

NO UGR

GEOCHEMICAL CHARACTERIZATION
OF
DEVONIAN GAS SHALE

RONALD E. ZIELINSKI
MONSANTO RESEARCH CORPORATION*
MOUND LABORATORY
MIAMISBURG, OHIO 45342

GEOCHEMICAL CHARACTERIZATION
OF
DEVONIAN GAS SHALE

RONALD E. ZIELINSKI
MONSANTO RESEARCH CORPORATION*
MOUND LABORATORY
MIAMISBURG, OHIO 45342

ABSTRACT

Detailed geochemical analyses are being used to provide an accurate assessment of the oil and gas resources present in the Devonian shales in the Appalachian and Illinois Basins. The suite of geochemical analyses is designed to evaluate the organic richness, the hydrocarbon potential, the type of organic matter and the thermal maturity of the organic matter.

Laboratory techniques such as pyrolysis gas chromatography and mass balance thermal extraction were also employed to measure thermally derived oil and gas yields from the Devonian shales.

Stable carbon isotope geochemistry has also been initiated. The first phase of this study involved the determination of stable carbon isotope values for shale core samples.

*Mound Laboratory is operated for the U. S. Energy Research and Development Administration by Monsanto Research Corporation (Contract No. EY-76-C-04-0053).

INTRODUCTION

Core samples from seven wells drilled in Illinois, Indiana, Kentucky and Virginia have been analyzed geochemically for the purpose of assessing their fossil energy resource potential. Organic geochemical data have been obtained for a better definition of the oil and gas contained in the Devonian shales.

The hydrocarbon source potential of fine-grained sediments from various worldwide locations has been studied by many researchers^(1,2). The hydrocarbon source rock studies were performed to investigate the organic richness, type (oil, condensate or gas), and state of thermal maturity of the hydrocarbon source rocks, and to determine their areal and stratigraphic distribution.

The location of the seven wells is displayed in Figure 1. In most cases, the entire stratigraphic unit of Devonian shale was cored. Samples for geochemical analyses were taken at 30-foot intervals and stored in air-tight metal containers. Shortly after arrival at the laboratory, the container air space was sampled for methane to heptane hydrocarbons. The container was opened and additional geochemical analyses were performed.

TECHNIQUES

The geochemical analyses performed on the Devonian shale samples are shown in Figures 2A and 2B. The abundance of methane through heptane hydrocarbons (C₁-C₇) was measured by summing the contents of the air space and core material stored in an air-tight container. Organic carbon was analyzed by combustion of the carbonate-free sediment. The kerogen was examined visually for morphological classification after being isolated from the inorganic matrix. Dried core material was crushed and extracted with a benzene-methanol solvent. The soluble extract was weighed, then separated into fractions by adsorption and liquid chromatography. The normal paraffin distribution was determined by gas chromatography. Vitrinite reflectance was measured using modifications of procedures described by Landes⁽³⁾, and Hacquebord and Donaldson⁽⁴⁾.

The pyrolysis gas chromatography involves the heating of a powdered sample of core material at a constant rate. The hydrocarbons produced during the pyrolysis process are analyzed using a flame ionization detector (FID) gas chromatograph.

The material balance assay is performed in a closed system under a cover of either helium or nitrogen. The condensable hydrocarbons formed during the pyrolysis process are collected along with water in a sidearm collector. The noncondensable products are carried over into a gas collection bottle. Following the pyrolysis event, the gaseous, liquid and solid products are characterized by additional analyses.

The stable carbon isotope studies performed to date have been performed only on the organic portion of the shale core. Prior to analysis, the inorganic carbon was removed by acidification.

DISCUSSION AND RESULTS

Abundance of C₁-C₇ Hydrocarbons

Gas and gasoline-range hydrocarbons are generated from organic matter at different levels of thermal maturity. Initially, at low temperature, microbial degradation forms methane or "dry" gas. With increasing time, temperature, and depth of burial, heavier hydrocarbons are generated. In the early stages of petroleum formation, gas-oil range hydrocarbons predominate with associated amounts of "wet" gas (C₂-C₄ hydrocarbons) and gasoline-range hydrocarbons. The content and distribution of C₁-C₇ hydrocarbons is primarily dependent on three geochemical parameters; namely, the organic richness, the type of organic matter, and its level of thermal maturity.

Shales from each of the wells analyzed to date, contained large quantities of C₁-C₇ hydrocarbons (Figure 3). The average C₁-C₇ values are listed in Table 1. For the I-1, O-1, P-1 and VA-1 wells, the dry gas, wet gas and gasoline-range hydrocarbons were uniformly distributed. The gas-

oline-range hydrocarbons in VA-1 are exceptionally low, but the lithology of the samples from this well indicated that coal was present in most of the samples. In the KY-2 well, however, the hydrocarbons varied significantly throughout the entire well profile. Also listed in Table 1 are the values of C₁-C₇ hydrocarbons released to the headspace of the sample canisters. These values indicate that most of the C₁-C₄ hydrocarbons are released from the samples and are not retained in the matrix. For well O-1, however, this was not true. Other investigators⁽⁵⁾ have indicated that samples from well O-1 contain ultramicroporous networks which inhibit the diffusion of hydrocarbon gases from the material.

The hydrocarbon concentrations listed in Table 1 are minimum values. The core samples are removed from the well and are exposed to the atmosphere for approximately 1 to 2 hours prior to being stored in the sample containers. This exposure time allows a significant amount of hydrocarbon gases to diffuse from the core. Although for most samples, the maximum exposure time is 2 hours, the P-1 samples were exposed to air for several weeks prior to canning for geochemical analysis.

Organic Carbon

The organic carbon content of fine-grained argillaceous sediments such as the Devonian shales is an indicator of organic richness. Organic matter comprised mostly of organic detritus is preserved by rapid burial. Alteration processes such as microbial degradation and thermal diagenesis transform the organic matter to the complex heterogeneous material called "kerogen." Kerogen is presumed to be the major precursor for oil and gas. As the sediments become thermally matured, oil and gas are generated. The amount of kerogen, expressed as the organic carbon content, shows the abundance of organic matter which may be altered to form hydrocarbons. The lower limit of organic carbon in shales from productive basins is 0.4 percent⁽⁶⁾. The worldwide average of organic carbon in shales and siltstones is 1.14 percent⁽⁷⁾.

The amount of organic carbon in Devonian shales varies from location to location (Figure 4). In general, the average organic carbon content of sediments from the I-1, O-1, P-1, KY-2 and VA-1 wells is 6.77, 8.75, 4.73, 2.04, and 1.96 percent, respectively. The organic matter appears to be more uniformly distributed in the I-1, O-1 and P-1 wells. However, to the east, the KY-2 and VA-1 shales vary considerably in organic carbon from a low of 0.16 to a high of 7.75 percent.

Using the average organic carbon contents and the Mott Factor (1350 ft³-gas/ton of organic matter), the predicted indigenous gas per unit volume (1 mile x 1 mile x 1000 feet) can be calculated. The existing indigenous gas can also be calculated using the experimentally determined average C₁-C₄ hydrocarbon contents. The results of these calculations are shown in Table 2. The existing indigenous gas values are very conservative. This conservatism is the result of the previously discussed loss of hydrocarbon during sample preparation at the well site. If the values were also corrected for downhole pressure and temperature they would be significantly higher.

Type of Organic Matter

The solid organic matter contained in fine-grained sediments visually reflects its source of deposition. Composed mostly of organic detritus, the kerogen is related to its depositional environment by the proportions of marine and continental organic matter it contains. Kerogen identified visually can be classified as amorphous, herbaceous, woody, or coaly (inertinite). After maturation by thermal diagenesis, the marine (amorphous) type is prone to generate abundant gaseous and liquid hydrocarbons. The nonmarine (woody-coaly) type is prone to produce mostly gaseous hydrocarbons^(8,9).

Of the five wells completed to date, the type of organic matter in the I-1, O-1 and P-1 wells is primarily herbaceous and amorphous kerogen (Figure 5). This liquid rich material (if present in sufficient quantities) has the potential to generate abundant oil and associated gas. In contrast, shales from the KY-2 well contain predominant amounts of either the herbaceous-amorphous kerogen or the woody-coaly kerogen. The VA-1 well contains organic matter that is predominantly herbaceous-woody. The high organic carbon content appears to be associated with the kerogen type. In most cases, the herbaceous-amorphous kerogen is present in shales which contain abundant organic carbon. The shales containing primary or secondary amounts of woody-coaly kerogen are lean in organic matter.

C₁₅₊ Extract

Core material was extracted with organic solvent to yield the C₁₅₊ extract or "bitumen." The bitumen is composed of hydrocarbon and nonhydrocarbon material. The bitumen in recent sediments is impoverished in hydrocarbons and contains mostly nonhydrocarbon material. As the sediments become thermally matured, increasing amounts of hydrocarbons are formed. The average worldwide concentrations of hydrocarbons in shales was found to be 96 ppm(7).

Shales from four of the wells were found to contain bitumen composed mostly of hydrocarbons. The distribution of hydrocarbon and nonhydrocarbon material extracted from the Devonian shales is shown in Figure 6. The hydrocarbon portion consists of paraffin-naphthene (P-N) and aromatic (AROM) fractions. The nonhydrocarbon material is separated into asphaltene (ASPH) and nitrogen-sulfur-oxygen containing compounds (NSO's). In the I-1, O-1, and P-1 wells, the average hydrocarbon content was 2159 ppm, 2463 ppm, and 3332 ppm, respectively. The average hydrocarbon content was 1469 ppm for the KY-2 shales and approximately zero for the VA-1 shales. The hydrocarbon content appears to be related to the organic carbon content and the kerogen type. In general, shales characterized by herbaceous-amorphous kerogen, and a high organic carbon content contain abundant C₁₅₊ hydrocarbons. Sediments with low organic carbon content and primary or secondary amounts of woody-coaly kerogen contain low amounts of C₁₅₊ hydrocarbons.

Thermal History

In order to assess the hydrocarbon generating capacity of potential source rocks, the thermal history and its diagenetic effect on petroleum generation must be evaluated. Two methods, kerogen coloration and vitrinite reflectance, were used to measure the thermal alteration of the Devonian shales. The kerogen coloration of the plant cuticle and spore-pollen debris is measured in transmitted light. The state of thermal alteration (Thermal Alteration Index or TAI) ranges from light greenish yellow at Stage 1 for unaltered kerogen to black at Stage 5 for severely altered kerogen. The thermal zone of oil generation corresponds to a moderately mature to mature kerogen of Stage 2 to 3 (Figure 7). The kerogen in the zone of oil generation is characterized by yellow-orange to light brown color. Vitrinite reflectance (R_o) is also used to measure the degree of thermal alteration. This technique has several advantages over other thermal maturation classifications. It is an absolute measurement; it is a rigorous analytical evaluation; and it is a universally accepted technique. R_o values ranging from 0.2 to 0.6 indicate that the sediments are too immature for oil generation. The zone of petroleum generation is usually interpreted to range from 0.6 to 1.2. R_o from 1.2 to 3.0 indicate a thermal history sufficient to form wet gas and methane. The severely altered or metamorphosed organic matter represented by R_o values greater than 3.0 is considered as a nonsource for hydrocarbons.

The thermal history of the Devonian shales analyzed in this study exhibit a small amount of variation (Figure 8). The organic matter in shales from the five wells is characterized by its yellow to orange-brown color. This coloration is consistent with a thermal alteration index of Stage 1+ to 3-. The average value of Stage 2 corresponds to a thermal history equal to the early stages of petroleum generation. The mean average vitrinite reflectance value in both the I-1 and O-1 wells is 0.45. In the P-1 well, a slightly higher value of 0.50 was measured. The value for KY-2 was 0.52, while that for VA-1 approached 1.0. Based on the vitrinite reflectance date, it appears likely that the Devonian shales will be increasingly more mature in an east-south easterly direction.

Material Balance Assay

Material Balance Assays (MBA's) are being performed on all the geochemical samples. For the assays approximately 100 grams of well-riffled, representative 4 to 8 mesh material are heated and destructively distilled at a maximum temperature of 500°. The assay is performed in a closed system and either helium or nitrogen is used as the flush gas. Oil and water are condensed in a centrifuge tube and noncondensable gases flow into an evacuated receiver. Following the pyrolysis process, the products are weighed and further analyzed.

The analyses performed on the pyrolysis products include oil, gas and water yield; gas compositional analysis; detailed oil and water analysis; percent post-assay organic carbon; and percent ash. These studies are designed to correlate the geochemical analyses with pyrolysis yield.

The average MBA product yields obtained to date are shown in Table 3. Table 4 lists the average gas analyses obtained for the samples from the three wells. These data support the previously determined geochemical data which indicated that the samples from the O-1 and I-1 wells would yield more hydrocarbon products than the samples from KY-2. The MBA of the KY-2 well samples also exhibited the same variations that characterized the other geochemical analyses. This is best indicated by the oil yields which varied from 0.1 to 4.6 gal/ton.

The other analyses are currently in progress on these samples, but a preliminary analysis of the oil product from the O-1 well produced the results shown in Table 5.

Pyrolysis-Gas Chromatography

To date, core samples from the I-1 well and the P-1 well have been analyzed by pyrolysis gas chromatography. Approximately 100 mg. of powdered sample was heated under helium from ambient temperature to 550°C at a constant rate of 30°C/min. The heating of the organic matter in the shale produces hydrocarbons which are swept by the carrier gas to a flame ionization detector. The amount of hydrocarbons generated vs. the temperature of generation is displayed on a recorder. The areas under the curves are computed by a digital integrator. The test data are listed in Table 6 and 7, and are shown in Figures 9 and 10.

A preliminary evaluation of the pyrolysis data from the analysis of I-1 and P-1 samples shows the following.

1. The total hydrocarbon yield is directly proportional to the C₁₅+ bitumen concentration and the organic carbon content.
2. The total amount of organic carbon available for hydrocarbons is less than the total organic carbon.
3. The Fischer Assay oil yields calculated by this method are similar to the yields obtained by the modified material balance method.
4. In order to obtain optimum hydrocarbon yields during the gas production of these shales, a heating process will be required not only for extraction, but also for pyrolytic cracking.

Stable Carbon Isotope Geochemistry

Samples of shale core from five wells have been analyzed by mass spectrometry for stable carbon isotope values. Prior to analysis, the inorganic carbon was removed by acidification. The total organic carbon was converted to CO₂ and its delta¹³C was measured relative to PDB. The delta¹³C results show a strong correlation to the organic matter type. In general, the samples classified as gas prone, restricted marine or nonmarine are characterized by delta¹³C values ranging from -24.6 to about -28. The oil prone, more marine type of organic matter composed mostly of herbaceous and amorphous kerogen is characterized by isotopically lighter delta¹³C values (-27 to -31). Four of the five wells have been exposed to a similar thermal history. The organic matter from the VA-1 is more thermally mature (Table 8). Delta¹³C values from the nonmarine shales (gas prone) from VA-1 appear to be isotopically lighter than the nonmarine shales in the other four wells. Increasing thermal maturation on kerogens of similar type usually produces a kerogen which becomes increasingly heavier relative to ¹³C/¹²C. The data indicate that the opposite effect has taken place, namely the organic matter has become slightly lighter. Previous studies performed on crude oils and kerogens have shown that delta¹³C values of -23 to -29 are indicative of marine derived organic matter. Values of -29 to -33 usually indicate marine organic matter. The initial results obtained on selected Eastern gas shales seems to show an inverse relationship when compared to previous carbon

isotope studies.

More samples from other wells are currently being analyzed to establish if this inverse relationship does exist and why it does occur. Stable carbon isotope work is also currently in progress on both the C₁-C₇ gas species and the Material Balance Assay oil product.

CONCLUSIONS

The Devonian shales are evaluated as a potential source of oil and gas based upon the type of kerogen present, its degree of thermal alteration, the nature of hydrocarbons which it has been generated and the hydrocarbons produced by pyrolysis. A preliminary evaluation of the geochemical data obtained from the core material seems to indicate that the samples from the western region have the greatest organic richness and contain the more abundant oil prone organic matter. The VA-1 well contained the most C₁-C₄ hydrocarbon gases, a minimum of 46 B Cu.ft./unit volume.

The degree of thermal alteration has been sufficient to initiate the hydrocarbon forming process in the Devonian shales in all the wells examined to date. Shales from the wells in the western region are at approximately the same level of maturation. The shales from the KY-2 and VA-1 wells are slightly more mature.

REFERENCES

1. Bailey, N. J. L., Evans, C. R., and Milner, C. W. D., "Applying Petroleum Geochemistry to Search for Oil: Examples from Western Canada Basin," Am. Assoc. Petroleum Geologists Bull., 58, 2284-2294, 1974.
2. Welte, D. H., "Petroleum Exploration and Organic Geochemistry," J. Geochem. Explor., 1, 117-136, 1972.
3. Landes, K. K., "Eometamorphism, and Oil and Gas in Time and Space," Am. Assoc. Petroleum Geologists Bull., 51, 828-841, 1967.
4. Hacquebord, P. A., and Donaldson, J. R., "Coal Metamorphism and Hydrocarbon Potential in the Upper Paleozoic of Atlantic Provinces, Canada," Can. J. Earth Sci., 7, 1139-1163, 1970.
5. Thomas, J. and Frost, R. R., "Internal Surface Area and Porosity in Eastern Gas Shales From the Sorption of Nitrogen, Carbon Dioxide, and Methane - A Status Report," Proceedings of the Third ERDA Symposium on Enhanced Oil and Gas Recovery and Improved Drilling Methods, The Petroleum Publishing Company, Tulsa, Oklahoma, August, 1977.
6. Ronov, A. B., "Organic Carbon in Sedimentary Rocks (in relation to the presence of petroleum)," Geokhim., 5, 510-536, 1958.
7. Gehman, H. M., "Organic Matter in Limestone," Geochem. Cosmochim. Acta, 26, 885-897, 1962.
8. Staphin, F. L., "Sedimentary Organic Matter, Organic Metamorphism, and Oil and Gas Occurrence," Bull. Can. Pet. Geol., 17, 47-66, 1969.
9. Tissot, B, et al., "Influence of Nature and Diagenesis of Organic Matter in Formation of Petroleum," Am. Assoc. Petroleum Geologists Bull., 58, 499-506, 1974.



WELL LOCATIONS

- I-1: EFFINGHAM COUNTY, ILLINOIS
- I-2: HENDERSON COUNTY, ILLINOIS
- I-3: TAZEWELL COUNTY, ILLINOIS
- KY-2: MARTIN COUNTY, KENTUCKY
- O-1: CHRISTIAN COUNTY, KENTUCKY
- P-1: SULLIVAN COUNTY, INDIANA
- VA-1: WISE COUNTY, VIRGINIA

FIGURE 1

MOUND LABORATORY

FLOW DIAGRAM FOR ORGANIC GEOCHEMICAL ANALYSIS

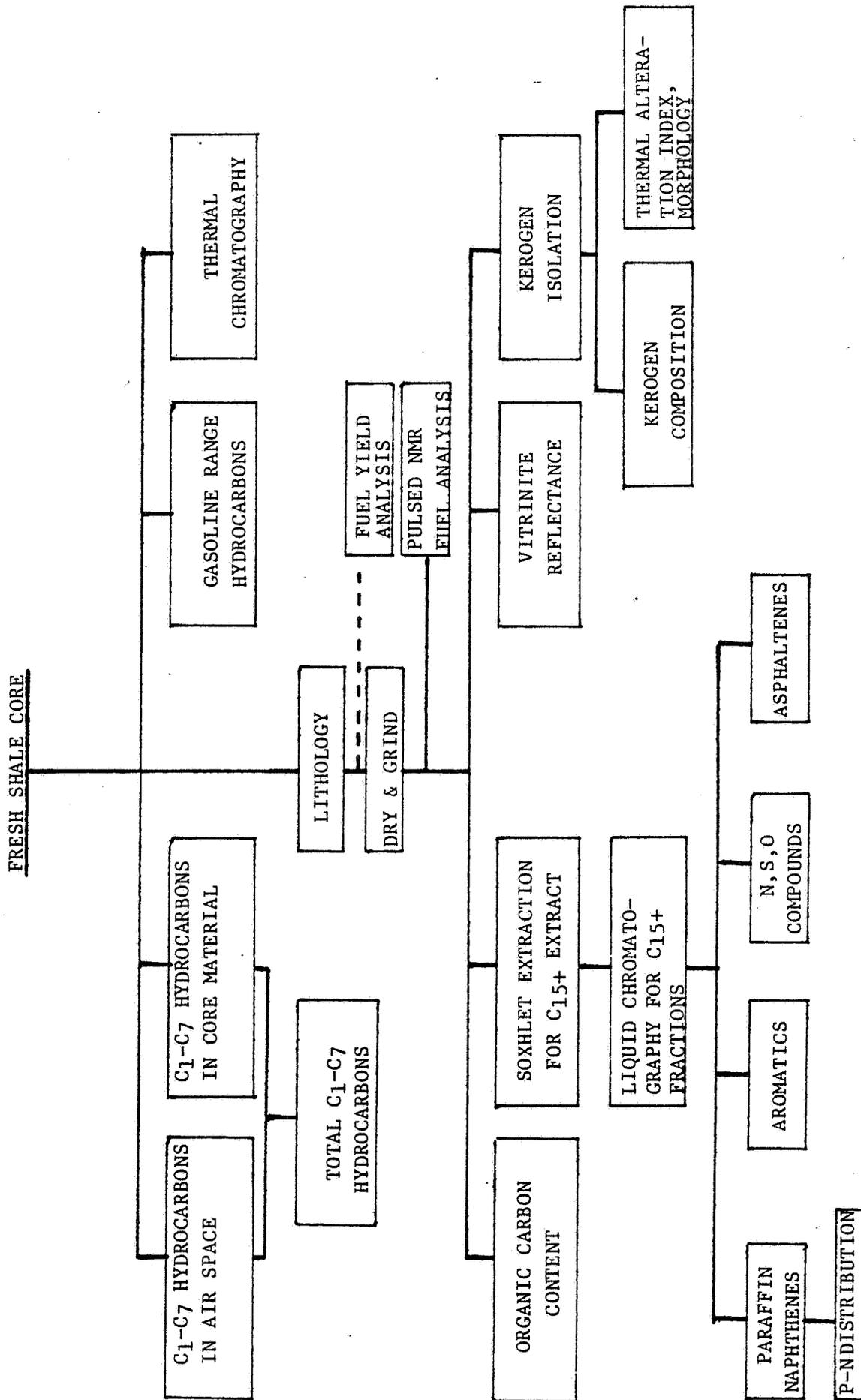


FIGURE 2A

MOUND LABORATORY
 FLOW DIAGRAM FOR FUEL YIELD ANALYSIS

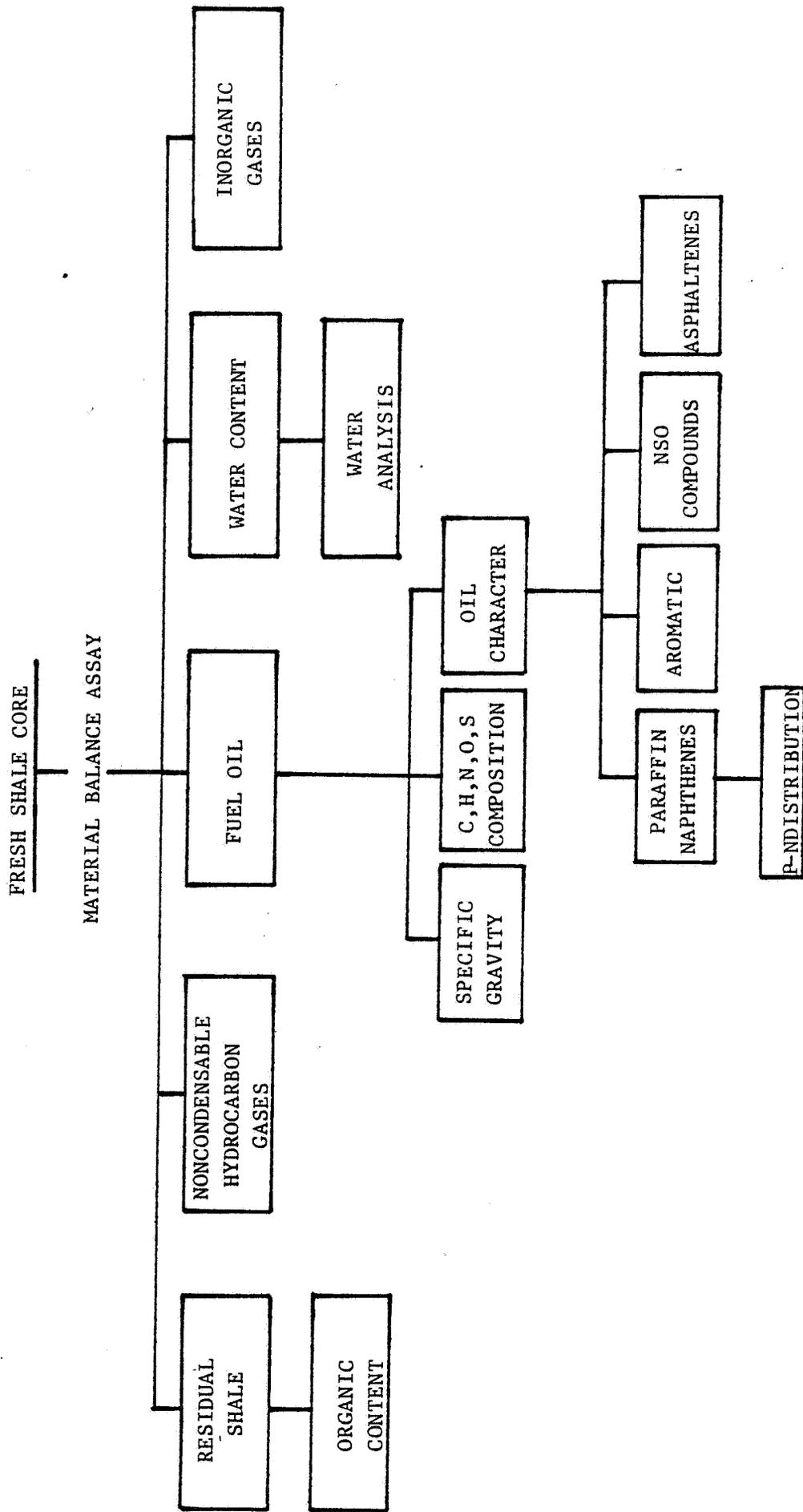
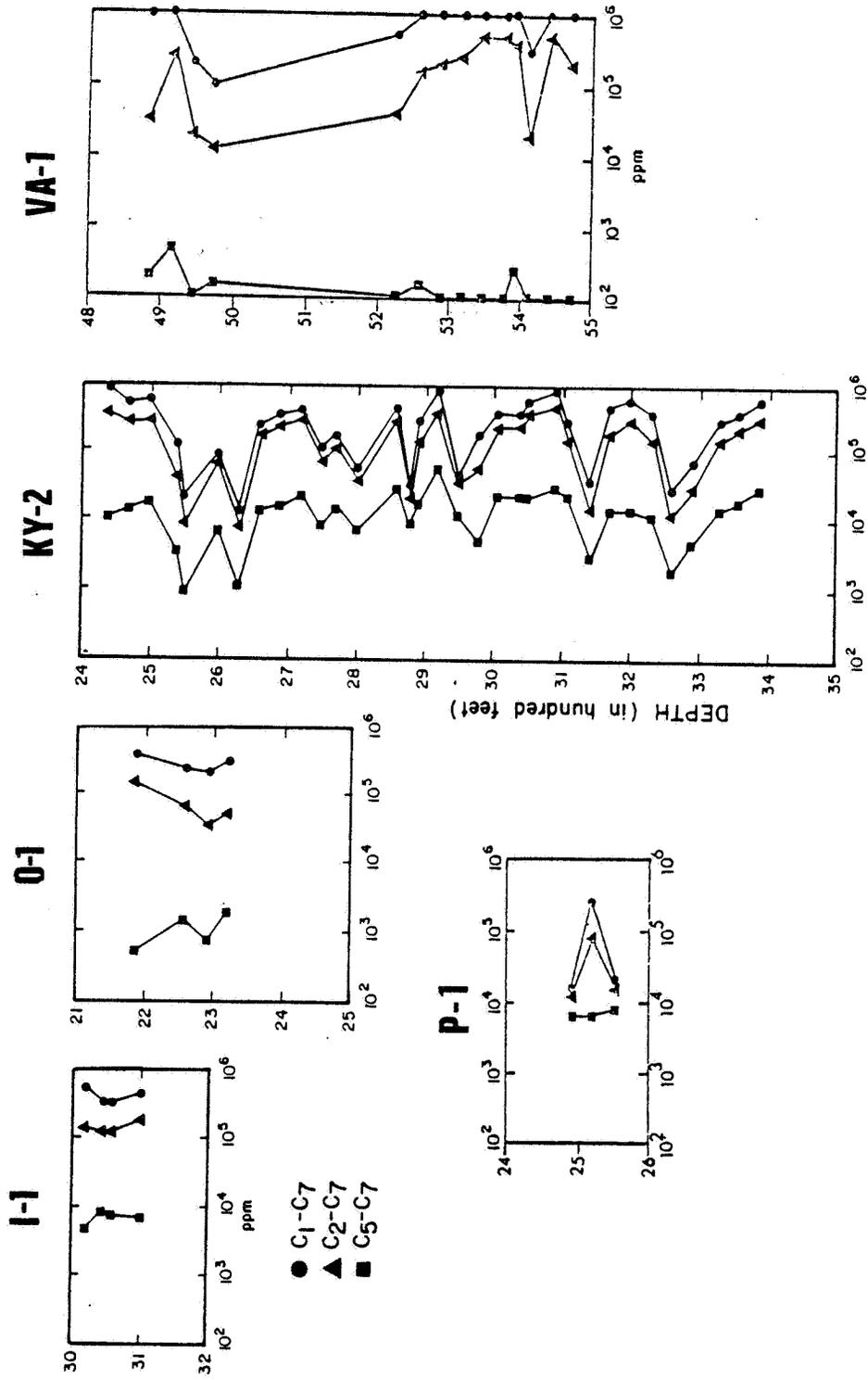


FIGURE 2B

TABLE 1

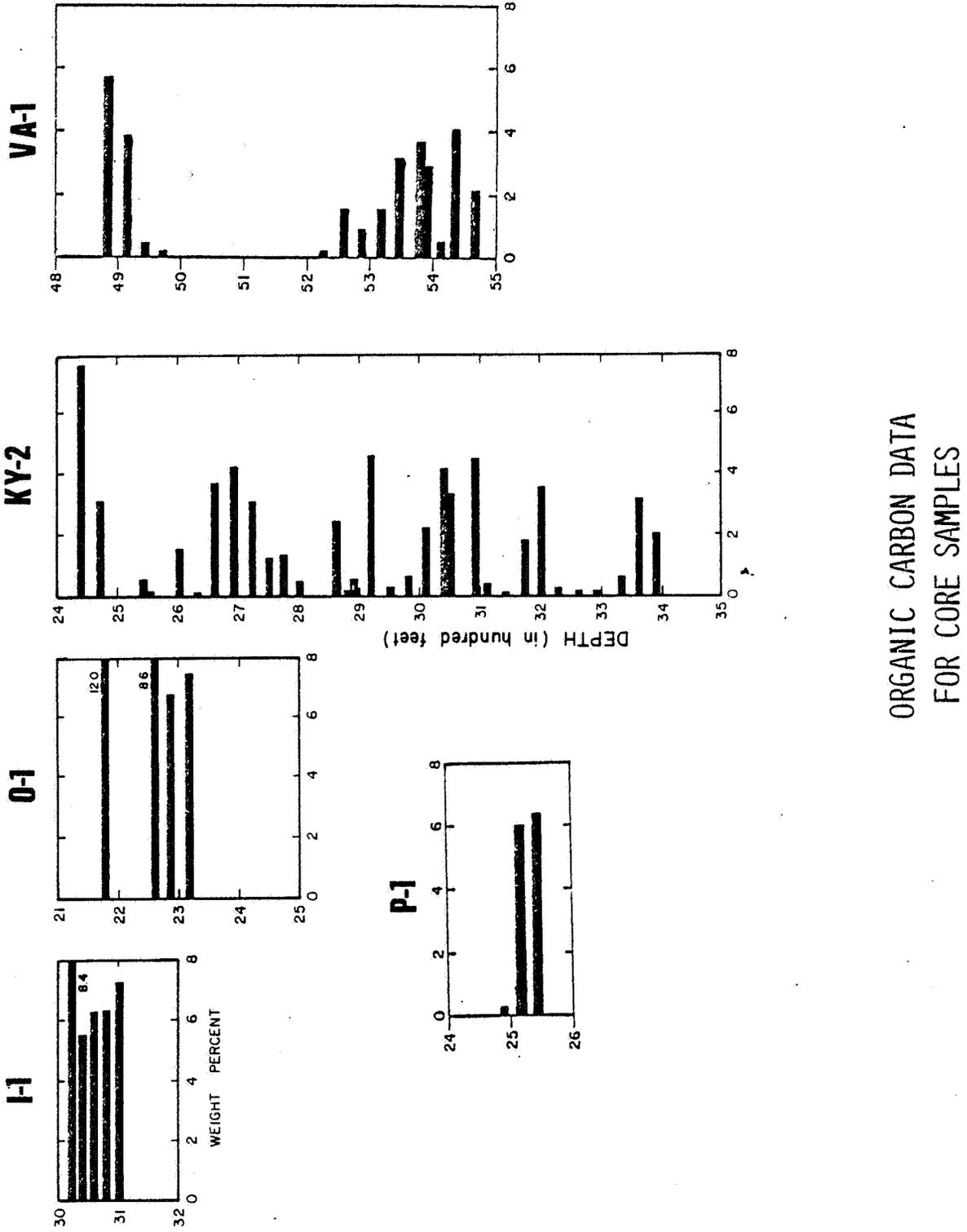
AVERAGE C₁-C₇ HYDROCARBON ANALYSES

| WELL NUMBER: | KY-2 | I-1 | O-1 | VA-1 | P-1 |
|------------------------------------------------|--------|--------|--------|---------|--------|
| \bar{C}_1 (PPM) HEAD SPACE | 139227 | 254529 | 110625 | 1392646 | 59989 |
| \bar{C}_1 (PPM) HEAD SPACE AND CORE | 152049 | 291438 | 236505 | 1415673 | 70509 |
| % RELEASED TO HEAD SPACE | 92 | 87 | 47 | 98 | 85 |
| $\overline{C_1-C_4}$ (PPM) HEAD SPACE | 235955 | 338082 | 150602 | 1569960 | 78065 |
| $\overline{C_1-C_4}$ (PPM) HEAD SPACE AND CORE | 313779 | 433160 | 311233 | 1642424 | 104384 |
| % RELEASED TO HEAD SPACE | 75 | 78 | 48 | 96 | 75 |
| $\overline{C_5-C_7}$ (PPM) HEAD SPACE | 6704 | 4329 | 213 | 32 | 3809 |
| $\overline{C_5-C_7}$ (PPM) HEAD SPACE AND CORE | 15939 | 7500 | 1283 | 116 | 6689 |
| % RELEASED TO HEAD SPACE | 42 | 58 | 17 | 28 | 57 |



C₁-C₇ HYDROCARBON DATA
 FOR CORE SAMPLES

FIGURE 3



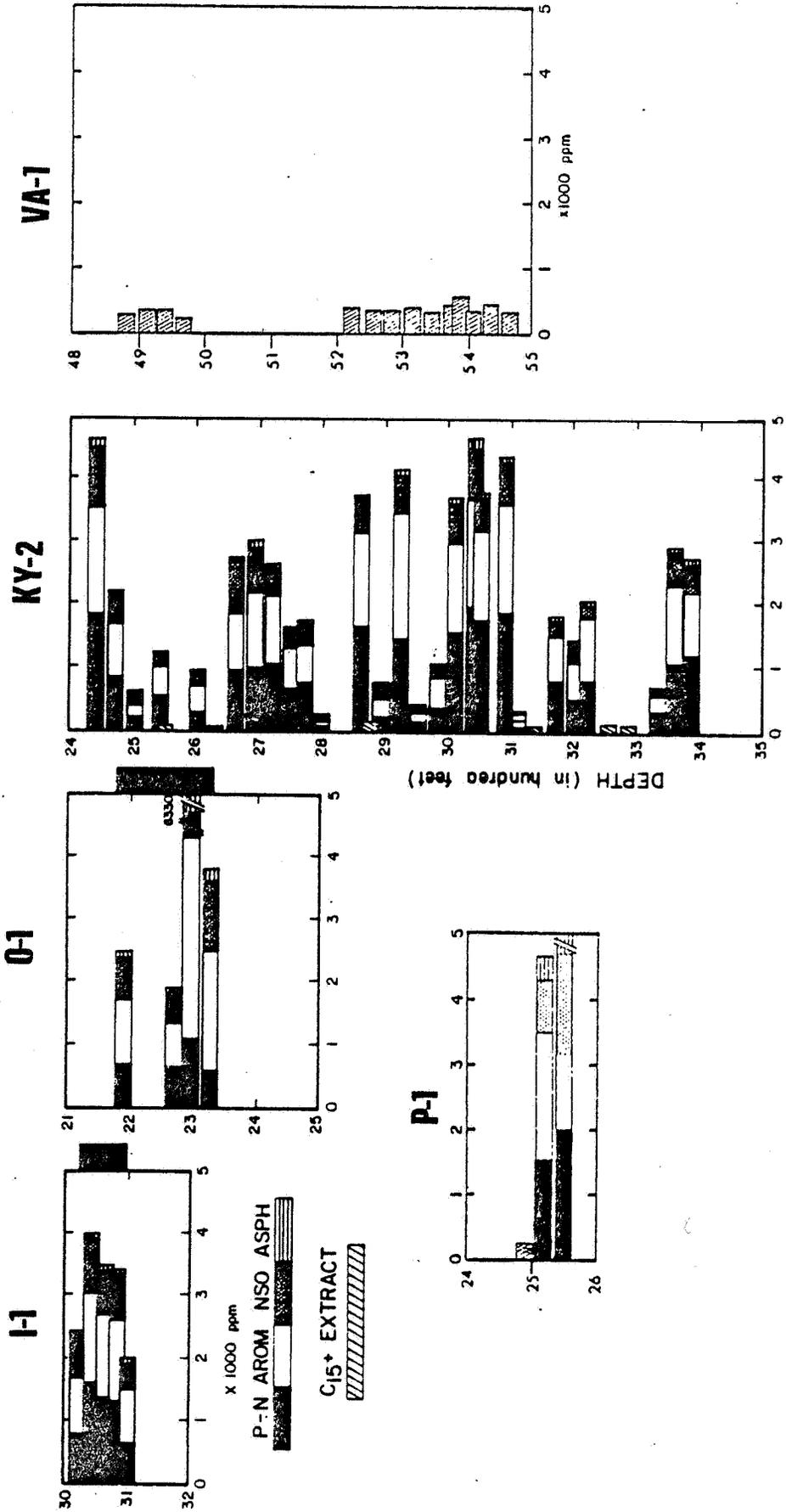
ORGANIC CARBON DATA
FOR CORE SAMPLES

FIGURE 4

TABLE 2

ESTIMATED INDIGENOUS GAS CONTENT

| WELL: | <u>I-1</u> | <u>0-1</u> | <u>KY-2</u> | <u>VA-1</u> |
|----------------------------------------------|------------|------------|-------------|-------------|
| PREDICTED INDIGENOUS GAS (B CU. FT./UNIT) | 237 | 306 | 71 | 69 |
| EXISTING INDIGENOUS GAS (B CU. FT./UNIT) | 12 | 9 | 9 | 46 |



C₁₅+ EXTRACT DATA
FOR CORE SAMPLES

FIGURE 6

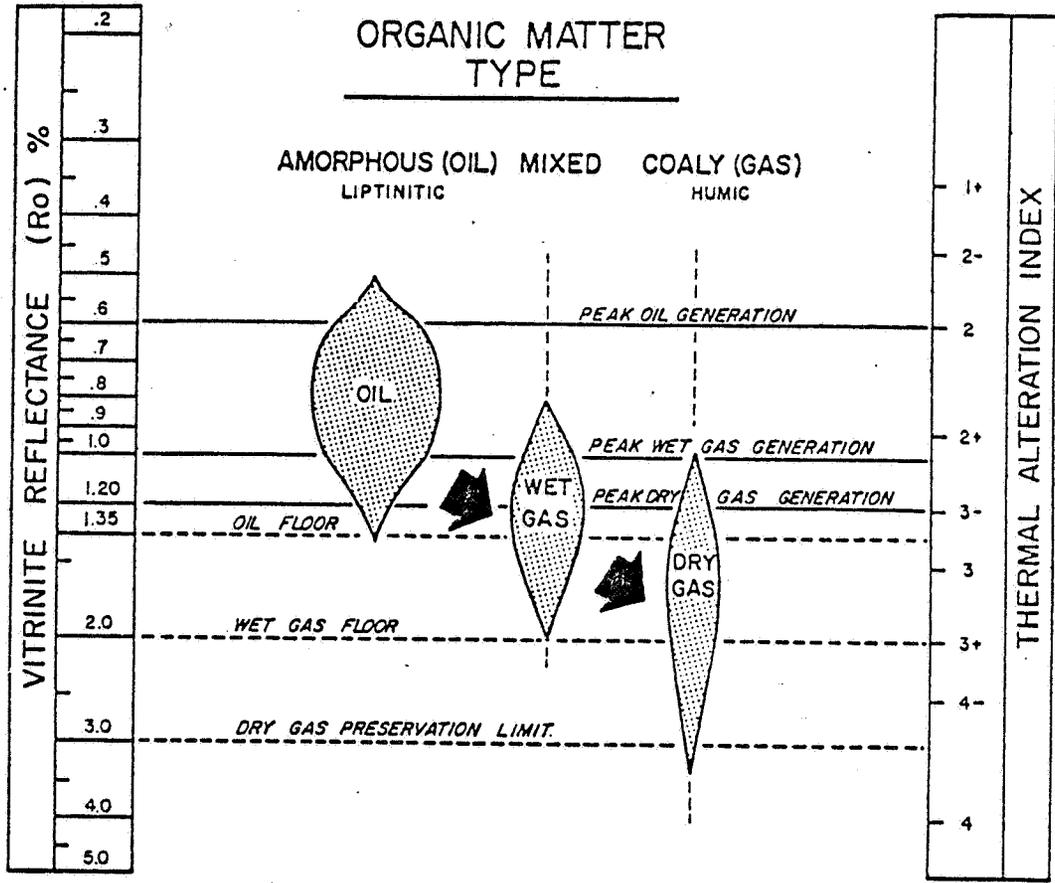
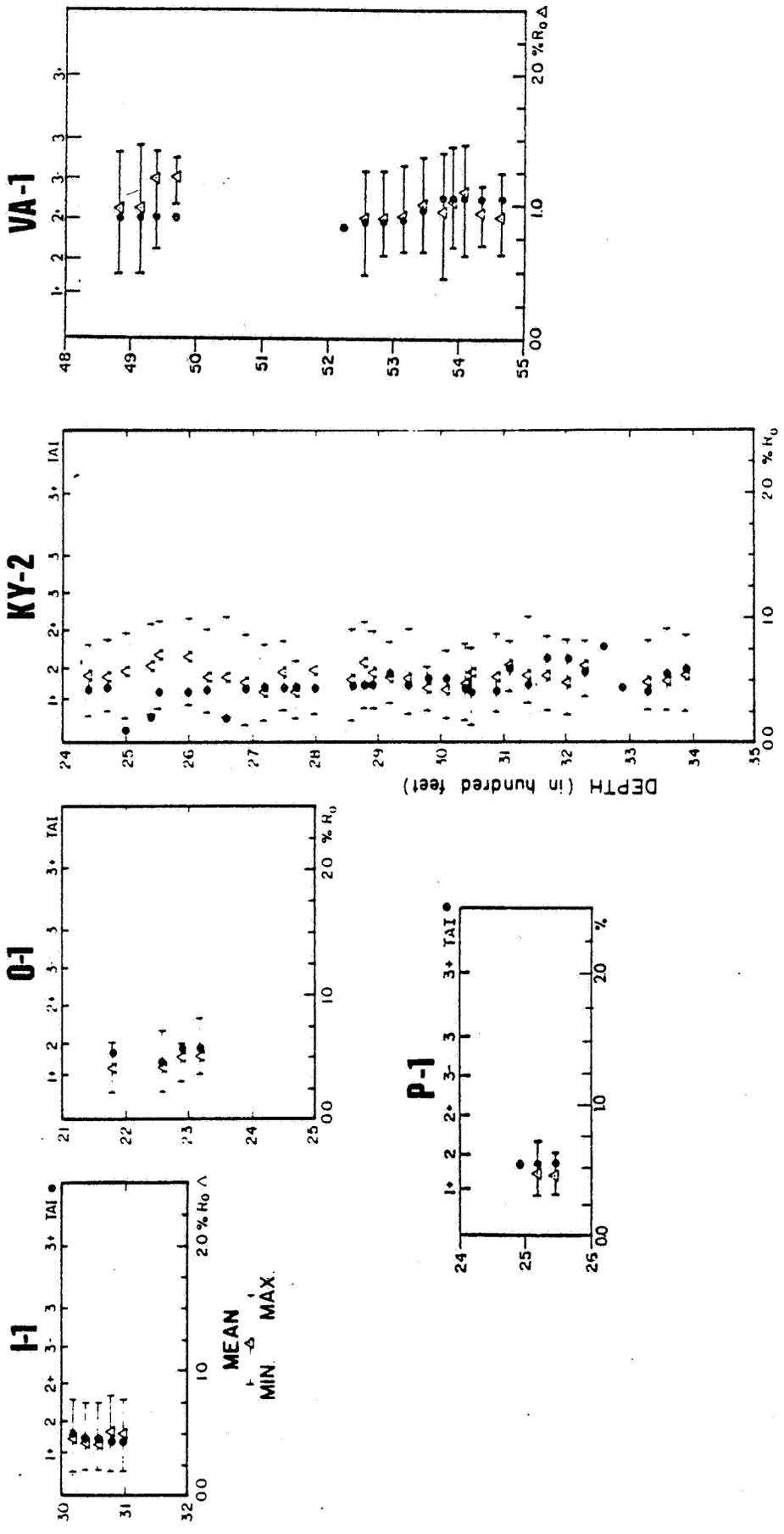


FIGURE 7



THERMAL ALTERATION INDEX AND VITRINITE REFLECTANCE FOR CORE SAMPLES

FIGURE 8

TABLE 3

MATERIAL BALANCE ASSAY

PRODUCT YIELD

| | | | |
|-----------------------------------------|------------|------------|-------------|
| WELL | <u>0-1</u> | <u>I-1</u> | <u>KY-2</u> |
| OIL YIELD (GAL./TON) | 12.75 | 9.04 | 1.63 |
| SPECIFIC GRAVITY (60/60) | 0.910 | 0.907 | 0.866 |
| °API-OIL GRAVITY | 24 | 25 | 32 |
| WATER YIELD (GAL./TON) | 2.224 | 4.134 | 4.130 |
| PH | 9.3 | 9.2 | 9.3 |
| HYDROCARBON GAS YIELD (FT. 3/TON) | 224.33 | 166.20 | 31.50 |

TABLE 4

MATERIAL BALANCE ASSAY

GASEOUS YIELD

| WELL | 0-1 | I-1 | KY-2 |
|---------------------------------------|-------|-------|-------|
| HYDROCARBONS (CM ³ /G) | | | |
| METHANE | 3.577 | 2.798 | 0.580 |
| ETHANE | 1.191 | 0.649 | 0.177 |
| ETHYLENE | 0.208 | 0.147 | 0.023 |
| PROPANE | 0.594 | 0.477 | 0.090 |
| PROPYLEN | 0.309 | 0.241 | 0.043 |
| I-BUTANE | 0.048 | 0.046 | 0.013 |
| N-BUTANE | 0.267 | 0.261 | 0.049 |
| BUTENE-1 | 0.135 | 0.103 | 0.017 |
| T-BUTENE-2 | 0.041 | 0.033 | 0.015 |
| C-BUTENE-2 | 0.027 | 0.022 | 0.016 |
| I PENTANE | 0.037 | 0.045 | 0.018 |
| N-PENTANE | 0.105 | 0.117 | 0.019 |
| PENTENE-1 | 0.035 | 0.036 | 0.005 |
| NON-HYDROCARBONS (CM ³ /G) | | | |
| HYDROGEN | 2.747 | 3.129 | 0.638 |
| HYDROGEN SULFIDE | 4.917 | 4.275 | 1.389 |
| CARBON MONOXIDE | 0.133 | 0.152 | 0.017 |
| CARBON DIOXIDE | 1.277 | 2.030 | 1.316 |

TABLE 5
 ANALYSIS OF PYROLYSIS OIL
 FROM WELL 0-1

C₁₅+ OIL COMPOSITION

| | |
|--------------------------|-------|
| HYDROCARBONS | |
| PARAFFIN-NAPHTHENE (P-N) | 19.6% |
| AROMATIC (AROM) | 32.0% |
| NON-HYDROCARBONS | |
| ASPHALTENE (ASPH) | 5.5% |
| ELUTED NSO | 24.6% |
| NON-ELUTED NSO | 18.3% |

DETAILED COMPOSITION OF C₁₅+ P-N HYDROCARBONS

| | |
|-------------------|-------|
| NC ₁₅ | 7.2% |
| NC ₁₆ | 15.5% |
| NC ₁₇ | 18.4% |
| NC ₁₈ | 16.6% |
| NC ₁₉ | 13.1% |
| NC ₂₀ | 10.0% |
| NC ₂₁ | 7.1% |
| NC ₂₂ | 4.7% |
| NC ₂₃ | 3.4% |
| NC ₂₄ | 2.2% |
| NC ₂₅ | 1.2% |
| NC ₂₆ | 0.5% |
| NC ₂₇ | 0.0% |
| % NORMAL PARAFFIN | 7.9% |
| % NAPHTHENE | 92.1% |

TABLE 6

PYROLYSIS - GAS CHROMATOGRAPHY

I-1 WELL - EFFINGHAM COUNTY, ILLINOIS

| | | | | | |
|-------------------------------|-------|-------|-------|-------|-------|
| DEPTH | 3023' | 3044' | 3057' | 3075' | 3099' |
| TOTAL HYDROCARBON YIELD (PPM) | 49015 | 34171 | 34077 | 38833 | 39783 |
| GALLONS PER TON | 13.05 | 9.10 | 9.08 | 10.34 | 10.59 |
| PEAK I | | | | | |
| TEMPERATURE (°C) | 272° | 242° | 200° | 260° | -- |
| PERCENT OF HYDROCARBONS | 7.2% | 8.4% | 10.3% | 7.7% | 6.0% |
| CONCENTRATION (PPM) | 3511 | 2883 | 3521 | 2985 | 2391 |
| PEAK II | | | | | |
| TEMPERATURE (°C) | 450° | 458° | 498° | 461° | 470° |
| PERCENT OF TOTAL HYDROCARBONS | 92.8% | 91.6% | 89.7% | 92.3% | 94.0% |
| CONCENTRATION | 45504 | 31288 | 30556 | 35848 | 37392 |

TABLE 7

PYROLYSIS - GAS CHROMATOGRAPHY
P-1 WELL - SULLIVAN COUNTY, INDIANA

| | | | |
|-------------------------------|-------|-------|-------|
| DEPTH | 2492' | 2521' | 2549' |
| TOTAL HYDROCARBON YIELD (PPM) | 605 | 35115 | 37779 |
| GALLONS PER TON | 0.16 | 9.35 | 10.06 |
| PEAK I | | | |
| TEMPERATURE (°C) | 290° | -- | 266° |
| PERCENT OF TOTAL HYDROCARBONS | 63.1% | 10.3% | 11.2% |
| CONCENTRATION (PPM) | 382 | 3624 | 4239 |
| PEAK II | | | |
| TEMPERATURE (°C) | 455° | 464° | 470° |
| PERCENT OF TOTAL HYDROCARBONS | 36.9% | 89.7% | 88.8% |
| CONCENTRATION (PPM) | 223 | 31491 | 33540 |

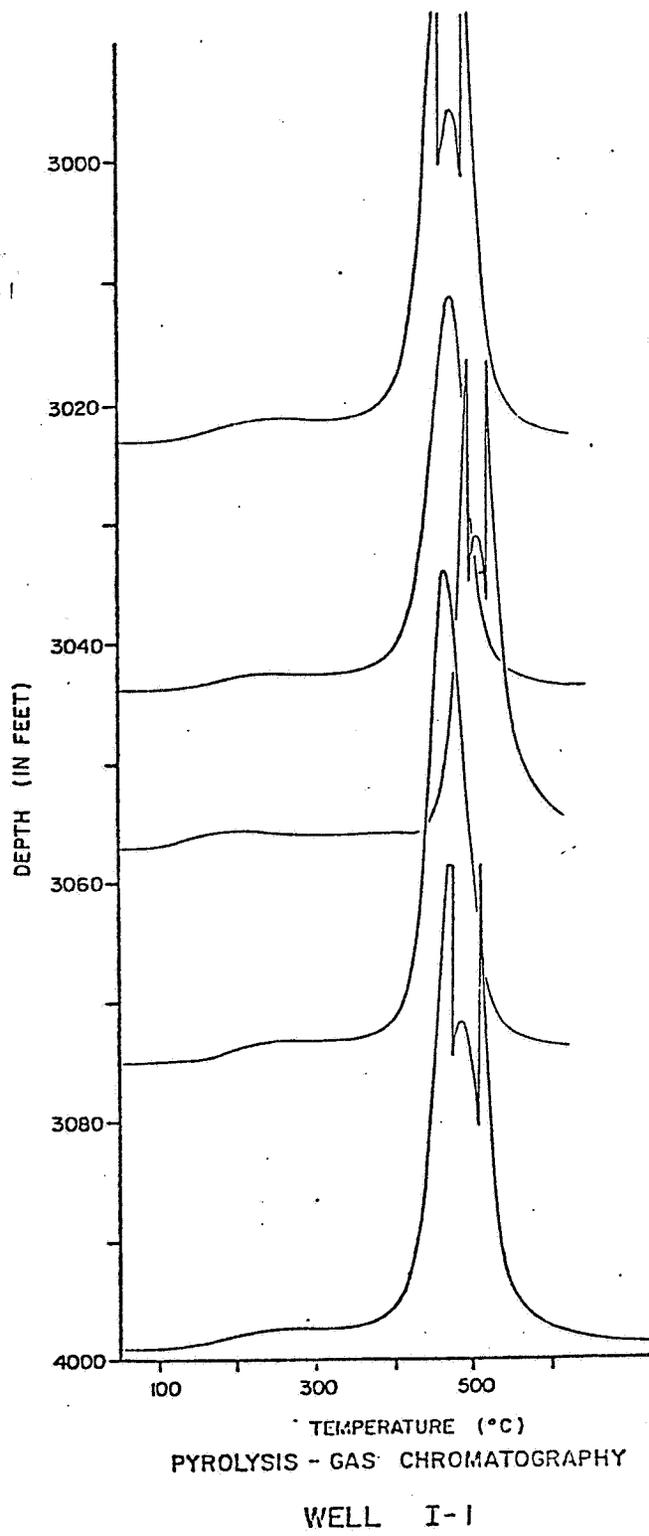


FIGURE 9

PYROLYSIS - GAS CHROMATOGRAPHY

WELL P-1

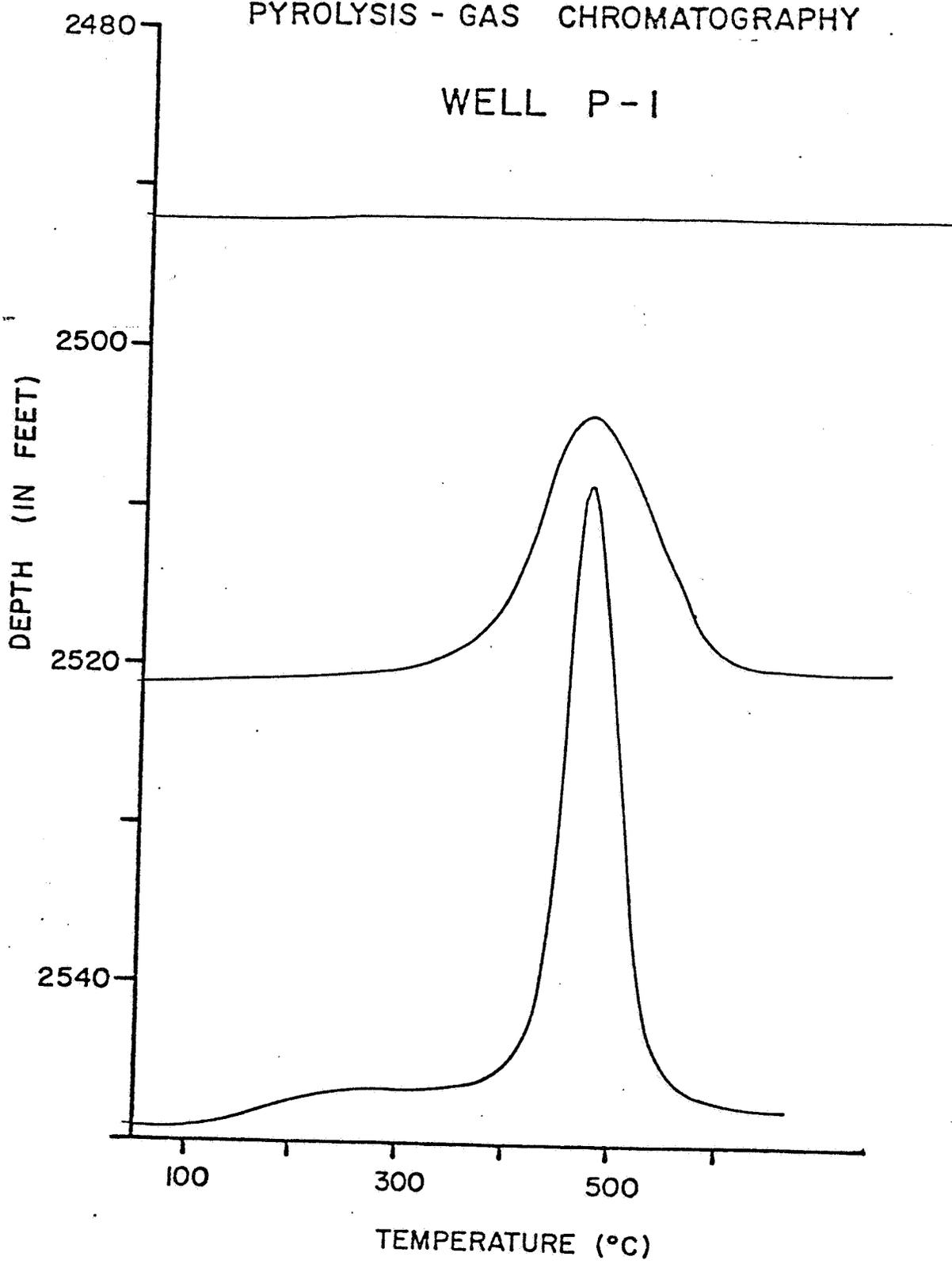


FIGURE 10

TABLE 8

DELTA ¹³C OF ORGANIC CARBON IN WHOLE ROCK

| WELL | DEPTH | ORGANIC MATTER TYPE* | DELTA ¹³ C PDB OF ORGANIC CARBON IN WHOLE ROCK |
|------|-------|----------------------|-----------------------------------------------------------|
| KY-2 | 2443' | H;AM;W(C) | -30.2 |
| | 2535' | W-C;H;- | -27.5 |
| | 2715' | H;AM;W-C | -30.0 |
| | 3085' | H;AM;- | -28.9 |
| | 3288' | H;W-C;- | -26.7 |
| VA-1 | 4885' | H;W;AM-C | -27.9 |
| | 4945' | W;H;C(AM) | -25.6 |
| | 5319' | H-W;-;AM-C | -28.1 |
| | 5393' | H;W;C(AM) | -29.3 |
| | 5469' | H;W;AM-C | -28.7 |
| P-1 | 2492' | W;C;H(AM) | -24.6 |
| | 2549' | AM;H;W-C | -28.0 |
| O-1 | 2184' | H;AM;W | -31.6 |
| | 2317' | AM-H;-;- | -30.3 |
| I-1 | 3044' | H;AM;W-C | -29.0 |
| | 3075' | H;AM;- | -28.9 |

*ORGANIC MATTER TYPE

| | | | |
|-------------------|----|---|--------------------|
| MARINE | AL | = | ALGAL |
| MARINE | AM | = | AMORPHOUS |
| RESTRICTED MARINE | H | = | HERBACEOUS |
| NONMARINE | W | = | WOODY |
| NONMARINE | C | = | COALY (INERTINITE) |