

25. GEOCHEMICAL ANALYSIS OF SAMPLES FROM HOLES 391A AND 391C, LEG 44: BLAKE-BAHAMA BASIN

Wallace G. Dow,¹ The Superior Oil Company, Houston, Texas

INTRODUCTION

Fifteen samples from Holes 391A and 391C were selected for geochemical analysis to evaluate the petroleum-generating capacity in a thick section of Cretaceous shale rich in organic carbon. Poorly oxygenated bottom water conditions are probably responsible for the preservation of organic matter in the Cretaceous black shales, but the origin of the organic material is not clearly understood. Bottom morphology, periodic nonreducing conditions, and a variable terrigenous contribution all affect sedimentation during the black shale episode.

Interest in the Cretaceous black shales centers on their capacity to generate oil and gas and hence whether they might be a source of petroleum under the Atlantic continental margins. To date, the black shale has been encountered in a number of relatively shallow DSDP holes but has always been thermally immature due to insufficient depth of burial for petroleum generation. The Site 391 samples offer an opportunity to study the black shale kerogen in detail and to evaluate its source capability should it also be present beneath thicker continental margin deposits. Data pertinent to the geologic history of the Blake-Bahama Basin was also be derived from geochemical study of the subject samples.

EXPERIMENTAL

The samples were oven dried at 40°C overnight and then freeze dried for 8 hours. A portion of the sample (0.6 g) was taken for carbonate and organic carbon analysis. This sample was pulverized and passed through a 60-mesh sieve. One-half (0.5) gram was reacted with 20 per cent HCl for 16 hours to remove carbonates. The residue was analyzed for carbon in a LECO WR12 Carbon Determinator. The remainder of the sample was ground and soxhlet extracted with benzene-methanol (azeotrope composition 3:2) for 20 hours. The residue was pulverized and extracted again for 40 hours. In both extractions, copper was added to the boiling flask to remove sulfur. The extracts were combined, the solvent evaporated, and the extracts weighed.

The extracts were separated by liquid chromatography. Asphaltenes were precipitated by the addition of hexane and removed by filtration through a

column packed with powdered teflon. The soluble fraction was further separated on a column containing 21.3 grams Merck No. 60 silica gel and 7.1 grams Alcoa F-20 alumina. Elution with hexane, benzene, and benzene-methanol yielded the saturate, aromatic, and NSO fractions, respectively. Asphaltenes were eluted from the teflon column with benzene-methanol and following solvent evaporation, washed with distilled water. All fractions were dried and weighed. The saturate fraction was analyzed by gas chromatography on a Varian 1400 equipped with a 6.1-meter eutectic column programmed from 160° to 350°C at 20°/minute.

The extracted sample (35 g) was treated with HCl (20%) and HF (70%) to concentrate the kerogen fraction. The residue was thoroughly washed with distilled water and freeze dried for 16 hours to remove all traces of moisture. A portion of the residue was mixed with epoxy to form a plug which was polished. Thermal maturity and visual kerogen type were determined with a Zeiss Universal reflecting microscope. A few samples yielded sufficient kerogen concentrate for elemental analysis. These samples were re-treated in HCl (20%) for 6 hours, washed, subjected to heavy mineral separation to remove pyrite, and freeze dried for 16 hours. Hydrogen-carbon ratios were determined with a Perkin-Elmer, Model 240 elemental analyzer. The analysis scheme is shown on Figure 1.

RESULTS

Dark gray to black Cretaceous shales at Site 391 are rated as marginal to very good, potential sources for primarily wet and dry gas. High percentages of amorphous, oil-generating organic matter are present in only a few samples containing little organic matter, and the overall capacity of the black shale section to yield crude oil is therefore limited. The top of the oil-generation maturity zone (0.6 R_o) occurs near the base of the Cretaceous system at about 1250 meters sub-bottom, and the beginning of significant wet gas generation (0.8 R_o) is in the Jurassic at about 1800 meters. Maturation studies also indicate that about 800 meters of section was lost to erosion at the Cretaceous/Miocene unconformity and that the two populations of recycled organic material were deposited as sub-bituminous and high-volatile "A" bituminous coal. If the samples analyzed are representative of the Cretaceous black shale sequence at Site 391, then very little crude oil would be generated even if the same interval were more deeply buried under continental margin deposits.

¹Present address: Getty Oil Company, 3903 Stoney Brooke, Houston, Texas 77063.

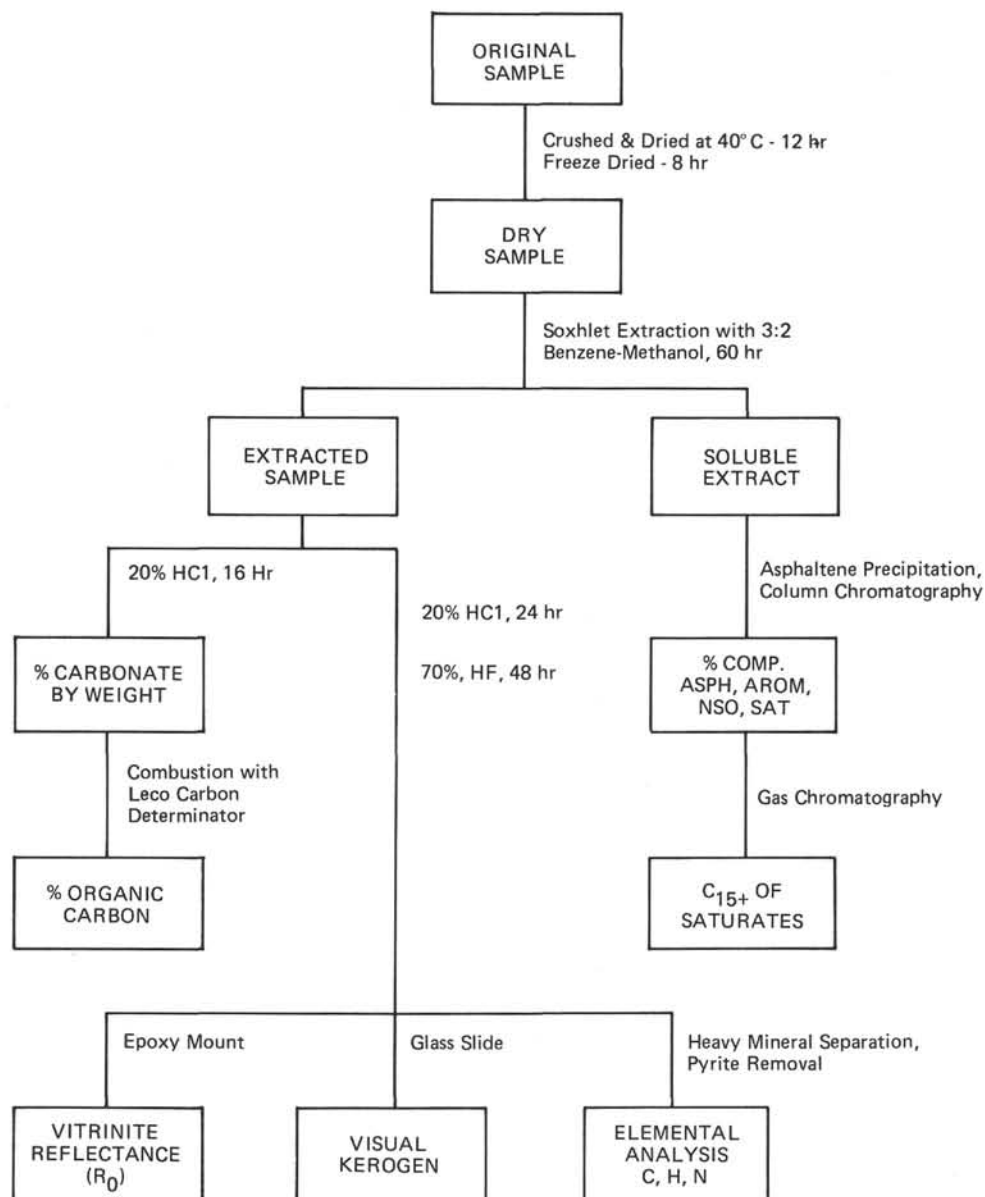


Figure 1. Analysis scheme for Site 391 samples.

DISCUSSION

Organic Carbon and Carbonate Content

Organic carbon and carbonate contents vary considerably even within the Cretaceous black shale section, but generally follow lithologic variations (Table 1). Green or olive colored samples are typically low in organic carbon and were probably deposited under oxidizing bottom conditions. Dark gray to black samples are relatively rich in organic carbon and represent reducing bottom conditions during deposition (Figures 2 and 3). The lower portion of the Cretaceous shale section is very calcareous, and most of the organic carbon in the underlying carbonate is concentrated in argillaceous laminations and streaks. Nine of the samples exceed the 0.4 weight per cent organic carbon limit generally accepted as the

minimum source quality rating, and only four of these are good quality ($>0.8\%$) petroleum source rocks. The organic carbon content of the overall section may be somewhat lower because only the darkest samples available were selected for analysis. This is particularly the case in the carbonate sections where most of the samples were taken from dark shale partings or laminations.

Organic Extract

Organic extract data are summarized on Tables 2 and 3, and gas chromatograms of the saturate fraction are shown on Figures 4-6. Also included are data on two hydrocarbon-rich materials used in drilling the well. Most of the samples do not appear to be contaminated with either of these two refined products with the possible exception of the three deepest samples (Figure 6). These three samples have anomalously high

extract/organic carbon ratios, high relative percentages of saturates, and gas chromatograms which resemble, in part, the sample of pipe dope. These three samples could be contaminated with pipe dope which is accentuated by their low natural extract content.

All of the extracts are low in saturates indicating the absence of oil-like liquid hydrocarbons while the high asphaltene and NSO fractions suggest thermal immaturity. Thermal immaturity is also revealed by a predominance of odd carbon number normal paraffins (high CPI), especially in the shallow, coaly samples.

TABLE 1
Organic Carbon Data

Sample (Interval in cm)	Time/Rock Unit	Lithology	HCl Sol. (wt %)	Org. Carb. (wt %)
391A-13-0, 3-27	L. Miocene	Green-gray claystone	29.3	1.58
391A-21-4, 0-2	U. Cretaceous	Olive-gray claystone	3.5	0.12
391C-6-3, 42-44	U. Cretaceous	Dark gray-black claystone	4.5	0.95
391C-7-2, 130-132	U. Cretaceous	Dark gray claystone	4.2	0.54
391C-8-2, 143-145	U. Cretaceous	Olive-gray siltstone	4.8	0.21
391C-9-3, 48-50	L. Cretaceous	Olive-gray black silty claystone	6.8	0.67
391C-10-3, 142-144	L. Cretaceous	Black, silty claystone and limestone	24.1	2.04
391C-11-2, 143-145	L. Cretaceous	Gray, silty calcareous claystone	50.4	0.31
391C-12-4, 46-48	L. Cretaceous	Very dark gray slightly calcareous claystone	10.8	1.44
391C-16-1, 110-120	L. Cretaceous	Gray-light gray laminated limestone	81.5	0.42
391C-21-3, 110-138	L. Cretaceous	Gray marl	44.7	0.63
391C-26-3, 130	L. Cretaceous	Light gray marl	58.5	0.25
391C-35-4, 5-11	L. Cretaceous	Light green-gray shaly limestone	75.0	0.11
391C-40-2, 0-3	U. Jurassic	Light gray limestone and siltstone	79.4	0.07
391C-52-2, 20-33	U. Jurassic	Dark green-gray and red calcareous shale	29.3	0.45

The three Cretaceous samples believed to be capable of yielding oil (Table 3) have extract data more typical of oil than gas source rocks even though they have not reached oil-generating maturities. The high CPI (356) of the Miocene sample reflects its thermal immaturity ($0.27 R_o$).

Kerogen Type

Most of the source quality samples (>0.4 weight per cent organic carbon) contain primarily gas generating kerogen. Three organic carbon-lean Cretaceous samples and one organic carbon-rich Miocene marl of very limited thickness, contain high percentages of oil-generating kerogen.

Kerogen type is determined by a combination of several parameters which represent both the kerogen and the extract fraction of the organic matter (Table 3). Amorphous and sapropelic organic matter is relatively high in hydrogen and will yield predominantly oil upon maturation; structured, coaly organic matter will yield only gas. Hydrogen/carbon ratios greater than 1.2 at maturity levels of about $0.6 R_o$ indicate high convertibility to oil and ratios of less than 0.8 reveal a capacity to generate mostly dry gas. Oil source rocks at a given maturity level should have a relatively low carbon preference index (CPI) and a relatively high extract/organic carbon ratio as compared to equivalent gas source rocks. These values, however, both change with maturity and can be affected by migrated hydrocarbons and by contamination. The primary source types for the samples analyzed, as determined by these parameters, is shown on Table 3. The absence of H/C values for many samples is because of insufficient kerogen for analysis.

Organic matter in most of the Site 391 samples analyzed is primarily terrestrial and suggests that abundant vegetation existed in the sediment source area. Bottom conditions appear to have been sufficiently reducing for preservation of allochthonous plant debris, but insufficient for more than partial conversion to autochthonous, amorphous organic

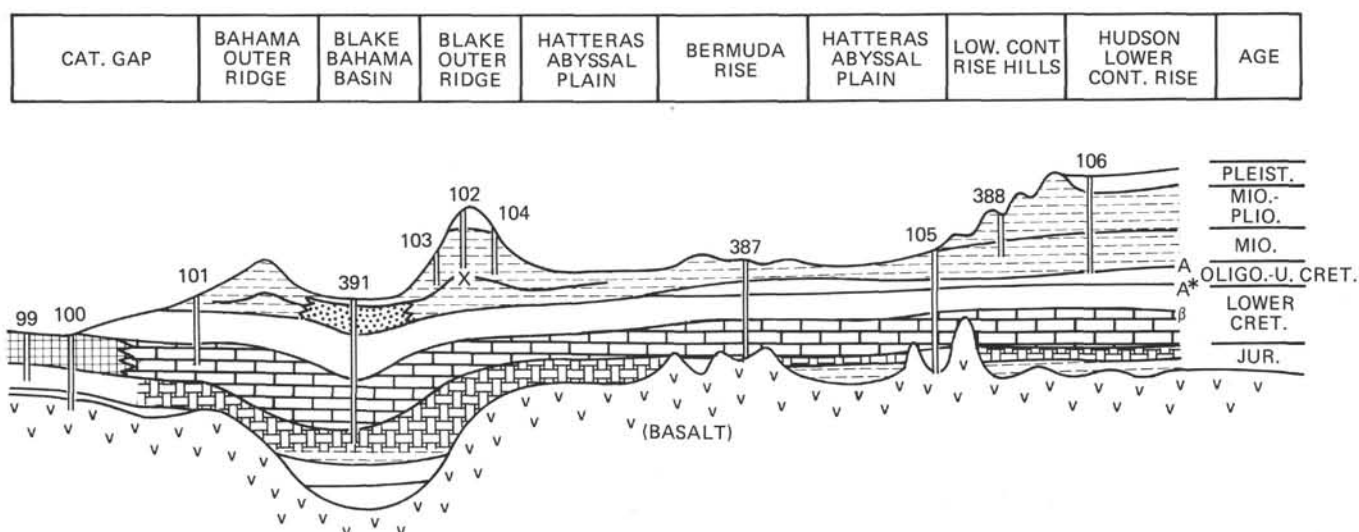


Figure 2. Regional cross section illustrating continuity of stratigraphic intervals in the outer North Atlantic, after this volume.

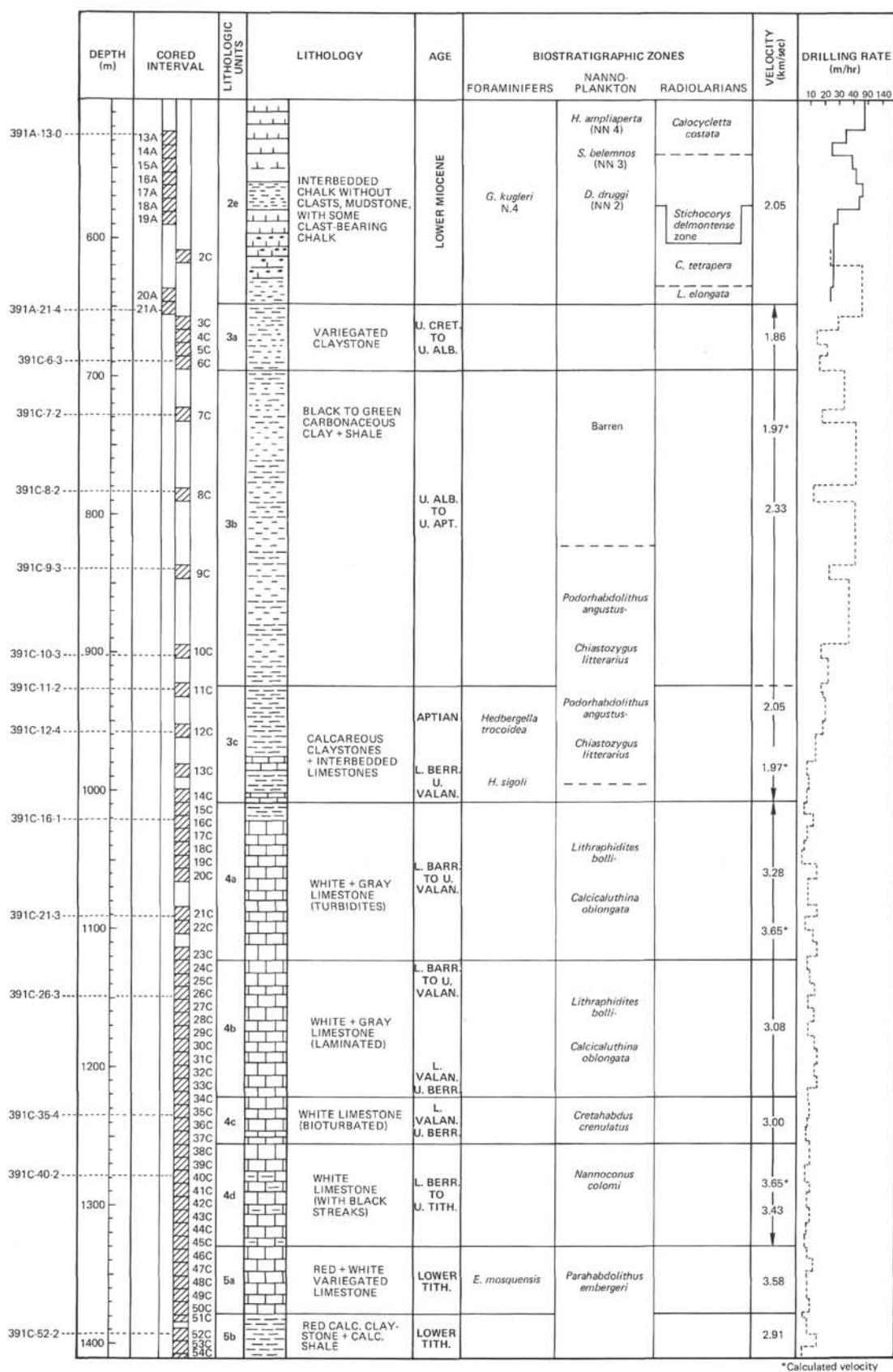


Figure 3. Columnar section of the Cretaceous shale section showing position of samples analyzed and superior sample numbers.

TABLE 2
Soxhlet Extraction Data

Sample (Interval in cm)	Total Extract (ppm)	Per Cent Composition			
		Asph.	Sat.	Arom.	NSO
391A-13-0, 3-27	607	35.9	9.2	11.1	43.8
391A-21-4, 0-2	686	50.9	6.0	13.2	29.9
391C-6-3, 42-44	750	49.1	4.9	11.2	34.8
391C-7-2, 130-132	326	14.4	9.2	24.0	52.4
391C-8-2, 143-145	613	52.6	3.7	10.6	33.2
391C-9-3, 48-50	398	40.1	6.8	13.0	40.1
391C-10-3, 142-144	885	45.8	9.8	7.3	37.1
391C-11-2, 143-145	551	54.9	3.9	9.8	31.5
391C-12-4, 46-48	651	63.6	1.5	6.0	28.8
391C-16-1, 110-120	147	33.2	7.8	12.5	46.5
391C-21-3, 110-138	317	53.5	6.2	6.8	33.5
391C-26-3, 130	339	12.7	7.5	8.4	71.5
391C-35-4, 5-11	167	14.9	42.4	7.7	35.0
391C-40-2, 0-3	158	8.0	31.8	11.9	48.3
391C-52-2, 20-33	185	23.9	13.5	9.7	52.9
Pipe dope	—	11.9	46.5	38.4	3.2
Cable grease	—	2.1	90.9	6.0	1.0

material. Depositional conditions during the Cretaceous black shale episode varied greatly and much higher percentages of oil-generating organic matter occur at some other locations (Dow, 1977a).

Kerogen Maturity

Thermal maturity of the samples is determined by vitrinite reflectance. Many of the samples have more than one population of vitrinite; only the lowest population is believed to be primary and therefore usable in maturity determinations. The higher populations both show some evidence of mechanical and chemical weathering and therefore probably represent recycled material derived from erosion of uplifted, previously buried sedimentary rocks. The average R_o values for each of the three populations of vitrinite in the samples is shown on Table 4.

The average R_o (reflectance in oil) values for each vitrinite population are plotted against depth which gives a kerogen maturation profile (Figure 7). In basins with uniform geothermal gradients this profile will almost invariably be a straight line if vitrinite reflectance is plotted on a log scale and depth on a linear scale. The slope of the profile is dependent on

TABLE 3
Source Rock Type

Sample (Interval in cm)	Kerogen Dominant O.M. Type	Extract			Source Type
		H/C	CPI	Ex/Org C.	
391A-13-0, 3-27	Amorphous	1.26	1.72	0.04	Oil
391A-21-4, 0-2	Amorphous	1.22	1.25	0.57	Oil
391C-6-3, 42-44	Coaly	0.54	1.51	0.08	Gas
391C-7-2, 130-132	Coaly	—	1.04	0.06	Gas
391C-8-2, 143-145	Amorphous	—	1.08	0.29	Oil
391C-9-3, 48-50	Coaly	—	1.26	0.06	Gas
391C-10-3, 142-144	Coaly	0.95	—	0.04	Gas
391C-11-2, 143-145	Coaly	—	1.10	0.18	Gas
391C-12-4, 46-48	Coaly	—	0.99	0.05	Gas
391C-16-1, 110-120	Coaly	—	1.54	0.04	Gas
391C-21-3, 110-138	Coaly	—	2.62	0.05	Gas
391C-26-3, 130	Amorphous	—	1.07	0.13	Oil
391C-35-4, 5-11	—	—	1.24	0.14	—
391C-40-2, 0-3	—	—	1.23	0.23	—
391C-52-2, 20-33	Coaly	0.58	1.16	0.04	Gas

both the temperature (geothermal gradient) and the exposure time (usually directly related to the geologic age of the sediments in continuously subsiding basins). When vitrinite first forms by diagenetic processes in the first thousand feet or so of burial, it has an average R_o value of about 0.2 ± 0.02 . Maturation profiles in simple basins (no major unconformities) will always originate at close to $0.2 R_o$ at the present surface. We also know that recycled organic matter matures more slowly than primary organic matter and the rate of maturation, as measured by the slope of the maturation profile, is dependent on its "inherited" coal rank at the time of deposition. High rank recycled organic matter will mature more slowly (steeper profile) than lower rank recycled material or primary organic matter. All of these observations have been well documented and are predictable under the rules for first-order chemical reactions (Dow, 1977b).

Comparison of the primary maturation profile (Figure 7) with the maturities of various oil- and gas-generation and destruction events (Figure 8) reveals that the entire Cretaceous section is thermally immature ($<0.6 R_o$) and therefore must be considered a potential generative sequence. Higher maturities are required for peak wet gas and dry gas generation (Figure 8) and these critical horizons occur at even greater depths. These depths can also be estimated by projection of the primary maturation profile. Recycled

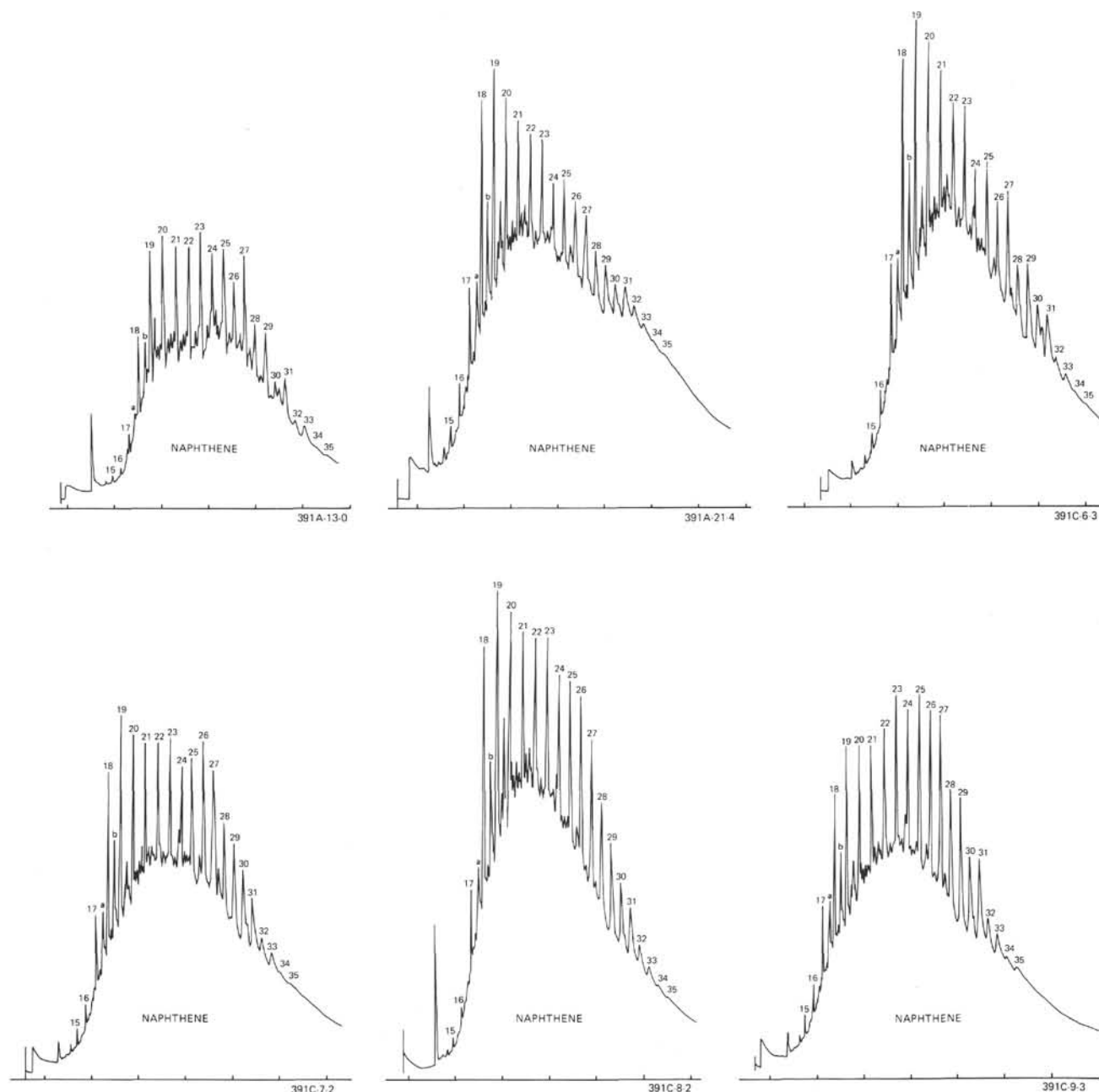


Figure 4. Gas chromatograms of saturate fraction analyzed with Varian 1400 equipped with a 6.1-meter eutectic column programmed from 160°C to 350°C at 20°/min.

organic matter, because of its commonly weathered state and previous thermal history, generally contributes very little to oil and gas-generating reactions. Because of this, the gas-generating capacity of Cretaceous organic matter is probably somewhat lower than would be anticipated if only primary organic matter were present.

Geologic History

Maturation data may be used to estimate the thickness of section lost at unconformities (including the present surface) to determine the rank of recycled organic matter when it was deposited, and to estimate the number of recycled vitrinite populations present

(Figure 7). If the primary maturation profile for Site 391, as established by Cretaceous organic matter, is projected to the rank of the organic matter immediately above the Cretaceous/Miocene unconformity, then about 800 meters of section were lost between the Cretaceous and Miocene sections. The Miocene profile is derived on the basis of only one, but reliable, data point and is drawn parallel to the Cretaceous profile. To express it another way, if 800 meters of section were added to the present sea floor, the primary maturation profile would project to 0.2 R_o and the profile would be typical of a continuously subsiding basin. The loss of section at the Miocene/Cretaceous unconformity, rather than at the present surface, is confirmed by the

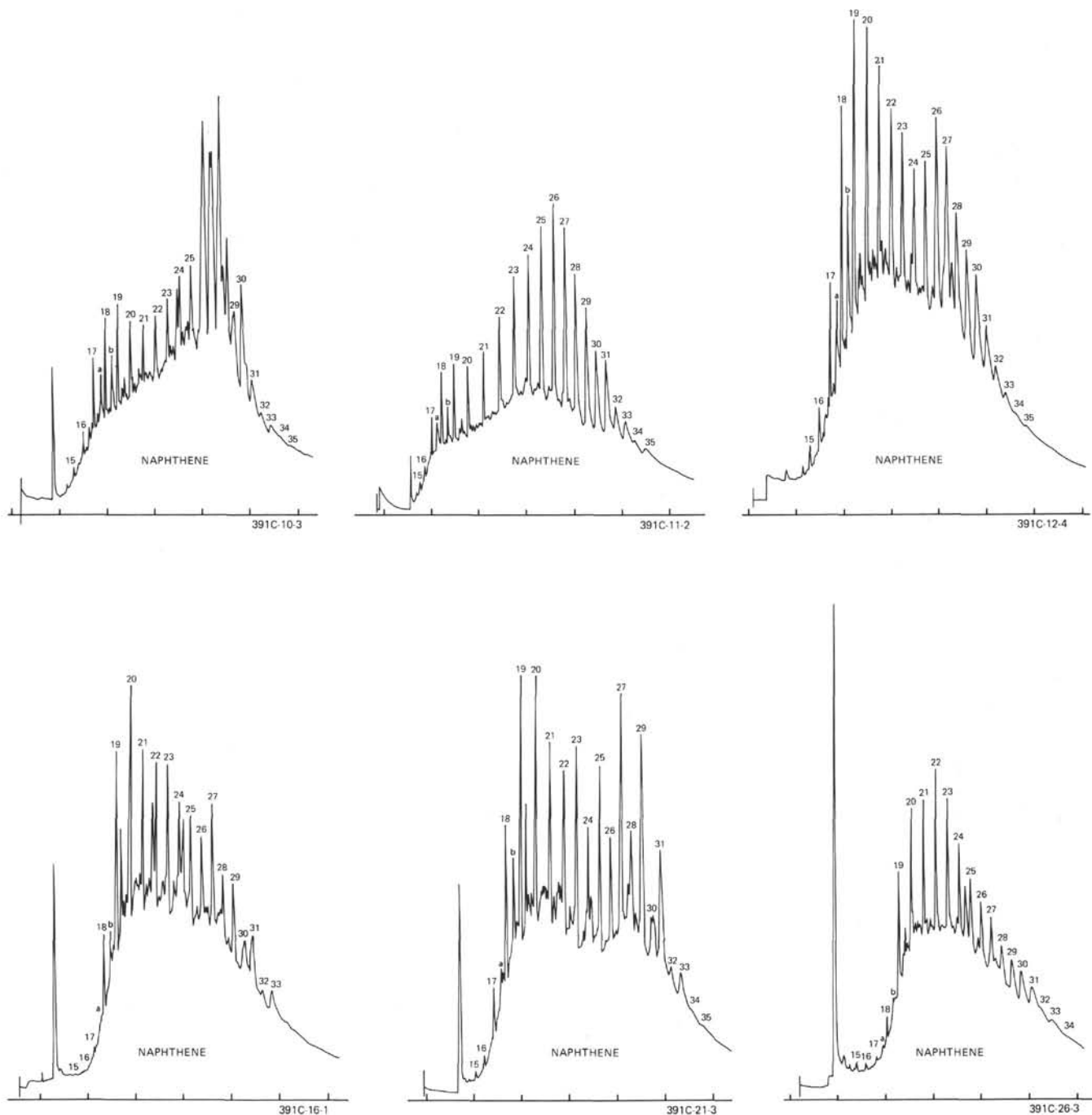


Figure 5. Gas chromatograms of saturate fraction analyzed with Varian 1400 equipped with a 6.1-meter eutectic column programmed from 160°C to 350°C at 20°/min.

relatively low rank of Miocene organic matter. Without these data, the loss of section might equally well have occurred at the Miocene/Quaternary unconformity. This geochemical interpretation is confirmed by geological data which indicates that ridges adjacent to Site 391 contain about 800 meters of section in the time interval represented by the Miocene/Cretaceous unconformity at Site 391 (Figure 2).

The maturity of the two populations of recycled organic matter at the time of deposition can also be estimated by projection of their maturation profiles (Figure 7). The addition of 800 meters of section above

the present sea floor results in 0.2 R_o for the primary vitrinite population and would represent a simple stratigraphic sequence uninterrupted by erosional surfaces. Projection of the two recycled vitrinite populations to this same position indicates their rank at the time of deposition. This secondary organic matter was therefore deposited as sub-bituminous coal (0.42 R_o) and high volatile "A" bituminous coal (0.77 R_o). These coal ranks are described on Figure 8. Estimation of the rank of secondary organic matter at the time of deposition provides important data on the provenance of the sediments from which it was derived.

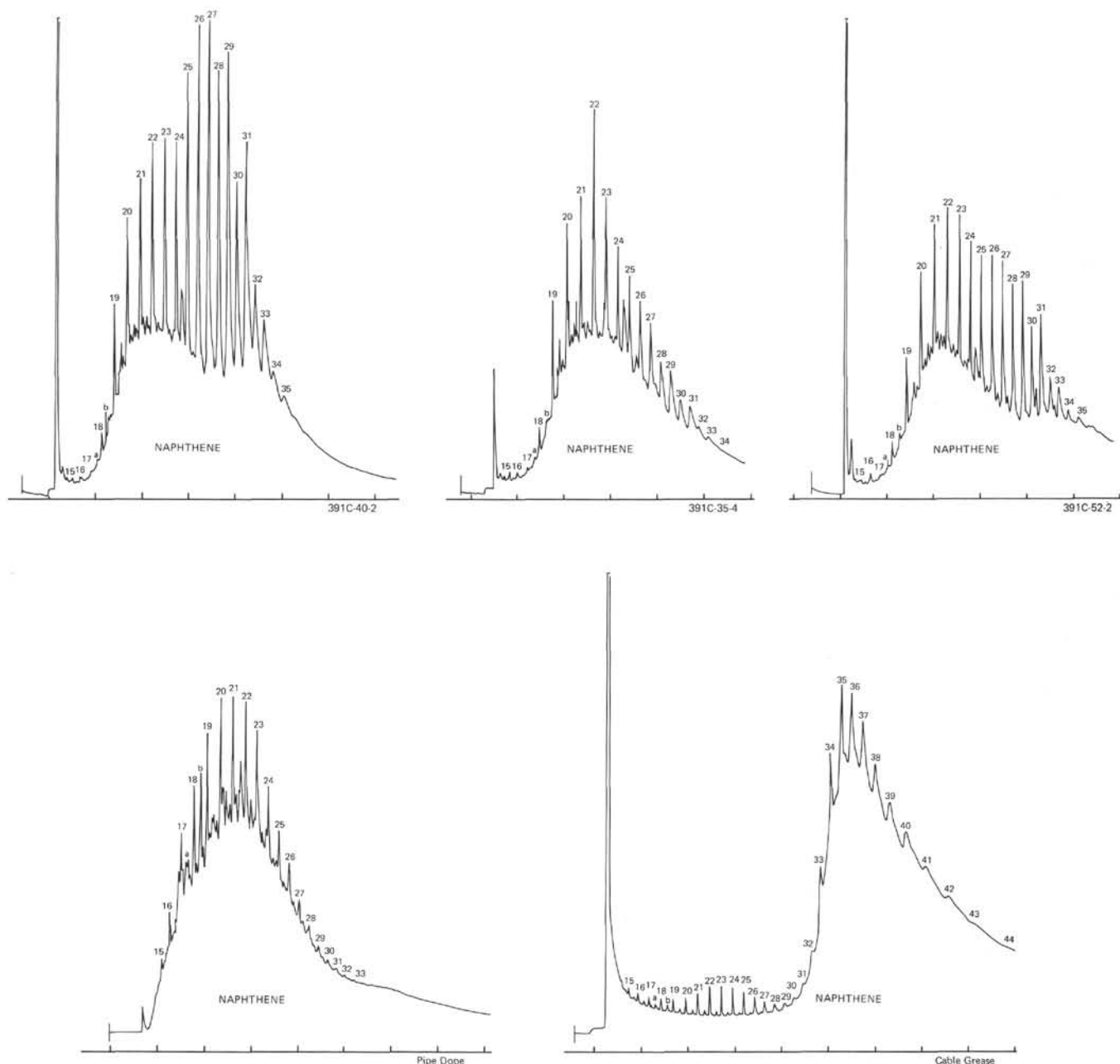


Figure 6. Gas chromatograms of saturate fraction analyzed with Varian 1400 equipped with a 6.1-meter eutectic column programmed from 160°C to 350°C at 20°C/min.

CONCLUSIONS

Geochemical analysis of the DSDP Site 391 cores is particularly discouraging because very little oil-generating capacity was found in the Cretaceous shale section. Possibly these samples are not truly representative of the section and that some sapropelic shales are present but were not sampled. It does appear, however, that the Cretaceous black shale cannot automatically be considered a good oil source and that

the Cretaceous seaway at the time of its deposition was not severely restricted.

Kerogen maturity data indicate that at least 2000 meters of burial is required to achieve oil generation (0.6 R_o) and 2500 meters for early gas generation (0.8 R_o) at the Site 391 location. Even greater burial may be required in thick continental margin deposits where geothermal gradients are probably lower. It is therefore doubtful that effective petroleum source beds are present in the deep ocean basins where maturation requirements are not met.

TABLE 4
Vitrinite Reflectance Data

Sample (Interval in cm)	Maturity ($R_0\%$)	Recycled Maturity ($R_0\%$)	
		Group 1	Group 2
391-13-0, 3-27	0.27		
391A-21-4, 0-2	—	—	—
391C-6-3, 42-44	0.43	0.78	—
391C-7-2, 130-132	0.47	—	—
391C-8-2, 143-145	—	0.76	—
391C-9-3, 48-50	—	—	—
391C-10-3, 142-144	0.51	0.81	—
391C-11-2, 143-145	—	0.83	1.21
391C-12-4, 46-48	0.50	0.85	1.19
391C-16-1, 110-120	—	—	—
391C-21-3, 110-138	0.54	0.91	1.21
391C-26-3, 130	0.55	0.89	1.34
391C-35-4, 5-11	—	—	—
391C-40-2, 0-3	—	—	—
391C-52-2, 20-33	—	1.04	1.37

ACKNOWLEDGMENTS

Appreciation is expressed to Don Mathews, formerly of The Superior Oil Company, for approving this project work and to Dolores Holt and John Allen for doing the analyses.

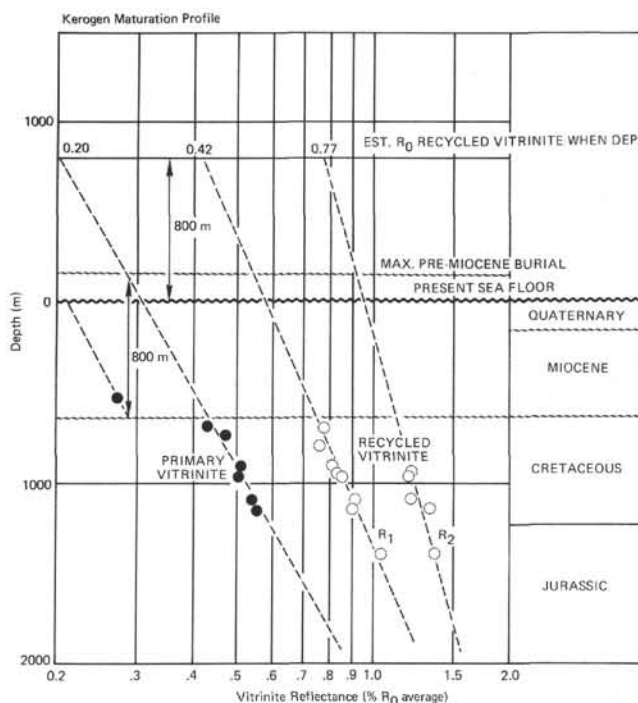


Figure 7. Maturation profile showing primary and recycled vitrinite. The method of estimating the amount of section lost at the Miocene-Cretaceous unconformity and the maturity of the recycled vitrinite when deposited are described in the text.

REFERENCES

- Dow, W.G., 1977a. Contact metamorphism of kerogen in sediments from DSDP Leg 41 sediments. In Lancelot, Y., Seibold, E., et al., Initial Reports of the Deep Sea Drilling Project, Volume 41: Washington (U.S. Government Printing Office), p.
- , 1977b. Kerogen studies and geological interpretations: J. Geochem. Explor., v. 7, no. 2, p.

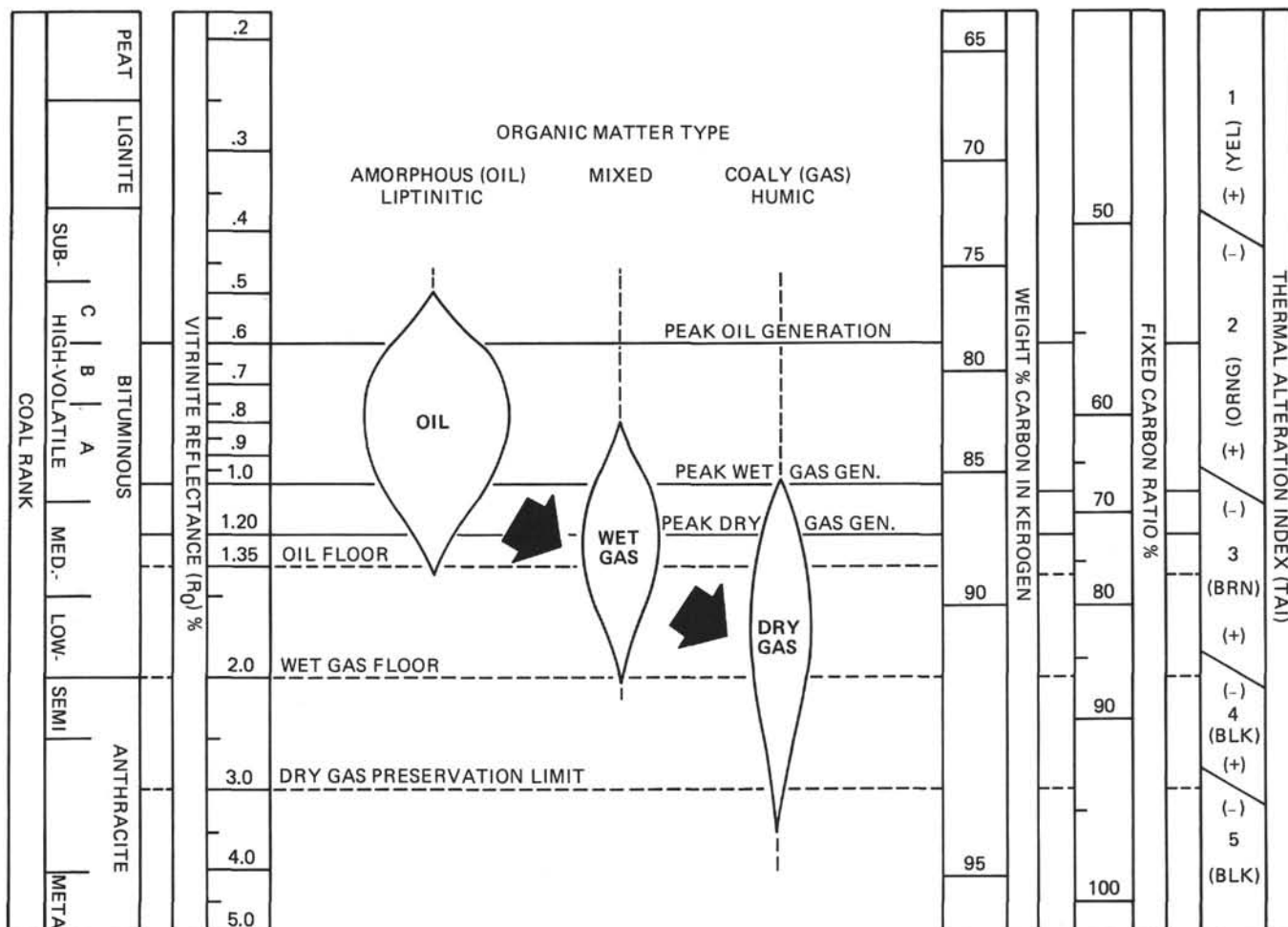


Figure 8. Correlation of the coal rank scale with various maturation indexes and the zones of petroleum generation and destruction. The relative importance of petroleum-generation zone depends on the composition of the original kerogen.