

## **Oil source bed hydrocarbon analysis: some methods and interpretations**

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**Abstract:** A well section, designated "Wildcat-1", has been evaluated by a suite of geochemical techniques including pyrolysis and gas chromatography. The operating principles of pyrolysis and gas chromatography are briefly discussed, and the basic interpretations that may be obtained from these data are presented. Pyrolysis alone was sufficient to screen out the poor source rocks but insufficient to unequivocally delineate the oil generation interval. However without pyrolysis neither the quantity of oil generation nor its unrealised potential could have been estimated.

### **INTRODUCTION**

#### **General**

The main functions of commercial petroleum geochemistry are to define which rocks generate, or have the potential to generate, oil, and if oil is found, to correlate it with such rocks. Oil is mainly a complex mixture of hydrocarbons (Speers and Whitehead, 1969) that have been generated by the thermal degradation (maturation) of oil-prone (sapropelic/liptinitic) fossil organic matter, (kerogen) (Tissot and Welte, 1978). Rock horizons that actually generate oil are called oil source beds; they are generally organic-rich shales located in zones of geothermal maturity (Dow, 1977).

Oil source beds contain two types of indigenous hydrocarbon:

- (a) free hydrocarbon—that which has already been generated from the kerogen and resides in its petroleum form in the rock/kerogen matrix, and
- (b) bound hydrocarbon—that which only exists as an integral part of the heteropolymeric molecular matrix of kerogen.

The quantity of free hydrocarbon in an oil source bed is set by the amount of hydrocarbon generated by the kerogen, but limited by the available porosity and surfaces of the mineral matrix and kerogen; excess hydrocarbon will be expelled from the rock (Jones, 1978). The quantity of bound hydrocarbon in an oil source bed is determined by the quantity and quality of kerogen, and how much has been converted to free hydrocarbon and expelled.

The quantity of free hydrocarbon in a source bed is readily determined by solvent extraction and weighing (Hunt, 1961; Vassoevich *et al.*, 1967). The quantity of bound hydrocarbon, which in the case of an immature source rock may account for nearly all

of its (potential) hydrocarbon content, can only be determined by pyrolysis analysis (Barker, 1974; Espitalie *et al.*, 1977). In certain cases this method can be further used to estimate the variable quantity of hydrocarbon that has migrated from a source bed. The composition of free hydrocarbons in source beds and reservoirs is readily characterised by gas chromatography (Dietz, 1965). This composition reflects the type and thermal history of the source bed kerogens and so may be used to distinguish between indigenous, migrant and contaminant hydrocarbon, which are indistinguishable by pyrolysis. It may be further used to correlate source beds and oils.

This paper sets out to explain the working principles of pyrolysis and gas chromatography, particularly the former as this is a relatively new technique, and how the data obtained by these analyses may be interpreted. To do this, the source rock evaluation data (including total organic carbon, kerogen composition, solvent extraction, extract fractionation, pyrolysis and gas chromatography) and maturity evaluation data (including vitrinite reflectance and spore colour index) of a real well section (made anonymous by some alterations) are presented. The well has been designated "Wildcat-1" and contains a major oil generating source, "the Wildcat shale".

### Hydrocarbons

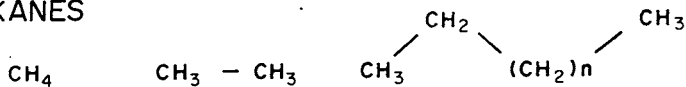
Hydrocarbons are basically carbon skeletons with a covering of hydrogen. The carbon skeleton configurations present in petroleum hydrocarbons are generally divided into only four groups, the types of possible configurations being somewhat constrained by the limited number of metabolic pathways that join carbon to carbon in nature. These configuration groups are (Figure 1):

- (i) normal (n-) alkanes                      (normal paraffins)
- (ii) branched alkanes                        (branched paraffins)
- (iii) cyclo alkanes                            (branched paraffins or "naphthenes")
- (iv) aromatics

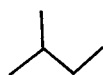
Petroleum mainly comprises a complex mixture of hydrocarbons; for example, the Ponca City crude contains an identifiable 256 hydrocarbons and 8 non-hydrocarbons representing about 60% of the crude's weight (Mair, 1965). However petroleum is much simpler than expected with respect to the number of compounds theoretically possible; only in the low molecular weight range have most of the possible isomers been found (Smith, 1966).

The amount of hydrocarbon that the kerogen of a rock can generate determines its capacity as a source rock. The range of molecular size of the generated hydrocarbons, and secondarily their structure, determine the properties of petroleum. For example n-C<sub>6</sub> (hexane) is a very light liquid, n-C<sub>16</sub> alkane (hexadecane) is a viscous liquid, and n-C<sub>20</sub> alkane (eicosane) is a waxy solid. It should also be noted that polycyclic alkanes are denser than their straight-chain counterparts, which is why biodegraded oil has a low °API gravity; straight-chain n-alkane components are removed by biodegradation, leaving mainly cyclic components.

## n - ALKANES



## ISOALKANES (CARBON "SKELETON" ONLY)



ISOPENTANE

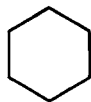


PHYTANE

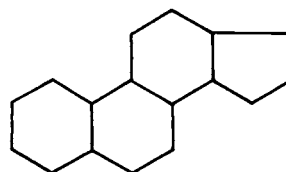
## CYCLOALKANES (CARBON "SKELETON" ONLY, SIDE CHAINS OMITTED)



CYCLOPENTANE

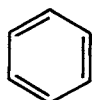


CYCLOHEXANE

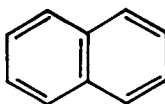


TETRACYCLIC "NAPHTHENE"

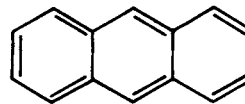
## AROMATICS (CARBON "SKELETON" ONLY, SIDE CHAINS OMITTED)



BENZENE



NAPHTHALENE



ANTHRACENE

Fig. 1. Basic hydrocarbon structures in petroleum

## METHODS

**General**

Cuttings samples from the Wildcat-1 well were subjected to routine petroleum geochemistry evaluation methods for thermal maturity and source potential. These methods are discussed elsewhere in the literature as outlined below:-

**Maturity Evaluation**

Vitrinite Reflectance

Bostick 1971, Hood *et al.* 1975, Teichmuller 1971.

Spore Colour

Cooper 1977, Staplin 1977

**Source Potential Evaluation**

|   |  |
|---|--|
| Total Organic Carbon and Extractable Hydrocarbons | Hunt 1961, Vassoevich <i>et al.</i> 1967, Welte 1972, Erdman 1975. |
| Kerogen Composition                               | Staplin 1969, Dow 1977.  |
| Pyrolysis*  | Barker 1974, Espitalie <i>et al.</i> 1977.                         |
| Gas Chromatography                                | Dietz 1965.  |

The exact procedures used vary from laboratory to laboratory; in this case standard Robertson Research procedures were applied. For the purposes of this work, only the pyrolysis and gas chromatography methods are discussed in detail.

**Pyrolysis Analysis**

Pyrolysis is one of the more modern methods of screening source rocks; it is used to give a rapid quantitative measure of the free hydrocarbon and bound hydrocarbon contents. The working principles of pyrolysis analysis are that the free hydrocarbons in a rock may be vapourised by heating, and with further heating the bound hydrocarbons may be progressively vapourised. A pyrolysis analyser is basically made up of:-

- (1) A crucible to hold a set quantity of rock powder while it is heated under a stream of helium, in an
- (2) oven, temperature programmed over a set range of temperature, and
- (3) a detector, to detect the bulk hydrocarbon contents as they are vapourised (see Figure 2).

The pyrolysis oven is commonly temperature programmed between 250° and 550°C at 25°C per minute. When the crucible is placed in this oven at 250°C, the free hydrocarbon content is rapidly vapourised. As the temperature increases the bound hydrocarbon is progressively vapourised. The vapourised hydrocarbon is carried to the detector by the helium carrier gas.

In hydrocarbon analysis, flame ionisation detectors are usually used. Hydrogen is added to the carrier gas as it exits from the oven, and the mixture is burned with a miniature flame tip situated in an air stream. The electrical potential from the base of the flame to an adjacent electrode is normally high. As a hydrocarbon is burned the charge particles created change this electrical potential; the greater the quantity of hydrocarbon, and thus number of charged particles, the greater the change in potential. This signal is recorded on a chart; the area under the peak is proportional to the quantity of hydrocarbon present.

The resultant pyrolysis chart, and the measured parameters are indicated in Figure 3. As the pyrolysis oven heats up, first the free hydrocarbon content and then the bound hydrocarbon content, are recorded. Pyrolysis is the only method by which

\*The pyrolysis data for this work was obtained on a Girdel Rock-Eval pyrolysis analyser.

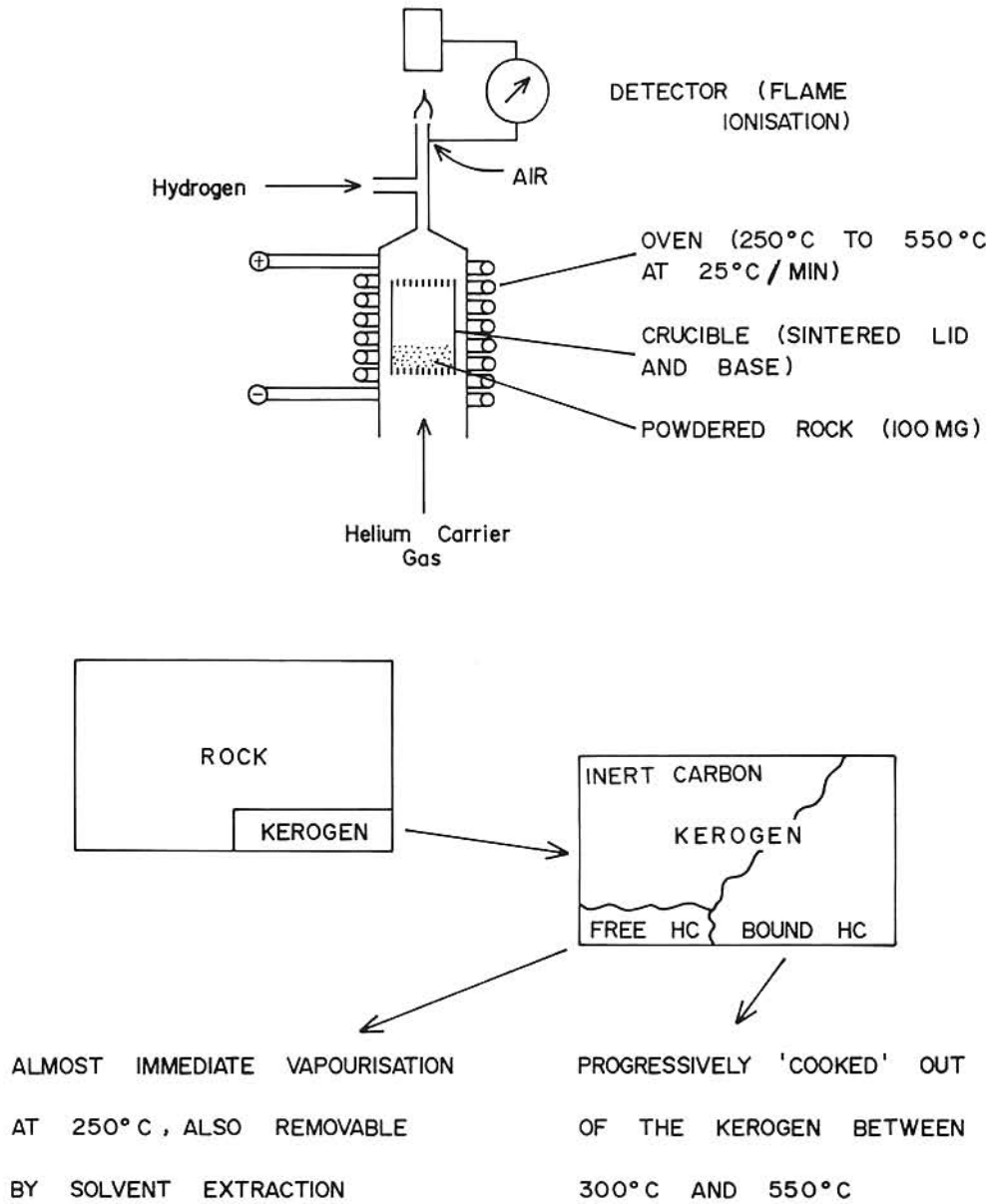
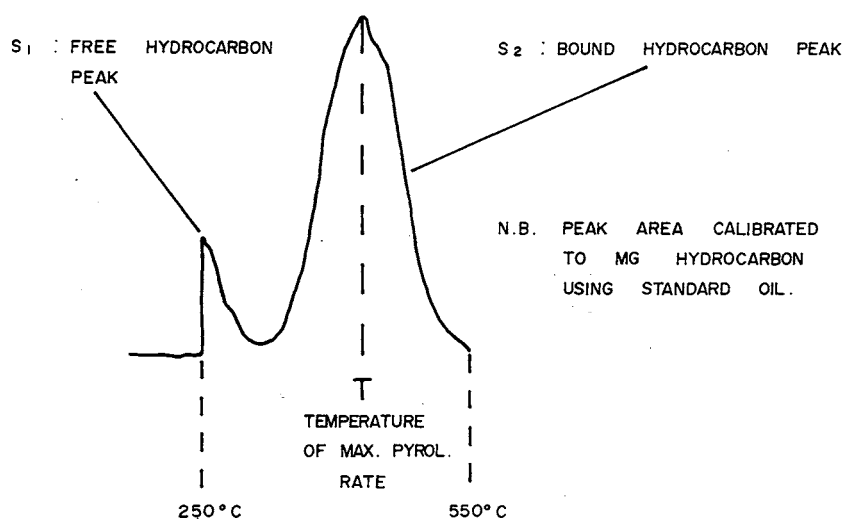


Fig. 2. Operating principles of pyrolysis



S<sub>1</sub> + S<sub>2</sub> IN MG HYDROCARBON PER GM ROCK (OR KG/TON)

= POTENTIAL YIELD

POTENTIAL YIELD 0 - 2 KG/TON — POOR

POTENTIAL YIELD 2 - 6 KG/TON — FAIR

POTENTIAL YIELD 6 - 20 KG/TON — GOOD

POTENTIAL YIELD > 20 KG/TON — VERY GOOD

S<sub>2</sub> / TOC = HYDROGEN INDEX, INDICATOR OF HYDROCARBON

POTENTIAL AND/OR MATURITY OF KEROGEN

T — INDICATOR OF MATURITY AND/OR TYPE OF KEROGEN

Fig. 3. Pyrolysis chart and basic interpretation

the future potential of an immature source bed (recorded as the  $S_2$  peak) can be estimated. As thermal maturity progresses in a rock the  $S_2$  peak will diminish, and the  $S_1$  peak will increase. However the  $S_1$  peak, or free hydrocarbon content can only increase up to the available pore capacity of the rock. Excess free hydrocarbon will migrate. Therefore in a succession of uniform source beds, the quantitative progress of hydrocarbon generation and migration can theoretically be monitored.

Some workers use a third peak (of trapped and regenerated carbon dioxide) to give an "oxygen index", from which information of kerogen quality may be obtained. However the apparatus complexity required to measure this parameter has been known to give problems with reliability and accuracy.

### Gas Chromatography Analysis

The principle behind gas chromatography (g.c.) is that molecules of different size and structure have different vapour pressures at particular temperatures. The equipment is basically made up of:-

- (1) An injector, to introduce the mixture onto the column,
- (2) a column, essentially a long micro-passage lined with extremely viscous liquid, which is situated in
- (3) an oven, temperature programmed over a set range of temperature, and
- (4) a detector, to detect individual components as they exit from the column (see Figure 4).

Injectors can be the flash vaporisation type, depending on high temperature to rapidly transfer the analysed mixture as a gas phase onto the column, or the more recent direct type, depending on a special isothermal solvent effect (Grob and Grob, 1978).

As shown in Figure 4, the hydrocarbon components will be in dynamic gas/liquid equilibrium in the column; this will be controlled by the vapour pressure of the hydrocarbon, which is determined by its molecular size and structure. When the temperature of the oven is raised, the equilibrium of a hydrocarbon will tend towards the gas phase; the more the hydrocarbon moves into the gas phase, the faster it can be moved along the column by the carrier gas. Hydrocarbons are progressively moved into the gas phase by the gradual increase in temperature of the oven. Flame ionisation detectors (as described in the previous section) are usually used to detect the individual hydrocarbon components as they exit from the column.

A gas chromatogram represents the successive quantification of individual hydrocarbon components in a hydrocarbon mixture such as oil, in order of increasing volatility. As shown in Figure 5, the peaks can be identified, the distribution of components identified can be used to indicate kerogen type and maturity and to compare an oil (migrated hydrocarbon) and source rock (free hydrocarbon only).

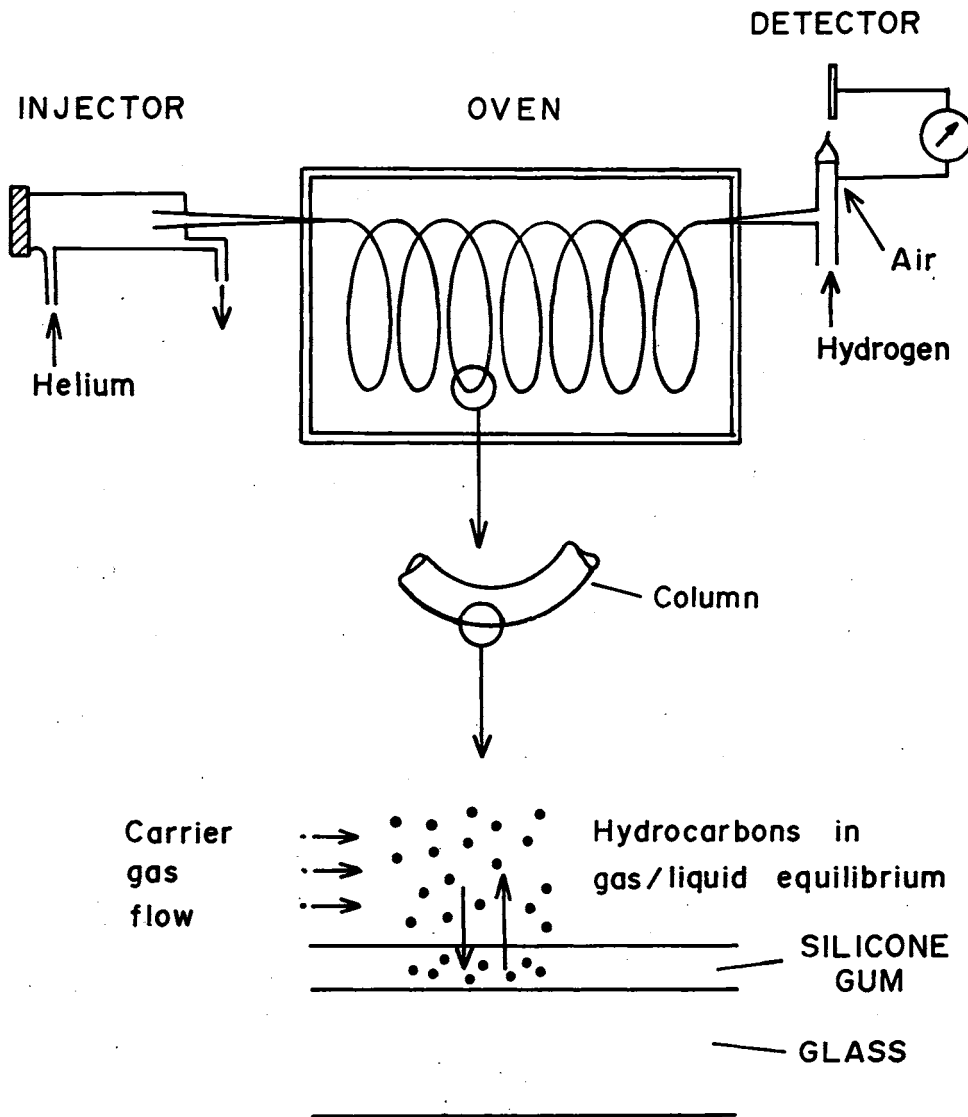
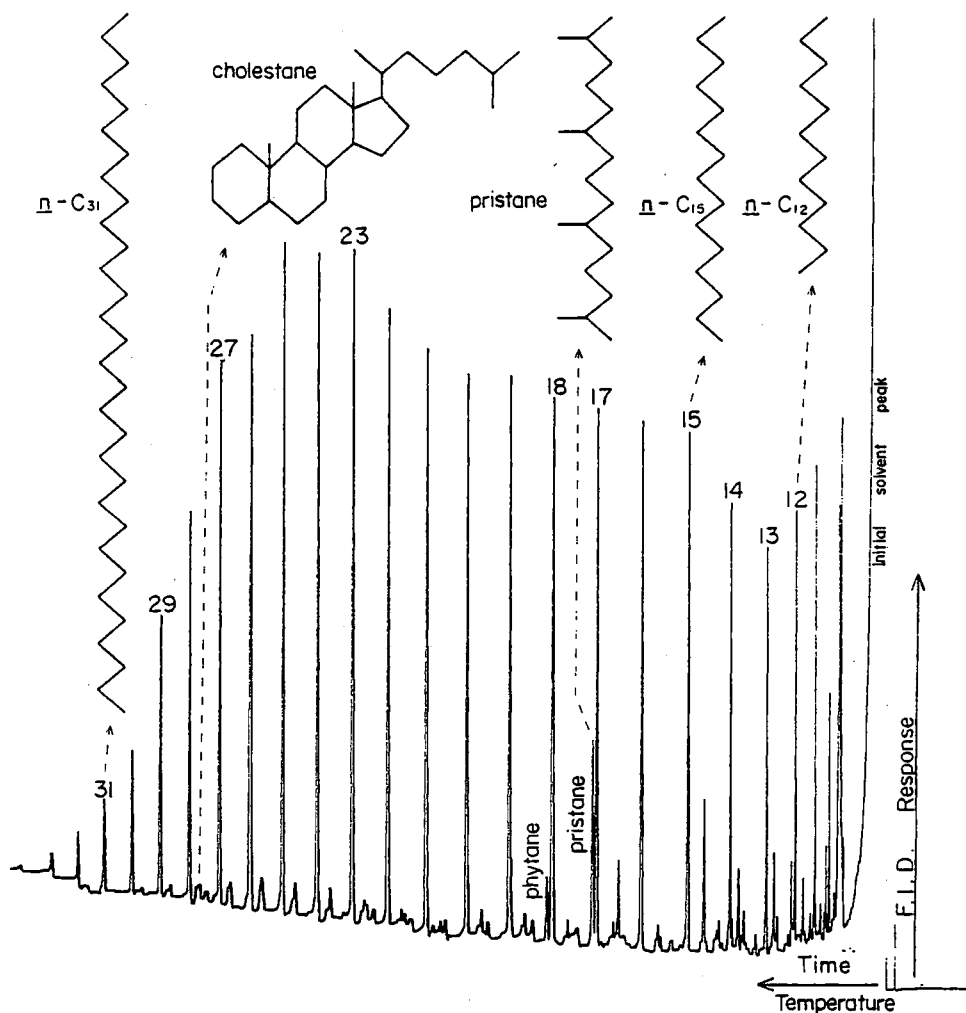


Fig. 4. Operating principles of gas chromatography





MEASURABLE PARAMETERS :

- 1) CPI, ie 
$$\frac{2 \sum (n-C_{27} + n-C_{29})}{\sum (n-C_{26} + n-C_{28}) + \sum (n-C_{28} + n-C_{30})}$$
- 2) pristane / phytane ratio
- 3) n-alkane distribution
- 4) sterane and triterpane distribution
- 5) n-alkane / branched and cyclic alkane ratio

Parameters 1 to 4 are indicators of kerogen type and or maturity, and are used in oil / source bed correlations

Parameter 5 is an indicator of kerogen type and (if the ratio is low) biodegradation.

Fig. 5. Gas chromatogram interpretation

## RESULTS AND DISCUSSION

**General**

The analytical data of Wildcat-1, are presented in Tables 1 (Maturity and Kerogen Composition Data), 2 (Pyrolysis Data) and 3 (Solvent Extraction and Fractionation Data). The data are illustrated in Figures 6 (Extract Hydrocarbon % Organic Carbon against Depth) and 7 (Pyrolysis Hydrocarbon against Depth), and the gas chromatograms of selected hydrocarbon fractions are presented as bar diagrams in Figure 8.

**Interval 1000 to 1800 metres**

Between 1000 and 1800 metres the analysed horizons are early mature, with vitrinite reflectance values of between 0.37% and 0.48%, and spore colour index values of between 3 and 4½ (see Table 1). Oil-prone kerogen at this level of maturity may generate minor quantities of hydrocarbon but unless very concentrated, is unlikely to form an oil source bed. (Thompson *et al.* 1979, Barnard and Cooper 1980).

The analysed horizons contain only average or below average organic carbon contents (see Table 3) which are mainly composed of inertinitic, non-generative and carbon rich, kerogen (see Table 1) and consequently contain little free or bound, (i.e. S<sub>1</sub> or S<sub>2</sub>) hydrocarbons (Table 2). The potential yield values (S<sub>1</sub> + S<sub>2</sub>) are all below 0.5 kg/ton. This interval therefore has little or no hydrocarbon generating potential at any level of thermal maturity.

TABLE 1  
WILDCAT-1: MATURITY AND KEROGEN COMPOSITION DATA

| Sample depth<br>in metres | Vitrinite<br>reflectance<br>% | Spore<br>colour<br>index<br>(1-10) | Kerogen composition |                |                |                 |
|---------------------------|-------------------------------|------------------------------------|---------------------|----------------|----------------|-----------------|
|                           |                               |                                    | Amorphous<br>%      | Liptinite<br>% | Vitrinite<br>% | Inertinite<br>% |
| 1000-050                  | 0.37(10)                      | 3(5)                               | 5                   | -              | 15             | 80              |
| 1450-1500                 | 0.42(15)                      | 3-3½(2)                            | 85                  | -              | 5              | 10              |
| 1550-1600                 | 0.45(12)                      | 3½(10)                             | 20                  | -              | -              | 80              |
| 1600-650                  | NDP                           | 4-4½(7)                            | 15                  | -              | 15             | 70              |
| 1900-950                  | 0.32(2)                       | 5(8)                               | 55                  | 30             | 5              | 10              |
| 2000-050                  | 0.52(10)                      | 5-5½(12)                           | 55                  | 30             | 5              | 10              |
|                           | 0.28(1)                       |                                    |                     |                |                |                 |
|                           | 0.57(18)                      |                                    |                     |                |                |                 |
| 2200-250                  | 0.69(2)                       | 5-5½(3)                            | 85                  | -              | 5              | 10              |
|                           | 0.28(2)                       |                                    |                     |                |                |                 |
|                           | 0.42(14)                      |                                    |                     |                |                |                 |
| 2300-350                  | 0.57(6)                       | 5½-6(8)                            | 90                  | -              | -              | 10              |
|                           | NDP                           |                                    |                     |                |                |                 |
| 2500-500                  | 0.60(6)                       | 5½-6(8)                            | 90                  | -              | -              | 10              |
|                           | 0.83(13)                      |                                    |                     |                |                |                 |
| 2600-650                  | 0.64(11)                      | 6(16)                              | 85                  | -              | 5              | 10              |
| 2750-800                  | 0.75(26)                      | 6½-7(8)                            | 90                  | -              | -              | 10              |
|                           | 0.97(1)                       |                                    |                     |                |                |                 |
| 2950-3000                 | 0.82(9)                       | 7½(5)                              | 85                  | -              | -              | 15              |

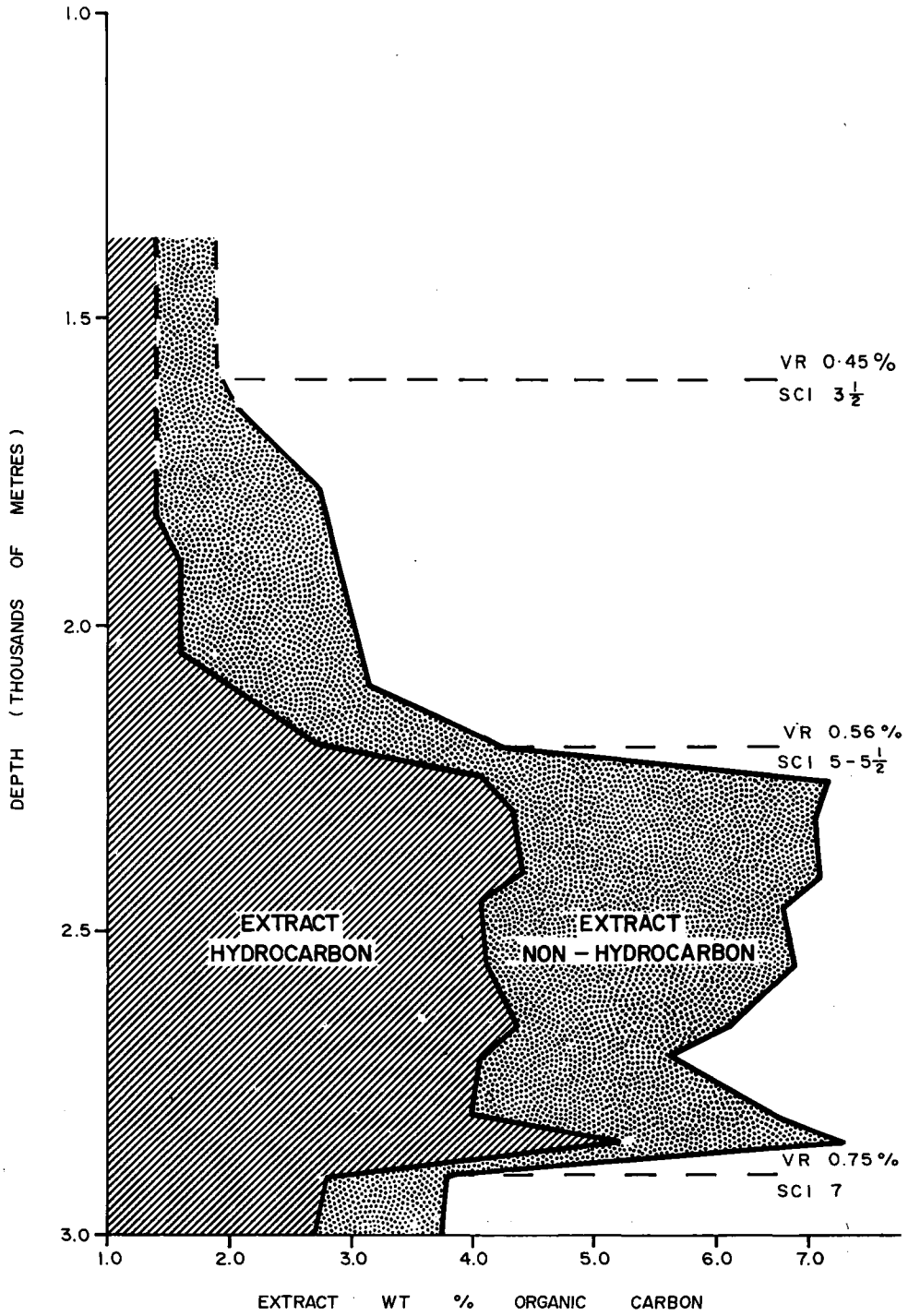


Fig. 6. Extract hydrocarbon % organic carbon against depth, Wildcat-1

TABLE 2  
WILDCAT-1: PYROLYSIS DATA

| Sample depth<br>(metres) | Lithology  | Organic<br>carbon % | Temperature | Hydrogen<br>index | Free HC S <sub>1</sub><br>(kg/ton) | Bound HC S <sub>2</sub><br>(kg/ton) |
|--------------------------|--|---------------------|-------------|-------------------|------------------------------------|-------------------------------------|
| 1000-050                 | ol-gy calc<br>sh/mdst                                | 0.50                | N.D.        | 45                | 0.09                               | 0.14                                |
| 1450-500                 | dk gy calc<br>sh + gy calc<br>mdst                   | 0.85                | 446         | 21                | 0.04                               | 0.14                                |
| 1550-600                 | dk gy sh +<br>ol-gy calc<br>sh/mdst                  | 0.99                | 442         | 41                | 0.08                               | 0.33                                |
| 1600-650                 | a/a + ol-gy<br>sh/slty mdst                          | 0.84                | 438         | 36                | 0.06                               | 0.24                                |
| 1700-750                 | brn-blk/dk gy<br>calc sh + dk<br>brn calc slty<br>sh | 1.24                | 441         | 37                | 0.09                               | 0.37                                |
| 1750-775                 | dk gy calc sh  | 0.73                | 440         | 56                | 0.12                               | 0.29                                |
| 1775-800                 | a/a  | 1.46                | 440         | 33                | 0.10                               | 0.38                                |
| 1800-825                 | dk brn/brn-blk<br>calc slty sh                       | 2.81                | 441         | 222               | 0.63                               | 5.62                                |
| 1825-850                 | a/a  | 3.02                | 440         | 270               | 0.64                               | 5.79                                |
| 1850-900                 | a/a  | 2.75                | 441         | 230               | 0.63                               | 5.70                                |
| 1900-950                 | brn-blk calc<br>slty sh/mdst                         | 2.26                | 445         | 195               | 0.54                               | 4.86                                |
| 1950-2000                | a/a  | 2.37                | 443         | 169               | 0.50                               | 4.50                                |
| 2000-050                 | brn-blk calc<br>slty sh/mdst                         | 2.34                | 440         | 209               | 0.49                               | 4.41                                |
| 2050-100                 | a/a  | 2.45                | 442         | 178               | 0.44                               | 3.94                                |
| 2100-150                 | a/a  | 2.16                | 443         | 193               | 0.42                               | 3.75                                |
| 2150-200                 | a/a  | 2.32                | 440         | 180               | 0.42                               | 3.77                                |
| 2200-250                 | a/a  | 2.70                | 445         | 154               | 0.42                               | 3.78                                |
| 2250-300                 | a/a  | 2.61                | 445         | 132               | 0.35                               | 3.10                                |
| 2300-350                 | dk brn-gy calc<br>slty sh/mdst                       | 2.61                | 448         | 134               | 0.70                               | 2.80                                |
| 2350-400                 | a/a  | 2.64                | 448         | 134               | 0.72                               | 2.83                                |
| 2400-450                 | dk brn-gy calc<br>slty sh/mdst                       | 2.85                | 449         | 125d              | 0.72                               | 2.88                                |
| 2450-500                 | a/a  | 2.74                | 450         | 121               | 0.67                               | 2.66                                |
| 2500-550                 | a/a  | 2.43                | 449         | 115               | 0.56                               | 2.42                                |
| 2550-600                 | brn blk calc<br>carb sh                              | 2.77                | 448         | 115               | 0.64                               | 2.56                                |
| 2600-650                 | a/a  | 2.83                | 452         | 110               | 0.60                               | 2.40                                |
| 2650-700                 | a/a  | 2.54                | 448         | 103               | 0.79                               | 1.84                                |
| 2700-750                 | a/a  | 2.54                | 450         | 93                | 0.71                               | 1.66                                |
| 2750-800                 | a/a  | 2.25                | 452         | 95                | 0.65                               | 1.50                                |
| 2800-850                 | a/a  | 2.12                | 450         | 94                | 0.60                               | 1.40                                |
| 2850-900                 | a/a  | 2.48                | 455         | 59                | 0.59                               | 0.89                                |
| 2900-950                 | a/a  | 2.80                | 455         | 55                | 0.62                               | 0.93                                |
| 2950-3000                | a/a  | 2.52                | 457         | 64                | 0.48                               | 1.13                                |

a/a—as above  
blk—black  
brn—brown  
calc—calcareous  
carb—carbon  
dk—dark  
gy—grey  
ol—olive  
mdst—mudstone  
sh—shale  
slty—silty

TABLE 3

## WILDCAT-1: SOLVENT EXTRACTION AND FRACTIONATION DATA

| Sample depth<br>(metres) | Sample<br>type | Analysed<br>lithology            | Organic<br>carbon %<br>of rock | Total<br>extract<br>p.p.m. | Extract<br>% of<br>organic<br>carbon | Hydro-<br>carbons<br>p.p.m.<br>of rock | Hydro-<br>carbons<br>% of<br>organic<br>carbon |
|--------------------------|----------------|----------------------------------|--------------------------------|----------------------------|--------------------------------------|--|--|
| 1000-050                 | C/S            | ol-gy calc sh/mdst               | 0.50                           |                            |                                      |  |  |
| approx. a/a to 1450m     |                |                                  |                                |                            |                                      |  |  |
| 1450-500                 | C/S            | dk gy calc sh<br>+ gy calc mdst  | 0.85                           |                            |                                      |  |  |
| 1500-550                 | C/S            | dk gy sh + lt gy<br>calc sh/mdst | 0.72                           |                            |                                      |  |  |
| 1550-600                 | C/S            | dk gy sh + ol-gy<br>calc sh/mdst | 0.99                           |                            |                                      |  |  |
| 1600-650                 | C/S            | dk gy sh + ol-gy<br>sh/slty mdst | 0.84                           | 120                        | 1.4                                  | -                                      | -  |
| approx. a/a to 1750m     |                |                                  |                                |                            |                                      |  |  |
| 1750-775                 | C/S            | dk gy calc sh                    | 0.73                           | 175                        | 2.4                                  | -                                      | -  |
| 1775-800                 | C/S            | dk gy calc sh                    | 1.46                           |                            |                                      |  |  |
| 1800-825                 | C/S            | dk brn/brn-blk<br>calc slty sh   | 2.81                           | 735                        | 2.6                                  | 380                                    | 1.4  |
| 1825-850                 | C/S            | a/a                              | 3.02                           |                            |                                      |  |  |
| 1850-900                 | C/S            | a/a                              | 2.75                           | 775                        | 2.8                                  | 440                                    | 1.6  |
| 1900-950                 | C/S            | brn-blk calc slty<br>sh/mdst     | 2.26                           | 650                        | 2.9                                  | 360                                    | 1.6  |
| 1950-2000                | C/S            | a/a                              | 2.37                           |                            |                                      |  |  |
| 2000-050                 | C/S            | a/a                              | 2.42                           | 795                        | 3.3                                  | 390                                    | 1.6  |
| 2050-100                 | C/S            | a/a                              | 2.23                           | 700                        | 3.1                                  | 415                                    | 1.9  |
| 2100-150                 | C/S            | a/a                              | 2.16                           |                            |                                      |  |  |
| 2150-200                 | C/S            | a/a                              | 2.32                           | 990                        | 4.3                                  | 615                                    | 2.7  |
| 2200-250                 | C/S            | a/a                              | 2.70                           | 1865                       | 6.9                                  | 1115                                   | 4.1  |
| 2250-300                 | C/S            | a/a                              | 2.61                           | 1770                       | 6.8                                  | 1115                                   | 4.3  |
| 2300-350                 | C/S            | dk brn-gy calc<br>slty sh/mdst   | 2.61                           |                            |                                      |  |  |
| 2350-400                 | C/S            | dk brn-gy calc<br>slty sh/mdst   | 2.64                           | 1805                       | 6.8                                  | 1160                                   | 4.4  |
| 2400-450                 | C/S            | a/a                              | 2.85                           | 1845                       | 6.5                                  | 1160                                   | 4.1  |
| 2450-500                 | C/S            | a/a                              | 2.74                           |                            |                                      |  |  |
| 2500-550                 | C/S            | a/a                              | 2.59                           | 1725                       | 6.7                                  | 1095                                   | 4.2  |
| 2550-600                 | C/S            | brn-blk calc<br>carb sh          | 2.77                           |                            |                                      |  |  |
| 2600-650                 | C/S            | a/a                              | 2.83                           | 1715                       | 6.1                                  | 1205                                   | 4.3  |
| 2650-700                 | C/S            | a/a                              | 2.54                           | 1410                       | 5.6                                  | 1050                                   | 4.1  |
| 2700-750                 | C/S            | a/a                              | 2.54                           |                            |                                      |  |  |
| 2750-800                 | C/S            | a/a                              | 2.25                           | 1455                       | 6.5                                  | 900                                    | 4.0  |
| 2800-850                 | C/S            | a/a                              | 2.12                           | 1490                       | 7.0                                  | 1120                                   | 5.3  |
| 2850-900                 | C/S            | a/a                              | 2.48                           | 935                        | 3.8                                  | 685                                    | 2.8  |
| 2900-950                 | C/S            | a/a                              | 2.80                           |                            |                                      |  |  |
| 2950-3000                | C/S            | a/a                              | 2.59                           | 975                        | 3.7                                  | 700                                    | 2.7  |

a/a—as above  
blk—black  
brn—brown

calc—calcareous  
carb—carbon  
dk—dark

gy—grey  
ol—olive  
mdst—mudstone

sh—shale  
slty—silty

In the case of hydrocarbon poor intervals such as that described here, pyrolysis analysis alone is sufficient to give a full evaluation. If the low hydrocarbon yield was due to late or post maturity rather than hydrocarbon poor or insufficient kerogen, this would be indicated by a higher temperature (approximately 450°C), and a greater proportion of free to bound hydrocarbon.

#### **Interval 1800 to 3000 metres**

From 1800 to 3000 metres, the analysed horizons are above average in organic richness, generally containing around 2.5% of organic carbon (Table 2) and this is mainly comprised of generally oil-prone (amorphous and liptinitic) kerogen (Table 1). The measured maturity levels over this interval increases from vitrinite reflectance 0.48%, spore colour index 4½ at 1800 metres, up to vitrinite reflectance 0.8%, spore colour index 7½ at 3000 metres. Thus there are about 1200 metres of organically rich, oil-prone shale, in a state of early maturity increasing up to late thermal maturity. The pyrolysis hydrogen indices over this interval do not (according to conventional interpretation) indicate oil-prone kerogen—they do not exceed 270. This is ascribed to the inertinitic (virtually pure carbon) component in the kerogen mixture.

The progress of thermal maturity and thus oil generation in the well section can be monitored by plotting the percentage of free (in this case for accuracy—extractable) hydrocarbons in the kerogen (measured as organic carbon) against depth (Figure 6). As the horizons become fully mature, hydrocarbon generation increases, the main exponential increase occurring at about 2200 metres—vitrinite reflectance 0.56%, spore colour index 5–5½. The concentration of hydrocarbon in the shale is then around 1000 ppm until around 2900 metres, where the concentrations rapidly decrease—a sign of late maturity—at vitrinite reflectance 0.75%, spore colour index 7. Thus maximum kerogen conversion to oil hydrocarbon and significant hydrocarbon generation, occur between 2200 and 2900 metres in the well section.

However, the horizons with the highest pyrolysis potential hydrocarbon yields occur between 1800 and 2050 metres, their yields (free hydrocarbon plus bound hydrocarbon contents) being greater than 5 kg/ton (Table 2 and Figure 7). The content of bound (S<sub>2</sub>) hydrocarbon progressively decreases from here down to 3000 metres, as maturity increases and the kerogen is converted to free hydrocarbon. At the same time the content of free hydrocarbon does not increase—probably because of saturation—so the excess hydrocarbon from the maturing kerogen must have been expelled, or migrated from the rock. As the shale between 1800 and 3000 metres exhibits only minor variations in quantity and quality of kerogen, the amount of migrated hydrocarbon may be assumed to be the difference in bound hydrocarbon content between the early mature and fully mature horizons, as shown in Figure 7. Thus on average the 700 metres of mature source bed between 2200 and 2900 metres may be estimated to have expelled around 3 kg/ton of hydrocarbon—in this case, oil.

Gas chromatography analysis of selected horizons between 1800 and 3000 metres (Figure 8) infers that the free hydrocarbon content of the horizons is predominantly indigenous rather than migrated-in, or contaminant. At 1900 to 1950 metres, the 30% liptinite contribution to the kerogen composition is reflected by the particularly high pristane contents. The progress of thermal maturity going down the section is reflected

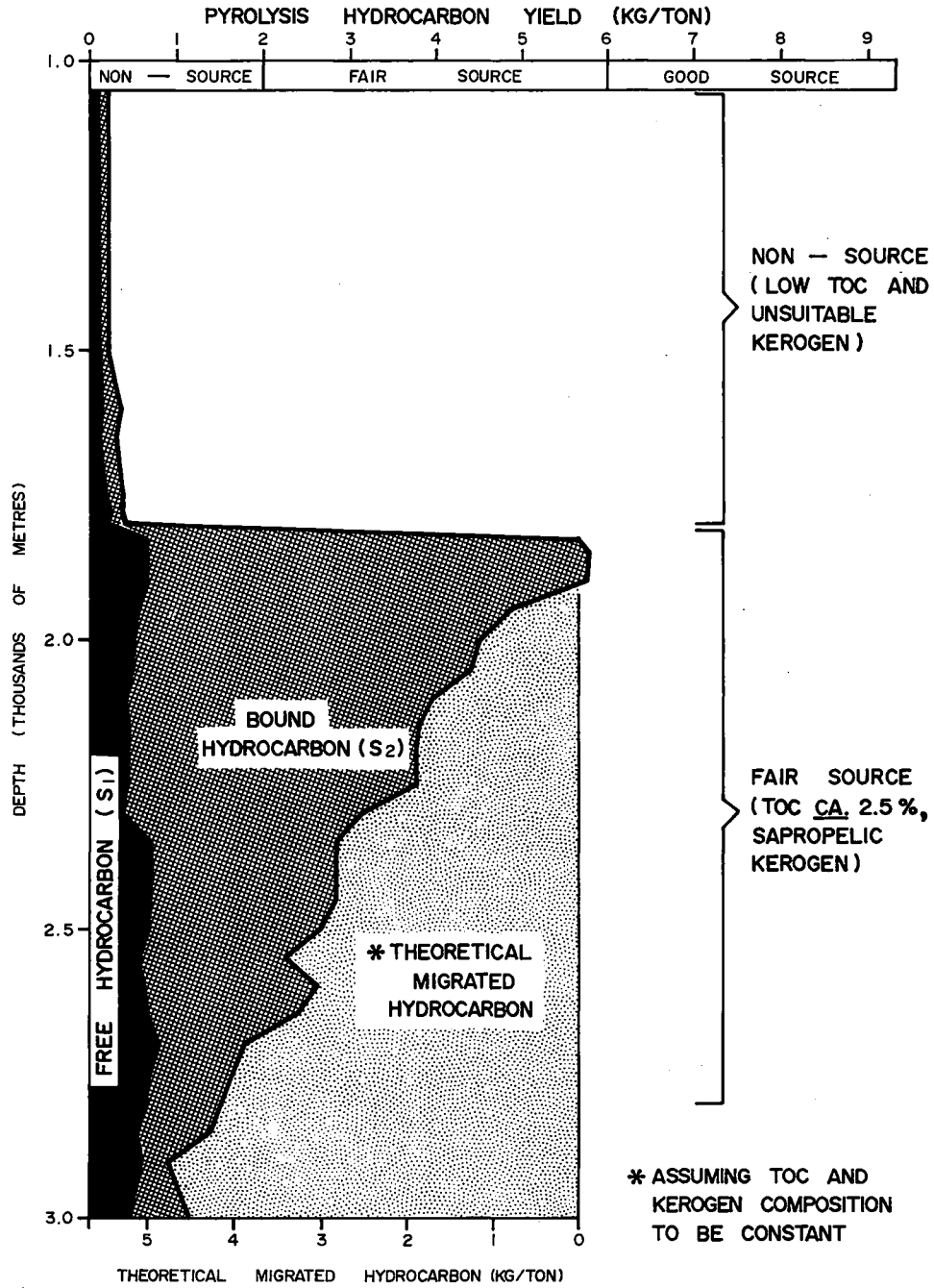


Fig. 7. Pyrolysis hydrocarbon against depth, Wildcat-1

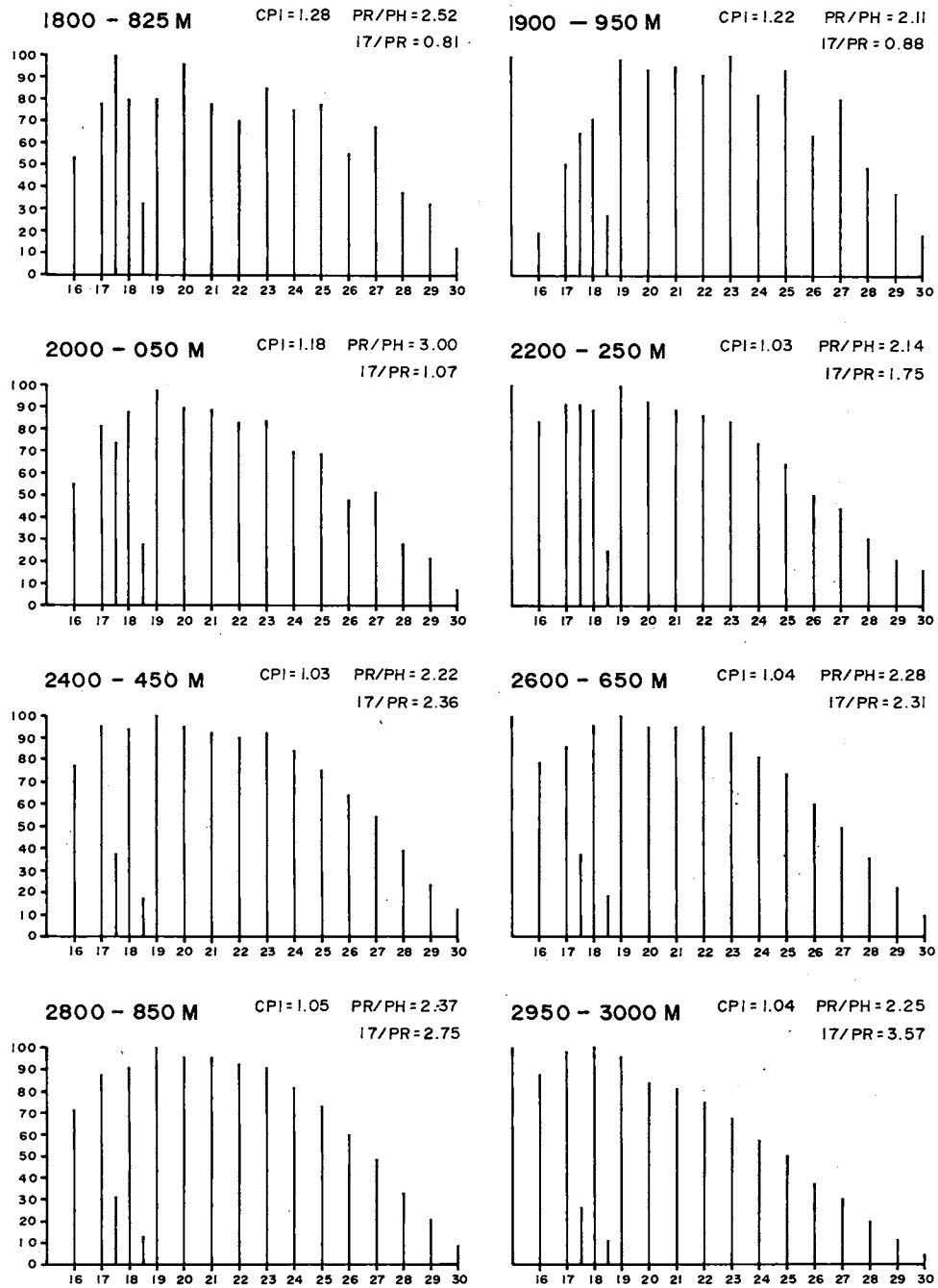


Fig. 8. Gas chromatograms of Wildcat-1 hydrocarbons



by the steady increase in  $n-C_{17}$  to pristane ratio (17/PR in Figure 8) and decrease in C.P.I. (carbon preference index). The odd-over-even predominance is most clearly marked in the 1800 to 2500 metres horizons—which are known to be not yet fully mature.

In the case of a hydrocarbon rich interval such as that described here, pyrolysis is invaluable in:

- (1) quantifying the potential hydrocarbon yield,
- (2) giving an estimate of the quantity of hydrocarbon that has migrated,
- (3) giving an estimate of the quantity of hydrocarbon that remains in the rock.

However the pyrolysis data in isolation could not be used satisfactorily to give these estimates, particularly regarding migrated hydrocarbon. If pyrolysis data only were available, it could as readily be interpreted as showing a decrease in oil generating potential (increase in inertinite content) with depth between 1800 and 3000 metres, coupled with a background of diesel oil contamination. Pyrolysis analysis whilst being a rapid and quantitative measure of hydrocarbon content, can give no indication of the type or source of free hydrocarbons, nor allow a comparison of simultaneously both kerogen type and maturity, especially in relation to total hydrocarbon generating potential.

### CONCLUSIONS

The summarised conclusions of the petroleum geochemical evaluation of Wildcat-1 are as follows:

The 1000 to 1800 metres interval has little or no hydrocarbon generating potential at any level of thermal maturity.

The 1800 to 3000 metres interval is a fair source rock that is generating moderate quantities of oil (around 3 kg/ton) between about 2200 and 2900 metres.

A further burial of more than 400 metres depth burial would optimize the hydrocarbon generating capacity of the 1800 to 3000 metres interval by bringing these rich but immature horizons into the zone of full maturity.

It should be noted that maturity, kerogen composition, solvent extraction and fractionation, and gas chromatography analysis as well as pyrolysis analysis are required to come to these conclusions. If the 1800 to 3000 metres interval of Wildcat-1 were examined by pyrolysis alone, the data could equally be interpreted as showing a decrease in oil generating potential with depth, coupled with a background of diesel oil contamination. However without pyrolysis the potential of this interval could not be fully quantified, or the actual progress of oil generation and migration monitored.

Thus the pyrolysis method is a very useful rapid screening method for poor source rocks, and a very useful quantitative method for rich source rocks. However in the case of kerogen rich source rocks it should always be used in conjunction with other techniques.

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