

CHARACTERIZATION AND RESOURCE ASSESSMENT
OF THE
DEVONIAN SHALES IN THE APPALACHIAN AND ILLINOIS BASIN

RONALD E. ZIELINSKI AND STEVEN W. HANCE
MONSANTO RESEARCH CORPORATION
MOUND FACILITY
MIAMISBURG, OHIO 45342

EGSP
OPEN FILE # 176

ABSTRACT

Upper Devonian shales from the Appalachian and Illinois Basins were evaluated to establish the depositional environment, organic source, thermal maturation, and hydrocarbon yields.

Cored shale samples from six Appalachian Basin wells and five Illinois Basin wells provided data for biostratigraphic studies and geochemical analysis of the kerogen. Fuel yields were determined using organic carbon content, material balance assays, and core gas analysis.

Woody and coaly material of a non-marine origin dominated the southern Appalachian Basin. Northern Appalachian Basin and Illinois Basin samples have a predominance of amorphous and herbaceous material indicative of a marine depositional environment. Appalachian Basin shales have experienced a sufficient degree of thermal maturation to yield hydrocarbons. Results from Illinois Basin samples are less definite. Hydrocarbon yields from the Appalachian shales were low and tended from oil and gas to gas-prone in a southeasterly direction. Illinois shales were oil- and gas-prone with comparatively higher yields.

*Mound Facility is operated for the U. S. Department of Energy by Monsanto Research Corporation (EY-76-C-04-0053).

INTRODUCTION

The national goal of increasing self-sufficiency in energy resources is resulting in the investigation of less-conventional sources for hydrocarbons. One such potentially major source is the Late Devonian-Early Mississippian organic-rich shales from the Eastern Interior Basins (Figure 1). These dark (black, brown, and gray) shales underlie hundreds of thousands of square miles near major energy-consuming population and industrial centers. Previous production from these low-permeability (0.001-0.0001 millidarcies) rocks has been restricted by marginal exploration economics⁽¹⁾. The Department of Energy (DOE) through the Morgantown Energy Research Center (MERC) has begun the Eastern Gas Shale Project (EGSP). The purpose of this project is to assess the hydrocarbon-producing potential (natural and induced) of the dark (gas) shales of the Eastern Interior Basins.

Mound Facility has initiated a detailed investigation of the chemical and physical characteristics of the dark shales in the Illinois and Appalachian Basins^(2,3,4,5,6). This information will provide the basis for characterizing the shale, identifying the source, assessing the resource, and locating the most promising reservoirs. The purpose of this paper is to summarize selected results from the project. Emphasis will be placed on recent information obtained from Appalachian Basin shales.

DATA AND TECHNIQUES

Shale samples were obtained from cores of eleven wells located in the Illinois and Appalachian Basins (Figure 1 and Table 1). In most instances, the entire Devonian shale interval was cored and representative samples were selected at approximately 30-ft intervals. The cores were placed in air-tight containers at the drilling site and shipped to the laboratory. The gases in the containers released by the shales and the shale samples were subjected to detailed geochemical and fuel yield analyses (Figures 2 and 3). The results of the analyses indicated by the cross-hatched areas of Figures 2 and 3, along with biostratigraphic studies of the shales, are discussed in this paper.

General details for the procedures are given in the following sections. Specific details of analytical procedures were not described here but have been previously reported^(2,3,4,5).

GEOLOGIC SETTING

Basin outlines and major structural elements are shown in Figure 1. The outline of the Appalachian Basin corresponds to the outermost occurrence of Silurian rocks. The outline for the Illinois Basin is delineated as the approximate outermost occurrence of Pennsylvanian-age sediments.

The Appalachian Basin extends east to the Blue Ridge Province and is bounded on the west and northwest by the Cincinnati and Findlay Arches, respectively. These arches became effective barriers by Ordovician time. The Appalachian highlands were the prominent source of clastics for the basin. However, the Cincinnati Arch may have acted as an intermittent source during the Devonian Period. As the basin matured, successive formations were generally thinner and the basin depocenter progressed westward as the sea retreated to the northeast⁽⁷⁾.

The Illinois Basin is bounded by a series of low-relief arches and domes which were emergent features by Ordovician time (Figure 1). The effectiveness of the Pascola Arch as a southern barrier during the entire Paleozoic Era is questionable⁽⁸⁾. Unlike the Basin, there was no major source of clastics near the Illinois Basin margin. This in part accounts for only 400 ft of Devonian dark shales in the Illinois Basin as compared to 1500 ft in the Appalachian Basin.

RESULTS AND DISCUSSION

Biostratigraphy

The ages and environments of basin deposits were determined by palynological studies of acritarchs and spores in samples from wells VA-1, KY-2, I-2, and I-3. Rock samples were treated with specific mineral dissolving acids to remove most of the silicate and carbonate matrices. The remaining organic material was studied by an experienced palynologist. Polymorphs of spores and acritarchs are known to be indicative of geologic age and environment of deposition. The shales from wells I-2, I-3, VA-1 and KY-2 are all Frasnian or Famennian in age^(5,9). The predominant environment of deposition for the Illinois Basin shales was initially marine, then restricted marine, with finally a greater influence of non-marine deposition (Figure 4)⁽¹⁰⁾. In contrast, shales at well VA-1 were almost entirely deposited under non-marine conditions, an obvious effect of the nearby Appalachian highlands. The more basinward KY-2 site was a basin hinge-line setting. Environments fluctuated rapidly from among marine, restricted marine, and non-marine as a function of variations in the sediment-influx and basin-subsidence^(9,10).

Organic Geochemistry

The organic material of the dark shales is primarily composed of the detritus from marine fauna and flora, with terrestrially derived organic debris from the Appalachian uplift and occasionally the Cincinnati Arch. Diagenesis of the organic debris proceeds through microbial degradation and thermal alteration to produce "kerogen". Kerogen, a complex heterogeneous material, is the precursor of oil and gas.

The biological precursor of kerogen can be determined by visual inspection(11,12). Kerogen is primarily composed of the remnants of the following: algal, amorphous (sapropel), herbaceous (spores, pollen, cuticles, and membrane debris), woody (structured), and coaly (inertinite) materials. This list proceeds for kerogen characterization from marine to non-marine environments. The analytical results from the Appalachian shale samples indicate that the marine-like kerogen, for the entire well profile, increases from wells VA-1 to CW-A, CW-B and R-109 (Figure 5). This is an indication of the basin environments during deposition. The influence of woody-coaly (non-marine) detritus supplied from the Appalachian highlands decreased in the wells located farther north. The wide range of kerogen types for samples from the KY-2 well (Figure 5) is consistent with the previous explanation of that basin position being affected by frequent depositional environment changes. The absence of a prominent bordering highland obviously resulted in the decreased presence of woody and coaly material in the Illinois Basin shales from wells I-2 and I-3 (Figure 5). The hydrocarbon potential of the organic debris in the dark shales will depend on the degree of thermal maturation, type of kerogen debris, and volume of organic material.

One method of determining maturation is kerogen coloration(12). The kerogen coloration of plant cuticle and spore pollen debris is measured in transmitted light. The measured degree of thermal alteration is compared to one of five stages of coloration. Light greenish-yellow kerogen corresponds to Stage 1 of the Thermal Alteration Index (TAI). Stage 1 is mildly altered kerogen. The sequence of color designations proceeds with increasing thermal effect through orange and brown to black (Stage 5). Stages 2 to 3 represent the degree of thermal maturation necessary for oil generation.

TAI values for all available samples (except from VA-1) from both the Illinois and Appalachian Basins were very uniform(6). The kerogen coloration was yellow to orange-brown. This gives a TAI of 1 to 2, indicative of the early stages of petroleum generation. A more detailed evaluation was made using vitrinite reflectance. This method has higher resolution and less subjectivity. Vitrinite reflectance (R_0) is the measure of the reflectivity of small organic grains exposed on a polished section of core. R_0 values of 0.2 to 0.6 indicate insufficient thermal alteration for efficient oil generation. An R_0 of 0.6 to 1.2 is the range for maximum petroleum generation. An R_0 of 1.2 to 3.0 indicates wet gas and methane production. R_0 values greater than 3.0 indicate exhaustion of hydrocarbon-generating capacity(13).

The method used was a modification of the technique described by Hacquebard and Donaldson(14). The Appalachian Basin results are given in Figure 6. Both the mean and the range of R_0 values are plotted versus depth. The mean values of R_0 for the entire well profiles of KY-2, OH-1, R-109, and VA-1 are 0.52, 0.71, 0.58, and 1.02, respectively. These values indicate adequate thermal

alteration for petroleum generation. There is also a trend of increasing maturation of the shale in a southeasterly direction. This may be an effect of the presence of older highly altered organic detritus from the Appalachian highlands being reworked and supplied to the southeast regions of the basin.

Vitrinite reflectance measurements of Illinois Basin shales (wells P-1 I-1, and O-1) yield mean R_0 values between 0.45 and 0.50⁽⁶⁾. This suggests that the dark shales from this basin have not experienced adequate thermal maturation to become a significant hydrocarbon source. Larger values with depth would be anticipated as a result of the temperature increase with greater depth of burial. Well KY-2 was sampled over an interval of 900 ft. No trend is apparent in Figure 6. This may be the result of a very small increase in R_0 values resulting from the variation in the source of organic material. Current analysis of well cores (sampled on a smaller interval) from the Devonian basin center will provide results for thicker sections with more uniform organic material. Perhaps then an R_0 -versus-depth relationship may be discerned.

The tendency for the dark shales to yield oil or gas is also controlled by the source of organic material. Algal and amorphous detritus tend to yield oil-prone hydrocarbons; woody and coaly materials, gas-prone hydrocarbons. The yield from herbaceous material is intermediate in nature^(15,16). Thus hydrocarbon yields tend from oil to gas from environments characterized as more marine to more non-marine, respectively. Elemental analysis of kerogen, expressed as ratios of H/C versus O/C, indicates source and potential of the sediments⁽¹⁵⁾. Non-marine environments tend to accumulate material rich in aromatics. This gives high O/C ratio and low H/C ratio (curve C in Figure 7). The kerogen capable of producing oil is rich in aliphatic structures and subsequently results in high H/C and low O/C ratios. These sediments indicate a marine environment of deposition (curve A in Figure 7). Curve B in Figure 7 represents the evolution path of organic material intermediate in nature. The first effects of increased thermal maturation are indicated by the elimination of oxygen, resulting in a decreased O/C ratio. Subsequently the H/C ratio is reduced by hydrocarbon generation⁽¹⁵⁾. These results are indicated by the arrow on curve C in Figure 7. The H/C versus O/C results from the Appalachian KY-2 and VA-1 wells are given in Table 2 and plotted on Figure 7. It is immediately evident that samples from VA-1 are gas prone and thermally mature. Samples from KY-2 suggest hydrocarbon yields will be of a nature intermediate between oil and gas. The scatter may be the result of the various organic sources evident at this basin location. In general, the sediment appears to be thermally mature. No correlation was evident between depth of sample and thermal maturation indicated by O/C versus H/C results.

The results for Illinois Basin wells were expressed as mean values of O/C and H/C for the entire vertical well profile (Table 3). The results in Figure 7 suggest these sediments will yield hydrocarbons intermediate in nature. The samples from this basin also indicate a relatively mild degree of thermal alteration.

The hydrocarbon potential of the shales is also related to the organic carbon content. The values of the organic carbon content in weight percent versus depth are given in Figure 8 for the Appalachian well profiles. The mean values for wells VA-1, KY-2, R-109, and OH-1 are 1.96, 2.04, 1.35, and 1.86, respectively. Comparatively, the averages for the Illinois Basin wells I-1, O-1 and P-1 are 6.77, 8.75, and 4.73, respectively⁽⁶⁾. The mean values all exceed the 0.4% minimum organic carbon content found in productive basins⁽¹⁷⁾. The range of values is large. For example, values at KY-2 vary from 0.01 to 7.75%. This indicates the rapid changes which can occur in a well profile and the subsequent need for a less-than-30 ft sampling interval. Part of this variation at KY-2 is due to its basinal position. As confirmed by the biostratigraphic study, frequent changes of environmental setting in the source area influence the volume and preservation of organic matter in shales at this site.

Hydrocarbon Yields

Estimates of total hydrocarbon potential in the dark shales were derived from the results of organic carbon content and material balance assay (MBA). The indigenous gas from shales can be estimated by using average organic carbon content, the Mott factor (1350 ft³ of gas per ton of organic matter), and assuming a shale density of 162 lb/ft³ and the weight of organic matter to be 1.25 times the weight of organic carbon⁽⁶⁾. Results indicate total gas reserves in MMCF per unit of reservoir rock (1 mi x 1 mi x 1000 ft) for wells KY-2, VA-1, OH-1, and R-109 are 77,900, 74,800, 71,200, and 51,600, respectively (Table 4). This reflects the large total reserves of the Appalachian Basin Devonian shales as has been discussed recently⁽¹⁸⁾. Results for Illinois Basin wells, per unit reservoir, were substantially higher. The indigenous gas reserves per unit of reservoir rock from wells I-1 and O-1 were 237,000 and 306,000, respectively⁽⁶⁾.

This approach for estimating reserves does not take into account the type of organic matter in the shales or their state of thermal maturation. Analysis of the volume of gas released from the shale core to the sample canisters and that retained within the shales more accurately indicates the actual volume of gas within the formation (Table 4). These results give a minimum value because of the unknown volume of gas released during coring and canning of the samples. The average gas contents (expressed in MMCF/unit of reservoir rock) from wells VA-1, KY-2, I-1, and O-1 are 96,000, 9,000, 12,000, and 9,000⁽⁶⁾. Comparison of these results with those predicted by using the organic carbon content indicates not only are actual gas yields likely to be lower, but also the yields depend on several variables rather than solely on organic carbon content. This interpretation assumes that the volume of gas released before sample canning is proportional to that measured.

Material balance assays were performed on selected samples from KY-2, VA-1, OH-1, and R-109. The MBA studies of shale samples determined the yields of oil, gas, and water as well as the API - gravity of the oil. MBA's are done on approximately 100 gram samples of 4 to 8-mesh shale material. Distillation of the sample is carried out in an inert helium or nitrogen atmosphere to 500°C. Results of the fluid yields are given in Table 5 for wells KY-2, VA-1, OH-1, and R-109. Values are expressed as average MBA product yields. Average oil yields, in gal/ton, for KY-2, VA-1, OH-1, and R-109 were 1.63, <0.5, 1.73, and 1.17,

respectively. The variation in yields was large both within vertical well profiles and throughout the basin. For example, well KY-2 gave oil yields from 0.1 to 4.6 gal/ton. There was no identifiable trend of hydrocarbon yields. The results from VA-1 suggest that the shales are relatively gas-prone. KY-2 yields a significant amount of oil hydrocarbons relative to VA-1. These results are consistent with the H/C and O/C kerogen studies. However, total gas yields in KY-2 are also higher. This is expected because of the lower hydrocarbon yields from the non-marine organic debris⁽¹³⁾.

Oil yields from Illinois Basin shales from I-1 and O-1 were 9.04 and 12.75, respectively⁽⁶⁾. MBA analysis of Illinois and Appalachian Basin shales indicates oil yields for these shales are less than the Western oil shales (Table 6). This secondary source of hydrocarbons will give added economic benefits during recovery from Eastern Shale gas wells.

CONCLUSIONS

The deposition of Upper Devonian dark shales of the Appalachian Basin was greatly influenced by the presence of the Appalachian highlands. The amount of terrestrially derived organic debris increases in a southeasterly direction. Burial with a moderate degree of thermal alteration throughout the basin has resulted in low-yield gas-prone shales in the southern regions with higher yield oil- and gas-prone sediments in the northern areas.

The dark shales of the Illinois Basin experienced a depositional setting similar to that of the northern Appalachian Basin shales. Thermal maturation is less in the Illinois Basin, but the hydrocarbon yields of these oil- and gas-prone shales are relatively greater.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the staffs of Geochem Research, Inc. and Mound Facility for their analytical efforts. Special acknowledgement is also due to R. McIver and S. Martin for their technical assistance.

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TABLE 1
LOCATION OF WELLS

ILLINOIS BASIN WELLS

I-2 Henderson County, Illinois
 I-3 Tazewell County, Illinois
 P-1 Sullivan County, Indiana
 I-1 Effingham County, Illinois
 O-1 Christian County, Kentucky

APPALACHIAN BASIN WELLS

R-109 Washington County, Ohio
 CW-A "Cottageville Wells" Jackson County,
 West Virginia
 CW-B "Cottageville Wells" Lincoln County,
 West Virginia
 KY-2 Martin County, Kentucky
 VA-1 Wise County, Virginia
 WV-5 Mason County, West Virginia
 OH-1 Carroll County, Ohio

TABLE 2
APPALACHIAN BASIN ATOMIC RATIO VALUES

VA-1

Depth	Atomic H/C	Atomic O/C
4890	0.69	0.33
4920	0.62	0.15
4980	0.56	0.07
5260	0.56	0.08
5290	0.59	0.16
5320	0.57	0.06
5350	0.60	0.09
5380	0.66	0.13
5390	0.74	0.11
5440	0.63	0.08
5470	0.63	0.06

KY-2

Depth	Atomic H/C	Atomic O/C
2440	1.07	0.10
2470	1.00	0.14
2540	0.91	0.13
2660	1.17	0.28
2690	1.13	0.39
2720	1.13	0.08
2770	1.04	0.10
2860	1.19	0.07
2920	1.14	0.10
3010	1.22	0.07
3040	1.34	0.04
3090	1.44	0.15
3110	1.22	0.25
3200	1.03	0.09
3230	1.28	0.08
3360	1.06	0.06

TABLE 3
ILLINOIS BASIN ATOMIC MEAN RATIO VALUES

Well	Atomic H/C	Atomic O/C
I-1	1.26	0.16
I-2	1.47	0.31
I-3	1.17	0.29
P-1	1.25	0.27
O-1	1.17	0.13

TABLE 5
MATERIAL BALANCE ASSAY RESULTS

Well	OH-1	R-109	VA-1	KY-2
Oil Yield (gal/ton)	1.73	1.17	<0.5	1.63
^o API - Oil Gravity	34.1	36.8	*	32
Water Yield (gal/ton)	3.56	2.75	2.53	4.13
pH	8.9	9.2	9.2	9.3
Hydrocarbon Gas Yield (ft ³ /ton)	31.13	35.14	16.56	31.50

* parameter not determined.

TABLE 4
ESTIMATED INDIGENOUS GAS CONTENT

Predicted Gas Content

<u>Well</u>	<u>VA-1</u>	<u>KY-2</u>	<u>R-109</u>	<u>OH-1</u>
Organic Carbon Content (weight percent)	1.96	2.04	1.35	1.86
Gas Content (MMCF/unit)	74,800	77,900	51,600	71,200

Measured Gas Content

<u>Well</u>	<u>VA-1</u>	<u>KY-2</u>	<u>0-1</u>	<u>I-1</u>
Mean C ₁ -C ₆ Hydrocarbon Content (cm ³ /gm)	0.710	0.147	0.135	0.165
Gas Content (ft ³ gas/ton sediment)	22.86	4.71	4.32	5.30
Gas Content (MMCF/unit)	45,700	9,400	8,600	10,600

TABLE 6
 FUEL OIL YIELD
 (Adapted from Zielinski²)

<u>Yield Based on Organic Carbon Content</u>	<u>Gal/Ton</u>
Colorado	16.9
Wyoming (GRB)	19.4
Wyoming (WB)	17.1
Utah	19.7
Kentucky	8.9

Oil Yield from MSA Analysis
 (mean value for all basin samples)

Appalachian Basin	1.4
Illinois Basin	9.6

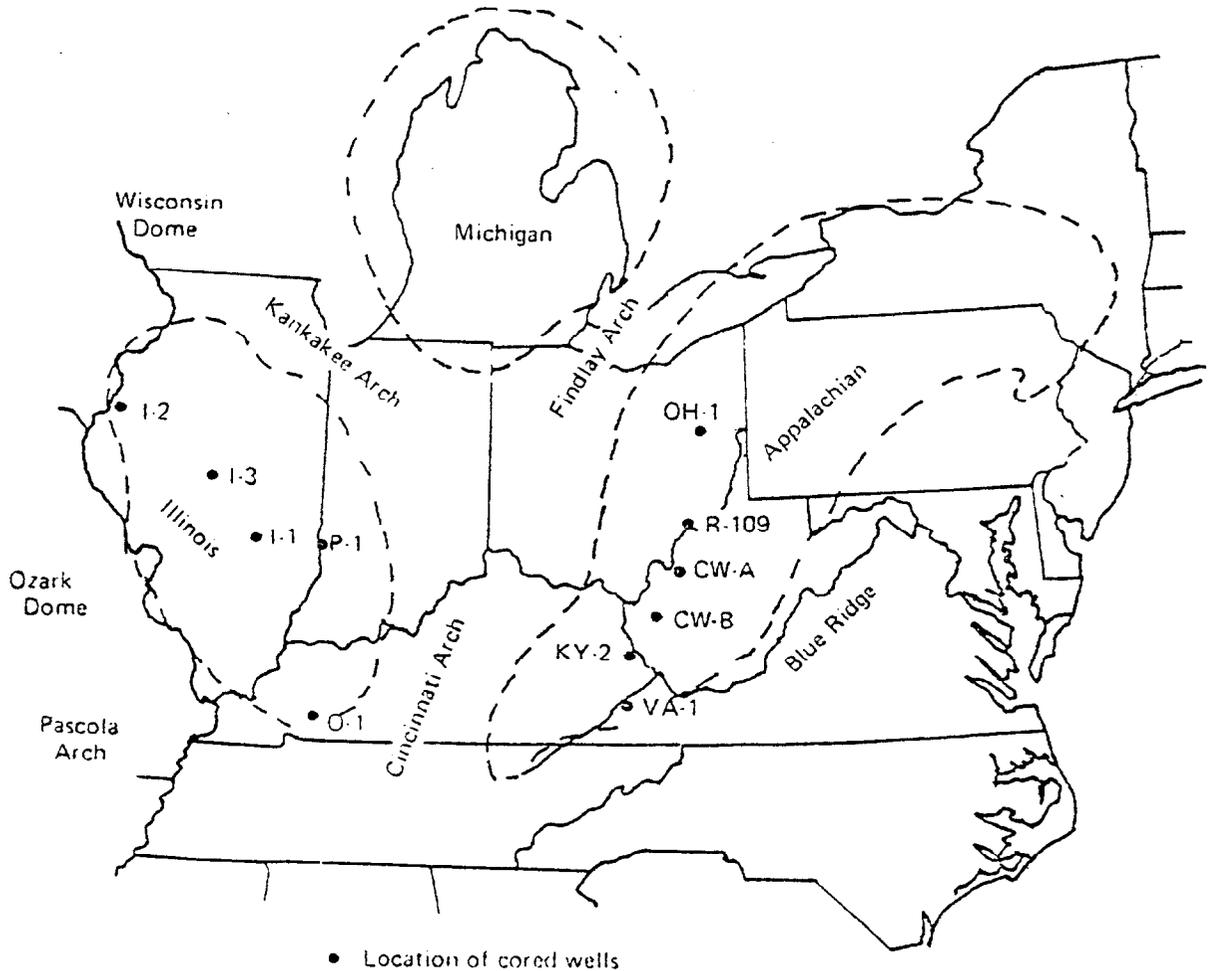


FIGURE 1 - Eastern interior basins.

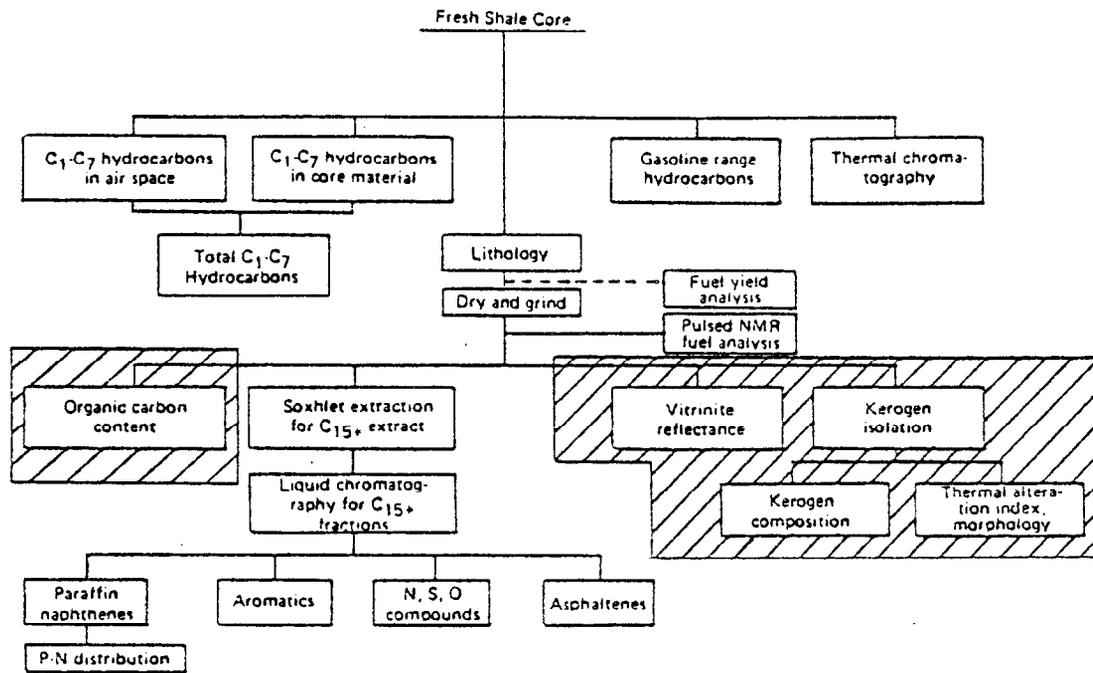


FIGURE 2 - Flow diagram for organic geochemical analysis.

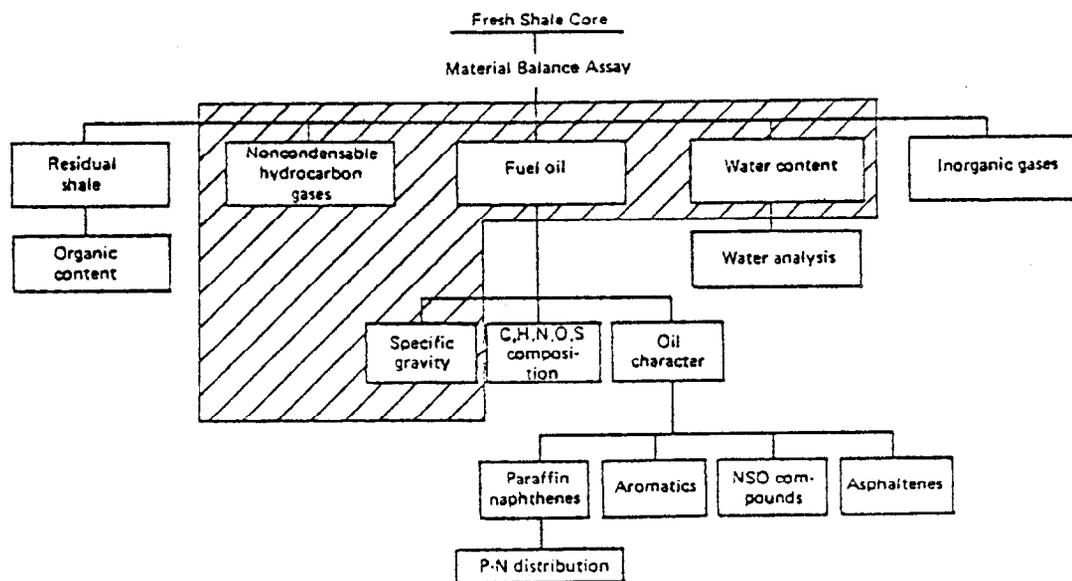


FIGURE 3 - Flow diagram for fuel yield analysis.

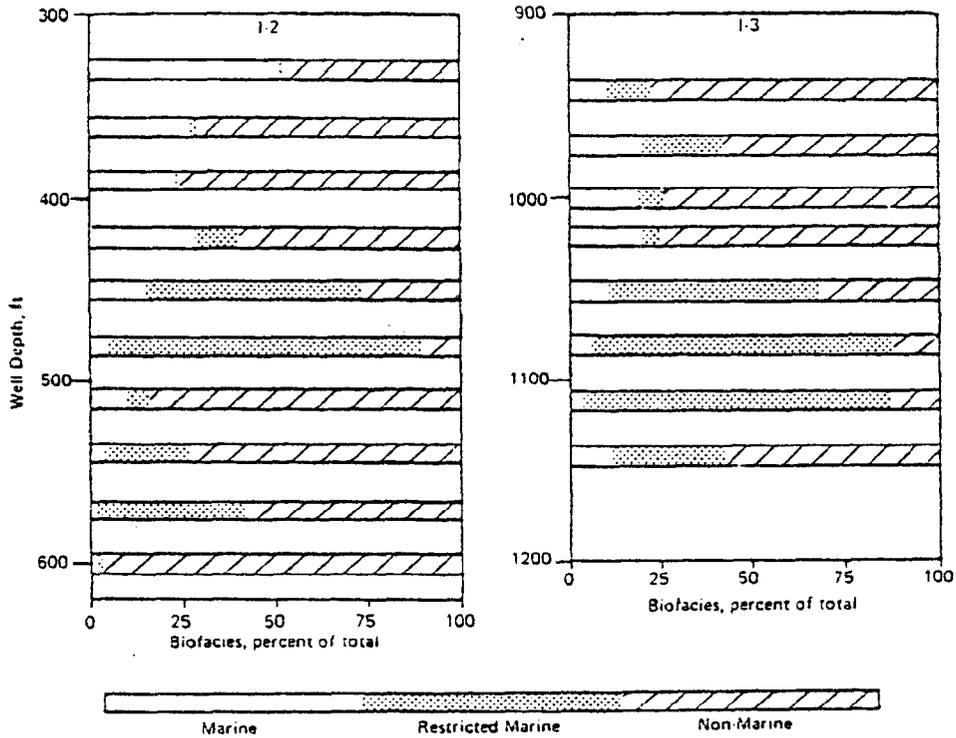


FIGURE 4 - Biofacies results.

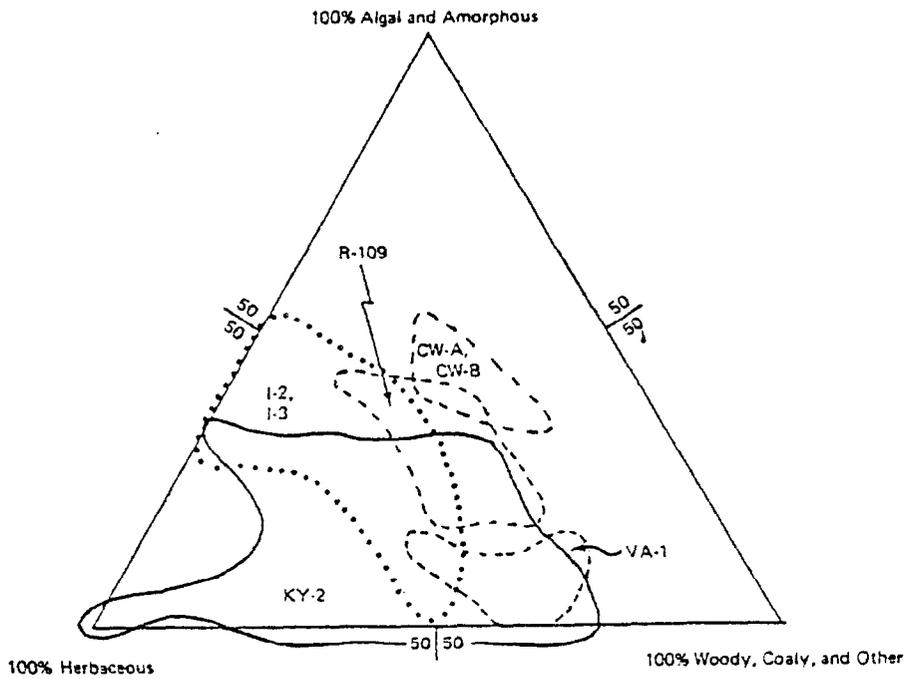


FIGURE 5 - Kerogen description zones.

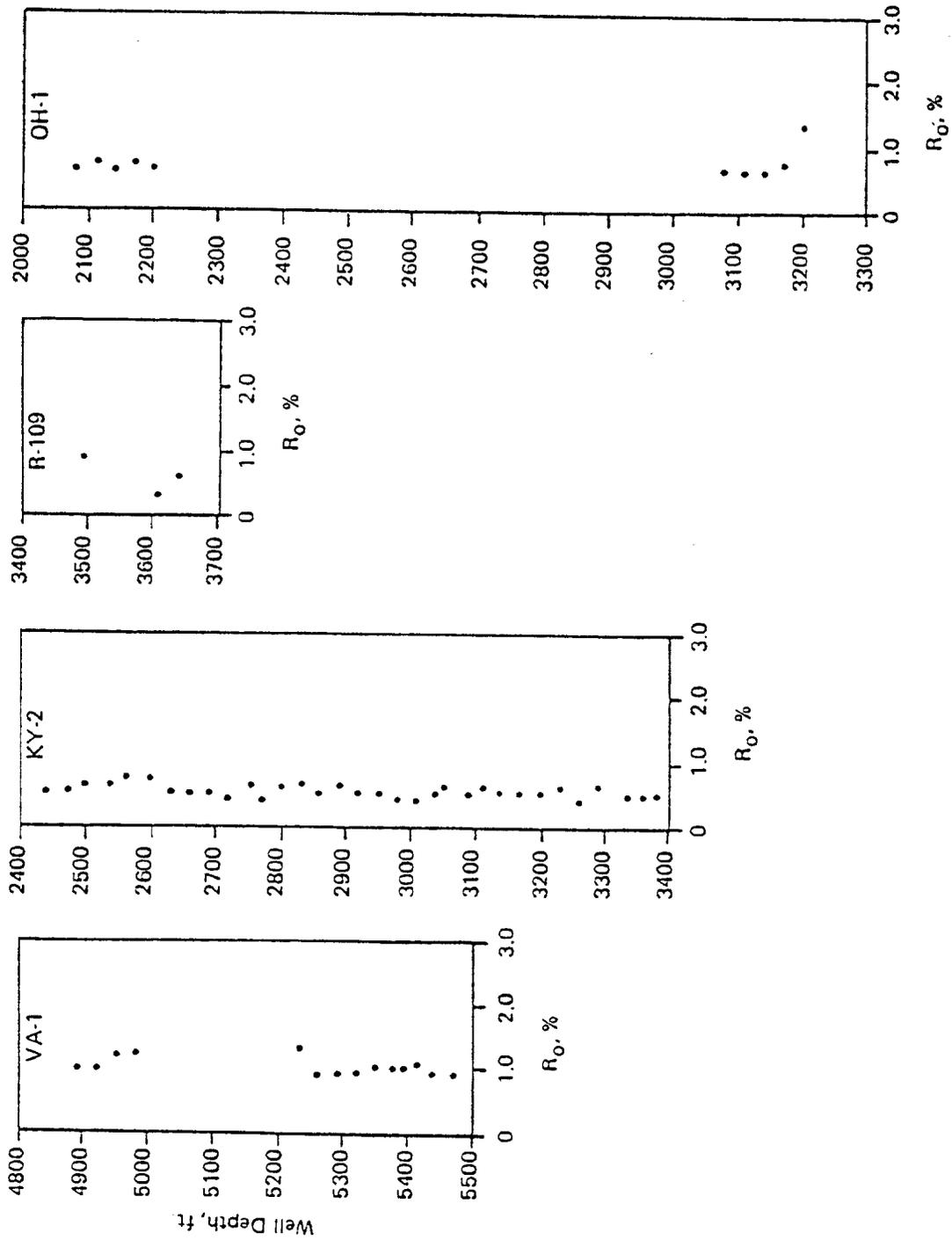


FIGURE 6 - Vitrinite reflectance results.

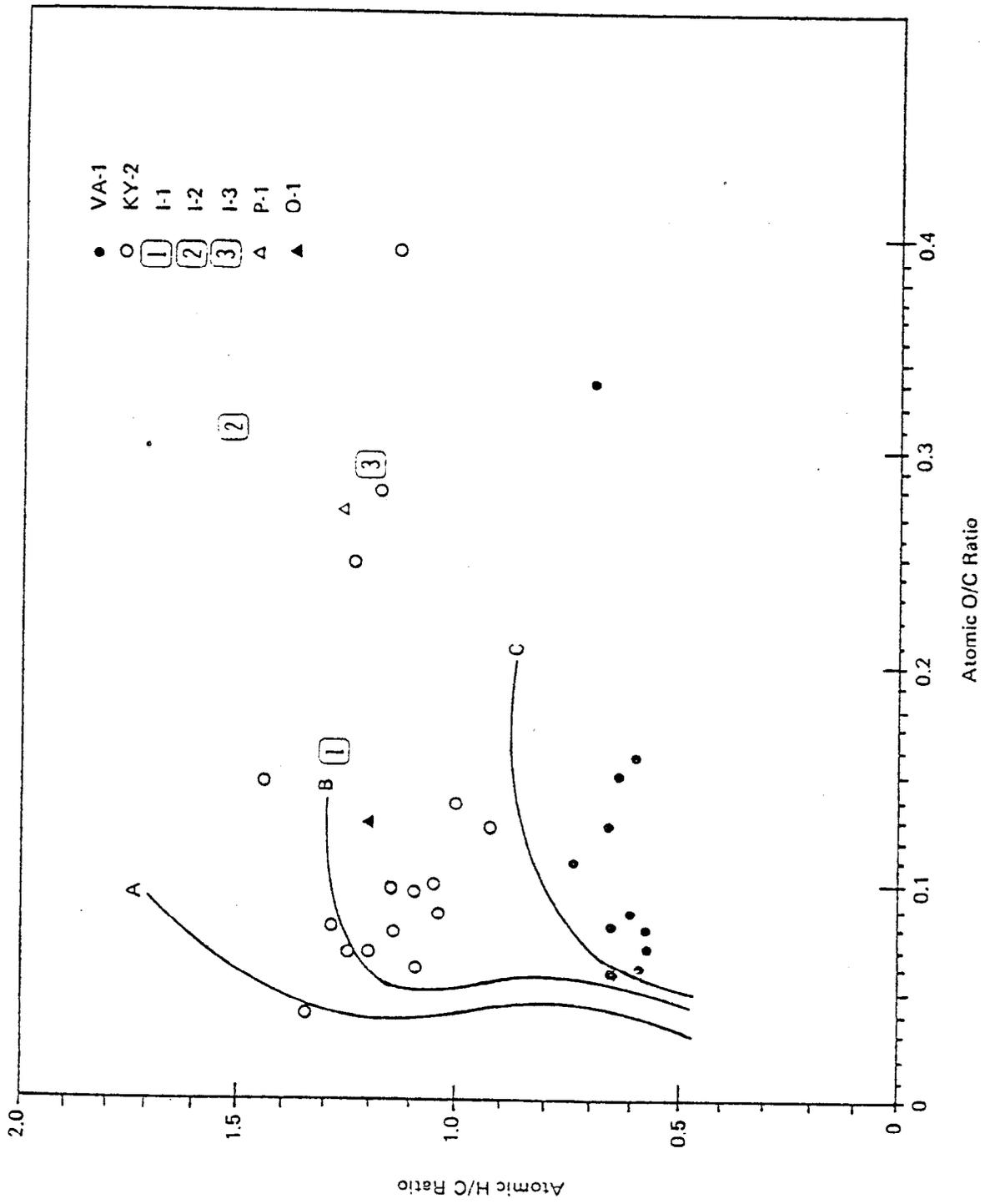


FIGURE 7 - Atomic ratio results (adapted from Tissot et al. 14).

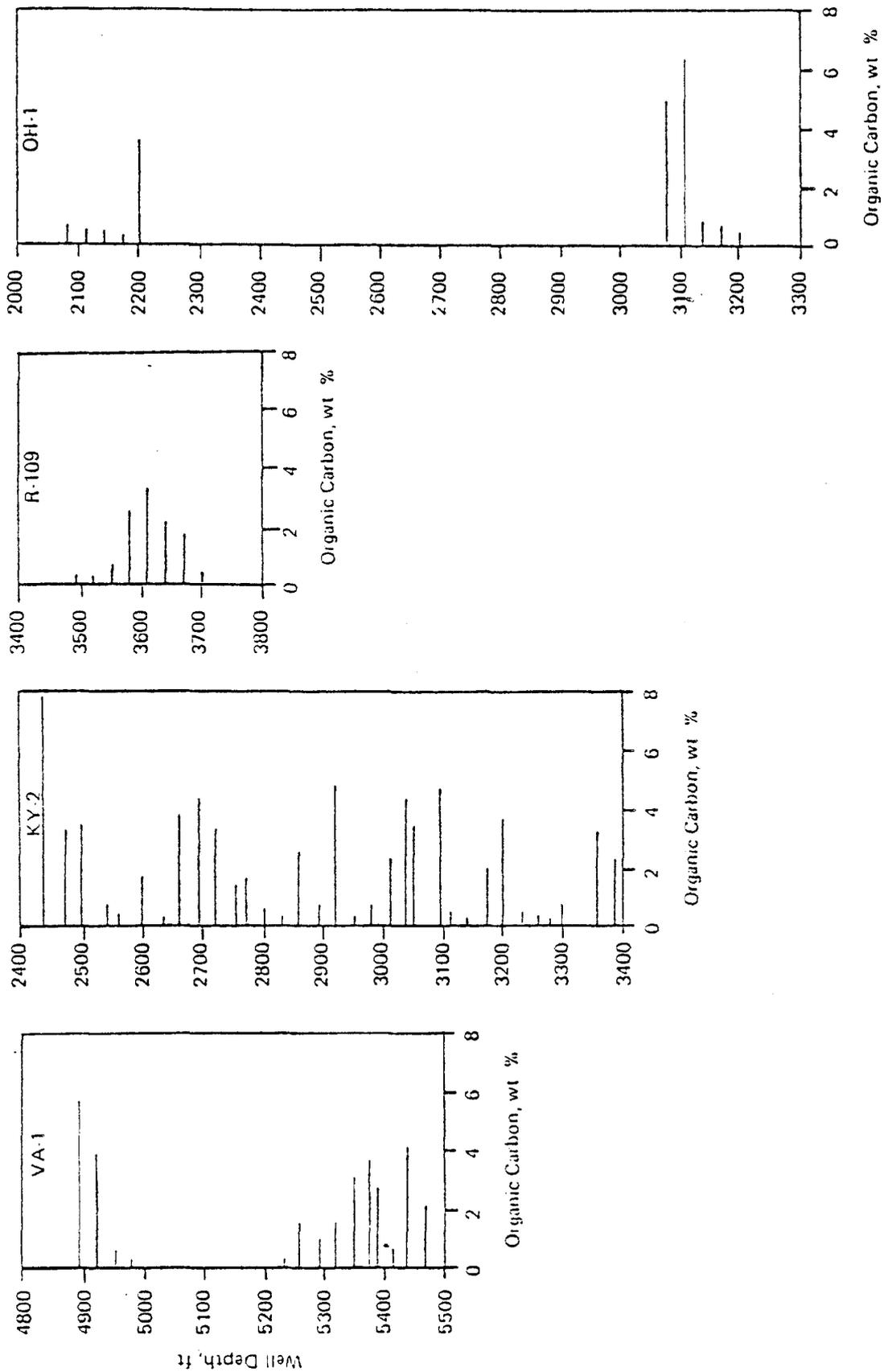


FIGURE 8 - Organic carbon content results.