30. DISTRIBUTION OF ORGANIC MATTER IN SEDIMENTS ALONG THE CALIFORNIA CONTINENTAL MARGIN[1]

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INTRODUCTION

As part of our continuing organic geochemical studies of sediments recovered by the Deep Sea Drilling Project, we have analyzed the types, amounts, and thermal alteration indices of organic matter in samples collected from the California continental margin on Leg 63 (Table 1). Some of the samples were frozen core; others were canned on site. Canned samples were analyzed for gas content (Table 2) using methods described by McIver (1972).

Our main objective was to see if the changes in surface circulation that had occurred through time off the California coast were reflected in changes in the type and amount of organic matter accumulating on the sea floor.

The samples fall into two groups: (1) the California Borderland group includes Site 467 in the San Miguel Gap (water depth = 2145 m) and Site 468 on the Patton Escarpment (water depth = 1752 m); (2) the other group, from the continental rise or deep sea, includes Site 469 at the foot of the Patton Escarpment (water depth = 3790 m), Site 470 near Guadalupe Island (water depth = 3750 m), Site 471 on the Baja continental slope (water depth = 3116 m), and Site 473 at the mouth of the Gulf of California (water depth = 3267 m) (Fig. 1). All samples are Cenozoic.

METHODS

After samples had been treated with warm, dilute HCl to remove carbonate minerals, the total organic carbon (here referred to as TOC) content of the samples was measured with a LECO carbon analyzer. Using a classification system described by Masran and Pocock (1979), we identified optically the different types of organic matter from slides prepared in the manner delineated by Staplin (1969).

TYPE AND AMOUNT OF ORGANIC MATTER

California Borderland (Site 467, 468)

At Site 468, the shallowest site, we analyzed one Pliocene(?) sample and four middle Miocene samples (Table 1). The younger sample is a nannofossil ooze that accumulated slowly at about 0.49 cm/1000 years; the older samples are diatomaceous silty clays that accumulated more rapidly at about 10 cm/1000 years. There is no change in organic facies (the assemblage of different types of organic matter) between the older and younger groups. Both are dominated by amorphous organic matter (probably marine-derived) with subordinate amounts of structured marine organic matter (Table 1).

At Site 467, Quaternary–upper Pliocene samples of diatomaceous silty clay have an average TOC content of 2.1%. The underlying middle Pliocene and upper Miocene sediments are lithologically similar but with a somewhat higher TOC content (averaging 3.9%). TOC content of the deepest upper Miocene sample reaches a maximum value of 7.8%. Below it are middle Miocene siliceous and calcareous silty claystones with an average TOC content of 2.3%. The organic-rich upper Miocene and younger facies are gassy and have velocities of 1.6 km/s; the middle Miocene facies contains less organic matter, is better cemented, less gassy, and has an average velocity of about 3.4 km/s. Rates of sedimentation change downcore from 7.5 cm/1000 years in the Quaternary, to 15 to 12.5 cm/1000 years in the Pliocene, to 5 cm/1000 years in the late Miocene and middle Miocene.

The three units defined by TOC content at Site 467 differ only slightly in organic facies. All are dominated by apparently marine-derived amorphous material. The youngest unit tends to have the most terrestrial material (pollen and spores, biodegraded and structured material), the middle unit has the most structured marine material, and the oldest unit has the least terrestrial material (Table 1).

Both of these shallow-water sites (Fig. 1) show a marked change in TOC from low values in the middle Miocene sediments to higher values in the younger sediments (Table 1).

Deep Continental Margin (Sites 469, 470, 471, 473)

Samples from relatively deep-water sites (i.e., water depth >3000 m) have TOC contents mostly less than 1% (averaging 0.9% for all samples analyzed). Amorphous organic matter is dominant. At Site 469, TOC content is lowest near the base of the section but slightly higher in the upper part of the section (Table 1). There is no enrichment in TOC in the upper Miocene, as at Site 467. From Site 470 we analyzed two samples, one upper Miocene, the other middle Miocene. Both are diatomaceous silty clays that accumulated at about 1.2 cm/1000 years and have low TOC contents (Table 1).

At Site 471, the TOC content is again moderately low (averaging 0.75%). Although there is a marked change in lithology (from porcelanites to turbiditic silty clays) and an attendant increase in sedimentation rate (from 2–5 cm/1000 years in the upper Miocene–Quaternary to 20 cm/1000 years in the middle Miocene), neither TOC content nor organic facies seem affected (Table 1).

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Table 1. Total organic carbon percents (TOC) and kerogen concentrations and thermal alteration indices (TAI) for samples from the California continental margin.

Site Hole No.	Core No.	Section	Interval (cm)	Depth below Sea Floor (m)	Chronostratigraphy	Total Organic Carbon (wt.%)	Kerogen Descriptions						
							Structured Marine	Amorphous	Pollen and Spores	Biodegradable Terrestrial	Structural Terrestrial	Coaly	TAI
467	7	5	Bottom	61.0	Quaternary	1.91	10	30	20	—	30	10	1+
467	8	4	Top	67.5	Quaternary-upper Pliocene	1.80	10	70	5	—	10	5	1+
467	9	2	Bottom	75.5	Quaternary-upper Pliocene	2.68	10	80	—	5	—	5	1+
467	9	3	Bottom	77.0	Quaternary-upper Pliocene	4.02	—	95	—	5	—	—	1+
467	9	4	Top	77.0	Quaternary-upper Pliocene	4.62	10	90	—	—	—	—	1+
467	10	5	Bottom	89.0	Pliocene	3.47	10	75	—	—	5	10	1+
467	11	1	Bottom	93.0	Pliocene	3.26	5	80	5	—	5	5	1+
467	11	3	Top	94.5	Pliocene	3.03	20	55	5	5	5	10	1+
467	11	4	Bottom	97.5	Pliocene	4.36	10	60	5	10	5	10	2−
467	13	1	Bottom	112.0	Pliocene	3.75	10	60	5	15	5	5	2−
467	13	5	Bottom	118.0	Pliocene	3.98	—	80	—	—	—	20	2−
467	14	1	Bottom	121.5	Pliocene	3.61	10	70	5	5	5	5	1+
467	14	2	Top	121.5	Pliocene	3.70	20	80	—	—	—	—	1+
467	14	2	Bottom	123.0	Pliocene	3.57	20	80	—	—	—	—	1+
467	14	3	Top	123.0	Pliocene	3.55	5	85	5	—	5	—	1+
467	16	1	Bottom	140.5	Pliocene	3.68	5	75	5	5	—	10	1+
467	16	2	Bottom	142.0	Pliocene	3.61	10	65	5	10	5	5	2−
467	18	1	Bottom	159.5	Pliocene	3.22	10	65	5	10	5	5	2−
467	18	2	Bottom	161.0	Pliocene	4.03	20	75	—	5	—	—	2−
467	18	4	Bottom	164.0	Pliocene	4.68	10	70	5	10	—	5	2−
467	26	1	Top	234.0	Pliocene	1.91	10	80	5	—	—	5	2
467	42	2	Bottom	392.0	Pliocene	4.13	10	90	—	—	—	—	2−
467	42	3	Bottom	393.5	Pliocene	3.93	10	90	—	—	—	—	2−
467	42	5	Top	398.0	Pliocene	4.03	10	90	—	—	—	—	2−
467	44	5	Bottom	412.4	Pliocene	4.67	5	90	—	5	—	—	2−
467	44	5	Top	411.0	Pliocene	3.08	5	90	—	—	5	—	2−
467	44	6	Top	412.5	Pliocene	3.21	5	90	—	—	—	5	2−
467	44	7	Bottom	414.0	Pliocene	3.52	10	90	—	—	—	—	2
467	54	2	108–118	502.6	Upper Miocene	4.36	—	99	—	—	—	—	1+
467	63	2	100–109	588.0	Upper Miocene	7.84	10	85	—	—	—	5	1+
467	85	4	145–150	801.5	Middle Miocene	1.69	—	90	—	—	—	10	1+
467	91	2	107–109	854.1	Middle Miocene	1.98	5	90	—	—	—	5	1+
467	97	2	118–123	911.1	Middle Miocene	2.42	30	70	—	—	—	—	1+
467	104	1	100–107	976.0	Middle Miocene	2.50	20	70	—	—	—	10	1+
467	110	3	55–58	1,035.0	Middle Miocene	2.85	20	70	—	—	5	5	1+
468	2	3	120–129	7.7	Pliocene?	2.68	20	70	5	—	—	5	1+
468	18	3	119–128	160.1	Middle Miocene	1.74	20	70	—	—	—	10	1+
468B	13	3	115–124	163.2	Middle Miocene	0.26	20	80	—	—	—	—	1+
468B	21	2	105–113	256.6	Middle Miocene	1.61	10	90	—	—	—	—	1+
468B	37	1	115–120	507.2	Middle Miocene	0.28	10	70	—	10	—	10	1+
469	2	2	100–109	10.1	Quaternary	0.65	—	90	—	—	—	10	1+
469	12	5	112–120	109.2	Upper Miocene	0.64	5	70	5	—	10	10	1+
469	20	3	127–134	182.8	Middle Miocene	0.45	—	85	5	—	—	10	1+
469	30	1	109–114	274.1	Upper middle Miocene	0.94	10	85	—	—	5	—	1+
469	37	1	140–145	341.4	Middle Miocene	0.37	5	90	—	—	—	5	1+
469	43	1	100–106	388.1	Upper Miocene	0.35	10	55	10	—	5	20	1+
470	8	1	100–109	69.6	Upper Miocene	0.24	15	40	5	—	15	25	2−
470	14	1	145–150	124.6	Middle Miocene	0.35	—	85	—	—	5	10	1+
471	3	2	141–149	21.6	Quaternary	0.80	10	60	5	10	5	10	1+
471	13	7	130–136	123.1	Upper Miocene	0.84	25	75	—	—	—	—	1+
471	39	2	100–109	363.6	Middle Miocene	0.93	10	75	10	—	5	—	1+
471	50	2	100–106	468.1	Middle Miocene	0.61	—	90	—	—	—	10	1+
471	63	3	100–115	593.1	Middle Miocene	0.64	—	85	—	—	10	5	1+
471	69	3	105–111	650.1	?	0.70	—	80	—	—	20	—	2−
473	2	2	125–131	3.3	Quaternary	1.90	10	80	—	—	—	10	2−
473	7	1	100–109	49.2	Quaternary	0.18	10	80	—	—	—	10	2−
473	23	2	123–130	193.2	Upper Miocene	0.91	10	75	—	—	10	5	2−

Note: — represents 0% of material present.

At Site 473, the organic facies do not change downhole, but the TOC content is quite variable (Table 1). This variability is also documented by DSDP shipboard analyses. We believe that the changes reflect the influx of turbidites. There is a surprisingly high proportion of terrigenous material in this section. Core 2 (where we measured 1.9% TOC) contains abundant angular and subangular quartz and feldspar, plus glauconite, plant debris, and carbonized wood fragments—all signs of mass transport downslope, presumably from the Mexican mainland.

THERMAL ALTERATION INDEX (TAI)

Using the method of Staplin (1969), we measured thermal alteration indices from spore and pollen color. All of the samples that we analyzed are thermally immature (Table 1). They have not been heated to the point where they might yield hydrocarbons.

GAS CONTENT

Gas from Site 467 cans consists almost entirely of methane (Table 2). Of the wet gas fraction, ethane

Table 2. Cuttings gas (C_1–C_4) concentrations (vol/vol) in air space of canned mud samples from Site 467: wet gas in C_2–C_4.

Core No.	Section	Interval	Vol. HC Gas (ppm)	CH_4 in HC Gas (%)	C_2-C_6 in HC Gas (%)	C_2H_6 in Wet Gas (%)
7	5	Bottom	4,704	100	0	68
8	4	Top	13,859	100	0	70
9	2	Bottom	402	100	0	58
9	3	Bottom	10,632	100	0	71
9	4	Top	9,242	100	0	63
10	5	Bottom	17,572	100	0	78
11	1	Bottom	11,318	100	0	57
11	3	Top	5,591	100	0	76
11	4	Bottom	4,459	100	0	50
13	1	Bottom	13,347	100	0	54
13	5	Bottom	11,659	100	0	72
14	1	Bottom	3,442	99	1	59
14	2	Top	47,053	100	0	63
14	2	Bottom	44,659	100	0	73
14	3	Top	10,580	100	0	62
16	1	Bottom	10,911	100	0	62
16	2	Bottom	8,882	100	0	77
18	1	Bottom	22,083	100	0	48
18	2	Bottom	6,288	99	1	70
18	4	Bottom	5,998	99	1	68
26	1	Top	53,686	100	0	77
42	2	Bottom	10,344	97	2	62
42	3	Bottom	3,201	94	3	57
42	5	Top	2,992	97	2	51
42	5	Bottom	2,856	95	2	35
44	6	Top	3,398	98	1	50
44	6	Top	16,161	97	2	47
44	7	Bottom	5,130	97	2	57

(C_2H_6) predominates. Preliminary shipboard data suggest that ethane increases in abundance downhole, resulting in a downward increase in the C_2/C_1 ratio. Our analyses confirm that ethane increases downhole relative to methane (Table 2); ethane averages 62% of the wet gas fraction (C_2H_6 to C_4H_{10}).

Gas abundances are consistently high (averaging 12,873 ppm) and slightly above gas levels typical of Tertiary and Quaternary sediments cored by the DSDP (see reports by McIver 1973a, 1973b). There is twice as much gas in the samples from the California margin as there is in continental margin samples from the Japan Trench (i.e., 6418 ppm—Gilbert et al., 1980). Some of the downhole variations in gas abundance listed in Table 2 may result from can leakage.

DISCUSSION

The southern California and Baja California continental margin differs considerably from the continental margin off Japan (Gilbert et al., 1980) in being so enriched in organic matter. Off Japan, which we consider to be typical of continental margins in areas where the water column is highly oxidizing, TOC values are low (average above 0.75%) and organic facies are dominantly terrestrial (amorphous and structured marine algal material is only about 30% of the kerogen fraction). Presently in the California Borderland, marine sediments become enriched in organic matter where surface waters are highly productive (ensuring a good supply of marine organic matter) and where bottom waters contain small amounts of oxygen (ensuring that dead organic matter will be preserved). Upwelling promotes high biological productivity at the surface, and the de-

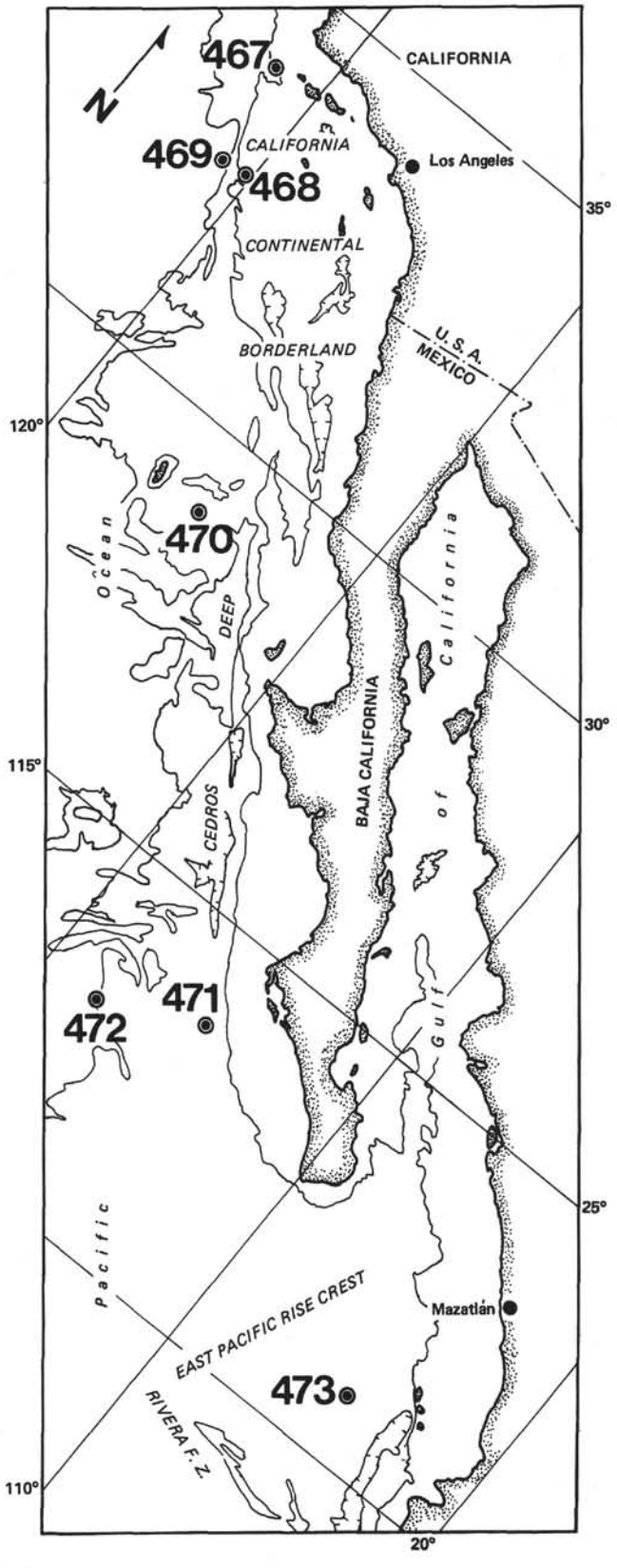

Figure 1. Location of Leg 63 sites.

cay of sinking organic remains depletes oxygen levels in the underlying water column resulting in a distinct oxygen minimum zone (Emery, 1960). Where dissolved oxygen levels fall below about 0.5 ml/l, benthic life is restricted. As a result, bottom sediments are often undisturbed, and large amounts of organic matter are preserved (Demaison and Moore, 1980). At slightly higher levels of oxygen (about 0.5 to 1.0 ml/l), burrowing benthic organisms can survive, although there still may be substantial preservation of organic matter (Demaison and Moore, 1980). At higher levels of oxygen, bioturbation is extensive, and benthic organisms and oxidation processes remove most of the organic matter that reaches the bottom.

In the California Borderland there is presently a well-developed oxygen minimum zone in which oxygen levels drop to 0.5 ml/l or less, which encourages the preservation of organic matter (Emery, 1960). This zone extends at least as deep as 2000 meters, at which depth the oxygen contents of bottom waters increase to 0.5 to 1.0 ml/l (Emery, 1960, fig. 97, p. 110). The Patton Escarpment site (468) falls within the present depth range of the minimum zone, the San Miguel Gap site (467) is just beneath it.

We suggest that the downhole changes in TOC content at Sites 467 and 468 reflect past fluctuations in the intensity of development of the oxygen minimum. Development of the minimum is linked to productivity; higher productivity at the surface leads to greater oxygen depletion at depth. Productivity, in turn, is linked to upwelling; sustained and vigorous upwelling promotes high productivity in surface waters. Changes in the pattern of upwelling reflect circulation changes that are also documented by a shift in regional isotherms (Ingle, 1973).

We interpret the vertical profiles of TOC content at Sites 467 and 468 in terms of an expansion of the oxygen minimum zone. This zone may not have intersected the sea floor at these sites in the middle Miocene. As a result, sediments of that age do not contain much organic carbon. In contrast, the zone probably intersected the sea floor in the late Miocene at Site 467 and in the Pliocene at both sites when more organic-rich sediments were deposited and preserved. It may intersect the sea floor presently at Site 468 (we have no modern samples, but this site is within the present oxygen minimum zone defined by Emery's fig. 97, 1960), but it does not do so at Site 467.

This interpretation does not account for vertical tectonic movements of the sea floor. The middle to late Miocene increase in TOC content at Site 467 could be explained, if the sea floor had risen into the oxygen minimum layer at this time. Similarly, the decrease in TOC values from the Pliocene into the Quaternary could reflect sinking of the sea floor below the oxygen minimum. We favor the oceanographic rather than the tectonic control, because paleontological data (Ingle, 1973) suggest significant temporal changes in the intensity of circulation in this region. Changes in rate of sedimentation appear to affect neither TOC content nor organic facies in the Borderland at Site 467.

The widespread occurrence of Miocene–Pliocene phosphorites may be an additional clue to unusual circulation conditions and nutrient supply in the California Borderland in the late Miocene–Pliocene (Emery, 1960). The association between phosphorites and organic-rich shales is well known (McKelvey and Chase, 1966). Both organic-rich shales and phosphorites require a massive source of nutrients abundant in centers of upwelling (Tooms et al., 1969). The absence of Quaternary phosphorites in the Borderland (Kolodny and Kaplan, 1970) suggests a change in some parameters critical to phosphorite formation between the Pliocene and the Quaternary. This change parallels the one we see at the top of the section at Site 467, where a decrease in TOC values suggests a lessening in the intensity of upwelling. More work is needed before the processes causing these changes are fully understood.

The deeper-water sites (469–473) contain little organic matter and do not show the vertical changes in TOC that we see in the Borderland. Apparently these deeper-water sites have been well below the oxygen minimum zone throughout their sedimentary histories.

CONCLUSIONS

The kerogen fraction of sediments of the deep sea off California (>2500 m) does not show any evidence for lateral shifts in surface currents, probably because the water is too deep and too oxidizing to permit extensive preservation of this material.

In the California Borderland we interpret the vertical changes in TOC content in terms of a late Miocene–Pliocene expansion of the oxygen minimum zone. This expansion probably was a response to increased upwelling and surface productivity caused by changes in surface circulation that occurred at the end of the middle Miocene. The result was more extensive accumulation of marine organic matter during the late Miocene and during the Pliocene. In the Quaternary, surface circulation changed again, making conditions less favorable for the accumulation of organic matter at the San Miguel Gap (though not in shallower basins; see Emery, 1960). The changes in TOC were accompanied by changes in phosphorite formation. Phosphorite formed extensively throughout the Borderland in the late Miocene–Pliocene. Presumably more nutrients were available at that time than before or since. Phosphorite formation peaked in the late Miocene and diminished during the Pliocene (Emery, 1960); TOC enrichment at Site 467 was less confined in time, extending through the Pliocene.

Although the sediments of the Borderland are rich in marine organic matter and make excellent potential source rocks for petroleum, they have not yet been heated sufficiently at these DSDP sites to yield liquid hydrocarbons. They contain abundant gas, mostly methane, of probable biogenic origin.

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