# 26. THERMAL ANALYSIS/PYROLYSIS OF CRETACEOUS SAPROPELS: DSDP LEG 44, HOLE 391C, BLAKE-BAHAMA BASIN

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Four samples of so-called sapropelic black shales of Albian-Aptian age from DSDP Hole 391C (Blake-Bahama Basin) were analyzed by the thermal analysis/pyrolysis technique to determine petroleum source rock potential. The results are given in Table 1.

All of these samples are thermally immature with respect to the temperature history required for petroleum hydrocarbon generation. Only one of the samples (391C-10-3, 110-138 cm) contains a sufficient amount of the right kind of organic matter to be considered a potential source rock, if it were elsewhere buried to depths on the order of 3 km.

Results reported in Table 1 are: weight percent organic carbon, pyrolytic oil yield in gallons per ton and weight percent (Fisher assay equivalent), pyrolytic oil yield as a percentage of organic carbon, oil content in weight ppm, and the temperature of maximum pyrolytic decomposition.

Organic carbon content reflects the amount of organic matter deposited and preserved in the sediment, and may indicate the petroleum hydrocarbon-generating potential of the rock. On the basis of low organic carbon content, two samples (391C-8-2, 115-143 cm, 391C-11-2, 110-143 cm) can be eliminated as potential oil source rocks.

A more direct indication of the oil-generating capacity of the rock is the thermal analysis/pyrolysis oil yield shown in Table 1. In this analysis the rock is heated in a stream of helium at a temperature increase of 40°C per minute from 30°C to 800°C. The volatile organic compounds evolved from the rock as a function of temperature are monitored with a hydrogen flame ionization detector. The materials evolved during the 30°C to 350°C heating period may be mostly volatile organic compounds pre-existing in the rock, which are reported as ppm oil content and generally show a direct correlation with the amount of solvent extractable substance in the same sample. The materials evolved during the 400°C to 800°C heating period are mostly thermal decomposition products from the cracking of the solid organic matter (kerogen).

The thermograms (flame-ionization response as a function of temperature) for these samples are shown in Figure 1. These samples all contain very small amounts of pre-existing volatile organic compounds, and the total pyrolytic oil yield ranges from 0.008 to 0.76 per cent. Immature sediments which yield less than 0.1 per cent of oil upon pyrolysis are probably inadequate source rocks, even under optimum burial (temperature) conditions for hydrocarbon generation.

The rate of thermal decomposition of the solid organic matter in sediments when heated at a regular rate of temperature increase (in this case 40 C/min), is an indication of (1) the temperature history of the sediment, and (2) the molecular structure or type of kerogen. Rocks which contain the typical mixture of sedimentary organic matter, and have never been heated to temperatures in excess of about 50°C

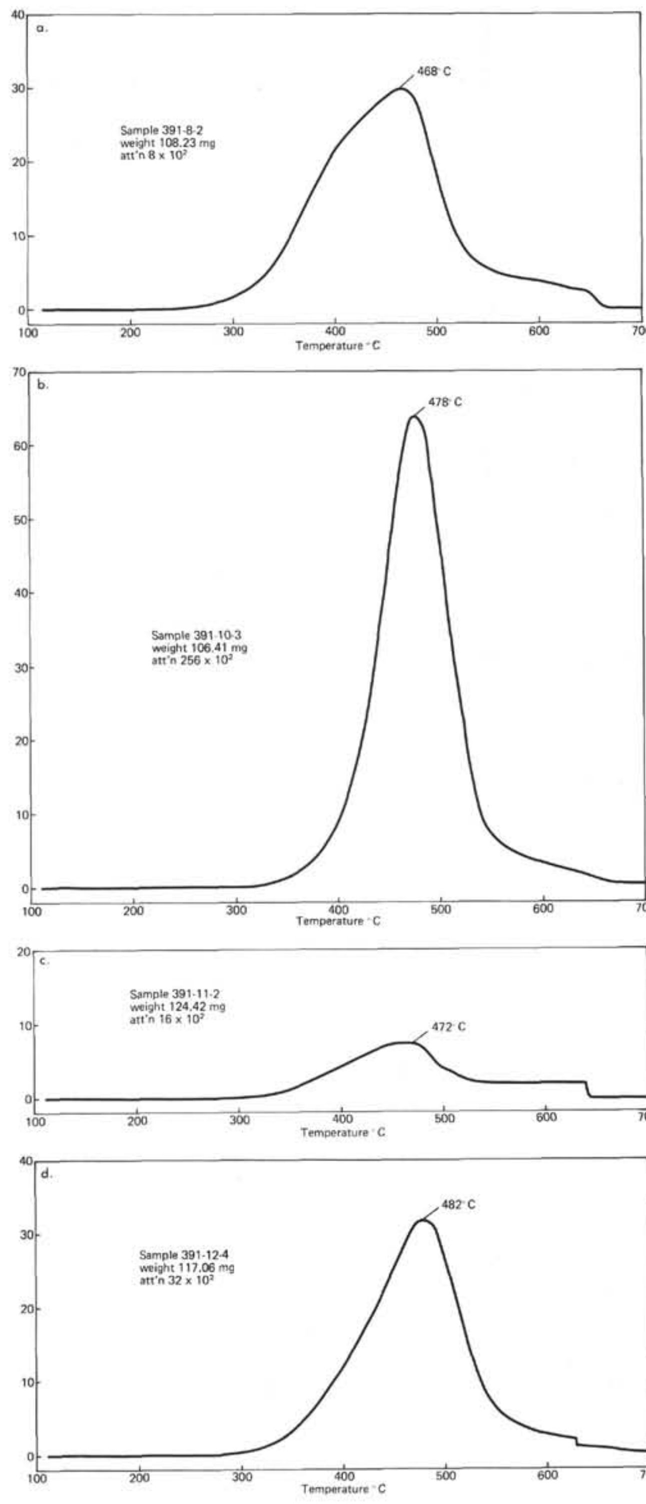


Figure 1. *Thermograms from analysis of Leg 44 samples.*

TABLE 1
Summary of Combustion and Thermal Analysis; Cretaceous Sapropels, DSDP Leg 44, Hole 391C, Blake-Bahama Basin

| | | | Thermal Analysis/Pyrolysis | | | | |
|---|---|---|---|---|---|---|---|
| Sample (Interval in cm) | Depth (m) | Organic Carbon (wt %) | Pyrolytic Oil Yield (gal/ton) | (wt %) | Oil Yield as % of Org. Carb. | Oil Content[a] (wt. ppm) | $T_{max}$ Yield (°C) |
| 391-8-2, 115-143 cm | 785 | 0.2 | 0.05 | 0.019 | 9.5 | 23 | 468 |
| 391-10-3, 110-138 | 901 | 2.5 | 1.98 | 0.76 | 30.4 | 122 | 478 |
| 391-11-2, 110-143 cm | 927 | 0.3 | 0.02 | 0.008 | 2.7 | 6 | 472 |
| 391-12-4, 30-60 cm | 958 | 1.2 | 0.16 | 0.062 | 5.2 | 31 | 482 |

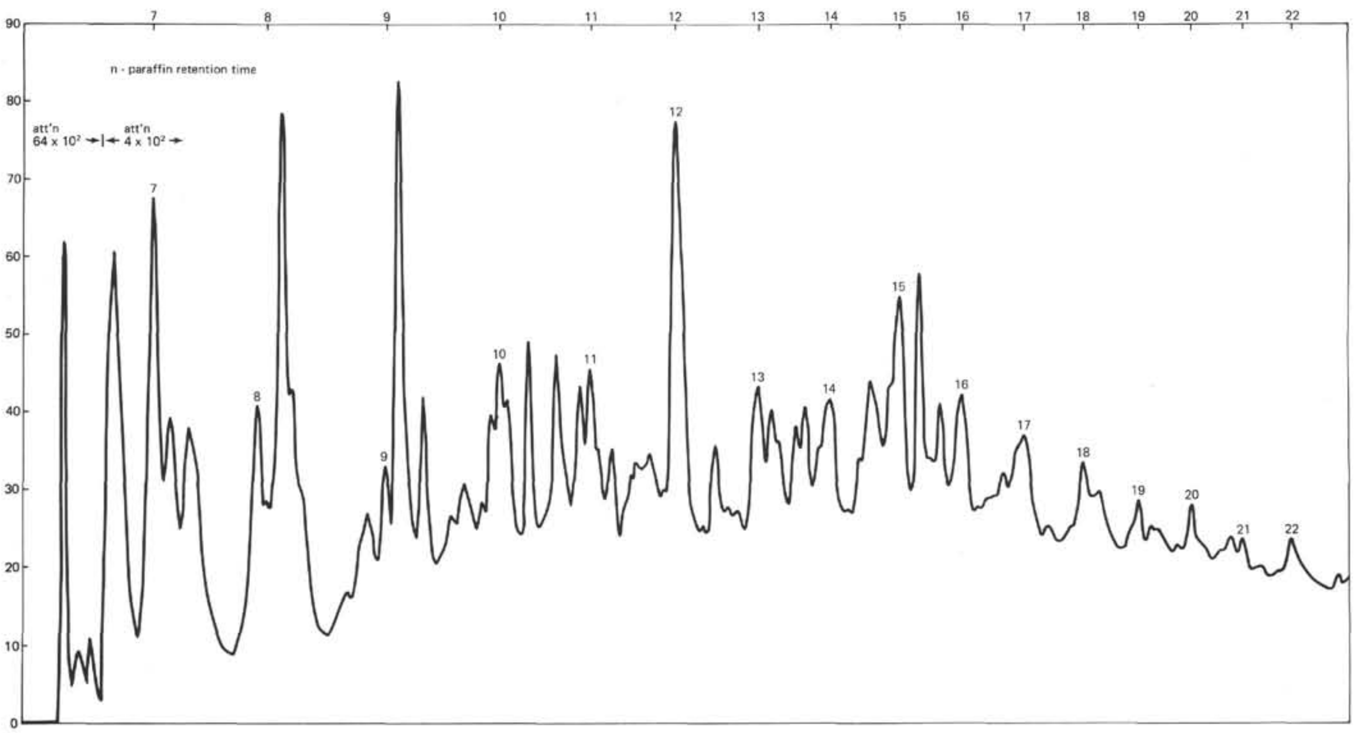


Figure 2. *Chromatogram of pyrolysis products Sample 391C, 10-3, 110-138 cm. Conditions: Trapped on poropak Q at 30°C; backflushed at 220°C onto 1.83 m X 3.13 mm ss column packed with 8% Dexsil 300 on Chromo W HP; temperature programmed from 60 to 340°C at 8°C/min. Chart speed 0.5 in./min. He carrier at 20 ml/min.*

during their burial history, will begin to decompose thermally at about 350°C when heated at 40°C/min, and will give a maximum (peak) in the production of pyrolysis products in the temperature range of 450° to 490°C. Mature petroleum source rocks, when heated under the same conditions, will begin to decompose at about 400°C and give a peak in the temperature range of 510° to 530°C. Incipiently metamorphosed sediments (i.e., sediments heated above 175°C during normal burial history) give a greatly diminished pyrolysis response with a peak in the range of 600°C. In these samples, the temperature of maximum pyrolysis yield shows a general increase with depth from 468°C at 785 meters to 482°C at 958 meters. Thus on the basis of pyrolysis response these samples are thermally immature.

Only two of the samples (391C-10-3, 110-138 cm, 391-12-4, 30-60 cm) game sufficient pyrolytic yield for gas chromatographic analysis, shown in Figures 2 and 3. Pyrolysis products from Sample 391C-10-3, 110-138 cm are primarily in the gas, gasoline, and kerosene molecular weight range, with very little heavy hydrocarbon product. Pyrolysis products from Sample 391C-12-4, 30-60 cm are almost all in the gas and gasoline range.

We do not know to what extent the composition of pyrolysis product accurately predicts the quality of the hydrocarbons which would be generated during the normal burial history of the same rock. The results, however, suggest that these samples of black shale are not particularly "oil-prone" compared to other immature sediments rich in organic carbon such as Green River Shale.

An indication of the type of organic matter is given by the oil yield as a percentage of the organic carbon content. Two samples, 391-8-2, 115-143 cm and 391-10-3, 110-138 cm, gave moderate to relatively high conversion of organic matter to pyrolytic oil (9.5% and 30.4%, respectively). The other two samples had lower degrees of conversion (2.7% and 5.2%) which suggests a lack of hydrocarbon-generating capability.

Note added in proof: All temperatures cited above and in Table 1 are furnace temperatures. Actual rock temperatures were found to lag behind furnace temperature by 25°C.

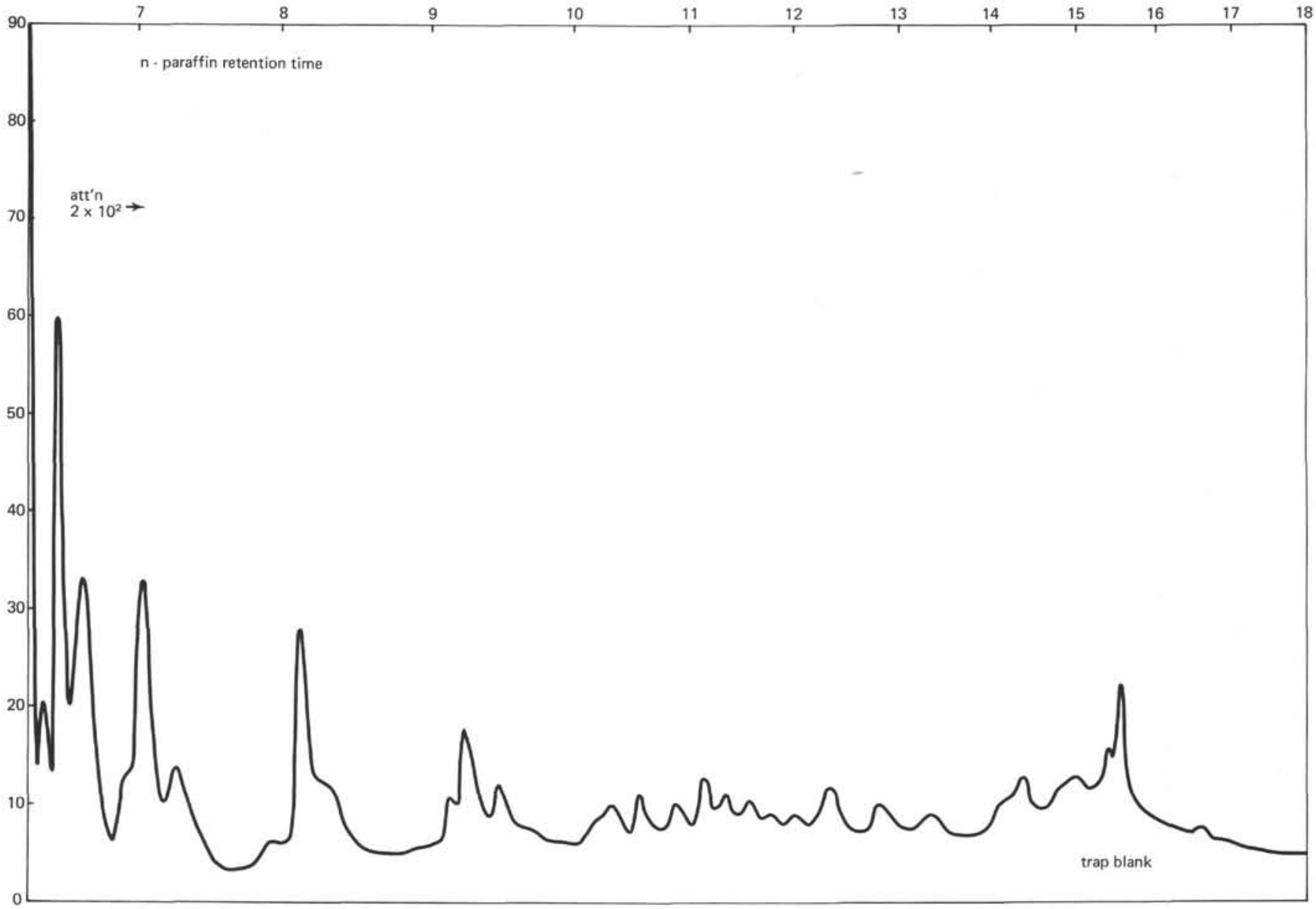


Figure 3. *Chromatogram of pyrolysis products, Sample 391C, 12-4, 30-6-cm. Conditions same as in Figure 2.*