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**THERMAL Maturity AND ORGANIC FACIES OF
DEVONIAN SHALES FROM SELECTED WELLS**

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ABSTRACT

An organic geochemical study was performed on core samples of the Devonian shale from wells in Ohio, Kentucky, and Illinois. The thermal maturity of the organic matter (kerogen) contained in the fine-grained sediments was investigated by vitrinite reflectance and kerogen coloration (Thermal Alteration Index). The results indicate that the organic matter has been thermally matured to the early stages of petroleum and associated gas generation.

A suite of geochemical analyses designed to evaluate the organic richness, the hydrocarbon potential for gas, condensate, and/or oil, and the type of organic matter was performed on the samples analyzed for thermal maturity. In general, two types of organic facies were encountered. The rich organic facies (A) is characterized by abundant gas, gasoline, and gas-oil hydrocarbons, a high organic carbon content, and organic matter prone to generate abundant oil and associated gas. Based on the geochemical data, a second type of organic facies (B) interbedded with the rich organic facies (A) was encountered in Kentucky and Ohio wells. Organic facies B consists of sediments relatively lean in organic carbon and gas-oil hydrocarbons, and abundant gas and gasoline hydrocarbons. In most cases, facies B is composed of woody and coaly types of kerogen. The woody-coaly kerogen is presumed to indicate a nonmarine derived depositional source prone to generate predominately gas (methane).

INTRODUCTION

Core samples from four wells drilled in Ohio, Kentucky, and Illinois 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 (Bailey et al., and Welte, 1972). The hydrocarbon source rock studies were performed to investigate the organic richness, type (gas, condensate, or oil), and state of thermal maturity of the hydrocarbon source rocks, and to determine their areal and stratigraphic distribution. Specific geochemical zones (organic facies) are also delineated.

The location of the four 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's 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 Figure 2. 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 (1967), and Hacquebard and Donaldson (1970).

DISCUSSION AND RESULTS

A. Organic Facies

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 (Ronov, 1958). The worldwide average of organic carbon in shales and siltstones is 1.14 percent (Gehman, 1962).

The amount of organic carbon in Devonian shales varies from location to location (Fig. 3). In general, the average organic carbon content of sediments from the I-1, 0-1, KY-2, and R109 wells is 6.77%, 8.75%, 2.04%, and 1.36% respectively. The organic matter appears to be more uniformly distributed in the I-1 and 0-1 wells. However, to the east, the KY-2 and R-109 shales vary considerably in organic carbon from a low of 0.16% to a high of 7.75%.

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 (Staplin, 1969 and Tissot et al., 1974).

Of the four wells studied, the type of organic matter in the I-1 and 0-1 wells is primarily herbaceous and amorphous kerogen (Fig 4). This lipid rich material (if present in sufficient quantities) has the potential to generate abundant oil and associated gas. In contrast, shales from the KY-2 and R-109 wells contain predominant amounts of either the herbaceous-amorphous kerogen or the woody-coaly (gas prone) kerogen. 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. For example, within the stratigraphic sequence represented by core material in the KY-2 well from 2440 \pm feet to 2550 \pm feet, the changes in kerogen type from herbaceous-amorphous to woody-coaly and in organic carbon content from 7.75% to 0.16%, probably represent a change in depositional environment. The environmental shift from marine to nonmarine kerogen types may be the result of a regressive depositional cycle.

C_{15^+} Extract

Core material was extracted with organic solvent to yield the C_{15^+} 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 concentration of hydrocarbons in shales was found to be 96 ppm (Gehman, 1962).

Shales from the four 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 5. 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 and 0-1 wells, the average hydrocarbon content was 2159 ppm and 2463 ppm, respectively. The average hydrocarbon content was 1469 ppm in KY-2 shales, and 1245 ppm in R-109 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 C_{15^+} hydrocarbons. These shales are represented in Figure 2 through 6 as organic facies A. Sediments with low organic carbon content and primary or secondary amounts of woody-coaly kerogen and low amounts of C_{15^+} hydrocarbons are designated as organic facies B. Based on the geochemical data, there appears to be a transitional zone where mixtures of organic facies A and B are present.

The geochemical zonation assigned to the shale intervals was based on their ability to satisfy the following conditions:

Organic Facies A

Organic Carbon Content: >1.0%
C₁₅+ Hydrocarbon Content: > 1000 ppm
Kerogen Type: Primary or Secondary Amounts of
Herbaceous or Amorphous Kerogen

Organic Facies B

Organic Carbon Content: <1.0%
C₁₅+ Hydrocarbon Content: < 1000 ppm
Kerogen Type: Primary or Secondary Amounts of
Herbaceous-Amorphous or Woody-Coaly Kerogen

Shales which did not satisfy these requirements were thought to represent a transitional zone.

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 well contained large quantities of C₁-C₇ hydrocarbons (Fig. 6). The average C₁-C₇ abundance in the I-1, 0-1, KY-2, and R-109 wells was 440,000

ppm, 313,000 ppm, 356,000 ppm, and 763,000 ppm, respectively. (The concentration is expressed as volumes of gas per million volumes of core material.) In the I-1, 0-1, and R-109 wells, the dry gas, wet gas, and gasoline-range hydrocarbons were uniformly distributed. However, in the KY-2 well, organic facies B characterized by its lean organic carbon content contained significantly lower amounts of C₁-C₇ hydrocarbons.

B. 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- (Fig. 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. 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 values 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 nonsource for hydrocarbons.

The thermal history of the Devonian shales analyzed in this study exhibit a small amount of variation (Fig. 8). The organic matter in shales from the four wells is characterized by its yellow to orange brown color. This coloration is consistent with a thermal alteration index of Stage 1+ to 2+. 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 0-1 wells is 0.45. In the KY-2 well, a slightly higher thermal alteration corresponding to a mean average R_o of 0.52 was measured. The mean average R_o for vitrinite particles in the R-109 well was 0.70. Based on the vitrinite reflectance data, it appears likely that the Devonian shales will be increasingly more mature in an east-south-easterly direction.

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, and the nature of hydrocarbons which it has generated. A preliminary evaluation of the geochemical data obtained from core material seems to indicate the following regional trend in an east-south-easterly direction:

Organic richness

0-1 > I-1 >> KY-2 > R-109

Abundance of oil prone organic matter

0-1 ≈ I-1 >> KY-2 > R-109

Liquid Hydrocarbon Abundance

0-1 > I-1 >> KY-2 > R-109

The stratigraphic interval penetrated by the four wells contains two distinct zones or organic facies, based on the organic carbon content, the abundance of C₁₅⁺ extract, and the organic matter type. Organic facies A is classified as a rich oil prone hydrocarbon source. Organic facies B is interpreted to be predominately a gas source. In some shales, organic matter consisting of both facies A and B constitute a transitional zone.

The degree of thermal alteration has been sufficient to initiate the hydrocarbon forming process in Devonian shales in all four wells. Shales from the I-1 and 0-1 wells are at the same level of maturation. KY-2 and R-109 shale are slightly more mature.

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Fig. 1 Location of core holes

Fig. 2 Organic geochemical analyses

Fig. 3 Organic carbon content

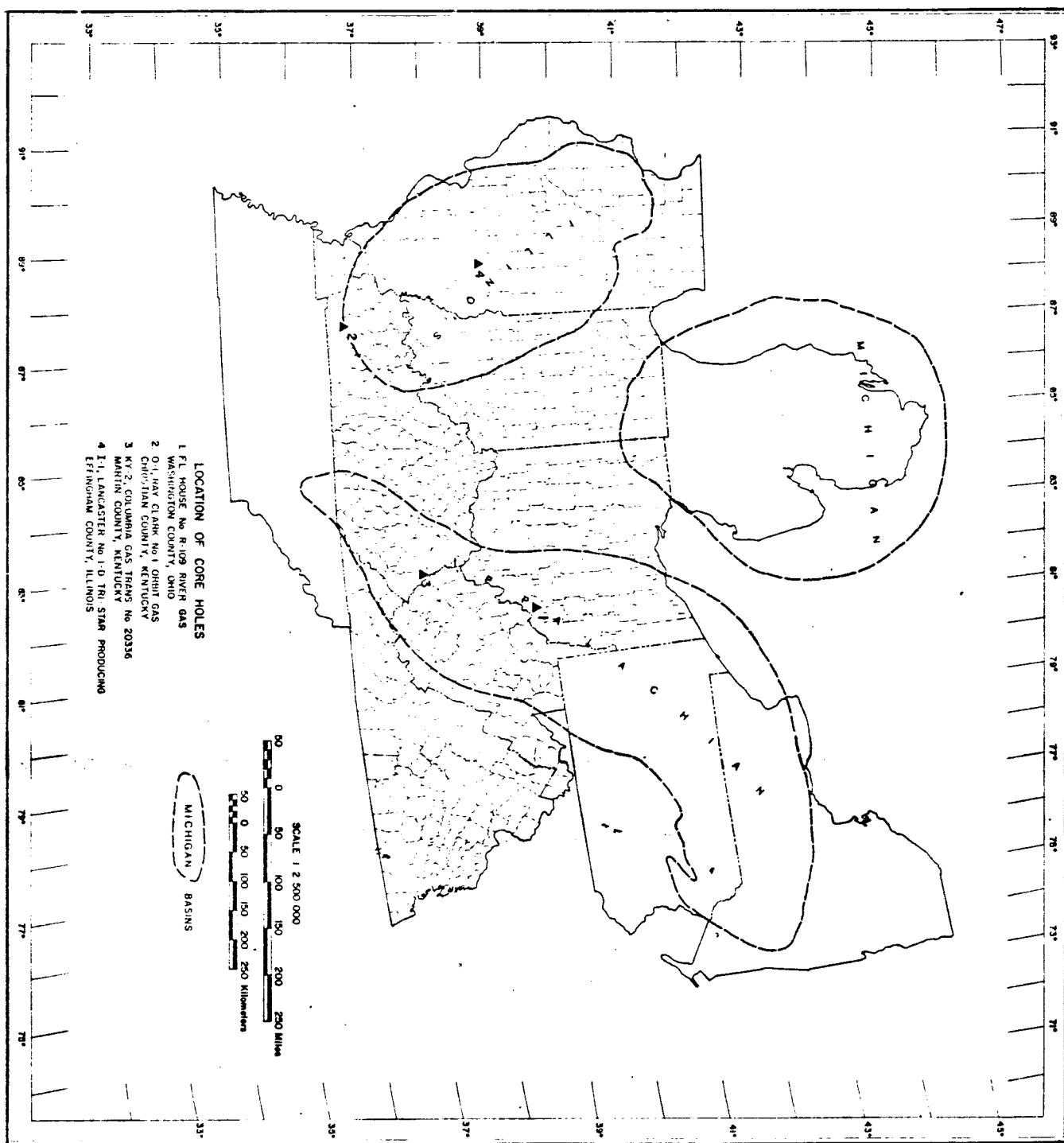
Fig. 4 Type of organic matter

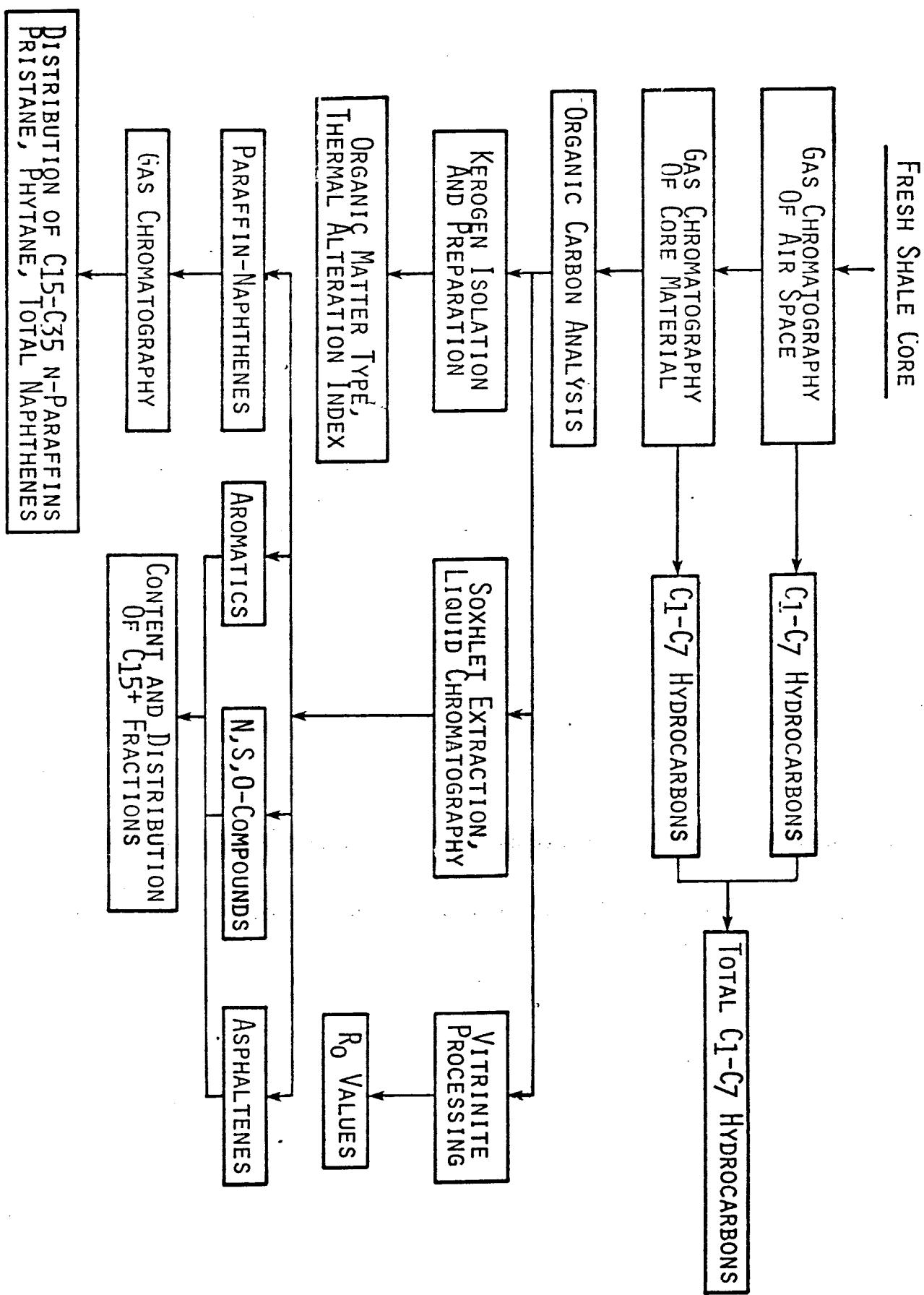
Fig. 5 Composition of C_{15}^+ extract

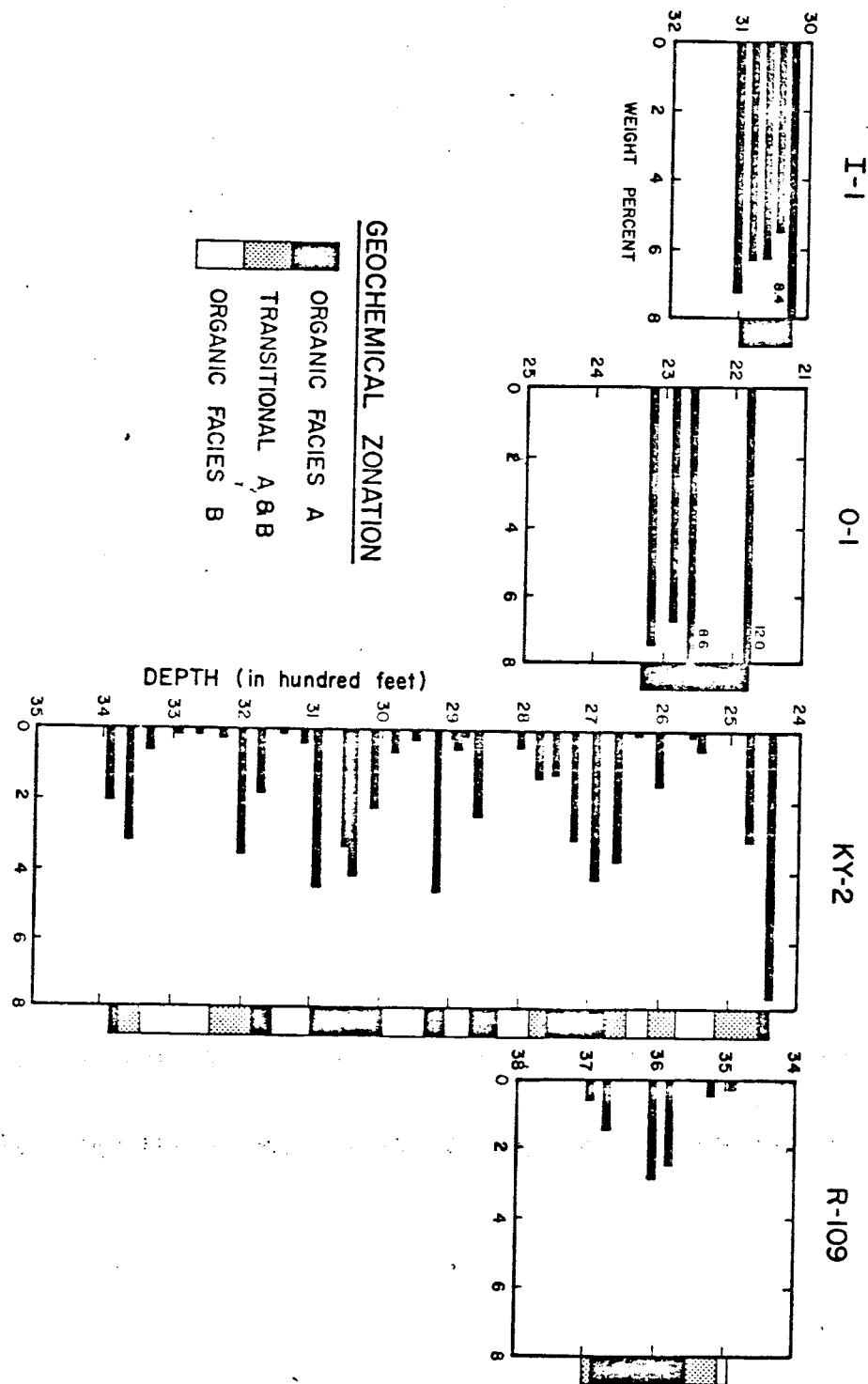
Fig. 6 C_1-C_7 hydrocarbons

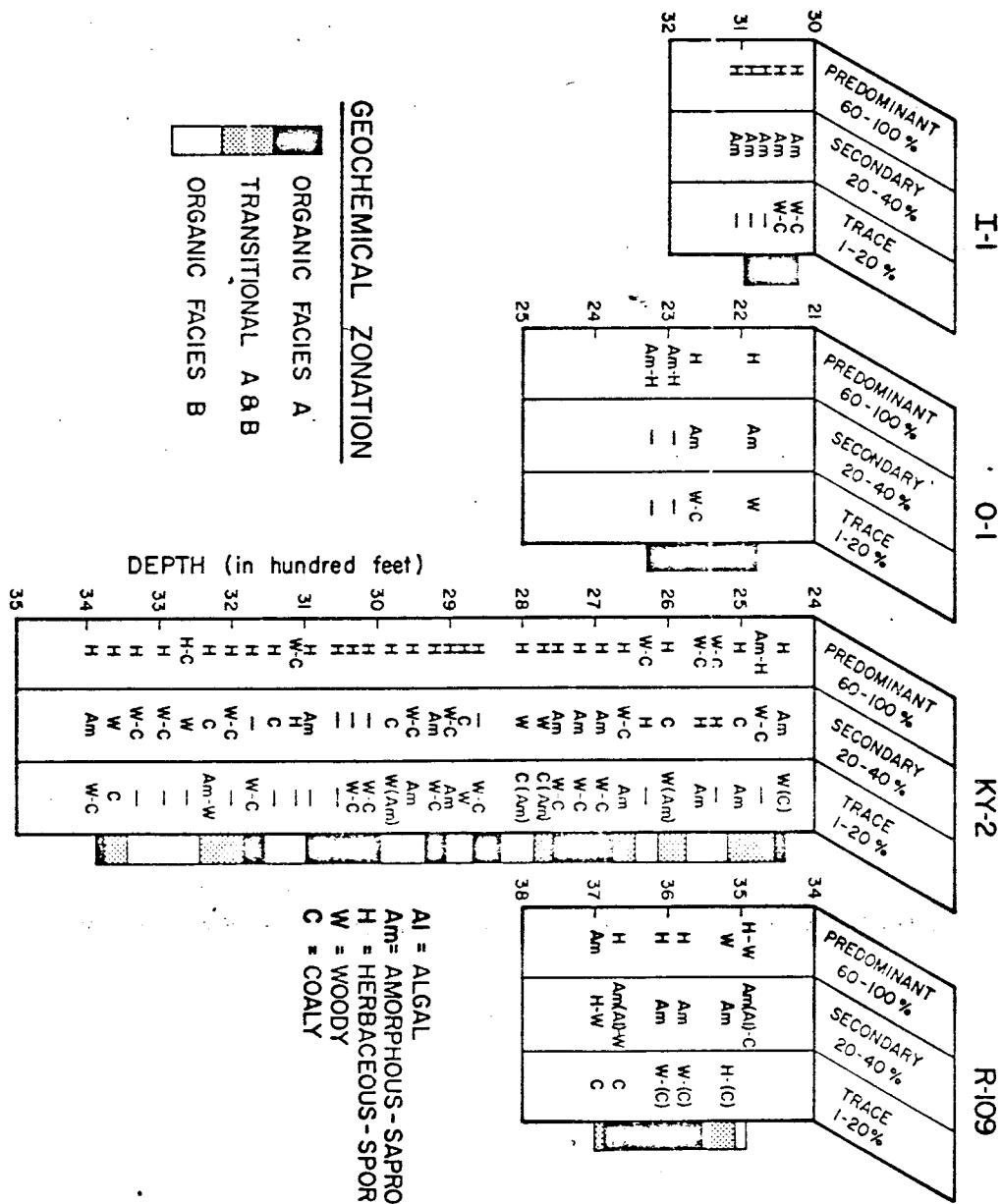
Fig. 7 Zones of hydrocarbon generation

Fig. 8 Thermal history of Devonian shales









A = ALGAL
A_m = AMORPHOUS - SAPROPEL
H = HERBACEOUS - SPORE/CUTICLE
W = WOODY
C = COALY

T-1

O-1

K-Y-2

R-109

