μm. The inner part of these particles generally is devoid of fluorescing material ("empty"). Relative percentages of the above-described macerals are listed in Table 4.

One of the most striking organic-matter characteristics in the sediments from the Peru upwelling area is the small particle size. Nearly all the alginites and liptodetrinites are smaller than 10 μm. With respect to the high organic-carbon values (Table 1) and the small percentages of detectable macerals in most samples, we conclude that the bulk of this organic matter is not visible by light microscopy, i.e., most organic particles are smaller than 1 μm. The size of vitrinites and inertinites depends on the fragmentation of organic clasts from higher land plants during transportation and potentially can be used as an indicator for the distance from land where the clasts originated (Stein et al., 1988). The size of vitrinites and inertinites in samples from Site 679 does not exceed 15 μm. The average diameter increases slightly from the youngest Quaternary sediments toward the lower Pliocene section. Organic particles at Site 681 are up to 30 μm in diameter throughout the whole section. The size of vitrinites and inertinites at Site 684 generally is less than 20 μm, but particles up to 80 μm long occur in Sample 112-684C-2H-4, 30–37 cm. The difference in size between organic clasts at Sites 679 and 681 probably reflects the distance from the coast (Fig. 1).

Because of the small percentage of organic matter that can be identified microscopically, the maceral composition is hardly reflected by bulk geochemical parameters. For instance, this is illustrated by a diagram showing the HI as a function of the relative amount of terrigenous macerals (Fig. 5). No negative correlation occurs between these two parameters, although organic matter of terrestrial origin is generally hydrogen-poor. However, such a correlation has been observed for other marine sediments in which most of the

Table 4. Percentages of identifiable macerals in the organic geochemistry samples.

Core, section, interval (cm)	Vitr.	Inert.	Algin.	Li-detr.	unstr. Lipt.	Spor.	Remarks
112-679C-1H-1, 30–37	16	38	24	7	15	0	
679C-1H-6, 133–140	15	38	7	1	37	0	Foraminifers
679C-2H-4, 30–37	13	32	38	6	9	0	Diatoms
679C-3H-4, 30–37	5	43	35	6	9	1	
679C-4H-4, 30–37	0	54	20	5	21	0	Diatoms
679C-5H-4, 30–37	8	56	24	2	10	0	
679C-6H-4, 30–37	0	12	38	9	41	0	
679C-7H-4, 30–37	0	0	48	10	41	0	
679C-8H-2, 30–37	2	8	35	8	47	1	
679C-8H-6, 30–37	6	15	6	4	68	0	
681C-1H-1, 30–37	12	23	8	1	55	0	
681C-2H-1, 30–37	7	13	60	5	14	0	
681C-2H-6, 5–12	15	17	20	1	47	0	
681C-3H-4, 30–36	25	34	31	6	3	0	
681C-4H-4, 30–36	17	20	8	6	45	3	Diatoms
681C-5H-4, 32–38	7	25	54	11	4	0	
681C-7H-4, 30–37	12	24	3	1	60	0	Coarse sedim.
681C-8H-4, 30–37	11	35	12	3	37	2	
681C-9H-4, 30–37	24	38	3	1	34	0	Coarse sedim.
681-10H-4, 30–37	24	40	7	3	26	0	
684C-1H-1, 30–37	0	28	13	0	56	2	
684C-1H-4, 30–37	15	42	4	2	36	0	
684C-2H-4, 30–37	23	50	0	0	26	0	Foraminifers
684C-3H-1, 30–37	15	28	16	9	31	0	
684C-3H-6, 30–37	4	20	14	15	45	2	Diatoms
684C-4H-3, 30–37	5	38	13	17	25	0	
684C-4H-7, 30–37	8	54	12	6	20	0	

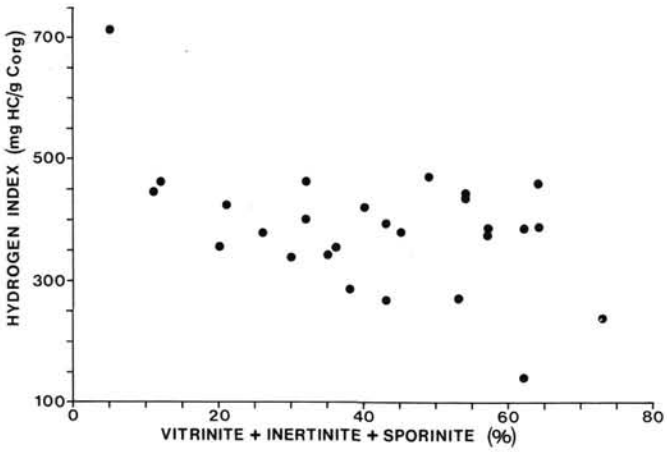

Figure 5. Cross plot of relative percentage of continent-derived macerals (vitrinite, inertinite, sporinite) vs. hydrogen index (HI) of organic matter.

organic matter is visible microscopically (e.g., Rullkötter et al., 1984; Stein et al., 1986). The high H/C ratios (Fig. 3; Table 2) point to a dominance of marine organic matter at Site 679. Clearly, volume percentages of pyrite are higher than those of total macerals. The ratio of pyrite to macerals exceeds ratios often observed in other marine black shales (e.g., Littke and Rullkötter, 1987). We interpret this as further supporting evidence for the hypothesis that most of the organic material is submicroscopically small.

A particular clue to the nature and mode of occurrence of the organic matter in samples from Leg 112 was obtained through the kerogen separation procedure using hydrochloric and hydrofluoric acid. Several samples were hardly affected by this procedure, i.e., little mass was lost and the residue contained not much more organic carbon than the starting material. This may be because finely disseminated organic matter impregnates some of the calcite and silicate particles and thus protects them from being destroyed by the acids.

Lipid Geochemistry

A total of 27 sediment samples (Table 1) were extracted, and these extracts divided into two parts. After derivatization, one part, the so-called total lipid fraction, was directly analyzed using GC and GC-MS. The other part was separated by medium pressure liquid chromatography (MPLC) into nonaromatic hydrocarbons, aromatic hydrocarbons, and heterocompounds. The heterocompound fractions of 14 samples were separated further by MPLC into alcohol, ester plus ketone, acid, base, and highly polar fractions. The alcohol, ester plus ketone, and acid fractions and, in one case, the highly polar fraction were analyzed using GC and GC-MS after appropriate derivatization. Extract yields and relative abundances of these compound classes, based on liquid chromatography, are given in Table 5. The compound classes are discussed separately, followed by a discussion of the total lipid fraction.

Nonaromatic Hydrocarbon Fraction

This class of compounds is mainly composed of a series of *n*-alkanes that range from *n*-C_{14} to *n*-C_{36} and show a strong odd-over-even carbon number preference of the higher homologs, with *n*-C_{31} as the most abundant alkane. Such a distribution is characteristic of terrigenous organic matter (Eglinton and Hamilton, 1963), but the nonaromatic hydrocarbon fraction alone cannot be used to estimate the relative amount of terrigenous organic matter in the sediments because other biogenic sources do not contribute major quantities of *n*-alkanes (cf., ten Haven et al., 1989).

Among the polycyclic nonaromatic hydrocarbons, sterenes, steradienes (C_{27} dominating; I, II), hop-17(21)-ene (III), 17β(H),21β(H)-homohopane (IV) and fern-7-ene (V) are ubiquitously present. The former two groups of compounds

Table 5. Extract yields and relative abundance of compound classes.

Core, section, interval (cm)	Extract (mg/g C_{org})	N. arom. (%)	Arom. (%)	Hetero (%)	Ketone (%)	Alcohol (%)	Acid (%)	Base (%)	H. polar (%)
112-679C-1H-1, 30–37	77	8	3	(89)	15	12	2	5	55
679C-1H-6, 133–140	19	9	4	87			—n.d.—		
679C-2H-4, 30–37	59	2	2	(96)	13	8	11	6	58
679C-3H-4, 30–37	48	4	2	94			—n.d.—		
679C-4H-4, 30–37	75	4	2	(94)	35	20	7	14	18
679C-5H-4, 30–37	54	5	1	94			—n.d.—		
679C-6H-4, 30–37	42	1	2	(97)	19	7	7	8	56
679C-7H-4, 30–37	54	12	6	82			—n.d.—		
679C-8H-2, 30–37	48	5	2	(93)	16	10	4	5	58
679C-8H-6, 30–37	54	4	1	95			—n.d.—		
681C-1H-1, 30–37	76	3	1	(96)	16	11	5	26	38
681C-2H-1, 30–37	43	4	2	94			—n.d.—		
681C-2H-6, 5–12	16	13	3	(84)	14	8	3	18	41
681C-3H-4, 30–36	12	6	2	92			—n.d.—		
681C-4H-4, 30–36	14	2	3	(95)	22	13	3	21	36
681C-5H-4, 32–38	15	3	1	96			—n.d.—		
681C-7H-4, 30–37	42	2	1	(97)	6	1	2	31	57
681C-8H-4, 30–37	13	2	4	94			—n.d.—		
681C-9H-4, 30–37	12	5	2	(93)	10	6	5	31	41
681C-10H-4, 30–37	18	5	2	93			—n.d.—		
684C-1H-1, 30–37	17	6	1	(93)	10	5	3	36	39
684C-1H-4, 30–37	14	4	1	95			—n.d.—		
684C-2H-4, 30–37	18	4	1	(95)	15	3	13	37	27
684C-3H-1, 30–37	12	5	2	93			—n.d.—		
684C-3H-6, 30–37	12	7	2	(91)	23	10	5	9	44
684C-4H-3, 30–37	11	4	3	93			—n.d.—		
684C-4H-7, 30–37	14	8	2	(90)	21	12	3	25	29

Note: Relative abundances are normalized to 100%, hence loss of material during work-up procedures was not taken into account. This loss is most pronounced for the highly polar fraction. n.d. = not determined.

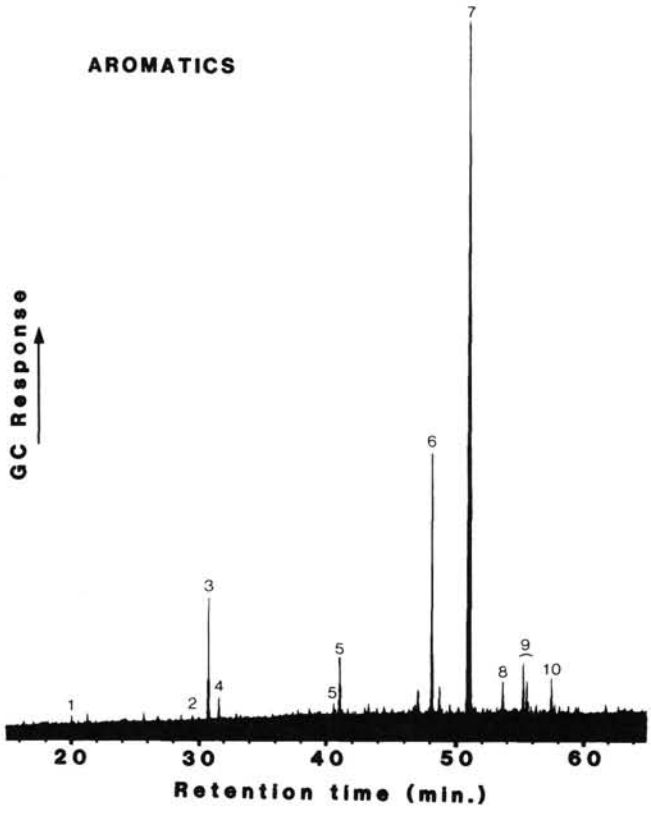

Figure 6. Partial gas chromatogram of the "aromatic hydrocarbon" fraction of Sample 112-684C-4H-7, 30–37 cm. Identification of numbered compounds is given in Table 6.

are derived from algae/phytoplankton sources (e.g., Volkman, 1986), while the latter three groups presumably have a bacterial origin (e.g., Brassell et al., 1981; Ourisson et al., 1984). In addition, a compound with a molecular ion at m/z 368 and characteristic fragments at m/z 147 and 191 is present in all samples. We have tentatively identified this compound as a trisnorhopene.

Interestingly, no traces of the highly branched C_{20}- and C_{25}-alkenes were observed, potential biological markers of diatoms (Nichols et al., 1988), although these compounds are present in high abundance in surface sediments at 15°S (Volkman et al., 1983; Farrington et al., 1988). However, these authors noted a strong decrease in concentration with depth (within 30 cm) of these labile compounds, which may explain their absence in our samples. A possible sink for these compounds is a reaction with H_2S or polysulfides with the formation of the sulfur-bearing derivatives (Sinninghe Damsté et al., 1989).

Aromatic Hydrocarbon Fraction

An example of a gas chromatogram of the aromatic hydrocarbon fraction of a sediment extract from Site 684 is given in Figure 6. The identified compounds are listed in Table 6. Perylene (7; VI), a pentacyclic aromatic hydrocarbon is the most abundant compound in most of the samples studied. The precursor of this compound is still a matter of debate, but must be omnipresent, judging from the widespread occurrence of perylene in the geosphere. Preliminary quantitative results indicate that its concentration increases with depth, which is in accordance with the suggestion that perylene is formed during early diagenesis under reducing conditions (see Gschwend et al., 1983, and references therein). A methylated

Table 6. Compounds identified in the aromatic hydrocarbon fraction of Sample 112-684C-4H-7, 30–37 cm (Fig. 6).

	M	BP	Struct.*
1. 2-ethyl-5-decyl-thiophene or isoprenoid thiophene	252	125	
2. 2-methyl-5-tridecyl-thiophene	280	111	
3. 3-methyl-2-(3,7,11-trimethyldodecyl)-thiophene	308	111	VIII
4. 3-(4,8,12-trimethyltridecyl)-thiophene	308	98	IX
5. monocyclic disulfides**	344	57	
6. monocyclic trisulfide**	376	57	
7. perylene	252	252	VI
8. 2-methylperylene	266	266	
9. B-ring monoaromatic 14β(H)-C_{27} anthrasteroid	366	211	VII
10. B-ring monoaromatic Δ^{N}-C_{28} anthrasteroid	378	211	

*See Appendix for molecular structures.
**Tentative identification.

perylene (8) was also present, and the methyl group is most likely located at position 2 of the aromatic ring system (Garrigues et al., 1988). Other aromatic hydrocarbons include C_{27} (9; VII), C_{28} and C_{29} B-ring monoaromatic anthrasteroids (C_{27} dominating). The C_{27} member also was found by Farrington et al. (1988) in a surface sediment from the Peru margin at 15°S. Compound 10 presumably is a C_{28} B-ring aromatic anthrasteroid with an additional double bond. The mass spectrum of this compound is presented in Figure 7A and shows the typical fragment ions of a C_{28} B-ring aromatic anthrasteroid, but the molecular ion and the common key fragment at m/z 251 have been shifted by two daltons to lower values, indicating the presence of an additional double bond.

The remainder of the aromatic hydrocarbon fraction is composed of several organic sulfur compounds, of which two C_{20} isoprenoid thiophenes (3, 4; VIII, IX) and an unknown sulfur compound (6) are most abundant. Isoprenoid thiophenes have been found in numerous marine sediments and are presumed to be diagenetic products of early sulfur incorporation into chlorophyll-derived phytol, or into diagenetic transformation products of phytanyl moieties from archaebacteria (Brassell et al., 1986; Rullkötter et al., 1988; in press). Several sulfur compounds (e.g., 5) with as yet unknown structures are present. These compounds have a molecular ion at m/z $330+14n$ (n = 0, 1, 2). All these compounds show a characteristic fragment of M^+-33 (M^+-SH) and, based on the response of the sulfur-selective flame photometric detector (FPD), they contain two sulfur atoms. Thus, the elemental composition is $C_nH_{2n}S_2$ (n = 19, 20, 21), which can be tentatively ascribed to alkyl- or isoprenoid monocyclic disulfides. In this respect, one should mention that Ciereszko and Youngblood (1971) reported the presence of *n*-hexadecyl and *n*-octadecyl disulfides (R'-S-S-R) in an artificially prepared sediment from the gorgonian *Pseudoplexaura porosa*. The mass spectrum of the most abundant unkown compound (6) is presented in Figure 7B. The molecular ion of m/z 376, and the ions at m/z 344 (M^+-S), and m/z 311 (344-SH), combined with the response signal of the FPD, indicate that we are dealing with an alkyl- or isoprenoid monocyclic trisulfide. The structural elucidation of these novel organic sulfur compounds is the subject of current investigation in collaboration with the Organic Geochemistry Unit of the Delft University of Technology (The Netherlands).

In a few samples, traces of two isomeric highly branched isoprenoid C_{25} thiophenes (X) were observed; these may result when sulfur is incorporated into corresponding olefinic dienes. These compounds have been proposed as potential

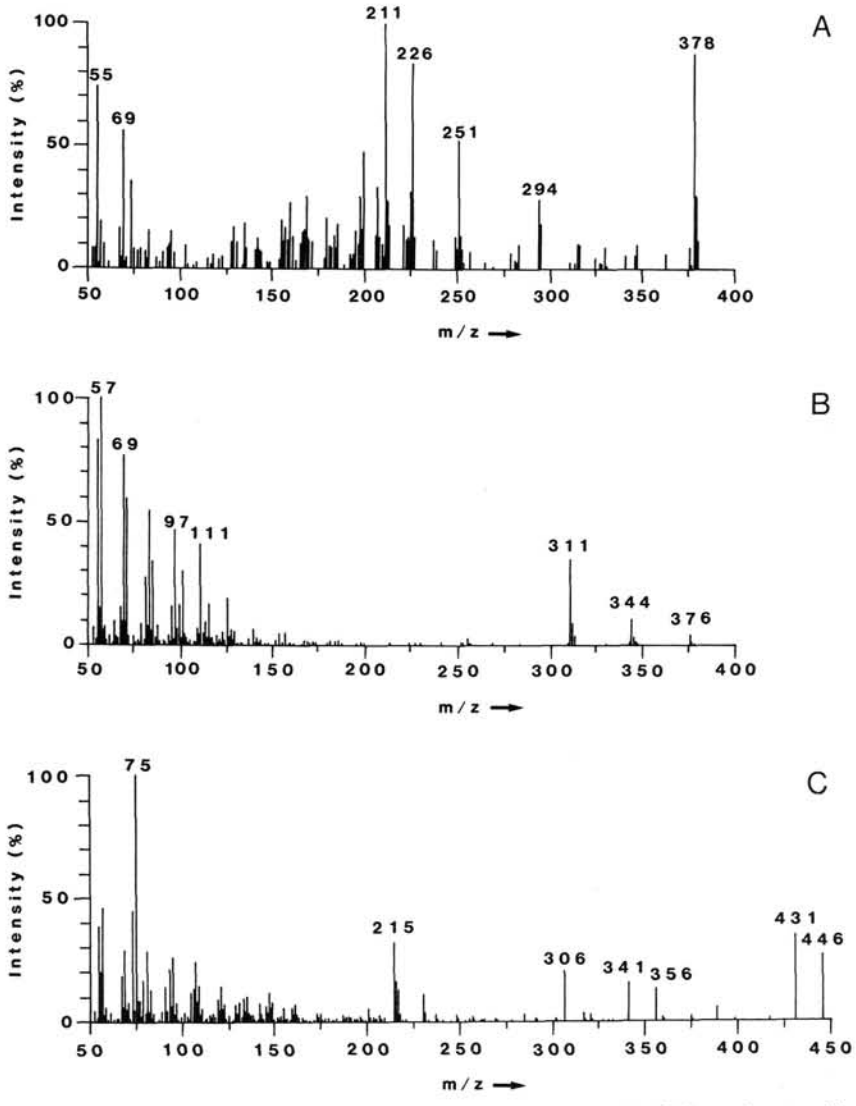

Figure 7. Mass spectra of compounds tentatively identified as (A) Δ^n-C_{28} anthrasteroid, (B) monocyclic trisulfide, and (C) 24-nor-5α(H)-cholestan-3β-ol.

biomarkers for diatoms (Sinninghe Damsté et al., 1989). They were observed as the most important compounds of the aromatic hydrocarbon fraction of various deep-sea sediments (Rullkötter et al., in press), and thus, their low abundance in the Peru margin sediments, despite the abundance of diatoms, is puzzling. Volkman et al. (1983) described the presence of highly branched alkenes in surface sediments from the Peruvian upwelling. Most of these compounds were trienes, and perhaps the double bonds were not in the right position to result in C_{25} thiophenes. An alternative explanation is that the sulfur compounds are present in the heterocompound fraction, cross-linked to higher-molecular-weight substances and only liberated during a later stage of diagenesis.

Carboxylic Acid Fraction

Saturated straight-chain C_{16} and C_{18} fatty acids, which have no diagnostic value because of their widespread occurrence in the biosphere, are the most abundant compounds here. Longer straight-chain fatty acids (C_{20}–C_{26}), maximizing at C_{22}, are present in trace amounts. No unsaturated or polyunsaturated fatty acids were observed, although such compounds were found by Smith et al. (1983a, 1983b) and Wakeham et al. (1983) in a surface sediment and in particulate matter, respectively. These authors saponificated the extract before the isolation of the acid fraction, and, hence, the mode of occurrence of these unsaturated fatty acids (e.g., free or esterified) is not known. Moreover, such compounds are highly labile, and, therefore, their absence in the extractable lipids of older deep-sea sediments is not surprising.

Ketone and Ester Fraction

The most important compounds of this fraction are C_{37} (3, 4; XI) and C_{38} (5, 6, 8, 9) di- and triunsaturated ketones (Fig. 8; Table 7), for which an origin from Prymnesiophyte algae (especially *Emiliania huxleyi* in late Quaternary sediments) has been presumed (e.g., Volkman et al., 1980; Marlowe et al., 1984). Other components are C_{39} unsaturated ketones (10, 11), 6,10,14-trimethylpentadecan-2-one (not shown in Fig. 8), hopanoid ketones (7; XIII), and a variety of steroid ketones, including C_{27}–C_{29} steran-3-ones, cholesta-3,5-dien-7-one, C_{28}–C_{30} 4-methylsteran-3-ones, and 4α,23,24-trimethylcholest-22-en-3-one (1; XIV; dinosterone). All these compounds originated from marine planktonic organisms, with the exception of the hopanoid ketones, which can be assigned to a bacterial

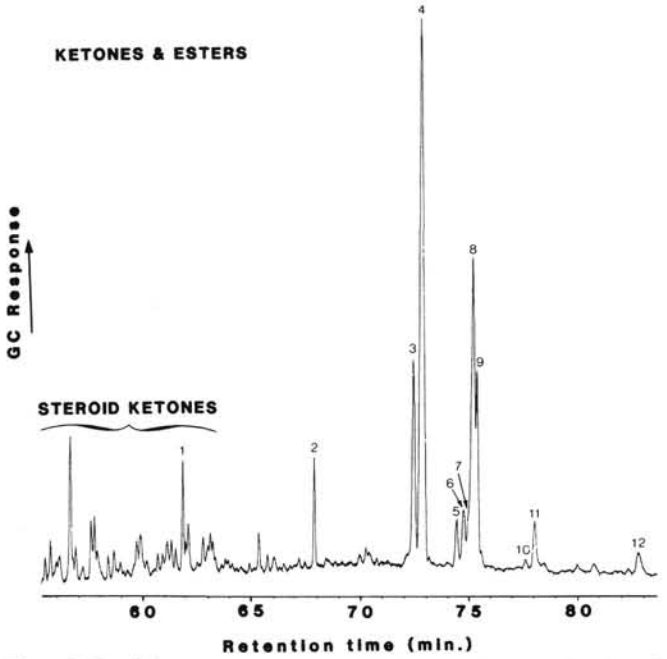

Figure 8. Partial gas chromatogram of the ketone plus ester fraction of Sample 112-681C-1H-1, 30–37 cm. Identification of numbered compounds is given in Table 7.

Table 7. Compounds identified in the ketone plus ester fraction of Sample 112-681C-1H-1, 30–37 cm (Fig. 8).

	M+	BP	Struct.*
1. 4α,23,24-trimethylcholest-22-en-3-one (dinosterone) or 4α-methyl,24-ethylcholest-22-en-3-one	426 426	69 69	XIV
2. 17β(H),21β(H)-hopan-30-oic methylester	456	235	XV
3. heptatriaconta-8(E),15(E),22(E)-trien-2-one	528	55	XI
4. heptatriaconta-15(E),22(E)-dien-2-one	530	55	
5. cluster of C_{38} diunsaturated wax esters** and octatriaconta-9(E),16(E),23(E)-trien-3-one	560 542	55 55	
6. octatriaconta-9(E),16(E),23(E)-trien-2-one	542	55	
7. 17β(H),21β(H)-trishomohopan-32-one	468	247	XIII
8. octatriaconta-16(E),23(E)-dien-3-one	544	55	
9. octatriaconta-16(E),23(E)-dien-2-one	544	55	
10. nonatriaconta-10(E),17(E),24(E)-trien-3-one	556	55	
11. nonatriaconta-17(E),24(E)-dien-3-one	558	55	
12. cluster of C_{40} saturated wax esters	592	57	e.g., XII

*See Appendix for molecular structures.
**Tentative identification.

origin. More specifically, dinoflagellates are a likely source for the 4-methyl steroid ketones (e.g., Brassell et al., 1983).

Several compounds having an ester group have been observed, of which 17β(H),21β(H)-hopan-30-oic acid methyl ester (2; XV), a cluster of C_{40} (12), and a cluster of putative diunsaturated C_{38} wax esters are most abundant among the GC amenable esters. We cannot exclude the possibility that the hopanoid ester is an artifact of our work-up procedure, during which we applied methanol. Thus, the mode of occurrence of this compound may be that of an acid. The mass spectrum of the cluster of C_{40} wax esters (12) is almost identical to that published by Boon and de Leeuw (1979). We conclude from the intensity distribution of typical fragment ions that a C_{40} wax ester (XII) having a C_{16} fatty acid and a C_{24} alcohol moiety is the most important isomer. Although the capillary column used for GC analysis was not ideally suited for analyzing wax esters, clearly the distribution in sediments differed from the distribution in particulate matter from the

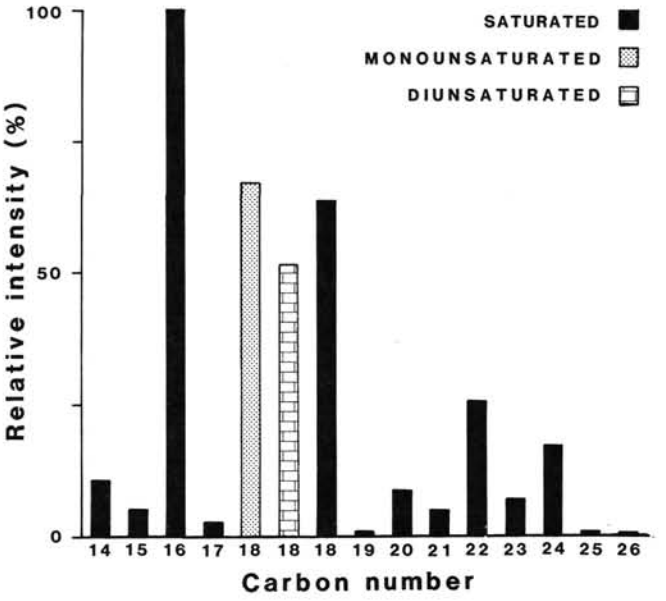

Figure 9. Bar graph showing the distribution of saturated and unsaturated straight-chain fatty acids obtained after saponification of the ketone plus ester fraction of Sample 112-679C-1H-1, 30–37 cm.

water column, as reported by Wakeham (1985) and Wakeham et al. (1983). In particulate matter off the coast of Peru, wax esters maximize either at C_{30}, C_{32}, or C_{34}, whereas in the studied sediment the maximum is at C_{38} or C_{40}. This latter distribution is similar that reported by Boon and de Leeuw (1979) for sediments deposited under the upwelling cell of Walvis Bay.

To substantiate the tentative identification of a diunsaturated C_{38} wax ester (5) and to look for the presence of steryl esters, which are not GC amenable, the ketone plus ester fraction of Sample 112-679C-1H-1, 30–37 cm, was saponified with KOH under reflux. The resultant extract was separated by MPLC into a ketone, an alcohol, and an acid fraction, all of which were analyzed by GC and GC-MS after appropriate derivatization. The distribution of the ester-bound fatty acids is given in Figure 9. The C_{16} saturated fatty acid is the most abundant acid, followed by a saturated, a monounsaturated, and a diunsaturated C_{18} fatty acid. No isoprenoid acids were observed. The highest homolog is the C_{26} fatty acid, which agrees well with the maximum chain length of the acid moiety of wax esters, as determined by Boon and de Leeuw (1979). The presence of an abundant C_{18} diunsaturated fatty acid corroborates to some extent our identification of the diunsaturated C_{38} wax ester. However, one must keep in mind that a large part of the fatty acids may come from steryl esters, which can, for instance, have a C_{16} acid moiety (e.g., Brassell et al., 1983).

The ester-bound alcohol fraction contains a series of saturated straight-chain alcohols (C_{14}–C_{28}) and a variety of sterols. The C_{16} and C_{18} members are the most important compounds among the n-alkanols, but are unimportant in comparison with sterols. The maximum chain length (C_{28}) is in accordance with the maximum chain length of the alcohol moiety of wax esters, as determined by Boon and de Leeuw (1979). The sterols have a variety of carbon skeletons (C_{26}–C_{30},), with various levels of unsaturation and almost exclusively without alkylation at C-4. A partial gas chromatogram showing the distribution of bound alcohols is given in Figure 10, and the identified peaks are listed in Table 8. Cholesta-5,22-dien-3β-ol (10; XVI), cholest-5-en-3β-ol (13) and 24-ethylcholest-5-en-3β-ol (26; XVII) are

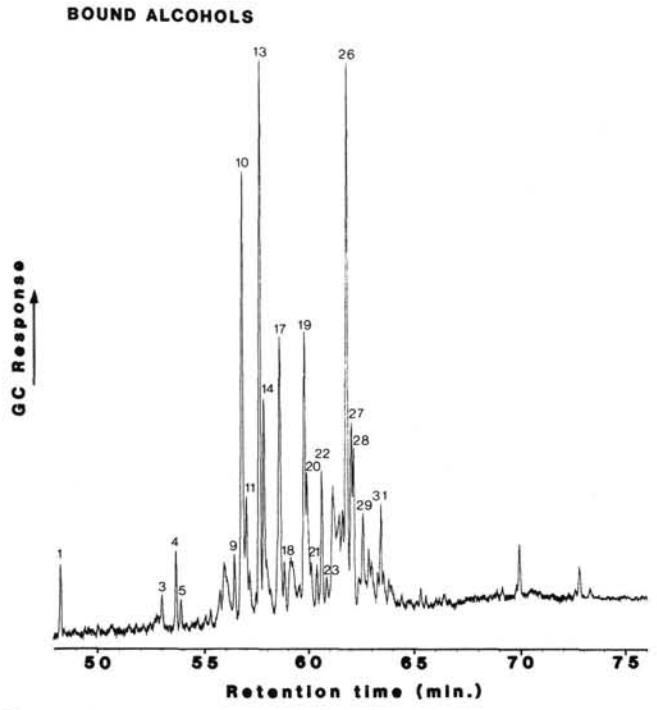

Figure 10. Partial gas chromatogram of the ester-bound alcohol fraction of Sample 112-679C-1H-1, 30–37 cm. Identification of numbered compounds is given in Table 8.

the most important compounds of the bound alcohol fraction. Only one 4-methyl sterol was found (4α,23,24-trimethylcholest-22-en-3β-ol;29; XVIII). A comparison of our results with those obtained from lacustrine sediments by Cranwell and Volkman (1981) shows that C_{27} sterols are much more abundant here, which we interpret as indicative of a marine origin for the sterol esters. There are, however, no published reports on the distribution of sterol esters in the Peru upwelling area. The dominance of ester-bound sterols over ester-bound straight-chain alcohols indicates that either sterol esters are more important than wax esters, or they are more resistant to degradation and, hence, enriched in relative quantities. However, this latter suggestion conflicts with the observation of de Leeuw et al. (1977) that sterol esters are rapidly hydrolyzed during early diagenesis.

Alcohol Fraction

Before discussing this fraction, we should mention that a comparison of the alcohols encountered in the alcohol fraction with those in the total lipid fraction revealed that alkan-15-on-1-ols were not recovered completely and that alkandiols were totally lost during the MPLC separation (see discussion of total lipid fraction). No apparent loss was observed for other alcohols discussed hereafter.

Partial gas chromatograms of the free-alcohol fraction of two representative samples are shown in Figure 11. A wide variety of sterols was identified (Table 8), including relatively rare sterols such as 5β(H)-cholestan-3β-ol (7; XIX), 5β(H)-cholestan-3α-ol (8), and 5α(H)-cholestan-3α-ol (15; XX). One compound had mass fragmental characteristics (Fig. 7C), which are consistent with the trimethylsilyl ether of 24-nor-5α(H)-cholestan-3β-ol (6; XXI). Traces of Δ^7 sterols were also noted. The 4α,23,24-trimethylcholest-22-en-3β-ol (29; XVIII) is the dominating sterol in most samples, although sometimes 24-ethylcholest-5-en-3β-ol (26, XVII) or the tentatively identified 24-propyl-5α(H)-cholestan-3β-ol (32) occur as

Table 8. Alcohols identified as TMS-ethers in the bound-alcohol fraction (Fig. 10) and the free-alcohol fraction (Fig. 11).

	M+	BP	Structure*
1. tetracosanol	426	411	
2. pentacosanol	440	425	
3. hexacosanol	454	439	
4. 24-norcholesta-5,22-dien-3β-ol	442	97	
5. 24-nor-5β(H)-cholest-22-en-3β-ol	444	75	
6. 24-nor-5α(H)-cholestan-3β-ol*	446	75	XXI
7. 5β(H)-cholestan-3β-,OL and heptacosanol	460 468	370 453	XIX
8. 5β(H)-cholestan-3α-ol	460	370	
9. 27-nor-24-methylcholesta-5,22-dien-3β-ol	456	111	
10. cholesta-5,22-dien-3β-ol	456	129	XVI
11. 5α(H)-cholest-22-en-3β-ol	458	75	
12. octacosanol	482	467	
13. cholest-5-en-3β-ol	458	129	
14. 5α(H)-cholestan-3β-ol	460	75	
15. 5α(H)-cholestan-3α-ol	460	75	XX
16. 24-methyl-5β(H)-cholestan-3β-ol	474	75	
17. 24-methylcholesta-5,22-dien-3β-ol	470	69	
18. 24-methyl-5α(H)-cholest-22-en-3β-ol	472	69	
19. 24-methylcholesta-5,24(28)-dien-3β-ol	470	73	
20. 24-methylcholest-5-en-3β-ol	472	129	
21. 24-methyl-5α(H)-cholestan-3β-ol	474	75	
22. 24-ethylcholesta-5,22-dien-3β-ol	484	83	
23. 24-ethyl-5α(H)-cholest-22-en-3β-ol	486	257	
24. 4α,24-dimethyl-cholest-22-en-3β-ol	486	69	
25. tricontanol	510	495	
26. 24-ethylcholest-5-en-3β-ol	486	129	XVII
27. 24-ethyl-5α(H)-cholestan-3β-ol	488	75	
28. 24-ethylcholesta-5,24(28)-dien-3β-ol	484	73	
29. 4α,23,24-trimethyl-5α(H)-cholest-22-en-3β-ol	500	69	XVIII
30. 24-propylcholest-5-en-3β-ol**	500	73	
31. 24-propylcholesta-5,24(28)-dien-3β-ol**	498	69	
32. 24-propyl-5α(H)-cholestan-3β-ol**	502	75	
33. two peaks: 4α,22,24-trimethyl-5α(H)-cholestan-3β-ol and/or 4α,23,24-trimethyl-5α(H)-cholestan-3β-ol	502 502	75 75	
34. triacontan-15-one-1-ol	524	509	
35. dotriaconten-15-one-1-ol**	550	535	
36. dotriacontan-15-one-1-ol	552	537	
37. tetratriacontan-15-one-1-ol	590	575	

*See Appendix for molecular structures.
**Tentative identification Table 9.

the most abundant compounds of this series. The 5α(H) stanols (e.g., 14, 21, 27) become more important with increasing burial depth. Dinoflagellates are the major source for the 4-methyl sterols (e.g., Boon et al., 1979; Robinson et al., 1984), and the feces and carcasses of fish and zooplankton for the cholest-5-en-3β-ol (Gagosian et al., 1983a, 1983b). Typical diatom-derived sterols, like 24-methylcholesta-5,22-dien-3β-ol (17) and 24-methylcholesta-5,24(28)-dien-3β-ol (19), also are present, although their relative abundance is not enhanced in samples having a high diatom content, observed under the microscope (Table 4). Sterol distribution is comparable to the distribution reported by Volkman et al. (1987), with the exception that dinosterol is relatively more enriched in the samples we have studied.

A significant difference can be observed in the abundance of C_{22}–C_{28} *n*-alkanols (Fig. 11). All four samples from the Pliocene section of Site 684 (Table 1) show this relative enrichment of continent-derived n-alkanols. An increased supply of wind-transported terrigenous organic matter to these four samples may be the reason for the high organic-carbon contents, which, as stated before, could not be attributed to an intensification of upwelling.

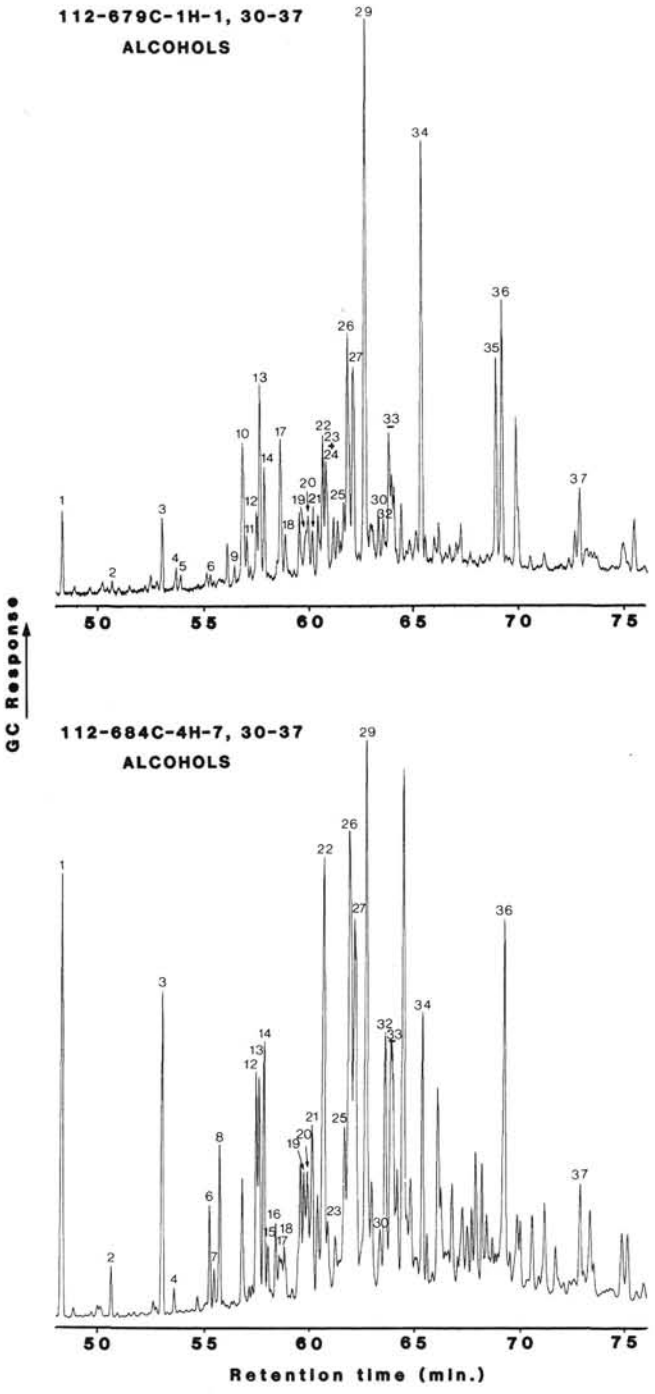

Figure 11. Partial gas chromatograms of the free alcohol fraction of Samples 112-679C-1H-1, 30–37 cm, and -684C-4H-4, 30–37 cm. Identification of numbered compounds is given in Table 8.

The distribution of hopanoid alcohols, as shown by an m/z 191 mass chromatogram, is similar to that reported by Volkman et al. (1987), i.e., a major C_{30} hopanol occurs in addition to small amounts of homohopan-31-ol and bishomohopan-32-ol. Volkman et al. (1987) tentatively identified this major compound as diplopterol, based on a mass spectrum of an acetate derivative. The mass spectrum that we obtained of the silylated compound is similar to that published by Venkatesan et al. (1987), who also ascribed the fragmentation as characteristic of diplopterol. However, we think this interpretation is erroneous because of the absence of the base peak fragment ion at m/z 131 [cleavage of side chain: $^{+}CMe_2(OSiMe_3)$] (cf. Bisseret et al., 1985; Zundel and Rohmer, 1985; ten Haven et al., 1987). Recently, we have shown that this compound is in fact tetrahymanol (ten Haven et al., 1989).

Highly Polar Fraction

Among the GC amenable compounds, loliolide (XXIII) and dihydroactinidiolide are important, next to several unknowns. Both are degradation products of carotenoids typically found in diatoms and dinoflagellates (Klok et al., 1984; Repeta and Gagosian, 1987).

Total Lipid Fraction

Partial gas chromatograms of the total lipid fraction of four samples are shown in Figure 12. In all samples, long-chain unsaturated ketones are the most important compounds (13, 14, 15; Table 9), even in sediments having a carbonate content of almost zero (Table 1). This latter observation may indicate that the calcareous nannoplankton *Emiliania huxleyi* is not a major contributor for this class of lipids in Peruvian sediments. The presence of *E. huxleyi* has been documented in today's Peru upwelling area, although its distribution is very patchy (Ryther et al., 1971). However, the age of most sediments investigated predates the first occurrence of *E. huxleyi*. Other algae from the class of Prymnesiophyte, including species not having formed coccoliths, are a more likely source for the long-chain ketones (cf. Marlowe et al., 1984). However, we cannot exclude that the calcareous nannoplankton record has been reduced by calcite dissolution and reprecipitation of dolomite.

The second most abundant group of compounds is composed of C_{30}- and C_{32}-alkandiols (9, 11), and C_{30}- and C_{32}-alkan-15-on-1-ols (10, 12). The 1,15-diol is the most important C_{30} member and the 1,13-diol the most important C_{32} member of the diols. The planktonic cyanobacterium *Aphemizomenon flos-aquae* may be a potential biological source (Morris and Brassell, 1988), but other sources cannot be excluded at present. Surprisingly, these compounds were not detected during the detailed studies of Smith and his coworkers (Smith, 1984; Smith et al., 1982, 1983a, 1983b, 1983c), despite their apparent abundance in Peruvian sediments (cf., Farrimond et al., this volume; Volkman et al., 1987). Other important compounds are sterols and, in some samples, *n*-alkanols, of which the details have already been discussed.

CONCLUSIONS

Drilling on the continental margin off Peru confirms that preservation of organic matter in deep-sea sediments is favored in areas of coastal upwelling. Although from the analysis of samples from only three sites one cannot expect the appropriate regional coverage, some distinct trends are obvious. Coastal upwelling at Site 679 apparently was strong during the Quaternary. However, mass accumulation rates of organic matter, in contrast to our expectations, were not higher than those in the Northwest African upwelling area. Values for the Peru margin may have to be revised toward higher accumulation rates when more precise sedimentation rates become available for this time interval. High organic-carbon contents in the early Pliocene at the same site coincide with low sedimentation rates and, thus, cannot be related to high surface-water bioproductivity in an upwelling cell. Although hard to imagine at present from a regional topography standpoint, reduced circulation of water masses may have been responsible for higher organic-carbon preservation during the early Pliocene at Sites 679. On the other hand, the

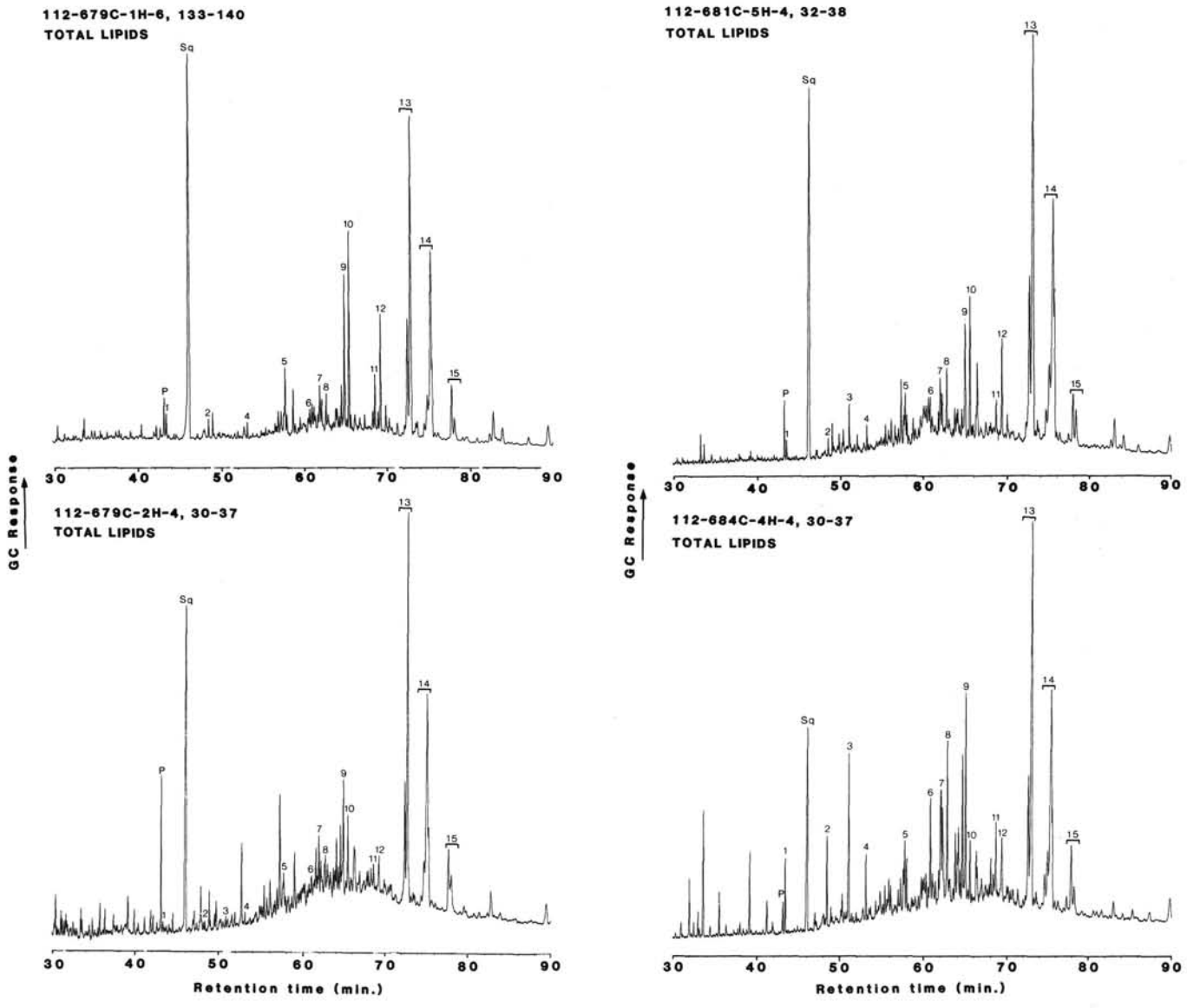

Figure 12. Partial gas chromatograms of the total lipid fraction of Samples 112-679C-1H-6, 133–140 cm, -679C-2H-4, 30–37 cm, -681C-5H-4, 32–38 cm, and -684C-4H-4, 30–37 cm. The amount of internal standard relative to weight of organic extract (squalane, indicated by Sq) is the same in all samples. Contamination by phtalate esters is indicated by P. Identification of numbered compounds is given in Table 9.

slope basin setting of Site 684 together with the strong increase of interstitial salts observed at this site (Suess, von Huene, et al., 1988; Site 684 Chapter) provide the possibility that a density stratification of the water column during Pliocene time led to a stagnant anoxic bottom water mass, which was then responsible for enhanced rates of organic-matter preservation.

The unusually small particle sizes of the organic matter in the Peru margin sediments indicate that fecal pellets, i.e., reworking in the food web, as well as anaerobic bacterial reworking and bacterial bioproductivity in surface sediments have a major influence on the organic facies. Molecular organic geochemical data on the extractable lipids confirm that marine planktonic organisms and bacteria are the main contributors to the sedimentary organic matter. Terrigenous material is subordinate, but over-represented among the larger macerals and in the nonaromatic hydrocarbon fractions (long-chain *n*-alkanes). Complexity of the preservation and transformation processes in the water column and in the sediment succession is reflected by lack of correlation between our data and published information on surface sediments and sediment trap material. Despite the details of the molecular composition of many compound classes documented in this study, any detailed conclusions may be premature. Several new compounds so far not reported in sediments were (tentatively) identified. The low relative abundance of organic sulfur compounds cannot be easily correlated with their significantly higher abundance in other organic-matter-rich deep-sea sediments. Particular emphasis will have to be placed on the relationship between the molecular composition of the extractable material and the distinct mode of occurrence of organic matter in the Peru margin sediments, i.e., this organic matter is finely disseminated and so closely mixed with the mineral matrix to the extent that the latter is even largely protected from destruction by strong mineral acids.

Table 9. Selected compounds identified in the total lipid fraction (Fig. 12).

Compound	Structure*
1. docosanol	
2. tetracosanol	
3. perylene	VI
4. hexacosanol	
5. cholest-5-en-3β-ol	
6. 24-ethylcholest-5,22-dien-3β-ol	
7. 24-ethylcholest-5-en-3β-ol	XVII
8. 4α,23,24-trimethylcholest-22-en-3β-ol	XVIII
9. triacontan-1,15-diol (also 1,13 and 1,14-diols)	
10. triacontan-15-one-1-ol	
11. dotriacontan-1,13-diol (also 1,14 and 1,15-diols)	
12. dotriacontan-15-one-1-ol	
13. C_{37} unsaturated ketones	e.g., XI
14. C_{38} unsaturated ketones	
15. C_{39} unsaturated ketones	

*See Appendix for molecular structures.

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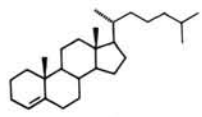
APPENDIX



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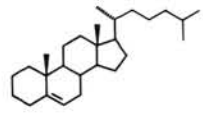

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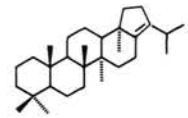

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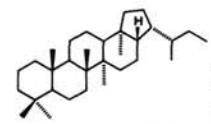

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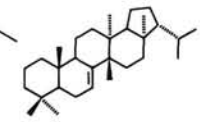
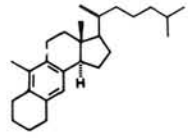


V. FERN-7-ENE

VI. PERYLENE



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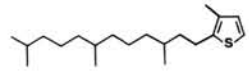
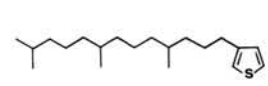
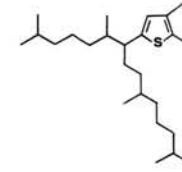


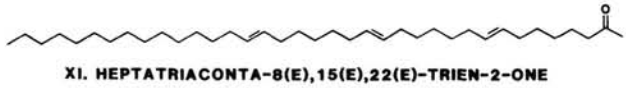
VIII. 3-METHYL-2-(3,7,11-TRIMETHYLDODECYL)-THIOPHENE



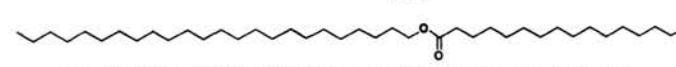
IX. 3-(4,8,12-TRIMETHYL-TRIDECYL)-THIOPHENE



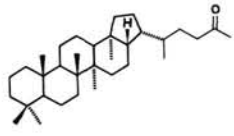
X. 2,3-DIMETHYL-5-(7'-(2',6',10',14'-TETRAMETHYL-PENTADECYL))-THIOPHENE



XI. HEPTATRIACONTA-8(E),15(E),22(E)-TRIEN-2-ONE



XII. TETRACOSANYL HEXADECANOATE (C24-C16 WAX ESTER)



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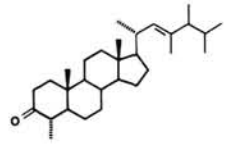

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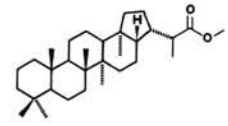
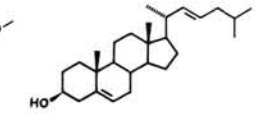


XV. 17β(H),21β(H)-HOPANOIC ACID METHYL ESTER



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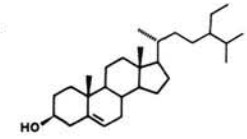

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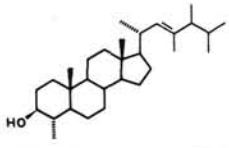

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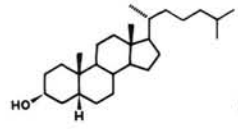
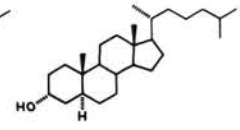


XIX. 5β(H)-CHOLESTAN-3β-OL



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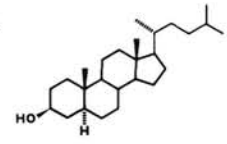

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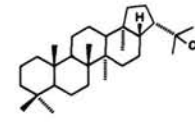

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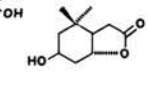

XXIII. LOLIOLIDE