

38. FACIES AND DIAGENESIS OF ORGANIC MATTER IN SEDIMENTS FROM THE BRAZIL BASIN AND THE RIO GRANDE RISE, DEEP SEA DRILLING PROJECT LEG 72¹

P. K. Mukhopadhyay, J. Rullkötter, and D. H. Welte, Institut für Erdol und Organische Geochemie, (ICH-5), Kernforschungsanlage Jülich GmbH, D-5170 Jülich, Federal Republic of Germany

ABSTRACT

The amount, type, and thermal maturation of organic matter in sediments from two DSDP holes in the South Atlantic (Leg 72) were investigated. Isolated kerogens were studied by microscopy, and nonaromatic hydrocarbons were characterized by capillary gas chromatography.

Organic carbon values are low in all samples and range between 0.05 and 0.21% in Hole 515B (Brazil Basin) and only between 0.02 and 0.10% in Hole 516F (Rio Grande Rise). The organic matter is predominantly terrigenous, mixed with some unicellular marine algae; it is severely oxidized in most samples. *N*-alkane distributions are usually dominated by long-chain wax alkanes with odd-over-even carbon number predominance; when the marine organic matter is relatively more abundant, however, significant amounts of *n*-alkanes are centered upon *n*-C₁₇. The organic matter is not mature enough in any sample to generate appreciable amounts of hydrocarbons.

INTRODUCTION

As a continuation of our investigation of deep-sea sediments from the South Atlantic ocean (von der Dick et al., in press), we have studied two suites of core samples from DSDP Holes 515B in the Brazil Basin (water depth 4252 m) and 516F on the Rio Grande Rise (water depth 1313 m). The Hole 515B sediments consist mainly of quartz-rich mudstones (siliceous limestones) or clay-rich nannofossil or terrigenous muds, and the deepest sample investigated was recovered at a sub-bottom depth of 596 m. The ages of the nannofossil limestones and chalks with minor siliceous or volcanoclastic material from Hole 516F (down to 1089 m) range from late Campanian-early Maestrichtian to early Miocene. The principal objective of this study is to investigate the amount and type of organic matter in these sediments and to assess the thermal maturation.

ANALYTICAL PROCEDURES

We dried the sediments at 50°C for 12 hours and ground them. After decomposing the carbonate carbon with 4N HCl, we determined the total organic carbon contents of all samples using a LECO IR-112 carbon analyzer. The remaining sediments were extracted with dichloromethane by the flow-through extraction method (Radke et al., 1978). Saturated hydrocarbon fractions were obtained by medium-pressure liquid chromatography (Radke et al., 1980). Kerogens were separated by treating the samples successively with 4N HCl, 48% HF, and heavy liquid (CdI₂ + KI with a density of 1.95 g/cm³). For details of the analytical procedures of gas chromatography and vitrinite reflectance measurements, see our earlier report (Rullkötter et al., 1981).

For organic facies analysis on isolated kerogens, we used both transmitted and normal/fluorescence-reflected light microscopy. The particulate (higher-plant) liptinite includes sporinite, cutinite, resinite, and suberinite (Stach et al., 1975). Bituminite I and II are fluorescence-microscopic terms (Teichmüller and Ottenjann, 1977). Bituminite I is degraded algae (whitish to golden yellow fluorescence, ~0.5% R_m), and bituminite II (yellow brown fluorescence, ~0.5% R_m), represents degraded phytoplankton, zooplankton, and zoobenthos. (R_m

is mean vitrinite reflectance in %.) Phytoclasts and zooclasts include acritarch, chitinozoans, conodonts, foraminifers, radiolarians, and so on. We did not observe bituminite III (degraded, terrestrial, humo-lipidic matter) in the Leg 72 sediments, and therefore it was not taken into consideration. The bituminites I, II, and III are very similar to the different amorphous organic-matter types proposed by Masran and Pocock (1981).

The thermal alteration index (TAI) was measured in accordance with Staplin (1969) and Jones and Edison (1978). Spectral fluorescence measurements were done according to the procedure described by Ottenjann et al. (1974), and the corresponding vitrinite reflectance values were calculated according to Teichmüller and Ottenjann (1977).

RESULTS

Brazil Basin, Hole 515B

Table 1 and Figure 1 show the amount of total organic carbon (TOC), the organic facies characteristics from maceral analysis, and the maturation trends for a total of 11 sediment samples from DSDP Hole 515B. The organic carbon contents are very low throughout the stratigraphic section and vary between 0.05 and 0.21%. The low amounts of organic carbon created problems in kerogen separation and chromatographic separation of the extractable organic matter (there are no quantitative data for extract amounts and relative proportions of separated fractions) and thus may influence the accuracy of the chemical data presented here.

The organic-facies analysis showed a distinct difference between Lithologic Units 1 and 2. The organic matter in Unit 1 consists mainly of degraded algae (Plate 1, Figs. 1-4). According to the organofacies criteria, the organic matter in Unit 1 belongs to the alginite/bituminite rather than the inertinite group, although the organic matter is mostly oxidized to inertinite. The influence of terrigenous organic matter in this unit is minor.

Unit 2, which stratigraphically extends from upper Oligocene to middle Miocene, shows minor variation in organic facies, and the samples are dominated by refractory or inertinitic terrigenous organic matter (e.g., trilete spore, inertodetrinite, or bimacerite) mixed with ma-

¹ Barker, P. F., Carlson, R. L., Johnson, D. A., et al., *Init. Repts. DSDP, 72*: Washington (U.S. Govt. Printing Office).

Table 1. Total organic carbon content (TOC) and maceral composition of sediment samples from DSDP Hole 515B (Brazil Basin).

Sample (interval in cm)	Sub-bottom depth (m)	Age	TOC (%)	Maceral composition						
				Huminite/vitrinite (%)	Inertinite (%)	Particulate liptinite (%)	Zooclasts/phytoclasts (%)	Alginite (%)	Bituminite I (%)	Bituminite II (%)
3-4, 120-135	119.75	late Miocene-Quaternary	0.05	11	11	3	8	17	50	—
6-6, 130-145	151.35	late Miocene-early Pliocene	0.08	6	6	3	12	—	73	—
14-4, 130-145	224.25	middle Miocene	0.20	2	67	4	10	17	—	—
25-4, 130-145	328.75	early Miocene	0.13	—	60	2	16	22	—	—
35-4, 135-150	423.75	early Miocene	0.12	—	61	—	16	22	1	—
38-4, 130-145	452.20	late Oligocene-early Miocene	0.09	7	61	—	10	22	—	—
41-6, 130-145	483.75	late Oligocene-early Miocene	0.09	7	56	—	25	12	—	—
44-4, 130-145	509.35	late Oligocene-early Miocene	0.14	8	56	—	18	13	5	—
47-4, 120-135	537.75	late Oligocene-early Miocene	0.10	8	56	5	14	17	—	—
50-4, 0-25	565.03	late Oligocene	0.21	4	49	4	9	29	5	—
53-4, 130-145	596.25	late Oligocene	0.17	—	54	4	9	27	6	—

Note: A dash indicates that the component is absent.

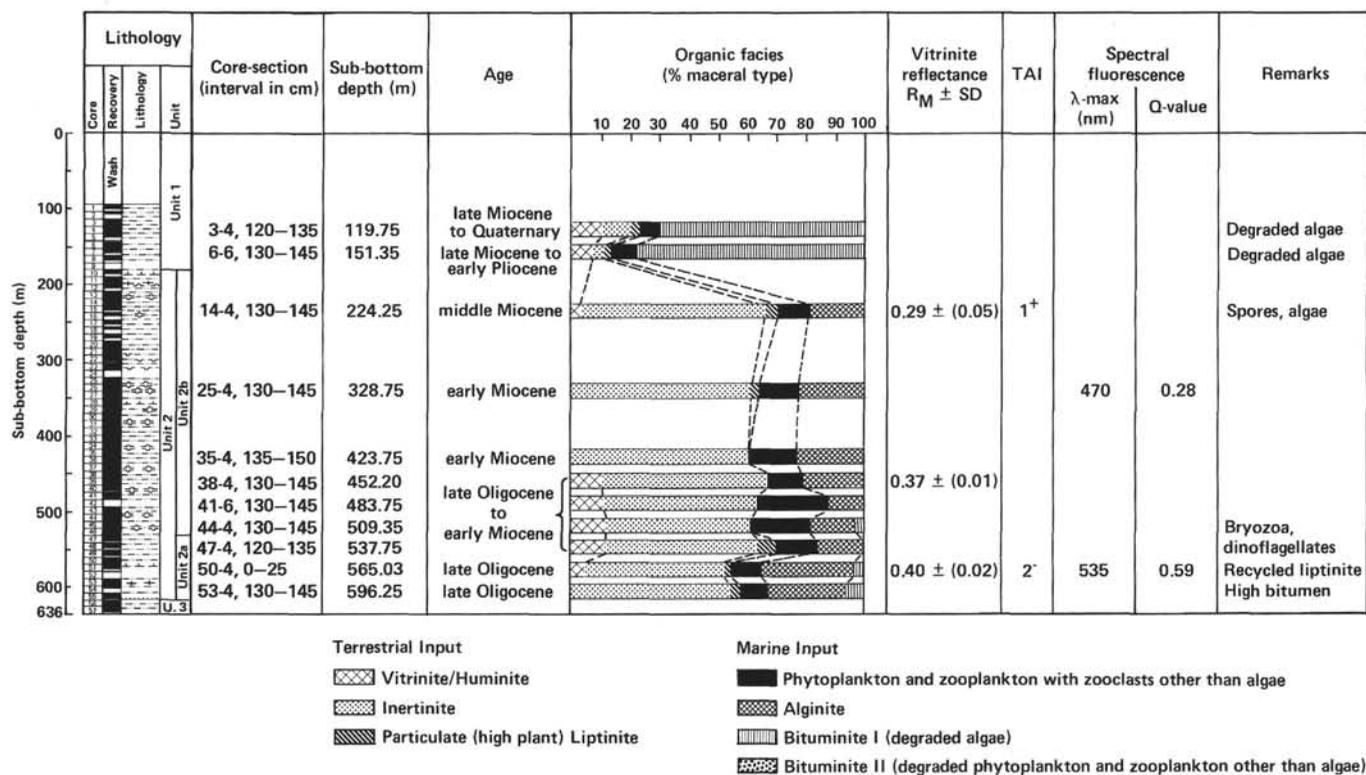


Figure 1. Correlation of data showing stratigraphy, organic facies, and different maturation parameters of samples from the Brazil Basin (515B). TAI, thermal alteration index after Staplin (1969), Jones and Edison (1978); spectral fluorescence measurement after Ottenjann et al. (1974).

rine unicellular algae, bryozoans, foraminifers, etc., Plate 1, Figs. 5-11 and 24). As in Unit 1, the oxidation phenomena in algae or phytoplankton and zooplankton are quite common. In general, the Unit 2 sediments contain a mixed inertinite and particulate, terrestrial and marine organic matter. A minor amount of bituminite (amorphous marine organic matter) occurs in the lower

sections of Hole 515B (Unit 2B). Unit 2A is slightly richer in phytoplankton (e.g., acritarch, dinoflagellates, Plate 1, Figs. 7-11), whereas Unit 2B is slightly enriched in foraminifers and bryozoan fragments (Plate 1, Figs. 5-6).

The *n*-alkane distribution of three selected samples from Lithologic Unit 2 of Hole 515B (Fig. 2) are consis-

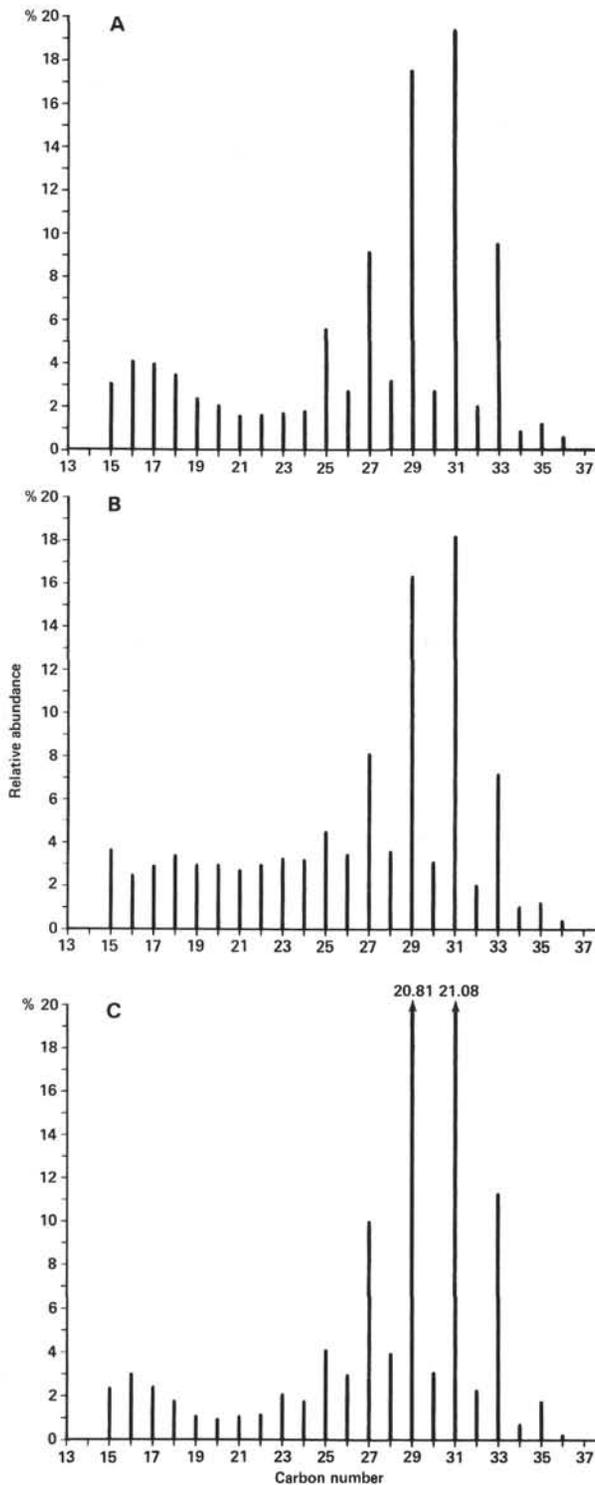


Figure 2. *N*-alkane distributions of sediment samples from DSDP Hole 515B. (Sub-bottom depth is in parentheses.) A, 14-4, 130-145 cm (224.25 m); B, 35-4, 135-150 cm (423.75 m); C, 50-4, 0-25 cm (563.03 m). Total *n*-alkanes equal 100%.

tent with the microscopy data. Long-chain *n*-alkanes, derived from terrestrial higher plant waxes (Eglinton and Hamilton, 1963), with a maximum at *n*-C₃₁, dominate and confirm the terrigenous imprint on the organic matter preserved in the sediments. Apart from the *n*-al-

kanes, small amounts of pristane and phytane in approximately the same abundance are the only other compounds found in significant concentration in the saturated hydrocarbon fractions.

The very high odd-over-even carbon number predominance of the long-chain *n*-alkanes (Fig. 2) indicates that the organic matter has suffered no major thermal stress. This low maturity is confirmed by the vitrinite reflectance, thermal alteration index (TAI), and spectral fluorescence values given in Figure 1. The primary huminite/vitrinite grains (mostly grey, homogeneous, smooth particles) are scarce in all these organic carbon-lean sediments (in most cases not more than 5-7 grains per sample). The standard deviation of the reflectance data (Fig. 1) shows the range of the primary vitrinite population. In general, reflectance of vitrinite in bimacerite grains (recycled vitrinite) ranged between 0.8 and 1.6%. The spectral fluorescence is determined on sporinite particles. In general, two nondegraded sporinite grains were measured in each sample. The Q-value and λ -max of these sporinites are compared with the data of Teichmüller and Ottenjann (1977), where

$$Q = \frac{\text{relative fluorescence intensity of liptinite at 650 nm wave length}}{\text{relative fluorescence intensity of liptinite at 500 nm wave length}}$$

and λ -max = maximum of the relative fluorescence intensity within the fluorescence spectrum between 400-700 nm. The Q-value of 0.59 in the deepest sample corresponds to 0.40% R_m at 596 m sub-bottom depth.

Rio Grande Rise, Hole 516F

Table 2 and Figure 3 show the amount of total organic carbon (TOC), the organic facies characteristics from maceral analysis, and the maturation trends for a total of 11 sediment samples from DSDP Hole 516F. The organic carbon contents are even lower than in the Brazil Basin sediments and range between 0.02 and an exceptional value of 0.10%; therefore, the same restrictions described above for the accuracy of Site 515 data also apply to the accuracy of chemical data from Hole 516F.

The maceral analysis revealed a fairly constant level of inertinite particles (close to 30% in most of the samples). Only in the deepest three samples investigated are the inertinite concentrations considerably higher, similar to the values measured in the Brazil Basin. The amount of vitrinite (8-27%) is considerably higher than in Hole 515B, but most of these particles are recycled, as is obvious from bimacerite grains (Plate 1, Figs. 25-26).

The Unit 1 sediments (lower Miocene) contain the highest amount of terrigenous material (particulate pollen and spores, inertinite, and vitrinite), with a subordinate admixture of unicellular algae. Unit 2 (upper Oligocene) is characterized by a significant contribution of zooclasts and phytoclasts and much less terrigenous material. In the lower part of Unit 2, algae and bituminite form a part of the marine organic matter. The Lithologic Unit 3 sediments (upper Eocene to lower Oligocene) show a mixed assemblage of a great variety of terrige-

Table 2. Total organic carbon content (TOC) and maceral composition of sediment samples from DSDP Hole 516F (Rio Grande Rise).

Sample (interval in cm)	Sub-bottom depth (m)	Age	TOC (%)	Maceral composition						
				Huminites/ vitrinite (%)	Inertinite (%)	Particulate liptinite (%)	Zooecists/ phytoclasts (%)	Alginite (%)	Bituminite I (%)	Bituminite II (%)
3-5, 130-145	195.45	early Miocene	0.06	10	35	35	—	20	—	—
9-3, 120-140	249.45	late Oligocene	0.05	15	32	5	32	16	—	—
15-5, 130-145	309.45	late Oligocene	0.10	12	22	13	41	8	4	—
19-2, 130-145	342.95	late Oligocene	0.05	15	38	10	29	6	2	—
26-4, 130-145	412.45	late Oligocene	0.05	15	34	12	18	9	12	—
35-2, 130-145	494.95	early Oligocene	0.03	27	31	14	10	18	—	—
40-1, 135-150	540.95	late Eocene	0.05	15	26	14	14	31	—	—
56-4, 120-135	697.45	middle Eocene	0.04	19	28	7	23	14	4	5
61-4, 135-150	734.95	middle Eocene	0.03	8	51	—	17	24	—	—
71-4, 120-134	806.95	middle Eocene	0.03	14	45	4	20	13	—	4
106-2, 120-135	1089.45	late Campanian- early Maestrichtian	0.02	11	81	—	3	3	—	2

Note: A dash indicates that the component is absent.

nous and marine maceral types (Plate 1, Figs. 12-22). The significant amount of 12% bituminite (bacterially degraded amorphous organic matter) in Sample 516F-26-4, 130-145 cm should be noted. Within Unit 4 (middle Eocene), the inertinite content starts to increase. Most of the phytoclasts and zooecists in the sediments from this unit exhibit oxidation effects; they are in the process of degradofusination (Stach et al., 1975). The organic matter in the only Cretaceous sample investigated (516F-106-2, 120-135 cm; Unit 6) consists almost entirely of inertinite and recycled vitrinite.

The *n*-alkane distributions of the Unit 2 samples (Figs. 4A and B) are dominated by long-chain wax alkanes with a maximum at *n*-C₃₁. Sample 516F-15-5, 130-145 cm (Fig. 4B) shows a second maximum at *n*-C₂₅. Similar distributions have been described as an effect of partial bacterial degradation of terrigenous organic matter (Simoneit et al., 1979). Microscopic detection of some bituminite I indicate bacterial action on the organic matter in this sample (Table 2). In the saturated hydrocarbons separated from the extracts of the Unit 3 sediments, the long-chain *n*-alkanes are much less abundant (Figs. 4C and D), which correlates with the enhanced alginite content in these samples. A very pronounced bimodal distribution is obvious from the *n*-alkanes of Sample 516F-61-4, 135-150 cm (Fig. 4E); these *n*-alkanes represent marine contribution in the lower molecular weight range near to *n*-C₁₆ and reduced terrigenous lipid contribution (Table 2) at the higher molecular weight end. In the Cretaceous sample from Section 516F-106-2, which revealed a very low absolute hydrocarbon concentration, the long-chain *n*-alkanes (maximum at *n*-C₃₁) become dominant again (Fig. 4F), and no alkanes at all could be detected below *n*-C₂₀, which confirms the nearly complete absence of marine organic matter in this sample (Table 2). As in the Brazil Basin, the saturated hydrocarbon fractions of all samples from Hole 516F predominantly consist of *n*-alkanes together with small amounts of pristane and phytane in about equal abundance.

None of the organic matter in the samples from DSDP Hole 516F is mature enough to generate appreci-

able amounts of hydrocarbons. The vitrinites are mostly recycled (R_m varies between 0.9 to 1.6%). Only a few grains (one or two grains per sample) of primary vitrinite were encountered. The thermal alteration index of pure spores or the spectral fluorescence of sporinites are thus taken as an index of maturation at this site. A thermal alteration index (TAI) of 2- corresponding to a vitrinite reflectance value of 0.40% was measured at 540 m depth (Fig. 3). At 697 m, a Q-value of 0.62 (equivalent to about 0.41% R_m) was obtained by fluorescence microscopy. The TAI value of 2.5 at 806 m depth corresponds to about 0.5% R_m . No microscopic maturation parameter could be measured for the deepest sample investigated in this series (1089 m) because no spores, primary vitrinites, or unoxidized algae were present. The immature nature of the organic matter at this depth, however, can be estimated from the large odd-over-even predominance of the long-chain *n*-alkanes in the saturated hydrocarbon fraction (Fig. 4F).

DISCUSSION AND CONCLUSIONS

From the organic geochemical point of view, the most important characteristics of all sediments from DSDP Leg 72 are the low organic carbon content and the high abundance of inertinite material. This suggests deposition of the sediments in an open marine environment where only chance preservation of autochthonous organic matter occurs and where the more resistant terrigenous organic matter has survived distal transport and has been incorporated into the sediment (Welte et al., 1979). Oxidation effects on algae and spores, which have been observed to be strong at both sites but more pronounced in the Brazil Basin, may have been reinforced at Site 515 by the oxygen-rich cold bottom waters that found their way from Antarctica into the Brazil Basin through the Vema Channel (Demaison and Moore, 1980). Slightly less oxidation of organic matter at Site 516 is obvious from the higher concentration of fresh spores and pollen and from a greater relative abundance of short-chain *n*-alkanes near to *n*-C₁₆. Nevertheless, apparently most of the other lipid material has been destroyed, leading to very low concentrations of branched

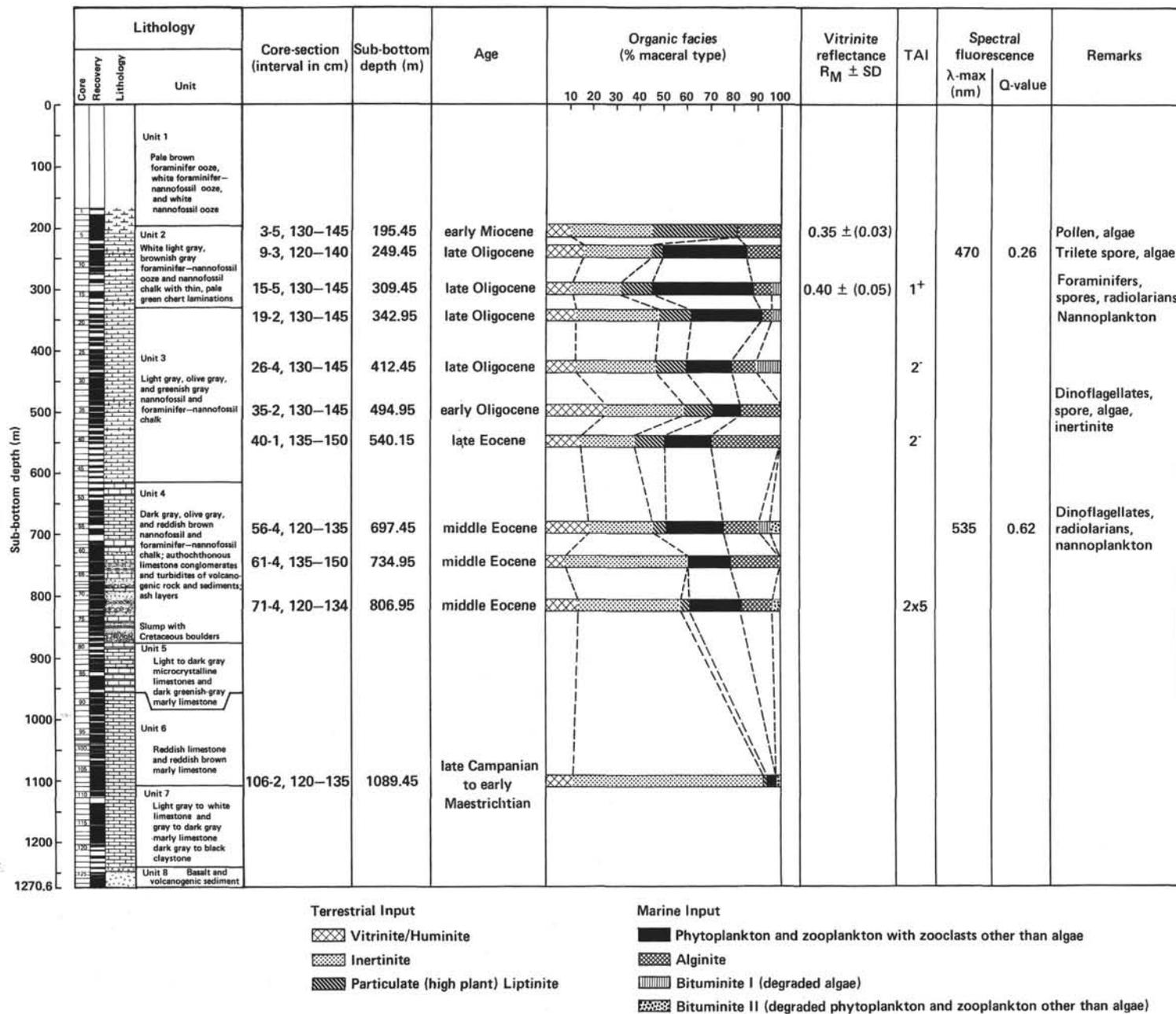


Figure 3. Correlation of data showing stratigraphy, organic facies, and different maturation parameters of samples from the Rio Grande Rise (516F). TAI, thermal alteration index after Staplin (1969), Jones and Edison (1978); spectral fluorescence measurement after Ottenjann et al. (1974).

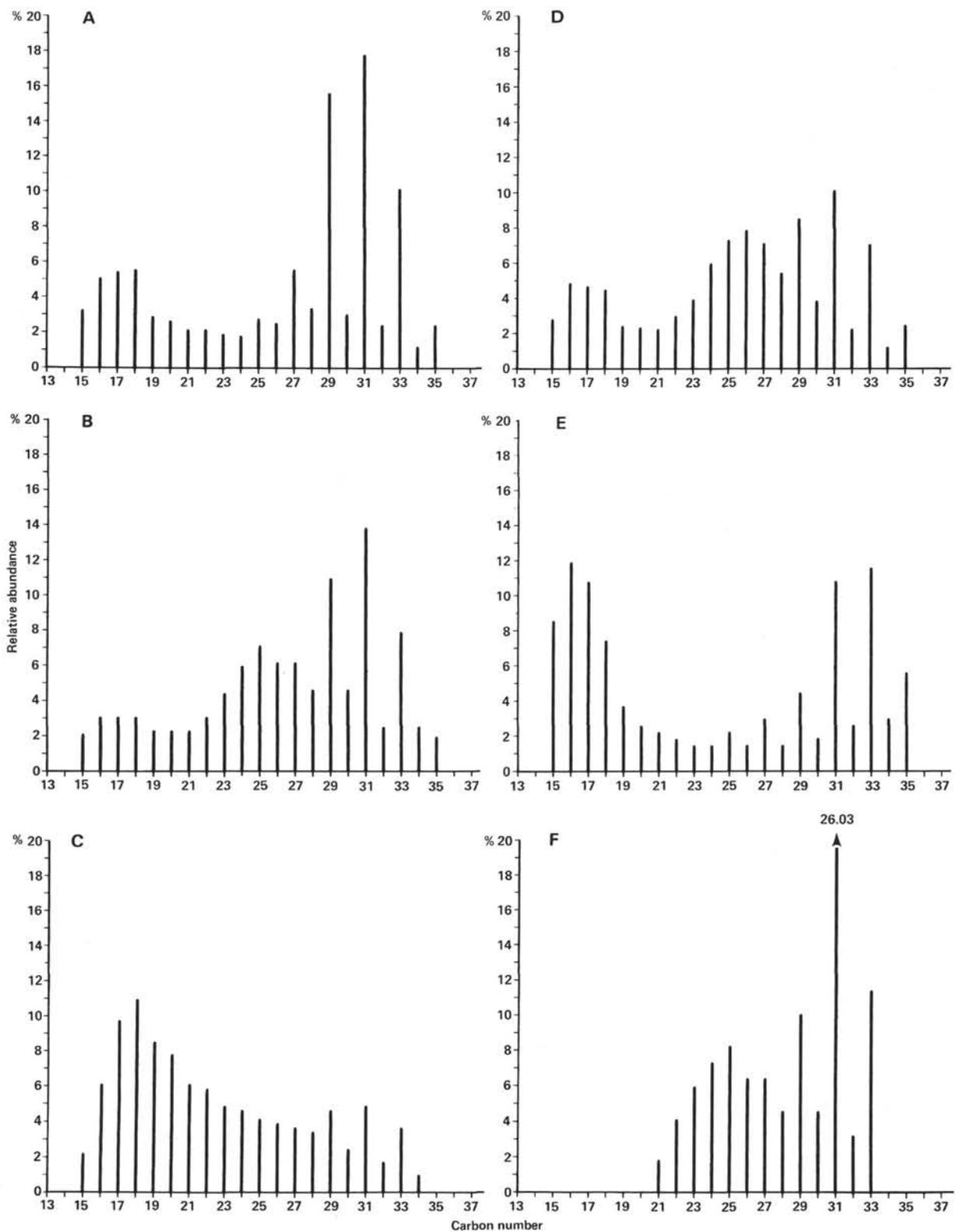


Figure 4. *N*-alkane distributions of sediment samples from DSDP Hole 516F. (Sub-bottom depth is in parentheses.) A, 9-3, 120-140 cm (249.45 m); B, 15-5, 130-145 cm (309.45 m); C, 35-2, 130-145 cm (494.95 m); D, 40-1, 135-150 cm (540.95 m); E, 61-4, 135-150 cm (734.95 m), F 106-2, 120-135 cm (1089.45 m).

and cyclic hydrocarbons in the extractable organic matter. In all sediments investigated, down to 1089 m in Hole 516F, the organic matter is thermally immature. This has been deduced from the strong odd-over-even carbon number predominance of the long-chain *n*-alkanes and the microscopic measurements of vitrinite reflectance, thermal alteration index, and liptinite fluorescence in selected samples.

ACKNOWLEDGMENTS

We would like to thank Drs. M. Radke, R. G. Schaefer, and J. Gormly for performing extraction/liquid chromatography, gas chromatography, and organic carbon analysis, respectively, and W. Benders, F. J. Keller, F. Leistner, and J. Schnitzler for their technical assistance. We are indebted to Drs. P. Robert (Elf-Aquitaine, Saint-Martory, France) and C. Summerhayes (Exxon, Houston) for carefully reviewing the manuscript. We would also like to thank Dr. H. W. Hagemann, Technische Hochschule Aachen, for providing facilities for spectral fluorescence analysis. Samples were made available by the Deutsche Forschungsgemeinschaft (Bonn) through its participation in the DSDP/IPOD Project. This is gratefully acknowledged as is the financial support given by the Deutsche Forschungsgemeinschaft, Grants We 346/23 and We 346/25.

REFERENCES

- Demaison, G. J., and Moore, G. T., 1980. Anoxic environments and oil source bed genesis. *Org. Geochem.*, 2:9-31.
- Eglinton, G., and Hamilton, R. F., 1963. The distribution of *n*-alkanes. In Swain, T. (Ed.), *Chemical Plant Taxonomy*: London (Academic Press), pp. 187-217.
- Jones, R. W., and Edison, T. A., 1978. Microscopic observations of kerogens related to geothermal parameters with emphasis on thermal maturation. In Oltz, D. F. (Ed.), *Symposium: Low Temperature Metamorphism of Kerogen and Clay Minerals*. Pacific Sect. Soc. Econ. Paleontol. Mineral., pp. 1-12.
- Masran, T. E., and Pocock, S. A. J., 1981. The classification of plant-derived particulate organic matter in sedimentary rocks. In Brooks, J. (Ed.), *Organic Maturation Studies and Fossil Fuel Exploration*: London (Academic Press), pp. 145-176.
- Ottenjann, K., Teichmüller, M., and Wolf, M., 1974. Spektrale Fluoreszenz-Messungen an Sporiniten mit Auflicht-Anregung, eine mikroskopische Methode zur Bestimmung des Inkohlungsgrades gering inkohlter Kohlen. *Fortsch. Geol. Rheinld. Westfalen*, 24:1-36.
- Radke, M., Sittardt, H. G., and Welte, D. H., 1978. Removal of soluble organic matter from rock samples with a flow-through extraction cell. *Anal. Chem.*, 50:663-665.
- Radke, M., Willsch, H., and Welte, D. H., 1980. Preparative hydrocarbon group type determination by automated medium pressure liquid chromatography. *Anal. Chem.*, 52:406-411.
- Rullkötter, J., von der Dick, H., and Welte, D. H., 1981. Organic petrography and extractable hydrocarbons of sediments from the eastern North Pacific Ocean, Deep Sea Drilling Project Leg 63. In Yeats, R. S., Haq, B. U., et al., *Init. Repts. DSDP*, 63: Washington (U.S. Govt. Printing Office), 819-835.
- Simoneit, B. R. T., Mazurek, M. A., Brenner, S., Crisp, P. T., and Kaplan, I. R., 1979. Organic geochemistry of recent sediments from Guaymas Basin, Gulf of California. *Deep-Sea Res.*, 26A: 879-891.
- Stach, E., Mackowsky, M. T., Chandra, D., Taylor, G. H., Teichmüller, M., and Teichmüller, R., 1975. *Coal Petrology*: Berlin (Gebrüder Borntraeger), p. 428.
- Staplin, F. L., 1969. Sedimentary organic matter, organic metamorphism and oil and gas occurrence. *Bull. Can. Pet. Geol.*, 17:47-66.
- Teichmüller, M., and Ottenjann, K., 1977. Liptinite and lipoid Stoffe in einem Erdölmuttergestein. *Erdöl Kohle*, 30:387-398.
- von der Dick, H., Rullkötter, J., and Welte, D. H., in press. Content, type and thermal evolution of organic matter in sediments from the eastern Falkland Plateau. In Ludwig, W. J., Krashennikov, V. A., et al., *Init. Repts. DSDP*, 71: Washington (U.S. Govt. Printing Office).
- Welte, D. H., Cornford, C., and Rullkötter, J., 1979. Hydrocarbon source rocks in deep sea sediments. *Proc. 11th Ann. Offshore Technol. Conf.*, 1:457-464.

Date of Initial Receipt: December 30, 1981

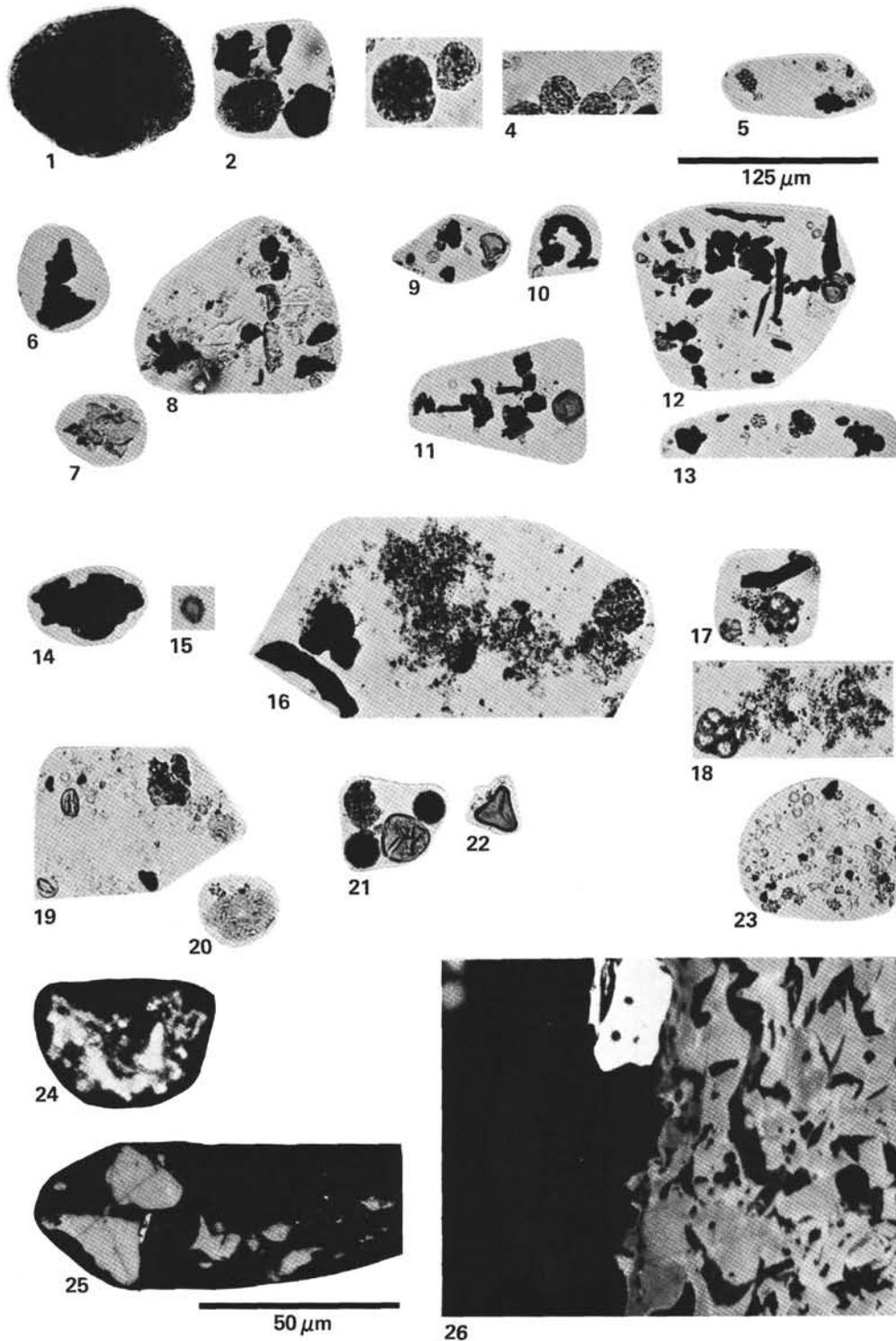


Plate 1. (Figs. 1-23 $\times 130$, in transmitted light. Figs. 24-26 $\times 324$, in reflected light.) 1-4. Degraded algae partly fusinized, Samples 515B-3-4, 120-135 cm and 515B-6-6, 130-145 cm. 5-6. Fusinized zooclasts, Sample 515B-47-4, 120-135 cm. 7. Dinoflagellate, Sample 515B-25-4, 130-145 cm. 8-11. Mixed organic facies: inertinite, algae, spores, and fusinized algae/phytoclasts, Sample 515B-25-4, 130-145 cm. 12-13. Mixed organic facies: inertinite, algae, phytoplankton, vitrinite, Sample 516F-19-2, 130-145 cm. 14-16. Inertinite, fusinized phytoplankton and bituminite, Sample 516F-26-4, 130-145 cm. 17-18. Foraminifers, inertinite, bituminite, Sample 516F-35-2, 130-145 cm. 19-22. Mixed organic facies: spores, algae, phytoplankton, inertinite, Sample 516F-40-1, 135-150 cm. 23. Nannoplankton and inertinite, Sample 516F-56-4, 120-135 cm. 24. Fusinized algae/phytoplankton. Sample 515B-53-4, 130-145 cm. 25. Recycled vitrinite, Sample 516F-9-3, 120-140 cm. 26. Bimacrite grain (vitrinite and fusinite) with inertodetrinite, Sample 516F-19-2, 130-145 cm.