

35. PYROLYTIC ASSAY OF SAMPLES FROM SITE 799¹

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ABSTRACT

Pyrolysis techniques were used to characterize the organic matter contained within the penetrated section and to assess the presence of heavy hydrocarbon shows. The Rock-Eval data indicate a change in organic hydrogen enrichment within the middle Miocene sequence. It appears that the level of organic enrichment may be controlled by sedimentation rate, while the organic hydrogen enrichment, as shown in the hydrogen index, may reflect differences in preservation potential. Higher sedimentation rates would result in higher organic carbon contents. Higher hydrogen index values would reflect higher degrees of organic preservation resulting from more restricted circulation.

The entire penetrated section is thermally immature and has not entered into the main phase of thermal hydrocarbon generation. Neither the Rock-Eval nor the pyrolysis-gas chromatographic data indicate the presence of thermally mature, migrated, heavy hydrocarbons. This absence of mature, heavy hydrocarbons includes Cores 128-799B-65R and 128-799B-66R, which exhibited cut fluorescence onboard the ship. Therefore, the fluorescence is considered to have resulted from indigenous, thermally immature bitumens.

INTRODUCTION

Site 799 is located in the Kita-Yamato Trough in the south-central Japan Sea (Fig. 1). Three holes drilled at the site penetrated 1084 m of sediment. The oldest sediment recovered is early Miocene in age.

The primary objective of Site 799 was to examine the depositional and tectonic environments of massive sulfide mineralization in a failed backarc rift. A secondary objective was to obtain a detailed paleoceanographic record of this backarc setting, including possible evidence of low-oxygen water masses during the initial formation of the basin. The original drilling plans called for total penetration of approximately 1610 mbsf (including 50 m of basement). However, drilling was terminated at 1084 mbsf prior to reaching this objective for safety reasons when samples from Cores 128-799B-65R and 128-799B-66R exhibited a slow, pale, yellowish-white cut fluorescence (Shipboard Scientific Party, 1990).

This study was initiated (1) to supplement the available shipboard organic geochemical data with information about downhole variability of the sedimentary organic matter and (2) to determine the significance of the cut fluorescence in Cores 128-799B-65R and 128-799B-66R. This was to include a determination about whether migrated, thermally mature, heavy hydrocarbons (C₁₀₊) are present in the stratigraphic column and whether the penetrated section is actively generating heavy hydrocarbons.

ANALYTICAL METHODS

One hundred and eight samples were selected for analysis, based on shipboard measurements of organic carbon (Shipboard Scientific Party, 1990). The stratigraphic distribution of these samples is presented in Figure 2. Upon receipt, each sample was oven-dried at 60° C and ground to approximately 325 mesh (44 µm). Organic carbon content (C_{org}) and total sulfur were determined for each sample using a LECO analyzer after decarbonation with HCl. Each sample was also subjected to whole-rock pyrolytic assay using the Rock-Eval system described by Espitalié et al. (1977). Selected samples underwent pyrolysis-gas chromatography, as described by Colling et al. (1986). This technique utilizes a pyroprobe which flash heats the sample to 700° C for 5 s, trapping the products in a liquid nitrogen cold trap. The products were then permitted to achieve thermal equilibrium with

the initial gas chromatograph oven temperature (50° C). After 18 min, the oven temperature was increased to 225° C at a rate of 8° per minute, and then to 310° C at a rate of 6° per minute. This final temperature was held for 6 min.

ANALYTICAL RESULTS

Organic Carbon and Total Sulfur

Organic carbon contents ranged from 0.90 to 5.08 wt%. These data are detailed in Table 1 and Figure 2. All of the samples contain above-average quantities of organic carbon (> 0.3 wt%) relative to deep-sea sediments (McIver, 1975), and all except seven samples contain above-average quantities of organic carbon (> 1.0 wt%) relative to all fine-grain sedimentary rocks (Bissada, 1982). In general, the lower and middle Miocene sections, below 454 mbsf (Core 128-799A-50X), display slightly greater levels of organic carbon enrichment than the younger sediments.

The shore-based organic carbon values measured as part of this study differ slightly from the shipboard measurements (Shipboard Scientific Party, 1990). In general, the shipboard measurements are slightly greater than the shore-based measurements (Fig. 3). Because there appears to be a systematic difference among the paired values, much of the difference may be attributable to a difference in analytical techniques. As noted previously, shore-based measurements were performed using a LECO analyzer, while shipboard values were determined by difference, with total carbon being determined using a Perkin Elmer (model 240C) CHN-elemental analyzer, while carbonate carbon was determined using a Coulometrics 5030 carbonate carbon apparatus. The generally depressed shore-based measurements may reflect losses of organic matter as a result of hydrolysis during decarbonation or depressed shipboard carbonate-carbon values because of the presence of both dolomite and siderite.

The few values that differ substantially from the observed trend may reflect sample inhomogeneity. Although measurements were performed using samples from the same intervals, they were not performed on splits of a homogenized powder.

Total sulfur data also are included in Table 1. Total sulfur contents range from 0.04 to 3.06 wt%. The observed carbon/sulfur ratios do not appear typical of open marine sediments (Fig. 4). In general, the sediments appear to contain a slight excess of sulfur. However, the sulfur excess is less than would be expected from a euxinic environment in which free H₂S is present in the water column and sedimentary iron is available (Bernier and Raiswell, 1983). The observed carbon/sulfur ratios may reflect an iron deficiency rather than differ-

¹Pisciotta, K. A., Ingle, J. C., Jr., von Breyman, M. T., Barron, J., et al., 1992. *Proc. ODP, Sci. Results, 127/128, Pt. 1*: College Station, TX (Ocean Drilling Program).

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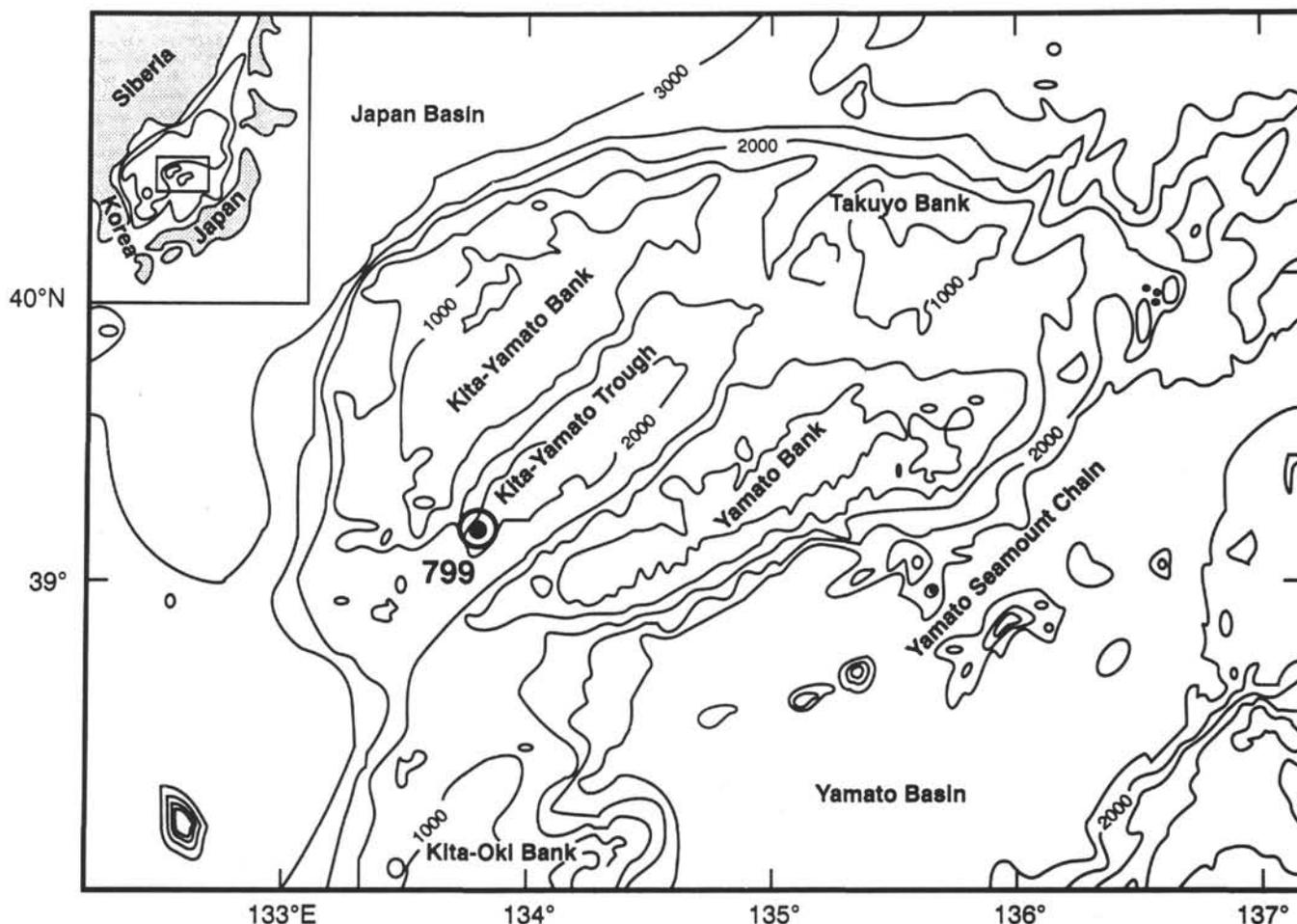


Figure 1. Location map for Site 799.

ences in the availability of either O_2 or H_2S in the water column. These observations are consistent with those of the Shipboard Scientific Party (1990).

Rock-Eval Pyrolysis

Pyrolytic assay provides information about hydrocarbon generation potential, organic character, the extent of thermal diagenesis, and the presence of "reservoired" hydrocarbons. Pyrolysis results are summarized in Table 1 and Figure 2.

Total pyrolytic hydrocarbon yields ($S_1 + S_2 =$ free distillable hydrocarbons [HC] + generatable HC) range from 0.69 to 18.83 mg HC/g rock. Good potential and/or effective hydrocarbon source rocks yield > 6 mg HC/g rock (Tissot and Welte, 1984). Within the present sample suite, sediments of this quality are limited principally to the section below 741 m (Core 128-799B-32R), i.e., the lower half of the middle Miocene and lower Miocene sequences. However, caution should be exercised when evaluating these data because of the suspected low levels of thermal maturity of the sediments. In samples having very low levels of thermal maturity, both the S_1 and the S_2 peaks may not contain exclusively hydrocarbons, but may instead contain significant amounts of hetero compounds (i.e., molecules containing O, N, and S). The presence of these labile compounds may result in a slight overestimation of the hydrocarbon yields.

Although complicated by such factors as thermal maturity (Espitalié et al., 1985), organic enrichment and mineral matrix effects (Katz, 1983), pyrolysis can be used to provide insight into the nature of the sedimentary organic matter. This interpretation is accomplished

using the hydrogen (mg " S_2 " HC/g C_{org}) and oxygen (mg CO_2 /g C_{org}) indexes and a modified van Krevelen-type diagram, as described by Espitalié et al. (1977).

Both the hydrogen and oxygen indexes samples from Site 799 exhibit wide variability (Fig. 5). However, these data do indicate that a marked change occurs in organic facies within the middle Miocene section (Fig. 2). The organic matter in the lower portion of the column, below 740 mbsf (Core 128-799B-32R), is more hydrogen enriched than the preserved organic matter contained within the upper portion of the stratigraphic column. The sediments in the lower portion of the stratigraphic column display hydrogen indexes of ~ 400 . This organic material might be classified type II according to the scheme of Tissot et al. (1974). Type II organic material is typically well-preserved marine organic matter. In the shallower portion of the column the hydrogen indexes typically range between 100 and 200. This material should be classified as type III organic matter according to the scheme of Tissot et al. (1974). Type III material typically is either oxidized marine or terrestrially derived organic matter. The elevated oxygen indexes ($> \sim 150$) are probably the combined result of an inorganic CO_2 contribution from the various carbonate minerals present (calcite, dolomite, and siderite; Palacas et al., 1981; Katz, 1983), as well as a contribution from the more functionalized components, including humic acids, typical of very thermally immature sediments.

An examination (Table 1) of the two pyrolysis thermal maturity indicators, T_{max} (temperature at which maximum pyrolytic hydrocarbon generation occurs) and the transformation ratio ($TR = S_1/[S_1 + S_2]$), suggests that the penetrated section is thermally immature (i.e., has not entered the main phase of the thermal hydrocarbon genera-

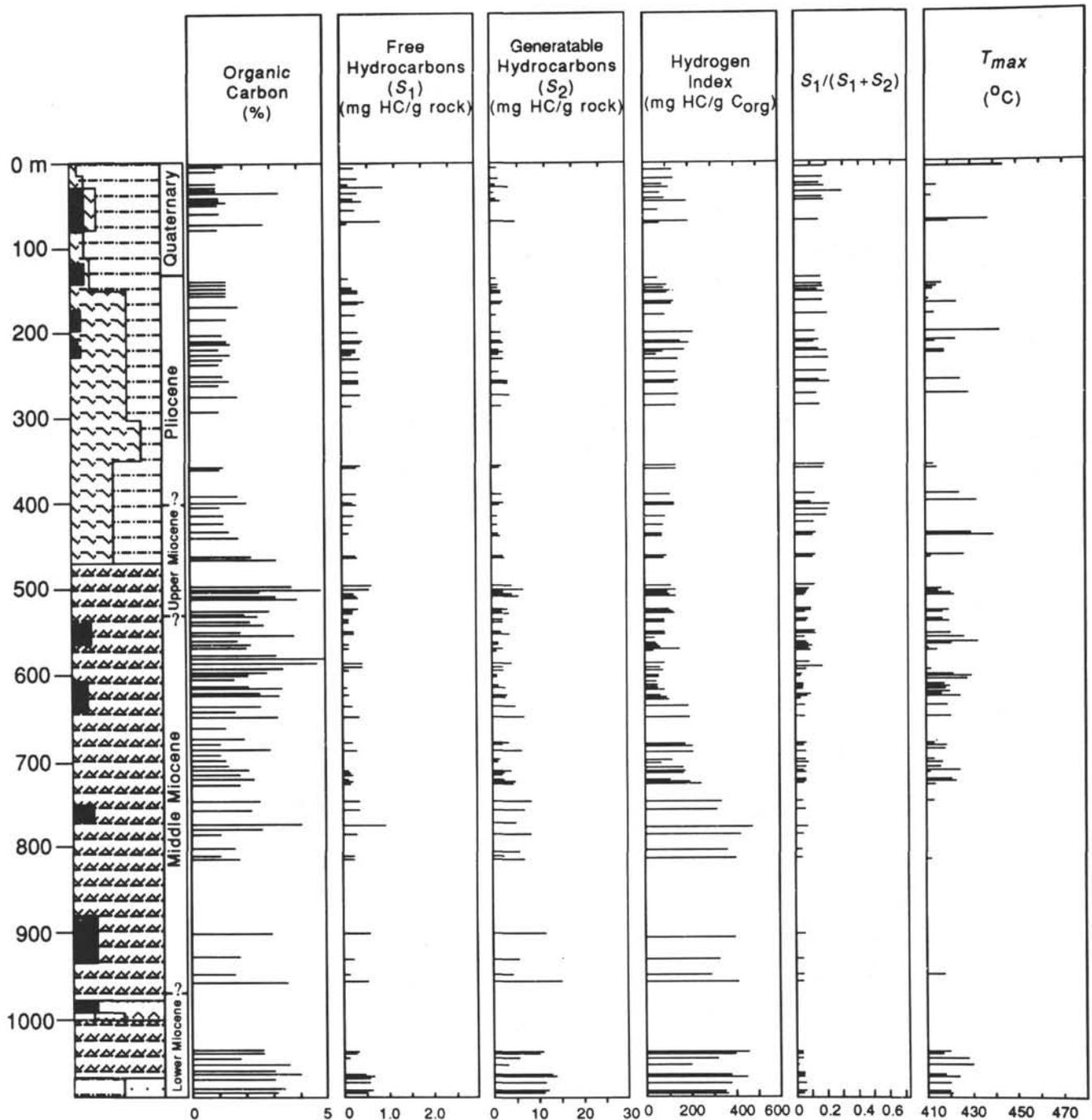


Figure 2. Lithostratigraphic and geochemical summary for Site 799.

tion). This is manifested by the typically low T_{max} values of $< 430^{\circ}C$ and the TR values of < 0.10 in the lower half of the sedimentary sequence.

These data further suggest that several samples (e.g., 128-799A-3H-6, 10–15 cm, and 128-799A-25X-4, 113–117 cm) contain high proportions of secondary, recycled, or inert organic matter. This is manifested by these samples' bimodal S_2 peak. Samples showing a bimodal S_2 peak appear to be largely restricted to the upper portion of the stratigraphic column. The presence of "residual" material is consistent with the suggested kerogen type, based on the hydrogen and oxygen indexes.

Although the TR values do indicate that the penetrated section is thermally immature, the observed trend in TR is anomalous and does

not represent a typically observed thermal maturation trend or profile. The highest TR values are observed in the upper portion of the sequence (Fig. 2). The inverted TR trend most probably reflects a decrease in the relative concentration of initial bitumens as a function of organic diagenesis. This inverted trend may, in part, be a result of the conversion from biopolymers represented largely in the S_1 fraction to geopolymers represented by the S_2 fraction (i.e., the kerogenization process).

Although anomalously high TR values may sometimes indicate the presence of migrated heavy hydrocarbons (petroleum), such is not considered to be the case at Site 799. Hydrocarbon shows or occurrences are normally restricted to discrete intervals and typically do not display

Table 1. Organic carbon and pyrolysis data, Site 799.

Core, section, interval (cm)	Depth (mbsf)	Organic carbon (wt%)	Total sulfur (wt%)	S ₁	S ₂	HI ^a	OI ^b	TR ^c	T _{max} (°C)
				(mg HC/g rock)					
799A									
1H-1, 44-49	0.44	1.25	0.04	0.59	2.78	222	128	0.18	420
2H-4, 74-78	6.44	1.01	0.70	0.31	1.32	130	140	0.19	^d B
3H-6, 10-14	18.30	1.11	0.85	0.38	1.58	142	95	0.19	B
4H-4, 20-25	25.00	0.99	0.40	0.17	0.84	84	213	0.17	B
4H-6, 20-25	28.00	3.34	1.30	0.94	3.87	115	83	0.20	415
5H-4, 20-25	34.60	1.01	0.89	0.37	0.78	76	478	0.32	B
6H-2, 20-25	41.20	1.36	0.84	0.28	1.28	94	208	0.18	412
6H-4, 20-25	44.20	1.01	0.66	0.47	1.94	191	75	0.20	B
7H-4, 40-45	54.00	1.10	1.30	0.33	0.70	63	231	0.32	<400
8H-6, 50-54	66.70	2.70	1.06	0.91	5.30	196	78	0.15	437
9H-2, 30-35	70.10	0.90	0.92	0.14	0.64	71	292	0.18	420
15H-6, 54-58	134.14	1.36	0.81	0.17	0.83	61	283	0.17	407
16H-4, 60-65	140.90	1.32	0.90	0.28	1.30	98	203	0.18	417
16H-6, 60-65	143.90	1.41	0.81	0.26	1.16	82	292	0.18	415
17H-2, 55-60	147.55	1.50	0.73	0.34	2.03	135	166	0.14	B
17H-4, 40-45	150.40	1.42	0.81	0.34	1.49	105	202	0.19	409
18H-4, 40-45	160.10	1.74	0.87	0.51	2.39	137	114	0.18	411
18H-6, 40-45	163.10	1.75	1.20	0.38	2.22	127	226	0.15	424
20H-2, 20-25	176.20	1.25	0.66	0.30	1.11	89	232	0.21	414
22X-2, 77-81	196.07	1.12	0.90	0.38	2.45	217	77	0.13	443
23X-2, 29-33	205.29	1.53	0.54	0.47	2.46	161	199	0.16	423
23X-4, 20-24	208.20	1.43	0.81	0.43	2.76	192	34	0.14	414
24X-2, 132-136	215.92	1.05	0.62	0.33	1.72	163	136	0.16	B
24X-4, 98-102	218.58	1.39	0.87	0.32	1.23	88	218	0.21	418
24X-6, 24-29	222.84	1.19	0.64	0.18	0.69	58	466	0.21	418
25X-4, 113-117	228.43	0.96	0.45	0.43	1.50	155	4	0.22	B
27X-2, 25-29	243.15	1.04	0.83	0.37	1.48	142	34	0.20	408
29X-2, 25-30	252.65	1.40	0.79	0.38	2.16	154	130	0.15	425
29X-4, 22-27	255.62	0.95	0.50	0.37	1.23	129	7	0.23	<400
30X-6, 50-55	268.55	1.74	1.12	0.41	2.62	150	169	0.14	429
32X-4, 50-55	283.20	0.90	0.77	0.26	1.23	136	168	0.18	410
39X-4, 40-44	350.80	1.20	0.68	0.41	1.67	138	35	0.20	414
39X-6, 40-44	353.80	1.05	0.73	0.33	1.44	137	141	0.19	415
42X-6, 80-85	383.30	1.74	0.74	0.30	2.08	119	211	0.13	425
43X-6, 40-45	392.50	1.99	1.06	0.26	2.57	129	183	0.09	432
44X-2, 10-15	395.90	0.91	0.50	0.33	1.20	132	37	0.22	<400
45X-4, 47-52	408.87	1.11	0.87	0.28	1.04	93	45	0.21	<400
46X-4, 20-25	418.30	1.07	0.54	0.25	0.97	90	44	0.20	405
47X-4, 126-130	429.06	1.37	0.93	0.15	1.04	75	449	0.13	430
47X-6, 144-148	432.24	1.69	1.16	0.08	1.29	76	343	0.06	440
50X-2, 88-92	454.68	2.12	1.09	0.31	2.01	94	263	0.13	427
50X-4, 93-97	457.73	3.07	1.15	0.34	2.75	89	53	0.11	412
799B									
5R-1, 90-94	490.50	3.61	1.17	0.63	4.32	119	46	0.13	410
6R-1, 33-38	494.93	4.92	2.07	0.61	6.69	136	57	0.08	417
6R-2, 10-15	496.20	2.42	0.97	0.19	2.47	102	57	0.07	415
7R-1, 20-25	499.90	3.10	1.00	0.32	4.06	130	52	0.07	421
7R-3, 30-35	503.00	3.85	1.18	0.36	5.50	142	70	0.06	422
8R-6, 16-20	516.96	2.85	1.29	0.35	3.06	107	50	0.10	409
9R-2, 91-95	521.41	1.77	1.57	0.23	2.37	134	109	0.09	420
9R-4, 123-127	524.73	2.40	1.63	0.24	3.51	146	72	0.06	417
10R-2, 127-131	531.37	2.02	1.12	0.15	1.70	83	50	0.08	417
10R-4, 64-67	533.74	2.57	1.10	0.15	2.10	81	132	0.07	420
11R-5, 29-31	544.59	1.67	0.61	0.22	1.49	89	39	0.13	400
11R-7, 32-35	547.62	3.78	1.45	0.21	3.62	95	61	0.05	421
12R-4, 71-74	553.11	1.58	0.51	0.04	0.65	41	394	0.06	427
13R-1, 56-61	558.16	2.10	1.60	0.07	1.17	55	174	0.06	433
13R-3, 60-65	561.20	1.93	1.52	0.15	1.31	67	222	0.10	421
14R-1, 85-90	568.15	2.22	1.56	0.08	0.85	38	380	0.09	415
14R-3, 55-60	570.85	3.03	1.47	0.23	1.87	61	21	0.11	416
15R-1, 25-30	577.25	5.08	1.62	0.89	8.09	159	21	0.10	414
15R-4, 5-10	581.55	4.92	2.16	0.43	4.24	86	39	0.09	400
16R-1, 80-85	587.40	3.21	1.97	0.43	2.16	67	23	0.17	<400
16R-3, 110-115	590.70	2.71	0.88	0.15	2.07	76	58	0.07	412
17R-1, 25-30	596.55	1.88	0.98	0.04	0.98	52	60	0.04	422
17R-3, 35-40	599.65	1.96	0.68	0.04	1.19	60	112	0.03	430
17R-5, 30-35	602.60	1.46	0.82	0.03	0.67	45	119	0.04	428
18R-1, 143-147	607.33	1.96	1.23	0.05	1.07	54	112	0.04	418
18R-3, 89-91	609.79	3.20	1.01	0.11	2.71	84	70	0.04	420
18R-4, 139-141	611.79	1.92	1.30	0.05	1.13	58	53	0.04	419
19R-1, 77-81	616.37	2.47	1.01	0.07	1.78	71	63	0.04	420
19R-3, 80-84	619.40	3.10	0.87	0.15	3.11	100	24	0.05	412

Table 1 (continued).

Core, section, interval (cm)	Depth (mbsf)	Organic carbon (wt%)	Total sulfur (wt%)	S ₁	S ₂	HI ^a	OI ^b	TR ^c	T _{max} (°C)
				(mg HC/g rock)					
19R-5, 55-59	622.15	2.43	1.00	0.07	2.70	111	30	0.03	425
20R-5, 108-112	632.28	2.40	1.00	0.26	4.64	193	19	0.05	419
21R-3, 80-84	638.70	1.53	0.39	0.09	1.20	78	102	0.07	417
22R-1, 6-9	644.66	3.17	0.99	0.34	6.42	202	19	0.05	421
23R-2, 50-55	656.20	1.17	0.81	0.15	1.82	154	22	0.08	411
25R-1, 60-65	674.10	1.78	0.94	0.24	3.21	180	20	0.07	413
25R-3, 90-95	677.40	1.09	0.72	0.10	2.27	207	54	0.04	419
26R-1, 120-125	684.40	2.85	0.98	0.30	6.04	212	59	0.05	418
27R-1, 108-112	693.58	1.10	1.23	0.09	1.30	117	24	0.06	413
27R-3, 112-117	696.62	0.98	1.15	0.06	0.72	73	113	0.08	417
28R-1, 40-45	702.50	1.19	0.99	0.12	1.96	164	32	0.06	416
28R-3, 40-45	705.50	2.01	0.98	0.14	3.68	182	91	0.04	425
28R-5, 40-45	708.50	1.58	1.27	0.18	2.61	165	25	0.06	411
29R-2, 100-105	714.30	1.70	0.77	0.12	2.35	138	38	0.05	421
29R-4, 75-80	717.05	2.20	0.99	0.21	4.41	200	48	0.05	423
30R-1, 85-87	722.25	1.62	1.40	0.17	4.07	251	4	0.04	414
32R-1, 59-61	741.09	2.40	1.07	0.37	8.32	347	63	0.04	413
33R-1, 69-72	750.89	2.11	1.42	0.35	6.90	326	16	0.05	402
35R-2, 42-44	771.42	3.91	1.97	1.17	18.83	481	9	0.06	403
36R-1, 137-141	780.57	1.98	1.09	0.32	8.47	428	23	0.04	408
38R-1, 65-67	799.15	1.47	0.74	0.23	5.40	366	62	0.04	410
39R-1, 103-105	809.13	1.69	0.88	0.27	6.85	405	17	0.04	412
48R-2, 96-100	897.06	2.86	1.39	0.62	11.68	407	8	0.05	408
51R-2, 78-82	925.58	1.72	1.08	0.26	5.72	331	4	0.04	409
53R-2, 0-4	944.10	1.40	1.00	0.17	4.20	300	2	0.04	418
54R-1, 19-23	952.39	3.52	1.83	0.56	14.94	424	33	0.04	410
62R-2, 13-17	1031.13	2.33	1.54	0.33	10.84	464	12	0.03	420
62R-4, 44-48	1034.44	2.44	1.31	0.32	9.76	400	36	0.03	417
63R-1, 119-123	1040.29	1.73	0.74	0.15	5.44	313	7	0.03	428
64R-1, 0-4	1048.80	1.61	1.02	0.08	3.24	201	9	0.09	430
65R-1, 83-85	1059.23	3.38	2.00	0.50	12.75	377	1	0.04	418
65R-2, 130-132	1061.20	3.68	2.58	0.66	14.06	381	7	0.04	424
65R-3, 14-16	1061.54	3.02	2.17	0.59	13.65	451	0	0.04	418
65R-3, 42-44	1061.82	2.80	2.76	0.49	10.43	372	6	0.04	423
66R-2, 53-55	1069.22	2.94	2.74	0.59	11.26	382	9	0.05	420
67R-1, 51-53	1078.21	3.25	2.43	0.65	11.70	360	11	0.05	420
67R-3, 72-74	1081.42	3.04	3.06	0.51	11.18	367	12	0.04	421

^a Hydrogen Index (mg "S₂" HC/g C_{org}).

^b Oxygen Index (mg CO₂/g C_{org}).

^c Transformation Ratio S₁/(S₁ + S₂).

^d Bimodal S₂ peak.

a depth trend. In addition, the samples with the elevated TR values do not consistently display unusually low T_{max} values (<400°C), which would be typical for a hydrocarbon show.

The general absence of nonindigenous (stains and/or drilling contaminants) hydrocarbons is consistent with the relationship between TR and T_{max} (Fig. 6), although several samples from Cores 128-799A-29X, 128-799A-44X, 128-799A-45X, and 128-799B-16R display slightly elevated TR values. The absence of nonindigenous hydrocarbons is also consistent with the relationship between S₁ and C_{org} (Fig. 7), in which all samples display low S₁/C_{org} values.

It is important to emphasize that the Rock-Eval data do not indicate the presence of migrated hydrocarbons in Cores 128-799B-65R, 128-799B-66R, or 128-799B-67R.

Pyrolysis-Gas Chromatography

Pyrolysis-gas chromatography provides additional information about the nature of kerogen (Larter and Douglas, 1980), as well as qualitative assessment of principal hydrocarbon products that may have been generated upon thermal maturation (Dembicki et al., 1983).

The chromatographic signatures obtained for all of the analyzed samples generally lack higher-molecular-weight, waxy, alkane-alkene doublets. The best developed alkane-alkene doublets typically range from C₁₃ to C₁₉. The lighter-end fraction is a complex hydrocarbon mixture that includes numerous aromatic species. In the higher molecular-weight range, a single peak tends to dominate in all sam-

ples independent of stratigraphic position or hydrogen index. This peak has tentatively been identified through its mass spectrum as squalene. Several samples (e.g., 128-799B-35R-2, 42-44 cm; Fig. 8D) also exhibit a well-developed naphthenic envelope. These same samples also appear to display the best-developed and most complete series of alkane-alkene doublets. In addition, these samples display a clearly defined harmonic decrease in peak height with increasing carbon number.

These characteristics may be largely independent of the hydrogen index value. Note the similarity in the chromatograms obtained from Samples 128-799B-6R-1, 33-38 cm, and 128-799B-35R-2, 42-44 cm (Figs. 8B and 8D), with hydrogen indexes of 136 and 481, respectively. This similarity in chromatographic character suggests that some of the hydrogen indexes may be depressed by the present of "inert" (strongly oxidized or recycled) organic matter, which contributes to the total organic carbon content but does not contribute to the hydrocarbon yield (Katz, 1988).

The poor peak development in samples (such as 128-799A-8H-6, 50-54 cm; Fig. 8A) is typical of samples containing organic matter that includes a large inert component. Such an interpretation is consistent with the slightly elevated T_{max} value of 437°C compared to the expected level of thermal maturity, based on the sample's age (Quaternary), depth of burial (66.70 mbsf), and *in situ* temperature (~7°C; Shipboard Scientific Party, 1990).

The absence of abundant waxy components (nC₂₂+) suggests that the reactive or "live" organic matter does not contain a significant

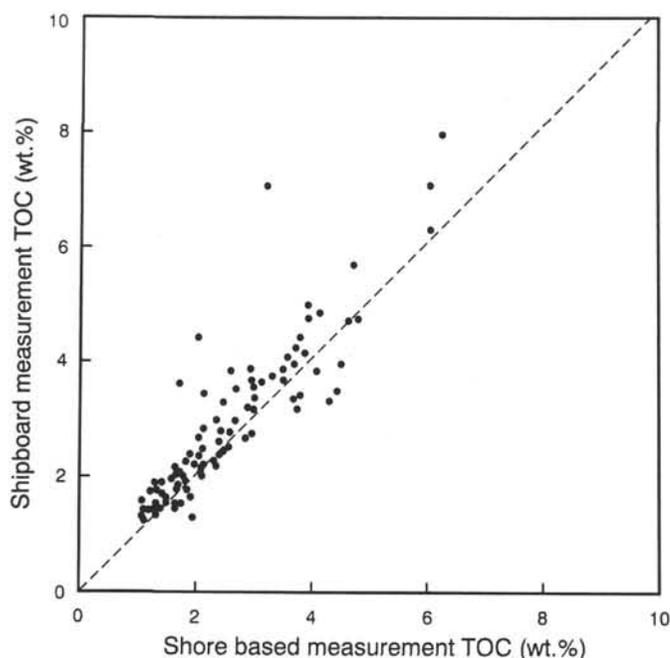


Figure 3. Comparison of shipboard with shore-based organic carbon determinations.

terrestrial component and was, in general, autochthonous (i.e., marine-derived). Such an interpretation is consistent with the presence of a naphthenic envelope, a harmonic decrease in peak height in some samples, as well as the presence of squalene, which has been found in planktonic organic detritus (Saliot et al., 1988). Differences in the calculated hydrogen indexes may reflect differences in the degree of preservation of the organic matter and/or the relative abundance of residual organic matter. The lower hydrogen index values might indicate poorer organic preservation and/or a larger relative proportion of residual organic matter. A common "live" organic matter source for the entire stratigraphic sequence is also consistent with the abundance of squalene in all of the pyrolysates.

The pyrolysis-gas chromatograph may also be used to thermally extract and analyze the S_1 hydrocarbons. These results are presented in Figure 9. Unlike mature extracts, which should be dominated by *n*-alkanes, these chromatograms are dominated by the isoprenoids pristane and phytane. *n*-alkanes are either absent or present in only trace quantities relative to the two isoprenoids. Such a chromatographic pattern is consistent throughout the penetrated section, including Cores 128-799B-65R and 128-799B-66R, which exhibited cut fluorescence on-board the ship.

As expected, a downhole increase in the complexity of the chromatographic pattern reflects the onset of thermal hydrocarbon generation, but not the presence of thermally mature hydrocarbons.

These thermal extracts also display variations in the pristane/phytane ratio and the relative abundance of specific compounds. For example, the pristane/phytane ratio of Sample 128-799B-65R-3, 14–16 cm, is ~1.0 (Fig. 9D) compared with 0.44–0.66 observed in the other samples. Such differences probably reflect temporal changes in both the biomass and the depositional environment.

DISCUSSION

Although all of the samples selected for this study were organically enriched, samples from the lower portion of the stratigraphic section (deeper than 454 mbsf; lower and middle Miocene) generally contain more organic matter than the shallow section. In addition, samples deeper than 740 mbsf display the most elevated hydrogen indexes. The discordance between organic enrichment and organic-

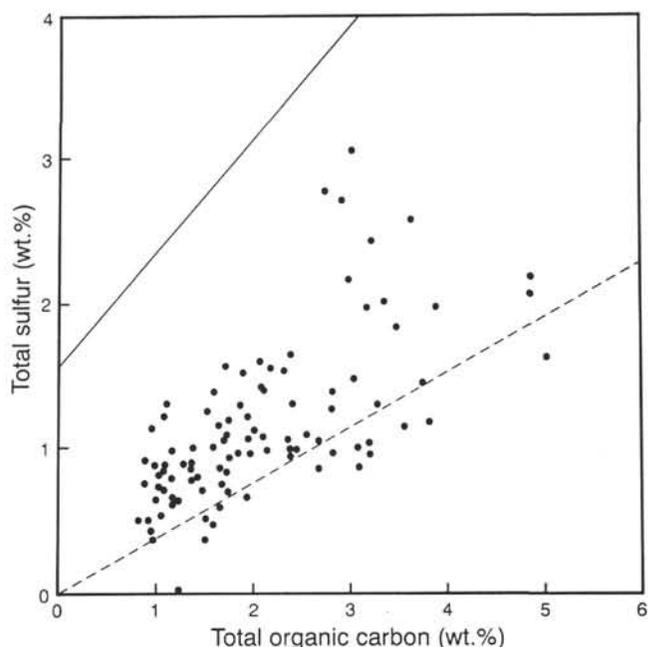


Figure 4. Relationship between total organic carbon and total sulfur. Dashed line = observed relationship for normal, modern marine sediments. Solid line = observed relationship for euxinic sediments of the Black Sea (Bernier and Raiswell, 1983).

hydrogen enrichment suggests possibly independent enrichment mechanisms. It is possible that the differences in organic carbon reflect differences in sedimentation rate, with higher TOC's associated with higher sedimentation rates (Müller and Suess, 1979), while differences in the hydrogen indexes may reflect differences in preservation efficiencies, with higher hydrogen index values reflecting better preservation, possibly as a result of more restricted circulation.

Kayoma et al. (1973) observed that organic hydrogen decreases at a greater rate than organic nitrogen, which in turn decreases at a more rapid rate than organic carbon during biochemical degradation of organic matter. Thus, the depletion in organic hydrogen associated with relatively constant organic carbon contents observed at Site 799 is probably the result of differences in the relative rates of elemental decomposition.

Possibly the most important results of this work are associated with the findings concerning the presence and generation of heavy hydrocarbons. The Rock-Eval maturity indexes clearly indicate that the penetrated section is thermally immature and has not yet entered into the main phase of hydrocarbon generation. This is consistent with the sediment's age, depth of burial, and geothermal gradient (98°C/km; Shipboard Scientific Party, 1990). In addition, these data indicate that migrated heavy hydrocarbons are not present within the penetrated section. No heavy hydrocarbon anomalies were detected, and those hydrocarbons that were observed appear to be thermally immature. Although the thermal extracts display increased complexity with depth, probably as a result of thermal hydrocarbon generation, such changes in composition are most probably associated with the earliest phases of thermogenic hydrocarbon generation. This interpretation is consistent with the Rock-Eval data and the interpretation of the volatile hydrocarbons by the shipboard party (Shipboard Scientific Party, 1990), who noted the presence of significant quantities of neopentane.

Although it was prudent and necessary to terminate drilling prior to reaching Site 799's objective, because of the observed cut fluorescence and the lack of shipboard data to determine the nature of the fluorescing material, this post-cruise investigation indicates that drilling might have proceeded safely if a more complete hydrocarbon monitoring program had been in use. This interpretation is significant

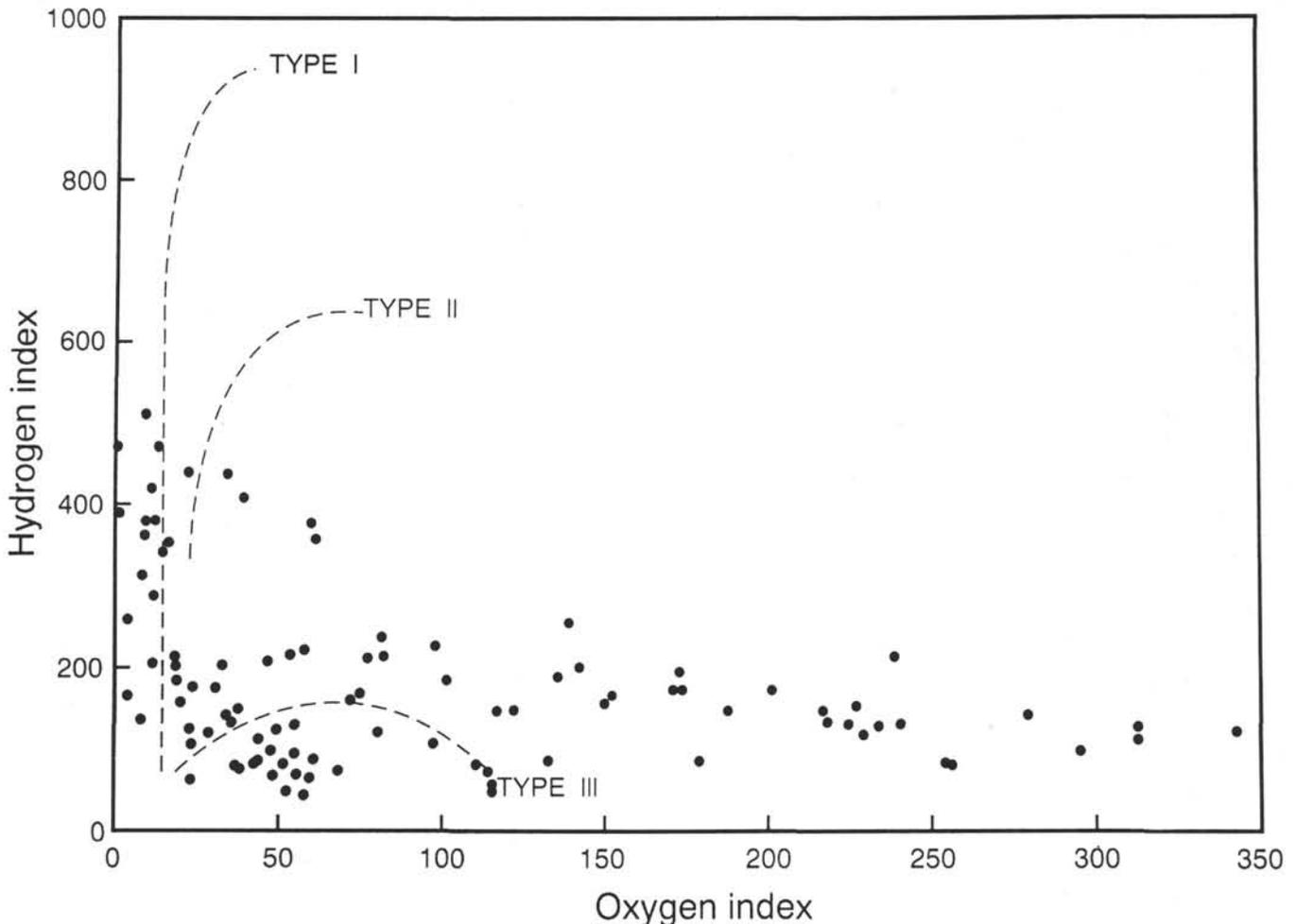


Figure 5. Modified van Krevelen-type diagram using the pyrolysis-derived hydrogen and oxygen indexes.

because a re-entry cone was left at the site and drilling might resume at Site 799 if the *JOIDES Resolution* returns to the Japan Sea.

SUMMARY

1. The lower portion (middle and lower Miocene) of the stratigraphic section is generally more enriched in both organic carbon and organic hydrogen. It appears that there may be different causes for the organic carbon and organic hydrogen enrichment. Organic carbon enrichment may reflect elevated sedimentation rates, while organic hydrogen enrichment may reflect increased preservation resulting from more restricted circulation.

2. Rock-Eval data do not indicate the presence of migrated heavy hydrocarbons in Cores 128-799B-65R, 128-799B-66R, or 128-799B-67R. Nor do these data indicate that the penetrated section experienced the necessary burial/thermal history for beginning the catagenic generation and expulsion of heavy hydrocarbons. This low level of thermal maturity is manifested in both Rock-Eval indexes.

3. The chromatographic fingerprint of the S_1 peaks obtained from Cores 128-799B-65R, 128-799B-66R, and 128-799B-67R are consistent with thermally immature bitumens and are similar to those obtained in the shallow portion of the section (Core 128-799A-4H). The thermal extracts are dominated by the isoprenoids pristane and phytane.

4. A decision to continue drilling could have been justified if a more complete shipboard hydrocarbon monitoring program had been in use on Leg 128.

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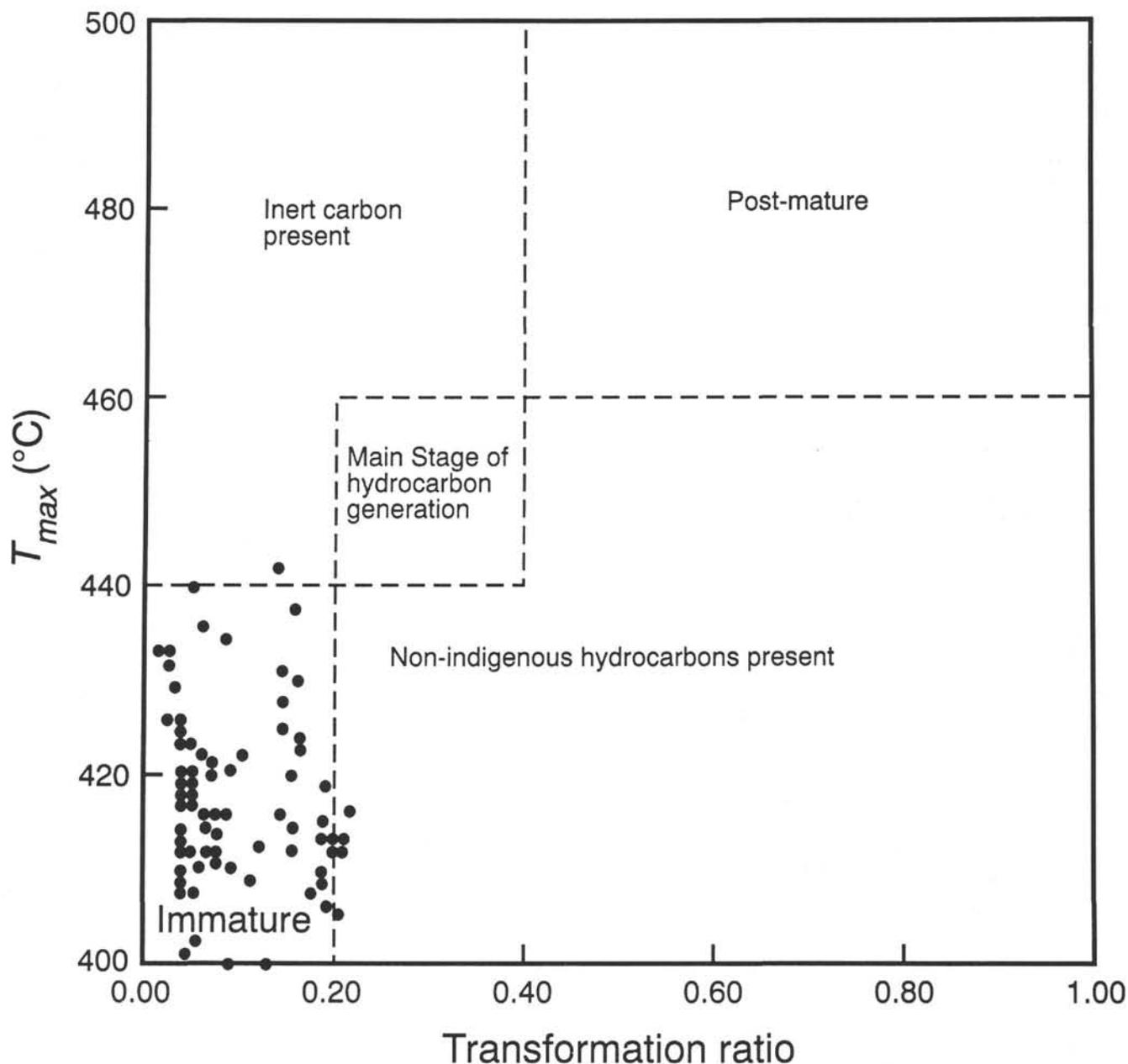


Figure 6. Relationship between T_{max} and TR, permitting an assessment of thermal maturity, the presence of inert carbon, and nonindigenous hydrocarbons.

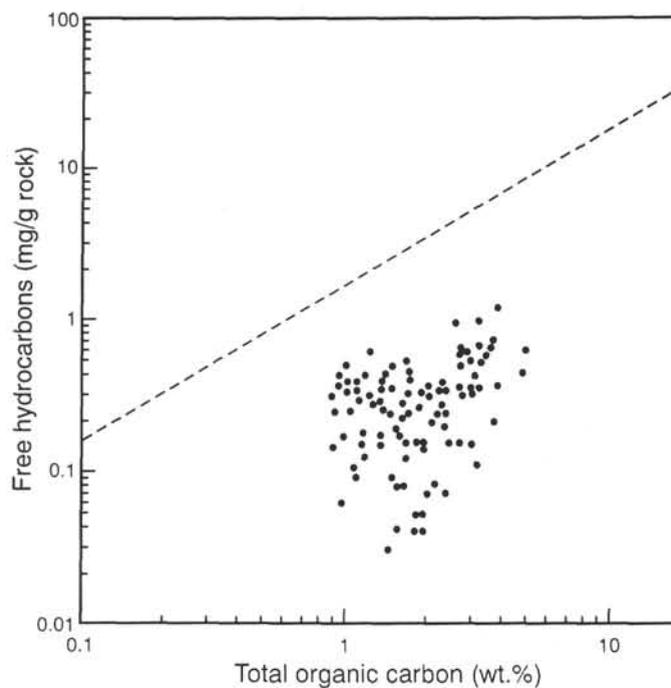


Figure 7. Relationship between S_1 yield and total organic carbon. Any samples plotting above the dashed line typically are contaminated or contain migrated hydrocarbons.

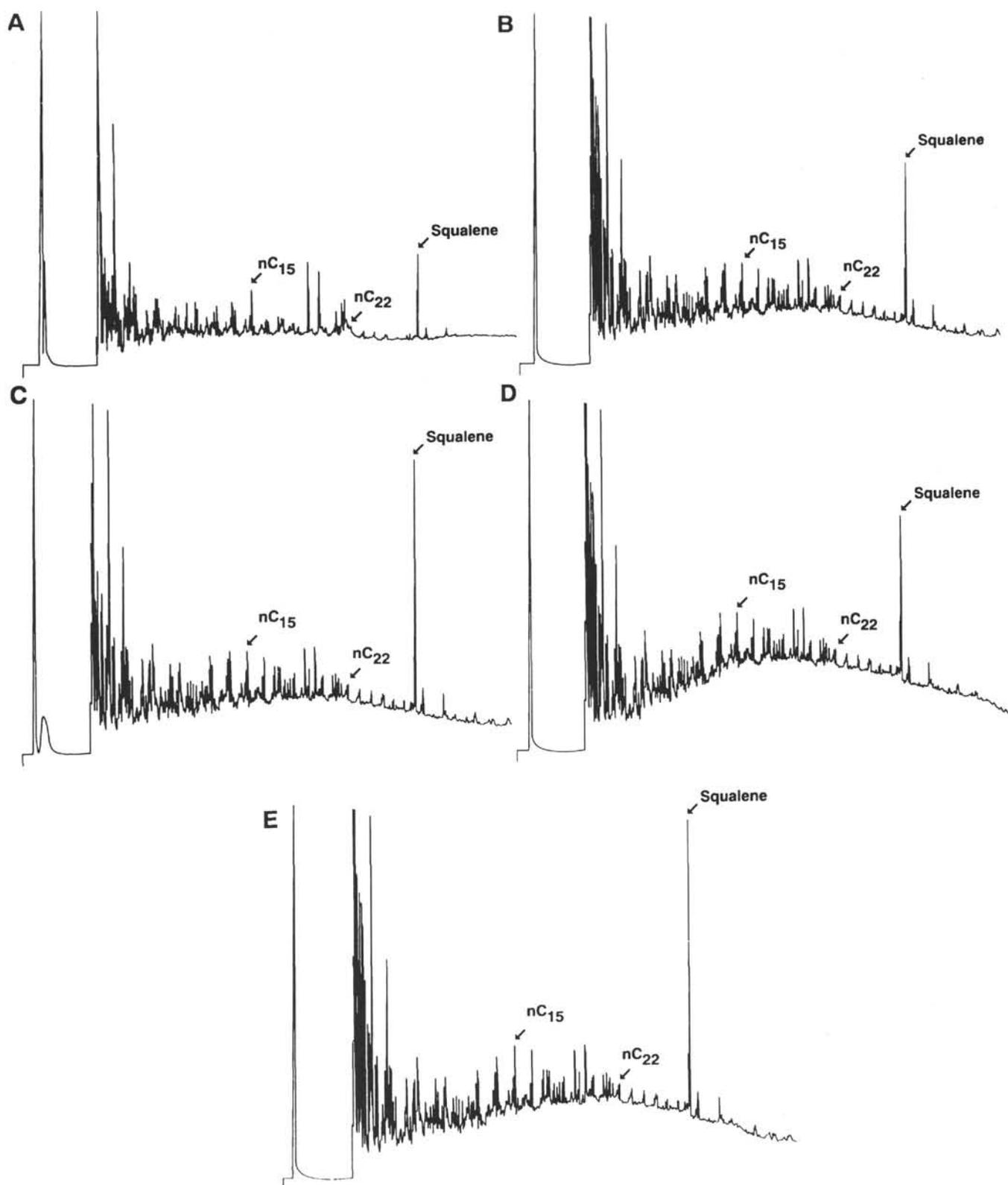


Figure 8. Pyrolysis-gas chromatograms. A. Sample 128-799A-8H-6, 50-54 cm. B. Sample 128-799B-6R-1, 33-38 cm. C. Sample 128-799B-22R-1, 6-9 cm. D. Sample 128-799B-35R-2, 42-44 cm. E. Sample 128-799B-67R-3, 9-11 cm.

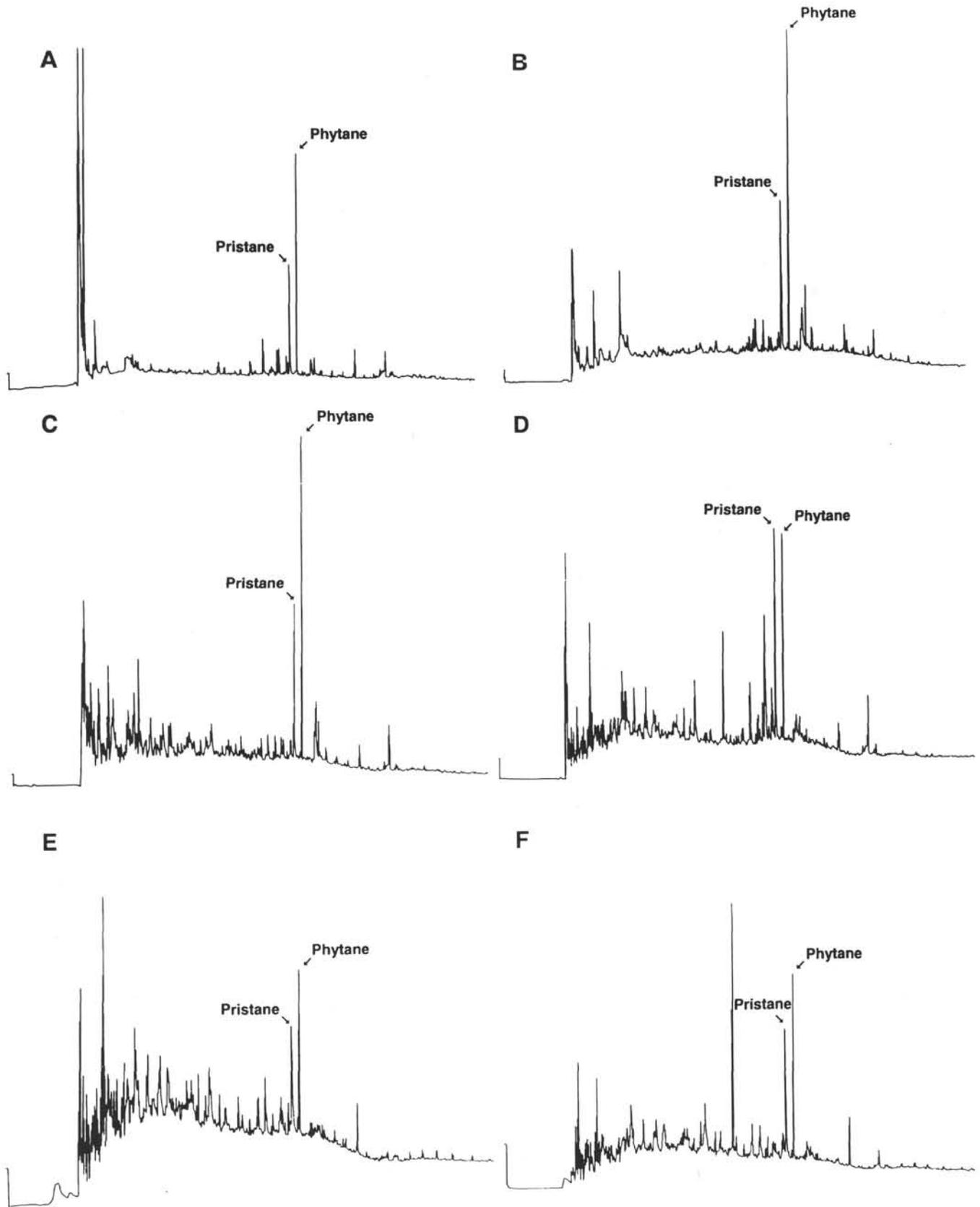


Figure 9. Gas chromatograms of thermally extracted S_1 hydrocarbons. A. Sample 128-799A-4H-6, 20–25 cm. B. Sample 128-799B-35R-2, 42–45 cm. C. Sample 128-799B-65R-2, 130–132 cm. D. Sample 128-799B-65R-3, 42–44 cm. E. Sample 128-799B-66R-2, 53–55 cm. F. Sample 128-799B-67-1, 51–53 cm.