38. ROCK-EVAL PYROLYSIS OF OUATERNARY SEDIMENTS FROM LEG 64, SITES 479 AND 480, GULF OF CALIFORNIA¹

K. E. Peters, Chevron Oil Field Research Company, Box 446, La Habra, California

and

B. R. T. Simoneit,² Institute of Geophysics and Planetary Physics, University of California–Los Angeles, Los Angeles, California

ABSTRACT

Geochemical analyses were carried out on Quaternary sediments from cores at Sites 479 and 480. The amount of organic matter indicates that these sediments have good to very good source-rock potential. Rock-Eval pyrolysis and microscopic examination show that many of the samples contain thermally immature, oil-prone, marine organic matter. Preliminary results show that Rock-Eval pyrolysis can distinguish oxic (bioturbated) and anoxic (laminated) organic facies in the cores.

More than 10% of the organic carbon in these immature sediments is normally lost as hydrolysate during conventional acid treatment for the removal of carbonates. The protokerogen remaining after solvent extraction and acid maceration constitutes only a fraction of the total organic matter. Elemental analysis, pyrolysis, and vitrinite reflectance of the kerogenous residue show that it is considerably less oil prone than the total organic matter.

INTRODUCTION

Demaison and Moore (1980) have suggested that studying the interaction of the oceanic oxygen-minimum layer with organic matter (OM) deposited in slope sediments will enhance our understanding of oil sourcebed genesis. Alternating laminated (anoxic) and homogeneous, bioturbated (oxic) zones were found in cores from the Deep Sea Drilling Project (DSDP)-International Phase of Ocean Drilling (IPOD) cores from Leg 64, Sites 479 and 480 (Curray et al., 1979; Schrader et al., 1980). These zones represent a unique opportunity to study the effects of periodic displacement of the oxygen-minimum layer on the geochemical and sedimentological parameters of young sediments. Both sites were drilled primarily in Quaternary marine sediments on the slope of the Guaymas Basin in the central Gulf of California. These unlithified sediments appear to represent modern analogs of shales, such as the Miocene Monterey Formation in California, which are rich in organic matter.

The concept of sedimentary organic facies is based on (1) the types of organisms that act as a source, (2) the depositional environment, and (3) conditions during early diagenesis. In ancient sediments, organic facies are mappable subdivisions of a stratigraphic unit that can be distinguished on the basis of the chemical composition of the organic matter. Examples of the use of various geochemical parameters in differentiating the organic facies characteristic of oxic and anoxic sedimentary environments include Pelet and Debyser (1977), Didyk et al., (1978), Byers and Larson (1979), and Jones and Demaison (1980). Facies determination by Rock-Eval pyrolysis produced negative (Favero et al., 1979) and positive (Demaison et al., 1980) results.

The purpose of this preliminary work is twofold: (1) to determine the quantity, quality, and degree of maturation of organic matter in these sediments to assess their hydrocarbon potentials and generative histories, and (2) to investigate the relation between Rock-Eval pyrolysis response and organic facies at Sites 479 and 480.

METHODS

Conventional "filtering" acidification procedures for the removal of carbonate prior to total organic carbon (TOC) analyses were conducted by DSDP. Each sample was acidified with 6N HCl in Leco filtering crucibles, and spent acid and wash water were removed by vacuum filtration. The dried residue was combusted, and organic carbon was measured as CO₂ (Gehman, 1962). Our "nonfiltering" acidification was modified from Wimberley

(1969). Aliquots of 100 mg of sediment were weighed into Leco nonfiltering combustion crucibles (No. 528-038). The samples were treated drop-wise with 6N HCl until all CO2 evolution ceased and were then allowed to react overnight. Crucibles containing the samples were oven-dried at 100°C for about 30 min. and analyzed as usual on the Leco carbon analyzer.

"Rock-Eval" is a pyrolysis instrument designed to rapidly measure hydrocarbon potential and generative history from whole-rock samples (Espitalié et al., 1977). The method is based on the selective detection of hydrocarbon compounds and carbon dioxide generated from organic matter in the rock during programmed heating in an inert atmosphere.

Several parameters are obtained by this technique. A flame ionization detector (FID) senses any hydrocarbons generated during pyrolysis. The first peak (S1) represents the quantity of free hydrocarbons (HC-bitumen) that is thermally distilled from the rock (mg HC/g sample). The second peak (S2) comprises hydrocarbons generated by pyrolytic degradation of the insoluble organic matter (kerogen) (mg HC/g sample). Carbon dioxide generated from the organic matter is analyzed as a third peak (S3) (mg CO2/g) using a thermal conductivity detector (TCD). Carbonate lithologies can pose a problem since some inorganic S3 can be produced (Peters, unpubl. data).

During pyrolysis the temperature is monitored by a thermocouple. The temperature at which the maximum amount of hydrocarbons are

¹ Curray, J. R., Moore, D. G., et al., Init. Repts. DSDP, 64: Washington (U.S. Govt. Printing Office). ² Present address: School of Oceanography, Oregon State University, Corvallis, Oregon.

generated is called T_{max} . The hydrogen index (HI) corresponds to the quantity of hydrocarbon compounds from S2 normalized to the TOC of the sample (mg HC/g organic carbon). The oxygen index (OI) corresponds to the quantity of CO₂ normalized to the TOC of the sample (mg CO₂/g organic carbon). As previously demonstrated (Espitalié et al., 1977), the HI and OI show good correlation with atomic H/C and atomic O/C, respectively.

Operating parameters for Rock-Eval pyrolysis were identical to those in Clementz et al. (1979). Homogenized samples of untreated or acid-treated dry sediments were pyrolyzed from 250 to 550°C in a helium atmosphere at a program rate of 25°C/min. Peak areas were calculated by digital integration.

Selected sediment samples were treated using the standard procedure for kerogen isolation applied to source rocks. Kerogen is defined as the acid-resistant, insoluble organic material isolated from ancient sediments. Site 479 and 480 samples were exhaustively extracted in a Soxhlet apparatus using carbon disulfide. The remaining material was treated with 6N hydrochloric acid for carbonate removal followed by repeated washing with water. Hydrofluoric acid (60%) removed most silicate minerals. The residue was rinsed with dichloromethane prior to drying at 40°C in a vacuum oven. Because of the thermally immature nature of these young sediments, we prefer to use the term "protokerogen" (Peters et al., 1981) to describe the insoluble residue. Protokerogen may contain a variety of biopolymers-such as lignin, cell wall debris, and weakly bound lipids or humic acids-subject to alteration during diagenesis. Our preliminary studies did not involve extraction of humic substances using basic solution. Thus, the protokerogen residues may contain some humic acids.

Carbon, hydrogen, and nitrogen contents of the protokerogen were measured using a Carlo Erba MOD 1106 elemental analyzer. Polished slides for microscopic analysis were prepared using the method described by Baskin (1979). Vitrinite reflectance measurements were completed by B. Alpern (CERCHAR, France).

DISCUSSION

Whole-Sediment Analyses

Total organic carbon, based on the nonfilter acidification procedure and Rock-Eval pyrolysis data for whole-sediment samples from Sites 479 and 480, are found in Tables 1 and 2, respectively. Total organic carbon values determined by DSDP on these samples are reported in parentheses in the tables. Four replicate analyses are included in these data. The average standard deviations, expressed as percentages of the respective measured values of TOC, HI, OI, and $T_{\rm max}$, are 0.5, 6.1, 5.5, and 0.7%.

Figure 1 plots TOC values for the nonfilter (hydrolysate-retained) versus filter (hydrolysate-lost) methods. It shows that, on the average, more than 10% of the organic carbon in a sample is lost as hydrolysate during conventional acid treatment. Additional loss of colloidal organic matter through the porous Leco filtering crucibles is possible. These results agree with those of Roberts et al. (1973), who showed a loss of up to 44% of the organic matter from Recent sediments in the acid filtrate. We have observed that sediments and rocks older than those found at these sites generally contain diagenetically mature organic matter, which is more resistant to hydrolysis.

Figure 2 is a plot of TOC versus total hydrocarbon yield (S1 + S2) obtained by Rock-Eval pyrolysis of the whole-sediment samples. These nonlinear results appear to result from differences in composition of the organic matter among samples. Preliminary optical studies by B. Alpern, for example, suggest that a difference in maceral composition exists between low- (< 2.5%) and high-(> 2.5%) TOC sediments at these localities. Low-TOC sediments commonly represent oxidizing depositional regimes dominated by recycled, hydrogen-poor macerals. Higher TOC sediments are characteristic of more reducing environments dominated by hydrogen-rich macerals. Upon pyrolysis, hydrogen-rich macerals yield more hydrocarbons per gram organic carbon than do hydrogen-poor macerals (Tissot et al., 1974). Low-TOC sediments at these localities seem to contain proportionally more recycled organic matter than high-TOC sediments. The variation in total hydrocarbon yield for samples with more than 2.5% organic carbon may also reflect differences in maceral composition. Additional optical studies are in progress.

An alternative explanation for the results in Figure 2 is absorption of pyrolytic hydrocarbons by the kerogen/ mineral matrix (Espitalié et al., 1980). This absorptive effect can be likened to the behavior of a sponge. When the supply of hydrocarbons to the sponge is low (low TOC), much of the hydrocarbon material is absorbed by the sponge. Once a specific threshold of hydrocarbon supply is reached, however, the sponge becomes saturated, and hydrocarbons flow through as rapidly as they are supplied.

All TOC values at Site 479 (Table 1) are greater than 1%, and most are over 2%. In more mature sediments this would indicate good to very good quantities of source rock organic material for hydrocarbon generation. (Organic carbon content does not, however, specify the proportion of the organic matter convertible to hydrocarbons.) $T_{\rm max}$ values range from 403 to 427°C. These low values, combined with negligible S1 (free hydrocarbon) content, verify the immaturity of the sediments. The transformation ratio, S1/(S1 + S2) (Tissot and Welte, 1978), for all these samples is approximately zero. Hydrocarbon-generating potential, as measured by S2, ranges from fair to very good. The variability with depth for values such as S2/S3, HI, and OI far exceeds the standard deviation for their measurement.

Rock-Eval and TOC results for Site 480 are similar to those from Site 479. TOC values range from 2.5 to 3.4%, indicating very good source rock potential in terms of quantities of organic matter. $T_{\rm max}$ values (400-420°C) and negligible S1 hydrocarbons again indicate immature sediments.

Figures 3 and 4 are HI versus OI plots based on pyrolysis results for Sites 479 (Table 1) and 480 (Table 2). Pathways I, II, and III represent the changing compositions of the principal types of organic matter in source rocks (Espitalié et al., 1977). Each pathway approaches the origin of the figure as a result of thermal maturation during burial. Organic matter plotting on the Type I pathway, such as that from shales of the Green River Formation, originates as very oil-prone material. Type II source rocks, such as those of the lower Toarcian of the Paris Basin, are moderately oil prone. Type III source rocks, such as the Upper Cretaceous rocks of the Douala Basin, are only gas prone. Most rocks contain mixtures of the principal types of organic matter.

By using different symbols, the data for each site are divided into three arbitrary depth intervals to show general depositional trends. At Site 479 (Fig. 3) the shallow Table 1. Rock-Eval pyrolysis and TOC results, Site 479.

Sample (interval in cm)	Sub-bottom Depth (m)	TOC ^b (wt.%)	S1 (mg HC/g)	S2 (mg HC/g)	S3 (mg CO ₂ /g)	T _{max} (°C)	S1/(S1 + S2)	S2/S3	HI (mg HC/gC)	OI (mg CO ₂ /gC)
3-2, 99-101	14.99	3.19 (2.8)	0	24.8	8.8	415	0	2.8	777	276
5-3, 107-109	36.57	2.92 (2.7)	0	19.1	10.6	417	0	1.8	654	363
6-4, 80-82	46.30	2.54 (2.3)	0.2	10.5	8.9	413	0	1.2	413	350
7-5, 108-110	56.58	2.96 (2.7)	0	31.2	7.0	405	0	4.5	1054	236
8-3, 45-47	63.45	2.73 (2.4)	0	14.5	10.7	419	0	1.4	531	342
9-3, 99-101	73.49	2.60 (3.0)	0	12.1	9.0	415	0	1.4	467	346
10-4, 65-67	84.15	2.72 (2.3)	0	14.4	12.0	420	õ	1.2	529	441
10-7, 24-26	89.24	2.68 (2.4)	õ	15.7	87	413	õ	1.8	586	325
12-6, 111-113	106.61	2 59 (2 4)	õ	15.3	77	417	õ	2.0	591	297
13-1, 110-112	108.60	3 26 (2.9)	ő	18.4	10.3	411	ő	1.8	564	316
14-2 52-54	119.02	2 83 (2 6)	ő	24 3	8.2	413	0	3.0	858	290
15-2, 97-99	128.97	3.16 (2.8)	õ	19.4	7.5	413	ő	3.4	614	221
15-5, 108-110	133.58	3 34 (2.9)	0.4	22.9	8.5	415	0	27	686	254
16-3, 126-128	140.26	3 48 (3 2)	0	27.2	0.3	415	0	1.8	782	267
18-1, 82-84	155.82	2 09 (1.9)	õ	10.9	4.9	403	0	2.2	522	234
21-5, 110-112	190.60	2.82 (2.5)	ő	12.4	75 4	412	0	0.9	440	191
22-5 101-103	200.01	2.98 (2.6)	ő	16.8	7.2	410	ő	23	564	242
23-4 73-75	207.73	2 34 (2 3)	0	12.0	9.1	420	0	1.5	513	346
24-3 86-88	215.86	2.80 (2.5)	0	17.8	6.0	410	0	3.0	636	214
25-2 131-133	224 31	2.00 (2.5)	0	14.7	5.4	415	0	27	544	200
26-1 82-84	231 82	1 77 (1.6)	ő	6.0	5.2	413	0	1 3	390	200
27-4 72-74	245 72	2 66 (2 5)	ő	20.8	5.5	413	ő	3.6	781	214
31-5 69-71	285 19	3.03 (2.6)	0	24.3	3.0	419	0	6.2	801	129
31-5 70-72	285.20	3.09 (2.8)	0.3	24.5	5.5	410	0	3.4	680	204
32-1 63-65	289.63	2.80 (2.5)	0.5	11.6	0.5	410	0	1.4	416	304
34-2 84-86	200.03	2.80 (2.3)	0	10.2	5.1	413	0	2.9	684	181
34-5, 108-110	314 08	2.02 (2.7)	0	17.5	5.1	412	0	2.6	546	200
34-5, 130-141	314.00	3.20 (3.0)	0	17.5	0.7	417	0	2.0	527	209
26a 2 70 72	322.39	2.36 (2.3)	0	13.0	0.5	410	0	2.1	327	232
36.3 70.72	329.70	3.24 (2.9)	0	14.9	1.2	410	0	2.1	522	212
37 2 78 80	329.70	3.21 (2.9)	0	17.1	0.8	421	0	2.5	533	212
202 5 120 121	357.70	3.02 (2.8)	0	18.8	10.0	410	0	1.9	023	331
30 -3, 129-131	352.29	3.40 (3.0)	0	21.1	7.2	410	0	3.8	800	208
30-5, 129-151	352.29	3.48 (3.0)	0	25.7	7.2	413	0	3.0	139	207
39-4, 107-109	360.07	3.80 (3.5)	0	25.2	9.0	419	0	2.8	603	237
40-6, 110-112	372.60	2.32 (2.1)	0	13.5	9.8	418	0	1.4	581	422
41-1, 99-101	3/4.49	3.06 (2.7)	0	12.0	8.6	418	0	1.4	392	281
432, 82-84	394.82	2.90 (2.6)	0	14.7	10.1	418	0	1.5	507	348
43-2, 82-84	394.82	2.91 (2.6)	0	14.7	10.8	413	0	1.4	505	3/1
44-3, 93-95	405.93	2.08 (1.9)	0	5.9	8.1	427	0	0.7	285	389
43-1, 81-83	412.31	2.22 (1.9)	0	9.8	6.3	407	0	1.6	441	284
4/4, 108-110	436.08	1.37 (1.2)	0	3.6	3.7	418	0	1.0	265	2/0
47-4, 108-110	436.08	1.36 (1.2)	0	3.2	3.0	418	0	1.0	235	221

a Replicate analyses. b TOC data using conventional acid treatment for carbonate removal in parentheses (DSDP data).

Table 2. Rock-Eval pyrolysis and TOC results, Site 480.

Sample	Sub-bottom Depth (m)	TOC ^a (wt.%)	S1 (mg HC/g)	S2 (mg HC/g)	S3 (mg CO ₂ /g)	T _{max} (°C)	S1/(S1 + S2)	S2/S3	Hl (mg HC/gC)	OI (mg CO ₂ /gC)
3,CC	14.20	2.68 (2.9)	0	18.5	8.7	418	0	2.1	690	325
5,CC	23.60	3.09 (2.8)	0	27.1	7.7	415	0	3.5	876	249
6,CC	28.40	2.86 (2.5)	0	17.6	6.1	420	0	2.9	763	265
7,CC	33.10	2.94 (2.9)	0	13.3	8.8	411	0	1.5	550	365
9,CC	42.60	3.36 (3.0)	0	16.5	14.0	417	0	1.2	491	417
11,CC	49.10	2.50 (2.5)	0	11.8	7.9	412	0	1.5	472	316
13,CC	66.30	2.69 (2.4)	0	14.5	6.0	410	0	2.4	539	223
17,CC	85.40	2.99 (2.7)	0	15.6	6.5	413	0	2.4	522	217
19,CC	94.90	2.73 (2.5)	0	19.6	4.8	417	0	4.1	718	176
21,CC	104.20	3.06 (3.2)	0	16.4	9.9	415	0	1.7	536	324
23,CC	113.90	2.74 (2.2)	0	23.5	5.3	413	0	4.4	858	193
25,CC	123.40	3.03 (2.8)	0	28.4	5.4	416	0	5.3	937	178
27,CC	132.90	2.90 (2.7)	0	29.7	5.8	408	0	5.1	1024	200
29,CC	142.40	2.62 (2.3)	0	25.4	4.2	411	0	6.0	969	160
31,CC	151.90	2.56 (2.2)	0	20.8	4.1	400	0	5.1	813	160

^a TOC data using conventional acid treatment for carbonate removal are in parentheses (DSDP data).



Figure 1. Nonfilter (hydrolysate-retained) versus conventional filter (hydrolysate-lost) TOC results for whole sediments, Sites 479 and 480. (Dashed line represents ideal correlation.)



Figure 2. Nonfilter TOC versus total hydrocarbon yield (S1 + S2) from Rock-Eval pyrolysis of whole-sediment samples, Sites 479 and 480.

interval (14.99–108.60 m) shows a range of HI and OI results, but most points cluster between the immature portions of the Type II (oil-prone) and Type III (gasprone) pathways. Thus, most of these sediments in the shallow interval are only weakly oil prone. Data for the intermediate interval (119.02–360.07 m) show that the general quality (oil-generating potential) of the organic matter was better than that deposited subsequently in the shallow interval. Most of the intermediate depth samples plot near the immature portion of the Type II pathway in Figure 3. Samples from the deep interval (372.60–436.08 m) are predominantly weakly gas prone, for they plot between immature Type II and Type III pathways.



Figure 3. Hydrogen index versus oxygen index for whole-sediment samples, Site 479.



Figure 4. Hydrogen index versus oxygen index for whole-sediment samples, Site 480.

At Site 479 the sediments were severely disturbed by biogenic gas partings and drilling. Unfortunately, the disturbed nature of the core does not allow a strict comparison of Rock-Eval pyrolysis results with lithology.

At Site 480, deposition of very oil-prone organic matter with a composition intermediate between immature Types I and II (Fig. 4) occurred in the deep interval (113.90–151.90 m). In an intermediate interval (33.10–104.20 m) most of the organic matter plots between immature Types II and III and is of lower quality than that of the overlying shallow interval (14.20–28.40 m) that plots near the immature Type II pathway.

The unlithified samples from Site 480 are core-catcher material, which is sometimes disturbed during collection. The core lithology is divided almost equally between two alternating sediment types (Schrader et al., 1980). Laminated zones, consisting of rhythmic couplets, are mixtures of diatom ooze and terrigenous clays. Homogeneous zones consist of diatomaceous mud to muddy ooze with evidence of extensive burrowing. The latter probably reflect times with a less-pronounced oxygen-minimum zone that allowed the existence of epifauna and infauna. The causes of these fundamentally different lithologies also appear to have determined the distribution of organic facies at this site.

Figure 5 plots TOC and some Rock-Eval parameters versus lithology at Site 480. An inverse relation exists between HI and OI as a function of depth. The results suggest different types of organic matter in the oxic, homogenous zones (low HI, high OI) than in the anoxic, laminated zones (high HI, low OI).

Note the striking change in HI, OI, and S2/S3 between 104.20 and 151.90 meters sub-bottom. The deeper interval is laminated and of sufficient thickness to be unaffected by mixing with homogenous layers from above during collection. The S2/S3 ratios and HI values for the deeper samples are significantly larger than those of the shallower sediments. The OI and T_{max} values of the deeper samples are smaller than those of the shallower sediments. The significance of these preliminary results is that Rock-Eval pyrolysis has been used successfully to differentiate organic facies in this core.

Protokerogen Analyses

Table 3 shows the results of elemental analysis, Rock-Eval pyrolysis, and microscopic examination of protokerogens isolated from selected Site 479 and 480 samples. The S2/S3 and HI and OI pyrolysis results in the table show that most of these residues are less oil prone than the total organic matter in the same sediment. This is particularly apparent for the very oil-prone organic matter in the deeper samples (113.90–151.90 m) at Site





Table 3. Microscopic, elemental analysis, and Rock-Eval pyrolysis results, Sites 479 and 480 kerogens.

Sample (level in cm)	Sub-bottom Depth (m)	Atomic H/C	$R_0^{1}(\%)$	S1 (mg HC/g)	S2 (mg HC/g)	S3 (mg CO ₂ /g)	T _{max} (°C)	S1/(S1 + S2)	S2/S3	HI (mg HC/gC)	Ol (mg CO ₂ /gC)
479-7-5, 108	56.58	1.18	0.26	0	240.8	74.4	409	0	3.2	553	171
479-12-6, 111	106.61	1.07	0.25	1.2	108.5	60.6	410	0	1.8	341	190
479-23-4, 73	207.73	1.09	0.28	0.2	116.8	52.6	422	0	2.2	355	160
479-36-3, 70	329.70	1.15	0.35	1.7	221.9	68.0	413	0	3.3	474	145
479-43-2, 82	394.82	1.09	0.35	1.2	172.3	79.4	421	0	2.2	384	177
479-47-4, 108	436.08	1.19	0.38	7.1	99.4	24.0	429	0.1	4.1	406	98
480-5,CC	23.60	1.16	0.35	2.8	148.0	96.6	415	0	1.5	418	273
480-11,CC	49.10	1.14	0.28	0	126.3	93.8	409	0	1.3	359	267
480-13,CC	66.30	1.08	0.25	6.6	142.1	90.1	410	0	1.6	424	269
480-17,CC	85.40	1.20	0.25	1.8	386.9	138.8	413	0	2.8	859	308
480-19,CC	94.90	1.15	0.27	0	166.3	84.4	409	0	2.0	509	258
480-21,CC	104.20	1.18	0.28	1.8	311.2	109.9	413	0	2.8	688	243
480-23,CC	113.90	1.11	0.31	0	230.8	118.0	407	0	2.0	715	366
480-25,CC	123.40	1.20	0.25	3.0	243.8	119.7	408	0	2.0	525	258
480-29,CC	142.40	1.13	0.34	0	246.8	129.1	413	0	1.9	577	302
480-31,CC	151.90	1.10	0.30	1.3	153.2	74.6	410	0	2.1	363	177

^a Oil immersion vitrinite reflectance of about 50 randomly oriented vitrinite particles per sample (by B. Alpern).

480. These residues constitute only a fraction of the total organic matter in the untreated samples. Apparently, oil-prone materials are preferentially removed from these immature sediments during acid maceration and solvent extraction (see Fig 1). Unlike the sediments at Sites 479 and 480, we find a general agreement between whole-rock and kerogen determinations of organic matter quality in older sediments and rocks. These results suggest that the Quaternary sediments at these localities on the Guaymas Slope are diagenetically immature. The production of kerogen from protokerogen, lipids, humic substances, and other classes of organic materials is still in progress (Peters et al., 1981).

Mean vitrinite reflectance values (Table 3) range from 0.25 to 0.38% at Site 479 and from 0.25 to 0.35% at Site 480. These values are characteristic of immature organic matter and agree with conclusions based on pyrolysis. Simoneit et al. (1979), reached similar conclusions by using elemental and isotopic analyses of protokerogens isolated from sediments near these locations. The reflectance studies also show varying quantities of recycled organic matter in Site 479 and 480 sediments.

Figure 6 is an atomic H/C versus O/C plot for the protokerogens and is based on data from Table 3. Location of points on the figure was determined using atomic H/C and vitrinite reflectance measurements (Jones and Edison, 1978). Lines I, II, and III in the figure are evolutionary pathways followed by the three principal types of kerogens during burial maturation (Tissot et al., 1974). This plot shows that samples from Sites 479 and 480 contain immature, moderately oil-prone protokerogen, whose composition is intermediate between Types II and III. The protokerogens are generally less oil prone than the whole-sediment samples shown in Figures 3 and 4.

CONCLUSIONS

Rock-Eval pyrolysis of whole sediments from Sites 479 and 480 shows that many consist of thermally immature, oil-prone, marine organic matter. In general, protokerogen isolated from these samples is less oil



Figure 6. Atomic H/C versus O/C plot for protokerogens isolated from selected Site 479 and 480 sediments.

prone than the total organic matter. Hydrolysis and loss of labile, oil-prone organic matter are significant during acid maceration and solvent extraction of young sediments. Preliminary results suggest that Rock-Eval pyrolysis is a useful geochemical method of mapping facies boundaries.

ACKNOWLEDGMENTS

We thank the management of the Chevron Oil Field Research Company for permission to publish this work. B. Alpern (CER-CHAR, France) completed vitrinite reflectance and maceral analyses of the kerogen isolates. We thank H. Halpern and P. C. Henshaw, Jr. for their reviews of this chapter. Special thanks are due R. W. Jones and G. J. Demaison for helpful suggestions and discussions. Contribution 2094 from the Institute of Geophysics and Planetary Physics, UCLA.

REFERENCES

- Baskin, D. K., 1979. A method of preparing phytoclasts for vitrinite reflectance analysis. J. Sediment. Petrol., 49:633-635.
- Byers, C. W., and Larson, D. W., 1979. Paleoenvironments of Mowry Shale (Lower Cretaceous), western and central Wyoming. Am. Assoc. Pet. Geol. Bull., 63:354-361.
- Clementz, D. M., Demaison, G. J., and Daly, A. R., 1979. Well site geochemistry by programmed pyrolysis [paper presented at the Offshore Technology Conference, Houston, April 30-May 3].
- Curray, J. R., Moore, D. G., Aguayo, J. E., et al., 1979. Leg 64 seeks evidence on development of basins. *Geotimes*, 24:18-20.
- Demaison, G. J., Bourgeois, F., and Melendez, F., 1980. Geochemistry and petrology of Miocene (Alcanar) carbonate source beds, Casablanca Field, Tarragona Basin, Spain [paper presented at the Geological Society of America Annual Meeting, Atlanta].
- Demaison, G. J., and Moore, G. T., 1980. Anoxic environments and oil source bed genesis. Org. Geochem., 2:9-31.
- Didyk, B. M., Simoneit, B. R. T., Brassell, S. C., et al., 1978. Organic geochemical indicators of paleoenvironmental conditions of sedimentation. *Nature*, 272:216–222.
- Espitalié, J., Madec, M., and Tissot, B., 1977. Source rock characterization method for petroleum exploration. 9th Ann. Offshore Technol. Conf., Houston, May 2-5, pp. 439-448.
- _____, 1980. Role of mineral matrix in kerogen pyrolysis: Influence on petroleum generation and migration. Am. Assoc. Pet. Geol. Bull., 64:59-66.
- Favero, V., Leplat, P., Mennig, J. J., et al., 1979. Exemple de distribution de la matière organique au Quaternaire sondage CNR VE-1, Venise. Rev. Inst. Fr. Pet., 34:351-370.

- Jones, R. W., and Demaison G. J., 1980. Organic facies—stratigraphic concept and exploration tool [paper presented at the AAPG-SEPM-EMD Annual Convention, Denver, Colorado, June 8-11].
- Jones, R. W., and Edison, T. A., 1978. Microscopic observations of kerogen related to geochemical parameters with emphasis on thermal maturation. In Oltz, D. (Ed.), Symposium in Geochemistry: Low Temperature Metamorphism of Kerogen and Clay Minerals: SEPM, Los Angeles, Oct. 5, 1-12.
- Pelet, R., Debyser, Y., 1977. Organic geochemistry of Black Sea cores. Geochim. Cosmochim. Acta, 41:1575-1586.
- Peters, K. E., Rohrback, B. G., and Kaplan, I. R., 1981. Geochemistry of artificially-heated humic and sapropelic sediments—I. Proto-kerogen. Am. Assoc. Pet. Geol. Bull., 65:688-705.
- Roberts, A. A., Palacas, J. G., and Frost, I. C., 1973. Determination of organic carbon in modern carbonate sediments. J. Sediment. Petrol, 43:1157-1159.
- Schrader, H., Kelts, K., Curray, J., et al., 1980. Laminated diatomaceous sediments from the Guaymas Basin slope (Central Gulf of California): 250,000-year climate record. *Science*, 207: 1207-1209.
- Simoneit, B. R. T., Mazurek, M. A., Brenner, S., et al., 1979. Organic geochemistry of Recent sediments from the Guaymas Basin, Gulf of California. *Deep-Sea Res.* Part A, 26:879-891.
- Tissot, B., Durand, B., Espitalié, J., et al., 1974. Influence of nature and diagenesis of organic matter in formation of petroleum. Am. Assoc. Pet. Geol. Bull., 58:499-506.
- Tissot, B. P., and Welte, D. H., 1978. Petroleum Formation and Occurrence: New York (Springer-Verlag).
- Wimberley, J. W., 1969. A rapid method for the analysis of total organic carbon in shale with a high-frequency combustion furnace. Anal. Chim Acta, 48:419-423.