36. ORGANIC GEOCHEMISTRY OF SEDIMENTS FROM DEEP SEA DRILLING PROJECT LEG 87, SITES 582 AND 583, NANKAI TROUGH, AND SITE 584, JAPAN TRENCH[1]

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ABSTRACT

Geochemical analyses of organic matter were carried out on Quaternary sediments from Sites 582 and 583 (Nankai Trough) and on Pliocene to Miocene sediments from Site 584 (Japan Trench), DSDP Leg 87, to evaluate petroleum-generating potential and to characterize the organic matter.

The vitrinite-huminite reflectances of indigenous materials for these sites are less than 0.3% indicating the immature nature of the sediments. The sediments, however, contain remarkable amounts of recycled organic materials. The Quaternary sediments from Sites 582 and 583 contain small amounts of amorphous organic matter (less than 0.75 wt.% organic carbon and 66–90% amorphous debris), which is composed of predominantly recycled, oxidized, and over-matured (or matured) Type III material. The amount of hydrocarbon yield indicates that those sediments have lean-source potential for commercial hydrocarbon generation. The Pliocene to Miocene sediments from Site 584 contain organic matter (0.3–1.09 wt.% organic carbon) of predominantly amorphous debris (68–96%) that originated in two sources, an indigenous Type II material and a recycled, over-matured material. Pyrolysis shows an upward increase in the section of hydrocarbon yield and the same trend is also observed in organic-carbon content. The amount of the yield indicates that the Miocene sediments have lean-to-fair source potential and the Pliocene sediments have fair-to-good source potential.

INTRODUCTION

The objectives of this study are to evaluate the petroleum-generating potential of Leg 87 sediments and to characterize the composition of the organic matter preserved in the sediments. Sites 582 and 583 were drilled in the Nankai Trough area and Site 584 near the Japan Trench (Fig. 1). Site 582 is located on the floor of the Nankai Trough, and the trench-fill deposits are dark olive gray to gray turbidites and hemipelagic clays and silts (site chapter, Site 582, this volume). Site 583 is located on the lowest structural terrace of the landward slope of the trough, and the sediments are dark gray to dark olive gray hemipelagic muds with generally thin and graded sand and silt layers (site chapter, Site 583, this volume). Site 584 is situated on the terrace of the landward trench slope, and the deposits are mainly composed of diatomaceous muds and mudstones (site chapter, Site 584, this volume).

For this study, we employed the techniques that we normally use to evaluate petroleum source-rock potential. From the whole-sediment analyses, we obtained (1) the contents of organic carbon and carbonate carbon present in a sample, and (2) the hydrocarbon-generating potential of the sample and the nature of organic matter included in the sample using a Rock-Eval apparatus. The vitrinite reflectance and the fractional composition of visual kerogen were obtained from the optical studies of the isolated kerogen concentrate, and elemental analyses of the kerogen concentrate were also performed to check the kerogen types obtained from both the optical examination and the Rock-Eval pyrolysis. Although these studies are sufficient to characterize the organic matter at these sites, complete analyses could not be performed because of limitations of sample volume.

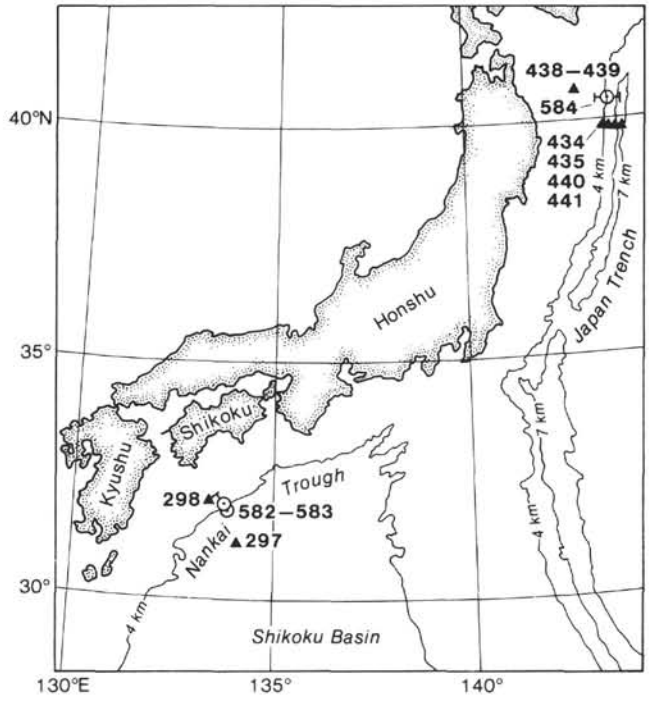

Figure 1. Location of Sites 582, 583, and 584, Leg 87, and of previous DSDP sites in the area.

EXPERIMENTAL PROCEDURES

Our laboratory received 224 frozen samples from Leg 87 cores that had been collected in plastic tubes 2.4 cm in diameter.

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Whole-Sediment Analyses

The selected samples were dried at 70°C for 10 hr. and then homogenized and passed through a 200-mesh sieve. The amount of organic carbon (C_{org}) was calculated by subtracting the measured carbonate-carbon content from the measured total carbon content of the whole-sediment sample. The total carbon was measured using a Perkin-Elmer Model 240 elemental analyzer. The carbonate carbon (C_{carb}) was determined gravimetrically by acidification of the powdered sample in order to dissolve the carbonate.

Rock-Eval pyrolysis was performed according to the method first described by Espitalié and others (1977). The 100-mg powdered samples were heated from 250 to 550°C (up to 590°C in some cases) at a programmed rate of 25°C/minute in a helium atmosphere. Free hydrocarbons present in the sample are first released at a temperature lower than 300°C and detected by a flame-ionization detector (FID). This first peak is called S_1 (mg HC/g sample). The second peak, S_2 (mg HC/g sample), records hydrocarbons produced by pyrolysis of kerogen between 300 and 550°C (or 590°C). All analyzed samples recorded a complex pattern of the S_2 pyrogram as described below. The organic-origin CO_2 is generated during the pyrolysis at temperatures up to 390°C and detected as the third peak, S_3 (mg CO_2/g sample), by use of a thermal conductivity detector (TCD). The total content of hydrocarbons ($S_1 + S_2$) represents the total petroleum-generating potential of the sample, whereas S_2 indicates the residual potential that still exists in the sample during subsequent maturation. The ratios of S_2/C_{org} and S_3/C_{org} are usually called the "hydrogen index" (HI, mg HC/g C_{org}) and the "oxygen index" (OI, mg CO_2/g C_{org}), respectively. These variables correlate with the H/C and O/C ratios, as previously demonstrated by Espitalié and others (1977). The pyrolysis temperature (T_m, °C) at the maximum generation of the S_2 hydrocarbons represents the maturation state of the organic matter present, and the T_m correlates with the vitrinite-reflectance R_o (Vandenbroucke and others, 1983).

Kerogen Analyses

Kerogen concentrate for microscopic investigation and elemental analysis was obtained from the 5-g ground sample (under 60-mesh size) by partial demineralization. We used 6N hydrochloric acid to remove carbonates, and a subsequent treatment with 56% hydrofluoric acid (HF) removed most of the silicates. HF treatment was carried out in a water bath adjusted to 95°C for 2 hours. Kerogen concentrate was floated off, using a $ZnBr_2$ solution of 2.0 g/cm^3 density. Our preliminary studies did not involve extraction of either humic substances or hydrocarbons, because our main objectives were to determine vitrinite reflectance and to obtain visual kerogen composition. Thus, the isolated kerogen residue may have contained some humic substances and hydrocarbons.

Where a sufficient amount of kerogen concentrate was obtained, we measured the vitrinite-huminite reflectance. Kerogen particles larger than 147 μm in diameter were embedded in a plastic mount. After grinding and polishing, a maximum value of reflectance (R_o) was measured by rotating an objective particle (collinite) under a microscope photometer equipped with a Leitz Orthoplan POL in monochromatic (546 nm) light and oil immersion. The Tertiary-Quaternary sequences in Japan usually contain degradinite (Fujii et al., 1979) which is an aggregate of fine particles of vitrinite and liptinite. Degradinite (Stach et al., 1975) closely resembles collinite in appearance under a microscope; so, when the particles are fine, it is difficult to distinguish the collinite component from an aggregate of collinite and degradinite. The reflectance of degradinite is always lower than that of collinite at low thermal levels, less than 1% R_o. This phenomenon yields an error in determining thermal maturity of organic matter. Therefore, we usually use large kerogen particles for the measurement of vitrinite reflectance. The measurements were displayed as a histogram with the number of counts per 0.02% R_o interval. An arithmetic mean and standard deviation were calculated for each discrete population in the histogram. The mean value for the lowest vitrinite-huminite reflectance population in each sample was considered to be an indicator of thermal maturity level of an indigenous organic matter.

From observation of the kerogen concentrate in transmitted light using an Olympus BHB microscope, a semiquantitative estimate of the "type of kerogen" was made using designations such as amorphous (AM), herbaceous (HB), and woody-coaly (WC) types based on the categories described by Staplin (1969), Burgess (1974), and McIver (1974). The "amorphous" group comprises fluffy or lumpy sapropelic material, algae, and fine organic material smaller than 5 μm in diameter. This fine material, however, may include some humic kerogen except opaque coaly material. The "herbaceous" group comprises nonopaque, recognizable plant material such as spores, pollen, cuticles, and resin. The "woody-coaly" group includes less opaque to opaque plant material of woody origin and opaque coaly material.

After drying at 100°C for about 30 minutes, the kerogen concentrate was analyzed for carbon, hydrogen, and nitrogen with a Perkin-Elmer Model 240 elemental analyzer.

RESULTS AND DISCUSSION

Details of data are reported in Appendixes A, B, and C. The organic-carbon content (C_{org}) and the hydrocarbon yield of the whole sediments ($S_1 + S_2$, called "genetic potential") and the visual kerogen composition are plotted in Figure 2 as a function of depth. The typical pyrograms by Rock-Eval assays and the hydrogen index (HI) versus oxygen index (OI) are shown respectively in Figures 3 and 4. The vitrinite-reflectance histogram and the vertical distribution of the mean reflectance (on a log scale) against depth (on a linear scale) are shown respectively in Figures 5 and 6.

Nankai Trough (Sites 582 and 583)

Organic Carbon and Carbonate Carbon

The Quaternary sediments from Sites 582 and 583 have organic-carbon contents ranging from 0.35 to 0.75% in

weight (Fig. 2, Appendix A). The samples above 500 m sub-bottom at Site 582 and all samples from Site 583 have more than 0.5 wt.% organic carbon; this value corresponds to the minimum level of organic carbon for a clastic source-rock of petroleum (Tissot and Welte, 1978). However, in our experience, 1 wt.% or more organic carbon is needed to consider a sediment as a potential source-rock of petroleum. The samples below 500 m at Site 582 are organic-poor sediments having less than 0.5 wt.% organic carbon.

The geochemical studies of the predominantly hemipelagic sediments of the Shikoku Basin (Sites 442, 443, and 444, Leg 58) by Rullkötter and others (1980) and by Waples and Sloan (1980) show that the organic-carbon values range from less than 0.1 wt.% in the Miocene sediments to around 0.4 wt.% in the Pleistocene and Holocene sediments. The organic matter in the Quaternary samples from Sites 582 and 583 was probably deposited in a sedimentary environment similar to the Quaternary sediments of the Shikoku Basin, because the values of the organic-carbon contents (about 0.4 to 0.6 wt.%) of our samples seem to agree with the above-mentioned trend of increasing organic-carbon values from the Miocene to the Holocene.

Most of the sediments from Sites 582 and 583 have a low carbonate-carbon content, ranging from 0.03 to 0.34 wt.% (Appendix A). Only one sample (583D-3-1) contains more than 1 wt.% carbonate carbon.

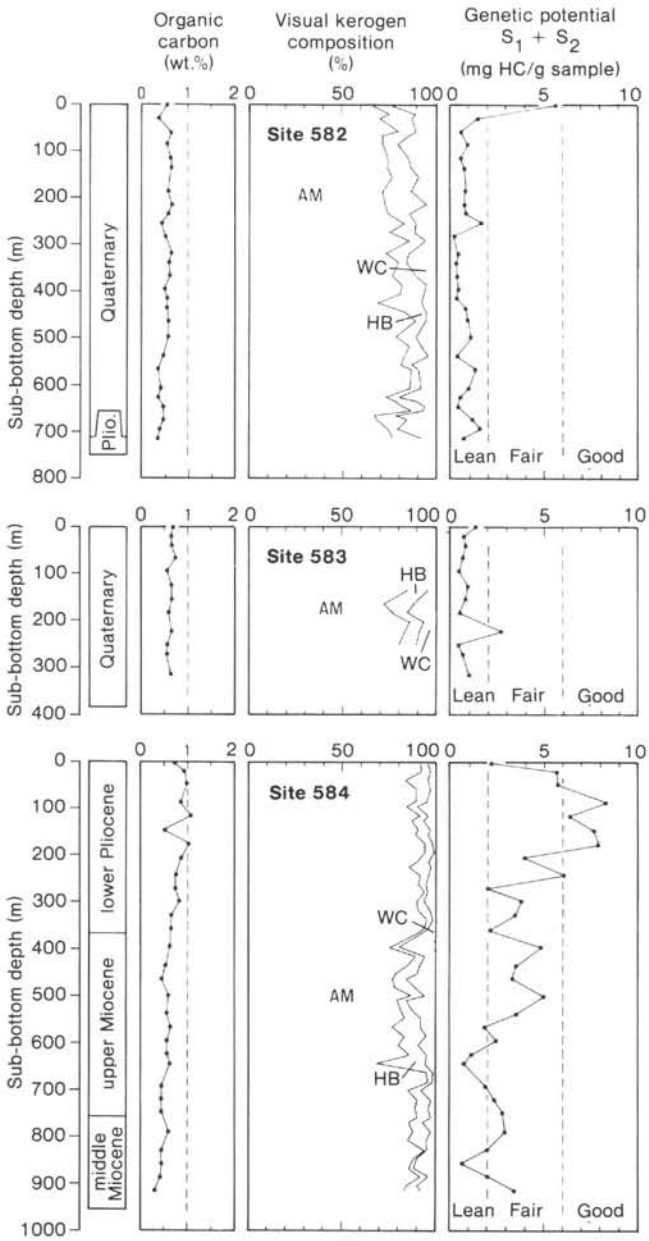

Figure 2. Vertical distribution of organic carbon, visual kerogen, and genetic potential in the sediments, Sites 582, 583, and 584. AM, HB, and WC represent amorphous, herbaceous, and woody-coaly kerogens, respectively.

Kerogen Type

The visual kerogen examinations of the samples from Sites 582 and 583 indicate kerogens dominated by amorphous debris (AM) ranging from 66 to 90% (79% on the average) as shown in Figure 2 and Appendix B. Rock-Eval assays indicate, however, that this is not sapropelic kerogen of marine origin.

The pyrograms produced by Rock-Eval assays of the whole-sediment samples are generally composed of three S_2 peaks (e.g., Samples 582A-15-3 and 582A-22-2, Fig. 3). Remarkably low amounts of hydrocarbons were generated from kerogens by pyrolysis at lower temperatures (up to 400°C), and because of the low T_m values (around 400°C), they are interpreted to be generated from indigenous kerogens. On the other hand, the peaks at higher temperatures, both around 450°C and especially above 550°C, are relatively large and are interpreted to result from recycled, matured, and/or over-matured kerogens.

The S_2 pyrogram of Sample 582A-22-2 is composed of three peaks [$S_2(I)$, $S_2(R_1)$, and $S_2(R_2)$] shown with dotted lines in Figure 3, because the characteristic pattern of the pyrogram does not come from base-line shift. We corrected this problem as follows. The sample was first heated from 250 to 480°C at a programmed rate of 25°C/minute, and then the heated sample was cooled to room temperature. After cleaning of the crucible, the column, and the FID detector of the apparatus by blank tests, the sample (preheated up to 480°C) was reheated from 250 to 590°C. There was no response between 250 and about 480°C, although a peak corresponding to the $S_2(R_2)$ in Figure 3 was counted up to 590°C. The characteristic S_2 pyrogram [small $S_2(I)$ and large $S_2(R_1)$ and $S_2(R_2)$] indicates that most of the kerogens are composed mainly of reworked materials.

Although HI and OI values are meaningful to a single kerogen in chemical composition, it is impossible to measure these values for each S_2 peak because we can not obtain an organic-carbon content that corresponds to each S_2 peak. We have, therefore, obtained only an integrated value including all S_2 peaks as the HI variable of the sample, counting only the hydrocarbons generated up to 590°C because that is the maximum programmed temperature of our apparatus. As shown in the HI-versus-OI diagram (Fig. 4), the kerogens indi-

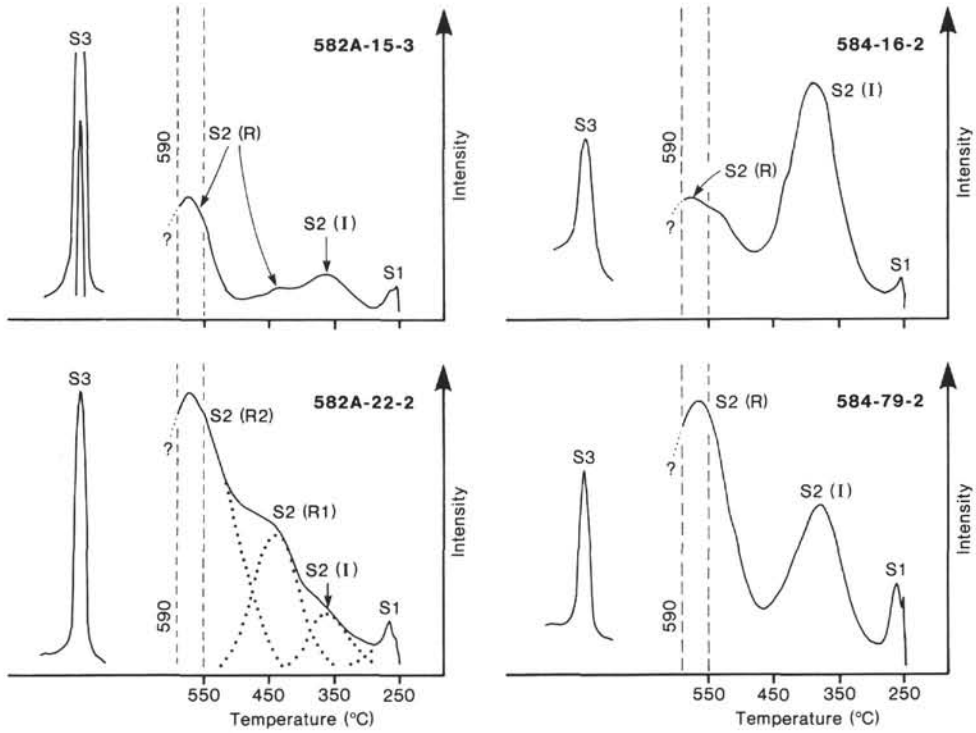

Figure 3. Typical pyrograms. (I) and (R) show indigenous and recycled S_2 peaks, respectively.

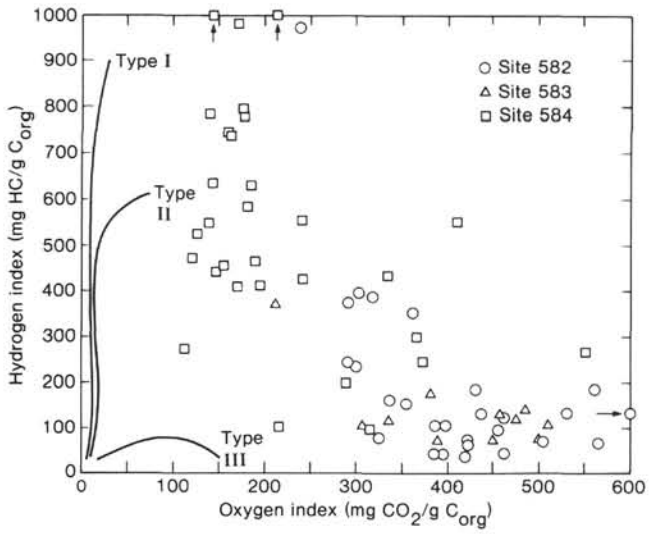

Figure 4. Hydrogen index versus oxygen index for Sites 582, 583, and 584.

cated by circles (Site 582) and triangles (Site 583) are mainly Type III (Tissot et al., 1974). The high OI values imply that most of the kerogens were oxidized during both erosion of their mother rocks and their redeposition.

In summary, the kerogens in the Quaternary sediments from Sites 582 and 583 are composed mainly of amorphous debris of terrigenous origin (Type III), and nearly all the kerogens have been derived from matured and/or over-matured older rocks. Similarly, Quaternary sediments of the Shikoku Basin contain a large amount of recycled organic matter (Rullkötter et al., 1980).

Thermal Maturity

Thermal maturity of the sediments from Sites 582 and 583 was estimated from the mean value of maximum vitrinite-huminite reflectance, and the temperature at the maximum generation of S_2 hydrocarbons was not applied because of its complex pyrolysis curve, as mentioned above.

Although some of the samples analyzed had more than one population of reflectance (Fig. 5, Appendix C), only the lowest population was believed to be the primary one, indicating the thermal maturity of the indigenous organic matter. The higher populations probably represent recycled materials derived from older rocks.

As shown in Figure 6, a combined depth distribution of reflectance values of Sites 582 and 583 is a maturation profile of indigenous kerogens present in those sites. This profile indicates that the sediments drilled at Sites 582 and 583 are immature. In the interval from the sea bottom to about 300 m sub-bottom, the indigenous-vitrinite reflectances are around 0.2%, and the reflectances increase with depth below 300 m. Because drilling at Site 582 penetrated no more than 700 m of sediment, it was very difficult to determine the true maturation trend of indigenous organic materials. If the three points circled with dots in Figure 6 are representative of recycled particles, the dashed line in the figure probably represents the *in situ* maturation trend. This trend implies that the underlying sediments may reach values of 0.5%

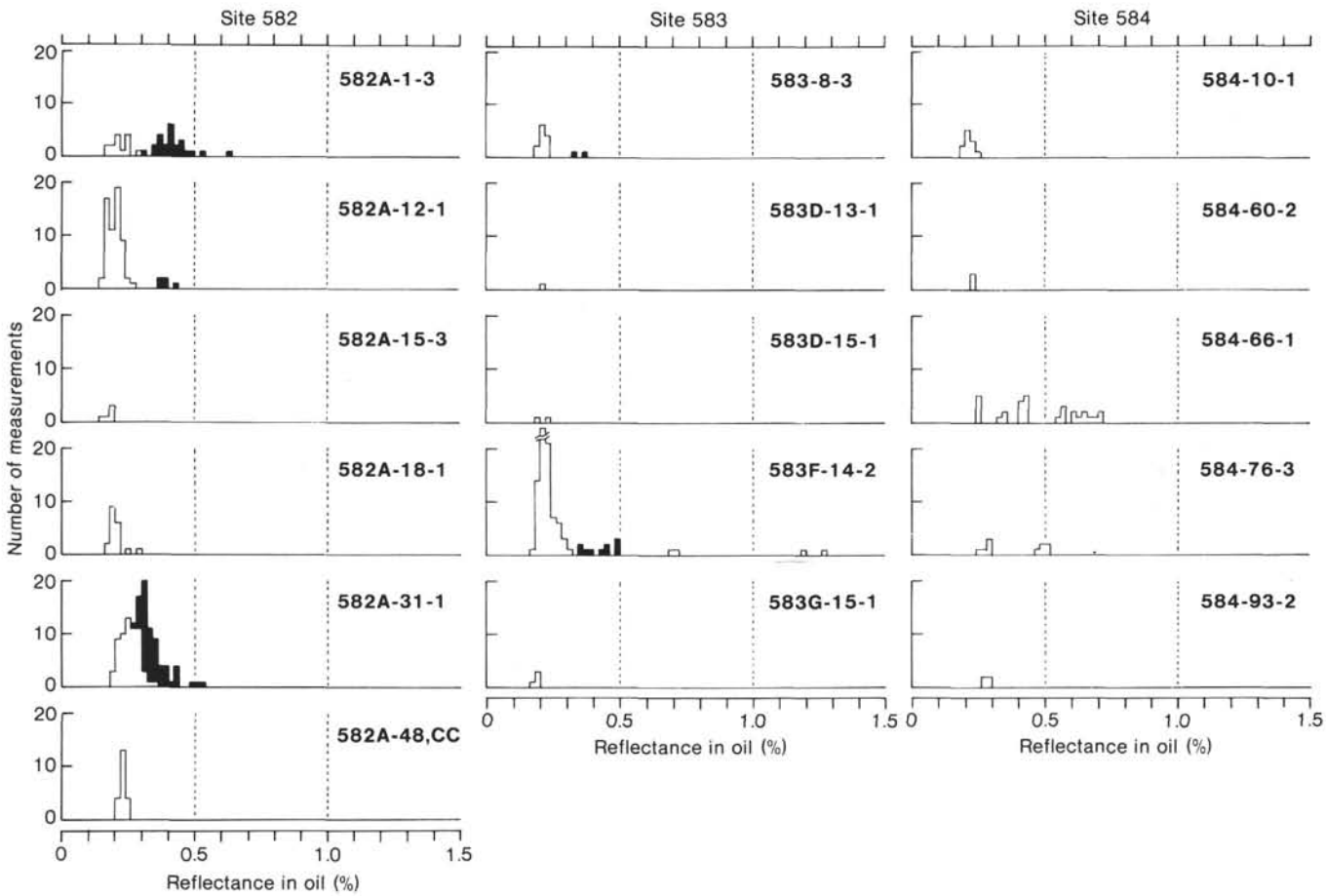

Figure 5. Reflectance histograms of vitrinite-huminite and inertinite, Sites 582, 583, and 584. White and black indicate vitrinite-huminite and inertinite, respectively.

R_o (petroleum-generating threshold) at about 1600 m subbottom.

Hydrocarbon Potential

Data concerning the quantity, quality, and maturity of the organic matter indicate that the Quaternary sediments drilled at Sites 582 and 583 have no source potential for commercial hydrocarbon generation. This conclusion is based on low hydrocarbon yields ($S_1 + S_2$, genetic potential), less than 2 mg HC/g sample (Fig. 2). Recycled organic material would generate a small amount of gas if subjected to higher-temperature metamorphism than it has experienced to date.

Japan Trench (Site 584)

Organic Carbon and Carbonate Carbon

Measured organic-carbon contents of sediments from Site 584 range between 0.30 and 1.09 wt.%; the highest value was found in a Pliocene sample (584-13-4) and the lowest one in a middle Miocene sample (584-96-1) (Appendix A). The Miocene sediments, with about 0.5 wt.% organic carbon on the average, are ranked among the poor sources for commercial hydrocarbon generation; on the other hand, the analyzed Pliocene sediments have organic carbon ranging from 0.64 to 1.09 wt.%; these are fair-to-good potential source rocks of petroleum. The organic-carbon values gradually increase from about 0.5 wt.% in the uppermost Miocene sediments to about 1 wt.% in the middle part of the lower Pliocene.

All samples from Site 584 have low carbonate-carbon content, with values ranging from 0.01 to 0.46 wt.% (Appendix A). These values are considerably less than those of the Nankai Trough area (Sites 582 and 583).

Kerogen Type

The visual-kerogen analyses of the samples from Site 584 indicate that kerogens are mainly composed of amorphous debris (AM), ranging from 68 to 96%, with an average of 87% (Fig. 2, Appendix B).

The S_2 pyrograms of all the whole-sediment samples analyzed are represented by a bimodal pattern including $S_2(I)$ and $S_2(R)$ peaks (Fig. 3). $S_2(I)$ occurs at low temperatures around 400°C (Appendix A) and probably results from thermal cracking of indigenous kerogens because of its low T_m value. $S_2(R)$ has its peak temperature above 550°C and is considered to be generated by thermal cracking of recycled, over-matured kerogens. According to the predicted path of kerogen evolution (Tissot et al., 1974), it is surprising for such recycled, over-matured materials to generate amounts of hydrocarbons as large as those shown in Sample 584-79-2 (Fig. 3). Although such a large $S_2(R)$ peak leads to a high HI value,

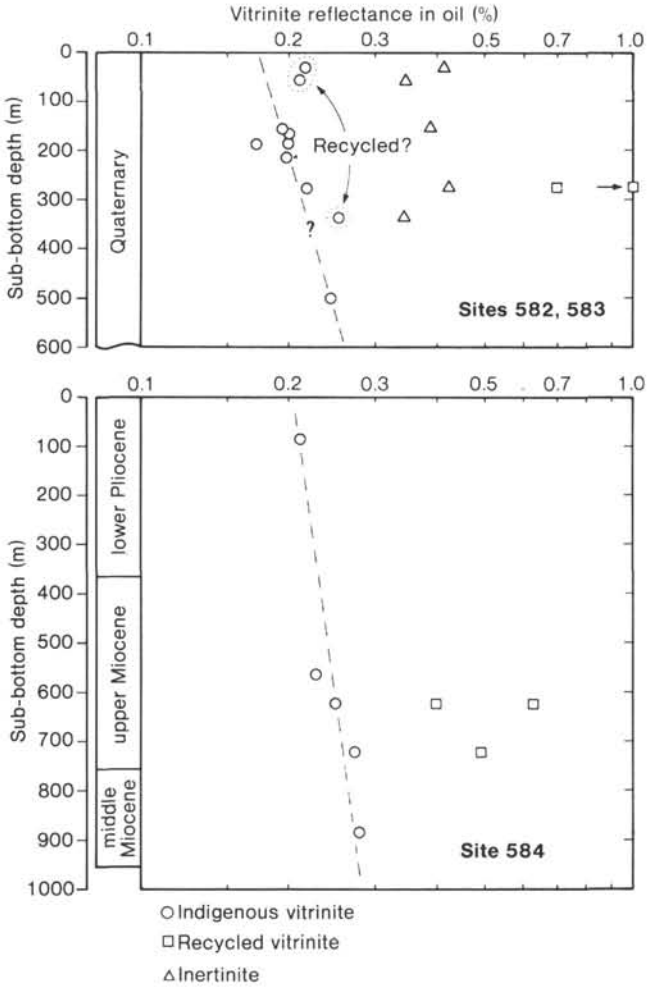

Figure 6. Mean reflectance as a function of sub-bottom depth for Sites 582, 583, and 584.

we could not determine the nature of the materials exactly.

Using the same methods as mentioned for the Nankai Trough, we obtained an integrated HI value composed of hydrocarbons generated from both indigenous and recycled kerogens; therefore, the kerogen typing using the HI and OI values gave false information on the type of kerogens present in the samples from Site 584. The values calculated, however, show remarkable differences between the results from the Nankai Trough and those from the Japan Trench. Specifically, most of the samples collected from Site 584 have higher HI values and lower OI values than those from the Nankai Trough area, Sites 582 and 583 (Fig. 4).

Samples having high HI values ($\geq$400 mg HC/g C_{org}) and low OI values ($\leq$250 mg CO_2/g C_{org}) are interpreted to be predominately immature Type II kerogens with some recycled, over-matured kerogens. The lower HI values (400 to 200) can probably be explained by dilution of such immature pyrolyzable kerogens with recycled, low-hydrogen and high-oxygen kerogens. Samples having the lowest HI values ($\leq$200) have no distinct S_2(I) peak at low temperatures around 400°C and mainly show the nature of recycled materials with peak temperatures above 550°C.

Therefore, most of the sediments from Site 584 contain immature Type II kerogens that are accompanied by recycled kerogens, and others contain mainly recycled kerogens.

Thermal Maturity

On the basis of the lowest population of vitrinite reflectance (Appendix C, Figs. 5 and 6), the thermal maturity of sediments from Site 584 is very low, below 0.3% R_o. This result is supported by the low T_m values around 400°C of indigenous kerogens (Appendix A).

Hydrocarbon Potential

The total hydrocarbon yields (S_1 + S_2) obtained from the Site 584 samples vary markedly throughout the analyzed section (Fig. 2). The deepest section, from about 921 to 560 m sub-bottom (the middle Miocene to the middle part of the upper Miocene), yields 0.24–3.47 mg HC/g sample (2.02 on the average), the lowest among the whole section analyzed. The intermediate section, from about 540 to 270 m (the middle part of the upper Miocene to the lower part of the lower Pliocene), yields 1.96–4.89 mg HC/g sample (3.49 on the average); these values correspond to fair source potential for commercial hydrocarbon generation. The shallowest section, above 240 m (the middle to upper part of the lower Pliocene), has high values of 2.18–8.32 mg HC/g sample (5.95 on the average); these values correspond to fair-to-good source potential. Vertical distribution of hydrocarbon yields, as mentioned above, is roughly comparable to that of organic-carbon contents (Fig. 2).

CONCLUSION

The organic material in the Quaternary sediments from Sites 582 and 583 in the Nankai Trough is predominately of amorphous type, of terrigenous origin (Type III), and oxidized and over-matured (or matured). This material probably originated from a recycled source from an adjacent land area. The maturity level of the sediments, however, is very low, an assessment based on the reflectance of substantially indigenous materials. The sediments have no source potential for commercial hydrocarbon generation.

The organic material from the Miocene to the Pliocene at Site 584 near the Japan Trench originated from two sources, an indigenous Type II material and a recycled, over-matured material. The latter was probably derived from an adjacent land area. Both reflectance and pyrolysis indicate that the sediments are immature. Pyrolysis shows progressive upward increases in hydrocarbon yield throughout the whole section, and the same trend is also observed in organic-carbon content. The Miocene sediments have lean-to-fair source potential and the Pliocene sediments have fair-to-good source potential for commercial hydrocarbon generation.

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REFERENCES

Burgess, J. D., 1974. Microscopic examination of kerogen (dispersed organic matter) in petroleum exploration. *Geol. Soc. Am., Spec. Publ.*, 153:19–30.

Espitalié, J., Laporte, J. L., Madec, M., Marquis, F., Leplat, P., Paulet, J., and Boutefeu, A., 1977. Métode rapide de caractérisation des roches mères, de leur potentiel pétrolier et de leur degré d'évolution. *Rev. Inst. Fr. Pet.*, 32:23–42.

Fujii, K., Yonetani, H., Sogabe, M., Sasaki, M., and Higashide, N., 1979. Coal petrological studies of the sub-bituminous coal in the Kushiro coal field, Hokkaido, Japan—as basic data for oil exploration off Kushiro. *J. Jpn. Assoc. Pet. Technol.*, 44:(3):134–143. (in Japanese)

McIver, R. D., 1967. Composition of kerogen—clue to its role in the origin of petroleum. *Proc. 7th World Petroleum Congr.*, 2:25–36.

Rullkötter, J., Flekken, P., and Welte, D. H., 1980. Organic petrography and extractable hydrocarbons of sediments from the northern Philippine Sea, Deep Sea Drilling Project Leg 58. *In* Klein, G. deV., Kobayashi, K., et al., *Init. Repts. DSDP*, 58: Washington (U.S. Govt. Printing Office), 755–761.

Stach, E., Mackowsky, M. T., Teichmüller, M., Taylor, G. H. Chandra, D., and Teichmüller, R., 1975. *Coal Petrology:* Berlin-Stuttgart (Gebruder Borntrager).

Staplin, F. L., 1969. Sedimentary organic matter, organic metamorphism, and oil and gas occurrence. *Can. Pet. Geol. Bull.*, 17:47–66.

Tissot, B., Durand, B., Espitalié, J., and Combaz, A., 1974. Influence of nature and diagenesis of organic matter in formation of petroleum. *Am. Assoc. Pet. Geol. Bull.*, 58(3):499–506.

Tissot, B. P., and Welte, D. H., 1978. *Petroleum Formation and Occurrence:* Berlin, Heidelberg, New York (Springer-Verlag).

Vandenbroucke, M., Durand, B., and Oudin, J. L., 1983. Detecting migration phenomena in a geological series by means of C_1-C_{35} hydrocarbon amounts and distributions. *In* Bjorøy, M., Albrecht, P., Cornford, C., de Groot, K., Eglinton, G., Leythaeuser, D., Pelet, R., Rullkötter, J., and Speers, G. (Eds.), *Advances in Organic Geochemistry 1981*: Chichester (John Wiley and Sons), pp. 147–155.

Waples, D. W., and Sloan, J. R., 1980. Carbon and nitrogen profiles in deep-sea sediments: new evidence for bacterial diagenesis at great depths of burial. *In* Klein, G. deV., Kobayashi, K., et al., *Init. Repts. DSDP*, 58: Washington (U.S. Govt. Printing Office), 745–754.

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APPENDIX A
Whole-Sediment Analyses: Carbon and Rock-Eval Data

Hole-Core-Section (interval in cm)	Sub-bottom depth (m)	Carbon		Rock-Eval pyrolysis							
									Tm (°C)		
		C_{org} (wt.%)	C_{carb} (wt.%)	S_1 (mg HC/g S)	S_2 (mg HC/g S)	S_3 (mg CO_2/g S)	HI (mg HC/g C_{org})	OI (mg CO_2/g C_{org})	I	R_1	R_2
Site 582											
582-1-4, 70–74	0.00–5.22	0.57	0.03	0.11	5.54	1.36	971	239			>550
582A-1-3, 130–134	29.10–33.42	0.38	0.17	0.07	1.33	1.37	350	361			>550
582A-2-3, 22–26	58.20–61.44	0.68	0.25	0.06	0.48	3.45	71	504		444	>550
582A-5-1, 63–66	87.30–87.96	0.57	0.19	0.08	0.91	1.92	160	337		451	>550
582A-8-2, 100–105	116.10–118.63	0.65	0.22	0.09	0.52	2.11	80	325		441	>550
582A-10-5, 82–87	135.50–142.35	0.67	0.30	0.07	0.71	2.59	106	387		447	>550
582A-15-3, 62–67	183.60–187.24	0.58	0.19	0.06	0.77	2.54	133	438	369		>550
582A-18-1, 45–50	212.50–212.97	0.67	0.19	0.07	0.69	2.66	103	397		461	>550
582A-20-1, 89–94	231.90–232.82	0.59	0.19	0.06	0.72	2.72	126	461			>550
582A-22-2, 61–65	251.10–253.23	0.42	0.02	0.06	1.63	1.34	388	319			>550
582A-25-1, 60–65	279.90–280.53	0.51	0.22	0.07	0.21	2.14	41	420			>550
582A-29-1, 116–120	318.30–319.48	0.65	0.34	0.05	0.42	2.74	65	422		451	>550
582A-31-1, 138–143	337.50–338.91	0.59	0.23	0.05	0.26	2.33	44	395		467	>550
582A-34-1, 68–73	365.90–366.61	0.60	0.33	0.06	0.29	2.77	48	462		445	>550
582A-37-1, 41–46	394.30–394.74	0.49	0.22	0.05	0.35	2.07	71	422		454	>550
582A-39-3, 24–29	413.20–416.47	0.55	0.29	0.05	0.25	2.12	45	385		445	>550
582A-41-2, 97–103	432.00–434.50	0.56	0.25	0.05	0.74	2.97	132	530		430	>550
582A-44-1, 70–73	460.50–461.22	0.58	0.12	0.04	0.88	2.06	152	355			>550
582A-48,CC	498.60–499.76	0.57	0.14	0.05	1.05	2.45	184	430		456	>550
582A-52-2, 28–30	537.00–538.79	0.47	0.20	0.04	0.46	2.15	98	457		468	>550
582A-55-2, 63–66	566.00–568.15	0.35	0.02	0.03	1.31	1.02	374	291			>550
582A-59-2, 60–62	604.50–606.61	0.40	0.10	0.03	0.93	1.20	233	300		460	>550
582A-61-1, 47–49	623.70–624.18	0.35	0.20	0.03	0.47	2.23	134	637		447	>550
582A-63-1, 84–86	642.90–643.75	0.46	0.50	0.04	0.32	2.60	70	565		442	>550
582A-66-3, 41–43	671.80–675.22	0.46	0.09	0.04	1.11	1.34	241	291			>550
582A-68-1, 146–148	691.20–692.67	0.39	0.06	0.03	1.54	1.18	395	303		474	>550
582A-70-2, 48–51	710.60–712.61	0.36	0.29	0.04	0.67	2.02	186	561	405		>550
Site 583											
583B-2-3, 24–26	5.00–8.25	0.68	0.14	0.08	1.20	2.60	176	382		456	>550
583C-5-2, 64–66	20.00–22.16	0.61	0.10	0.08	0.63	1.87	103	307			>550
583C-4-1, 44–48	40.00–40.46	0.67	0.13	0.05	0.77	2.25	115	336		447	>550
583D-3-1, 76–80	66.00–67.78	0.74	1.10	0.08	0.55	3.70	74	500	415		>550
583D-6-2, 64–68	95.00–97.16	0.55	0.20	0.06	0.39	2.14	71	389		454	>550
583D-9-2, 110–114	123.70–126.32	0.65	0.21	0.08	0.83	2.97	128	457		442	>550
583D-12-1, 136–140	152.60–153.98	0.66	0.26	0.06	0.71	3.36	108	509		442	>550
583D-15-1, 40–45	181.70–182.13	0.59	0.27	0.05	0.42	2.65	71	449		451	>550
583D-19-1, 124–128	220.20–221.46	0.65	0.02	0.07	2.41	1.38	371	212		450	>550
583D-22-2, 23–28	249.30–251.06	0.55	0.21	0.06	0.39	2.76	71	502		441	>550
583D-24-4, 90–95	268.70–274.13	0.53	0.19	0.06	0.63	2.52	119	475		445	>550
583D-29-2, 20–25	316.90–318.63	0.64	0.23	0.05	0.91	3.10	142	484		437	>550
Site 584											
584-1-3, 118–123	0.00–4.21	0.75	0.46	0.18	2.00	4.13	267	551		425/>550	
584-3-2, 89–94	20.00–22.42	0.94	0.03	0.19	5.48	1.71	583	182		433/>550	
584-6-1, 113–118	48.20–49.36	0.99	0.12	0.24	5.47	4.06	553	410	419	>550	
584-10-1, 113–118	86.50–87.66	0.83	0.01	0.19	8.13	1.42	980	171	390	>550	
584-13-4, 83–85	115.10–120.44	1.09	0.08	0.24	6.03	2.62	553	240		437/>550	
584-16-2, 113–118	144.00–146.66	0.49	0.01	0.16	7.41	0.71	1512	144	400	>550	
584-19-1, 113–118	173.10–174.26	1.03	0.01	0.25	7.65	1.66	743	161	394	>550	
584-22-1, 63–64	202.10–202.73	0.86	0.07	0.17	3.72	2.87	433	334		441/>550	
584-26-1, 74–76	240.30–241.05	0.74	0.01	0.17	5.90	1.31	797	177	411	>550	
584-29-2, 114–117	268.80–271.46	0.74	0.22	0.15	1.81	2.76	245	373	403	>550	
584-32-1, 79–81	297.30–298.10	0.82	0.02	0.18	3.63	1.21	443	148	420	>550	
584-35-3, 32–36	326.00–329.34	0.64	0.01	0.15	3.36	0.81	525	127	395	>550	
584-38-1, 92–94	354.60–355.53	0.67	0.23	0.14	2.00	2.45	299	366	394	>550	
584-42-4, 80–82	392.90–398.21	0.61	0.01	0.15	4.74	1.08	777	177		447/>550	
584-46-1, 62–66	431.50–432.15	0.53	0.02	0.09	3.37	0.76	636	143		435/>550	
584-49-2, 125–128	460.10–462.87	0.43	0.02	0.11	3.18	0.70	740	163		>550	
584-53-1, 86–89	498.50–499.38	0.60	0.03	0.17	4.71	0.84	785	140		>550	
584-57-3, 92–94	536.60–540.53	0.53	0.06	0.15	3.34	0.98	630	185		433/>550	
584-60-2, 12–15	565.10–566.74	0.65	0.02	0.07	1.76	0.73	271	112		436/>550	
584-63-1, 64–67	593.60–594.26	0.57	0.05	0.12	2.33	0.97	409	170	396	>550	
584-66-1, 7–9	622.40–622.48	0.58	0.04	0.05	1.16	1.67	200	288		495/>550	
584-68-1, 109–112	641.80–642.90	0.61	0.03	0.06	0.63	1.32	103	216		489/>550	
584-73-1, 114–116	690.20–691.35	0.44	0.01	0.09	1.81	0.86	411	195		436/>550	
584-76-3, 40–45	719.10–722.53	0.47	0.02	0.13	2.20	0.89	468	189		460/>550	
584-79-2, 30–33	748.00–749.82	0.46	0.03	0.23	2.53	0.64	550	139	379	>550	
584-83-2, 144–146	786.40–789.35	0.60	0.01	0.15	2.73	0.93	455	155	411	>550	
584-87-1, 133–134	825.20–826.54	0.44	0.06	0.15	1.88	1.06	427	241		>550	
584-90-1, 118–121	854.00–855.20	0.47	0.12	0.12	0.46	1.48	98	315	410	>550	
584-93-2, 7–10	883.10–884.69	0.42	0.01	0.12	1.98	0.51	471	121	424	>550	
584-96-1, 147–149	911.20–912.68	0.30	0.03	0.10	3.37	0.64	1123	213	428	>550	

Note: C_{org} = organic carbon; C_{carb} = carbonate carbon; g S = gram of sample; HI = hydrogen index; OI = oxygen index; T_m = pyrolysis temperature; I = indigenous S_2 peak; R_1 and R_2 = recycled S_2 peaks. Blanks indicate not detected. See text for definitions of S_1, S_2, and S_3.

APPENDIX B
Kerogen Analyses: Visual Composition and Atomic Ratio Data

Hole-Core-Section (interval in cm)	Sub-bottom depth (m)	Composition AM (%)	HB (%)	WC (%)	Atomic ratio H/C	N/C
Site 582						
582-1-4, 70–74	0.00–5.22	66	11	23		
582-3-6, 44–48	19.40–27.36	75	14	11		
582A-1-3, 130–134	29.10–33.42	70	17	13	0.81	0.0320
582A-2-3, 22–26	58.20–61.44	80	9	11	1.09	0.0404
582A-3-3, 11–16	67.90–71.04	72	14	14	1.04	0.0454
582A-5-1, 63–68	87.30–87.96	72	7	21	1.12	0.0344
582A-8-2, 100–105	116.10–118.63	75	11	14	0.99	0.0378
582A-10-5, 82–87	135.50–142.35	74	13	13	1.06	0.0356
582A-12-1, 123–128	154.80–156.06	77	14	9	0.86	0.0307
582A-15-3, 62–67	183.60–187.24	72	15	13	0.99	0.0324
582A-18-1, 45–50	212.50–212.97	73	22	5	0.94	0.0308
582A-20-1, 89–94	231.90–232.82	74	12	14	0.90	0.0342
582A-22-2, 61–65	251.10–253.23	83	6	11	0.81	0.0327
582A-24-1, 108–112	270.30–271.40	76	12	12	0.95	0.0472
582A-26-3, 60–65	289.50–293.13	86	8	6	0.89	0.0314
582A-29-1, 116–120	318.30–319.48	73	13	14		
582A-31-1, 138–143	337.50–338.91	80	4	16	0.79	0.0297
582A-34-1, 68–73	365.90–366.61	77	12	11	0.88	0.0351
582A-36-1, 60–65	384.80–385.43	82	13	5	0.85	0.0316
582A-38-2, 75–81	403.80–406.08	81	12	7	0.79	0.0292
582A-40-2, 33–38	422.60–424.46	68	24	8	1.14	0.0338
582A-42-1, 76–78	441.50–442.27	83	11	6	0.97	0.0399
582A-44-1, 70–73	460.50–461.22	89	5	6		
582A-48,CC	498.60–499.76	78	11	11		
582A-50-3, 33–35	517.80–521.14	86	6	8	0.84	0.0295
582A-52-2, 28–30	537.00–538.79	83	13	4	0.87	0.0285
582A-54-1, 92–94	556.30–557.23	81	6	13		
582A-55-2, 63–66	566.00–568.15	87	3	10		
582A-59-2, 60–62	604.50–606.61	86	6	8	1.00	0.0327
582A-61-1, 47–49	623.70–624.18	73	7	20	0.86	0.0353
582A-62-2, 87–90	633.30–635.68	79	11	10		
582A-63-1, 84–86	642.90–643.75	81	12	7	1.07	0.0419
582A-64-3, 92–94	652.50–656.43	87	5	8	1.00	0.0404
582A-65-1, 24–26	662.10–662.35	67	11	22	1.25	0.0444
582A-66-3, 41–43	671.80–675.22	68	16	16	1.12	0.0443
582A-68-1, 146–148	691.20–692.67	74	5	21	0.92	0.0431
582A-70-2, 48–51	710.60–712.60	77	15	8		
Site 583						
583-1-1, 18–21	0.00–0.20	81	10	9		
583-3-3, 91–93	15.00–18.92	76	15	9		
583-5-3, 94–97	32.50–36.45	78	13	9		
583-7-1, 90–93	45.90–46.82	84	6	10		
583-8-3, 120–122	55.40–59.61	74	15	11		
583-11-1, 90–93	73.50–74.42	82	8	10	0.94	0.0362
583-13-1, 83–85	87.00–87.84	78	8	14	0.89	0.0344
583-17-1, 10–13	107.00–107.12	79	14	7	0.79	0.0288
583-19-1, 60–63	117.00–117.62	79	13	8	0.94	0.0323
583D-10-1, 45–48	133.20–133.67	85	11	4	1.03	0.0399
583D-13-1, 90–95	162.30–163.22	72	16	12	1.19	0.0375
583D-15-1, 40–45	181.70–182.13	77	8	15		
583D-17-1, 40–45	201.00–201.43	86	7	7		
583D-19-1, 124–128	220.20–221.46	83	8	9		
583D-22-2, 23–28	249.30–251.06	80	9	11	1.20	0.0362
583F-14-2, 46–49	275.70–277.68	80	10	10	1.10	0.0296
583F-16-1, 42–45	295.00–295.43	77	10	13		
583F-18-3, 40–43	314.20–317.62	78	13	9		
583F-20-2, 69–74	333.60–335.82	85	8	7		
583F-22-1, 116–120	352.90–354.08	87	5	8		
583F-25-1, 132–134	381.80–383.13	90	6	4		
583F-26-2, 43–46	391.50–393.45	76	16	8		
583F-27-2, 50–51	401.20–403.21	83	10	7		
583F-29-2, 24–27	420.40–422.16	88	9	3		
583G-15-1, 138–140	442.00–443.39	80	13	7		
Site 584						
584-1-3, 118–123	0.00–4.21	92	4	4		
584-3-2, 89–94	20.00–22.42	92	5	3		
584-5-3, 113–118	38.80–42.96	83	13	4	1.25	0.0587
584-7-1, 113–118	57.80–58.96	89	8	3	1.31	0.0602
584-10-1, 113–118	86.50–87.66	89	6	5	1.20	0.0586
584-11-4, 69–71	96.00–101.20	84	10	6	1.20	0.0564
584-13-4, 83–85	115.10–120.44	92	4	4		
584-14-1, 42–47	124.70–125.15	87	6	7	1.21	0.0581

Appendix B. (Continued).

Hole-Core-Section (interval in cm)	Sub-bottom depth (m)	Composition AM (%)	HB (%)	WC (%)	Atomic ratio H/C	N/C
Site 584 (Cont.)						
584-16-2, 113–118	144.00–146.66	91	6	3		
584-17-1, 113–118	153.70–154.86	89	7	4		
584-19-1, 113–118	173.10–174.26	94	4	2	1.27	0.0654
584-21-1, 113–118	192.50–193.66	94	5	1		
584-23-1, 113–118	211.70–212.86	90	6	4	1.19	0.0549
584-24-4, 78–83	221.30–226.60	85	12	3	1.20	0.0585
584-26-1, 74–76	240.30–241.05	92	4	4		
584-28-1, 111–114	259.30–260.43	91	4	5		
584-30-1, 90–93	278.30–279.22	94	2	4		
584-32-1, 79–81	297.30–298.10	90	3	7		
584-34-2, 75–78	316.40–318.67	91	6	3		
584-36-1, 4–7	335.60–335.66	95	3	2		
584-38-1, 92–94	354.60–355.53	93	3	4	1.16	0.0548
584-39-3, 92–94	364.10–368.03	90	2	8		
584-42-4, 80–82	392.90–398.21	75	2	20	1.11	0.0485
584-44-4, 99–101	412.30–417.80	89	5	6		
584-46-1, 62–66	431.50–432.15	85	7	8		
584-48-2, 110–112	450.50–453.11	78	12	10		
584-49-2, 125–128	460.10–462.87	77	7	16		
584-51-1, 123–126	479.30–480.55	78	11	11		
584-53-1, 86–89	498.50–499.38	87	7	6		
584-54-4, 99–101	508.10–513.60	79	5	16	1.19	0.0485
584-56-1, 69–71	527.10–527.80	81	6	13		
584-58-1, 125–127	546.10–547.36	83	9	8	1.21	0.0524
584-60-2, 12–15	565.10–566.74	77	15	8	1.25	0.0380
584-62-1, 44–47	584.10–584.56	83	12	5	1.28	0.0473
584-64-1, 51–53	603.20–603.72	80	11	9	1.20	0.0484
584-66-1, 7–9	622.40–622.48	86	9	5	1.36	0.0379
584-68-1, 109–112	641.80–642.90	68	26	6		
584-70-1, 38–40	661.20–661.59	95	3	2		
584-72-1, 75–77	680.60–681.36	96	2	2	1.00	0.0395
584-74-1, 118–121	699.80–700.99	85	7	8		
584-76-3, 40–45	719.10–722.53	90	7	3	1.10	0.0467
584-78-1, 32–34	738.50–738.83	89	7	4		
584-80-4, 12–15	757.50–762.14	90	7	3		
584-81-1, 63–65	767.00–767.64	86	7	7		
584-83-2, 144–146	786.40–789.35	88	9	3	1.15	0.0533
584-85-1, 60–61	805.80–806.40	85	10	5		
584-87-1, 133–134	825.20–826.54	94	2	4		
584-89-2, 53–58	844.40–846.46	88	2	10	1.17	0.0462
584-91-1, 40–44	863.70–864.12	86	2	12		
584-93-2, 7–10	883.10–884.69	92	4	4		
584-95-1, 93–96	902.50–903.45	84	6	10	1.15	0.0514
584-96-1, 147–149	911.20–912.68	83	9	8		

Note: AM = amorphous; HB = herbaceous; WC = woody-coaly; blanks indicate not analyzed.

APPENDIX C
Reflectance Data of Vitrinite-Huminite and Inertinite

Hole-Core-Section (interval in cm)	Sub-bottom depth (m)	Number of observations	Mean reflectance (%)	Standard deviation	Remarks
Site 582					
582A-1-3, 130–134	29.10–33.42	14	0.215	0.038	
		24	0.412	0.066	Inertinite
582A-12-1, 123–128	154.80–156.06	61	0.193	0.027	
		5	0.386	0.029	Inertinite
582A-15-3, 62–67	183.60–187.24	5	0.172	0.016	
582A-18-1, 45–50	212.50–212.97	19	0.197	0.025	
582A-31-1, 138–143	337.50–338.91	63	0.251	0.039	
		57	0.341	0.054	Inertinite
582A-48,CC	498.60–499.76	21	0.244	0.013	
Site 583					
583-8-3, 120–122	55.40–59.61	12	0.210	0.014	
		2	0.345	0.035	Inertinite
583D-13-1, 90–95	162.30–163.22	1	0.20		
583D-15-1, 40–45	181.70–182.13	2	0.200	0.028	
583F-14-2, 46–49	275.70–277.68	83	0.218	0.027	
		2	0.695	0.021	Recycled vitrinite
		2	1.22	0.057	Recycled vitrinite
		10	0.420	0.055	Inertinite
583G-15-1, 138–140	442.00–443.39	4	0.180	0.008	
Site 584					
584-10-1, 113–118	86.50–87.66	11	0.210	0.016	
584-60-2, 12–15	565.10–566.74	3	0.227	0.006	
584-66-1, 7–9	622.40–622.48	5	0.248	0.005	
		12	0.396	0.039	Recycled vitrinite
		13	0.626	0.055	Recycled vitrinite
584-76-3, 40–45	719.10–722.53	5	0.272	0.022	
		5	0.490	0.016	Recycled vitrinite
584-96-1, 7–10	883.10–884.69	4	0.278	0.010	