

H) C<sub>15+</sub> EXTRACTION, DEASPHALTENING AND CHROMATOGRAPHIC SEPARATION

Sections "A" and "E" dealt with analyses covering the light end of the hydrocarbon spectrum. This section is concerned with the solvent extractable organic material in the rock with more than fourteen carbon atoms in the molecule (i.e. the heavy end). The amount and composition of this extract indicates source richness and type, the level of thermal maturation and the possible presence of migrated hydrocarbons.

These results are integrated with those derived from the pyrolysis, visual kerogen, organic carbon and light hydrocarbon analyses.

The techniques involved in this analysis employ pure solvents and have been designed to give reproducible results. Hand picked samples are ground and then solvent extracted in a soxhlet apparatus, or by blending, with dichloromethane (the solvent system can be adapted to client's specifications). After asphaltene precipitation, the total extract is separated by column chromatography or high pressure liquid chromatography into the following fractions: paraffin-naphthene hydrocarbons, aromatic hydrocarbons, eluted NSO's (nitrogen-, sulphur-, and oxygen- containing non-hydrocarbons) and non-eluted NSO's. Note that the non-hydrocarbons are split into three fractions and not reported as a gross value. These fractions can be submitted for further analyses (carbon isotopes, gas chromatography, high mass spectroscopy) including correlation studies.

For convenience and thoroughness, the data are reported in three formats: the weights of the fractions, ppm abundances and normalised percentage compositions. The data are also presented diagrammatically.

J) GC ANALYSIS OF C<sub>15+</sub> PARAFFIN-NAPHTHENE HYDROCARBONS

The gas chromatographic configurations of the heavy C<sub>15+</sub> paraffin-naphthene hydrocarbons reflect source type, the degree of thermal maturation and the presence and character of migrated hydrocarbons or contamination.

Not only is this analysis an integral part of any source rock study but it also provides a fingerprint for correlation purposes and helps to define the geochemical/palynological environmental character of the source rocks from which crude oils were derived.

The paraffin-naphthene hydrocarbons obtained by column chromatography are separated by high resolution capillary chromatography. Excellent resolution of the individual normal paraffins, isoprenoids and significant individual isoparaffins and naphthenes is achieved. Runs are normally terminated at nC<sub>35</sub>. A powerful in-house microprocessor system is being introduced to correct for the change in response factor with chain length.

The normal paraffin carbon preference indices (C.P.I.) indicate if odd (values in excess of 1) or even (values less than 1) normal paraffins are dominant. Strong odd preferences ( $\pm$  strong pristane peaks) are characteristic of immature land plant organic matter whilst even preferences ( $\pm$  strong phytane peaks) suggest a reducing environment of deposition. With increasing maturity, values approach 1.0 and oils are typically close to 1.0. The indices are calculated using the following formulae:

$$\text{C.P.I.A} = \frac{\text{C}_{21} + \text{C}_{23} + \text{C}_{25} + \text{C}_{27}}{\text{C}_{20} + \text{C}_{22} + \text{C}_{24} + \text{C}_{26}} + \frac{\text{C}_{21} + \text{C}_{23} + \text{C}_{25} + \text{C}_{27}}{\text{C}_{22} + \text{C}_{24} + \text{C}_{26} + \text{C}_{28}}$$

$$\text{C.P.I.B} = \frac{\text{C}_{25} + \text{C}_{27} + \text{C}_{29} + \text{C}_{31}}{\text{C}_{24} + \text{C}_{26} + \text{C}_{28} + \text{C}_{30}} + \frac{\text{C}_{25} + \text{C}_{27} + \text{C}_{29} + \text{C}_{31}}{\text{C}_{26} + \text{C}_{28} + \text{C}_{30} + \text{C}_{32}}$$

Chromatograms are reproduced in the report for use as visual fingerprints and in addition, the following data are tabulated: normalised normal paraffin distributions; proportions of paraffins, isoprenoids and naphthenes in the total paraffin-naphthene fraction; C.P.I<sub>A</sub> and C.P.I<sub>B</sub>; pristane to phytane ratio; pristane to nC<sub>17</sub> ratio.

#### K) PYROLYSIS

The process of thermal maturation can be simulated in the laboratory by pyrolysis, which involves heating the sample under specified conditions and measuring the oil-like material which is freed/generated from the rock. With this analysis, the potential richness of immature sediments can be determined and, by coupling the pyrolysis unit to a gas chromatograph, the liberated material can be characterised. These results are correlated with those obtained from the organic carbon, kerogen and C<sub>15+</sub> analyses.

Small amounts of powdered sample are heated in helium to release the thermal bitumen (up to 340°C) and pyrolysate (340-550°C). The thermal bitumen correlates with the solvent extractable material (see above) whilst the pyrolysate fraction does not exist in a "free" state but is generated from the kerogen, thus simulating maturation in the subsurface. Abundances (weight ppm of rock) are measured with a flame ionisation detector against a standard. Thermal bitumen includes source indigenous, contaminant and migrated hydrocarbons but the pyrolysate abundance is a measure of ultimate source richness. The capillary gas chromatogram of the pyrolysate is used to evaluate the character of the parent organic matter and whether it is oil or gas prone. Peak temperature(s) of pyrolysate evolution is recorded. Carbon dioxide can be measured if requested but is normally ignored as the separation of the organic and inorganic species has been found to be artificial and unreliable.

Pyrolysate yields provide a definitive measure of potential source richness which avoids the ambiguities of the organic carbon data and the problem of contamination. This analysis is also used to evaluate the quality and character of the organic matter and the degree to which it has realised its ultimate hydrocarbon potential. Geochem does not employ the pyrolysis technique to evaluate maturation, preferring the kerogen and vitrinite reflectance analyses which avoid the problem of reworking and hence, are more reliable.

Capillary chromatograms produced for the pyrolysate hydrocarbons range from C<sub>1</sub> (methane) out towards C<sub>35</sub> but exhibit considerable variations. They are used to define whether a source rock will yield oil, condensate or gas. With this new technique, it is now possible to complete the evaluation of a source rock.

The data are tabulated and presented graphically. MINI-PYROLYSIS includes ppm thermal bitumen and ppm pyrolysate. PYROLYSIS also provides the above together with the temperature of peak pyrolysate evolution. The capillary chromatograms of the pyrolysate obtained by PYROLYSIS-GC are reproduced in the report. The Mini-Pyrolysis analysis is recommended as a screening technique.

#### L) CORRELATION STUDY ANALYSES

Oil to oil and oil to parent source rock correlation studies require high resolution analytical techniques. This requirement is satisfied by some of the analyses discussed above but others have been selected specifically for correlation work. Many of these analyses also provide information upon the character of the environment of deposition of the parent source rocks.

- detailed C<sub>4</sub>-C<sub>7</sub> hydrocarbon (gasoline range) analysis. See Section E. Although these hydrocarbons can be affected by migrational/alteration processes, they commonly provide a very useful correlation parameter.
- capillary gas chromatography of the C<sub>15</sub>+ paraffin-naphthenes. See section J. The branched+normal paraffin distributions are used to "fingerprint" the samples.
- capillary chromatograms of whole oils and of the C<sub>8</sub>+ fraction of source rocks.
- capillary gas chromatography of C<sub>15</sub>+ aromatic hydrocarbons. Separate chromatograms of the hydrocarbons and of the sulphur-bearing species are reproduced.
- high pressure liquid chromatograms.
- mass spectrometric carbon isotope analyses of crude oil and rock extract fractions and of kerogen separations. A powerful tool for comparing hydrocarbons and correlating hydrocarbons to organic matter. With this technique the problem of source rock contamination can be avoided. The data are recorded on x-y or Galimov plots.
- mass fragmentograms (mass chromatograms) of fragment ions characteristic of selected hydrocarbon groups such as the steranes and terpanes. The fragmentograms provide a convenient and simple means of presenting detailed mass spectrometric data and are used as a sophisticated fingerprinting technique. This provides the ultimate resolution for correlating hydrocarbons and facilitates the examination of hydrocarbon classes.
- vanadium and nickel contents.

Suites of (rather than single) analyses are employed in correlation studies, the actual selection depending upon the complexity of the problem. See also section N.

#### M) ANALYSES FOR SPECIAL CASES

##### M-1) ELEMENTAL KEROGEN ANALYSIS

This analysis evaluates source quality, whether the sediments are oil or gas prone, the character of the organic matter and its level of thermal maturation. It is the chemical equivalent of the visual kerogen analysis. The pyrolysis analysis is generally preferred to this technique, both methods providing similar information.

##### M-2) SULPHUR ANALYSIS

The abundance of sulphur in source rocks and crude oils.

##### M-3) CARBONATE CONTENT

The mineral carbonate content of sediments is determined by acid treatment. These data are particularly useful when used in conjunction with organic carbon contents as a screening technique.

##### M-4) NORMAL PARAFFIN ANALYSIS

Following the removal of the branched paraffins and naphthenes from the total paraffin-naphthene fraction, a chromatogram of the normal paraffins is obtained. The resulting less complicated chromatogram facilitates the examination of normal paraffin distributions.

M-5) SOLID BITUMEN EVALUATION

Residual solid bitumen after crude oil is generated by three prime processes: the action of waters, gas deasphalting, thermal alteration. Thus it provides a means of determining the reservoir history of a crude and of evaluating whether adjacent traps will or will not be prospective for oil. In carbonate sections, where organic matter is sometimes sparse, this technique is also used to evaluate thermal maturation levels.

The analysis involves the determination of the solubility (in CS<sub>2</sub>) of the solid bitumen and of the atomic hydrogen to carbon ratio of the insoluble fraction.

N) CRUDE OIL ANALYSIS

N-1) API GRAVITY

This can be performed upon large (hydrometer) and small (SG bottle, pycnometer) samples and even upon stains extracted from sediments (refractive index).

N-2) SULPHUR CONTENTS (ASTM E30-47)

N-3) POUR POINT (ASTM D97-66, IP15/67)

N-4) VISCOSITY (ASTM D445-72, IP71/75)

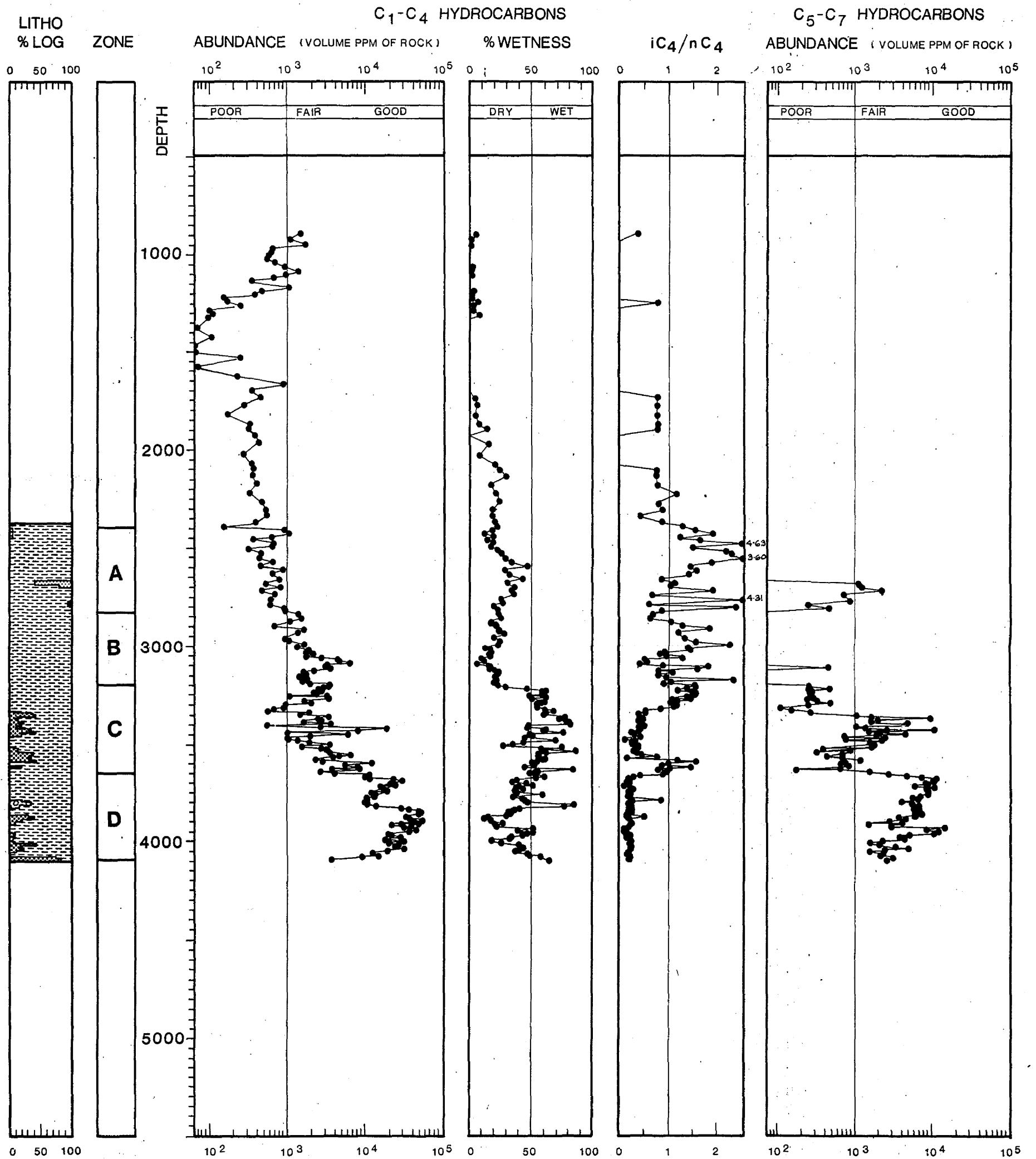
N-5) FRACTIONAL DISTILLATION

Graph of cumulative distillation yield against temperature. Five percent cuts taken for further analysis. Mass spectrometric studies of these fractions provide a detailed picture of the distribution of paraffins and of the various naphthene and aromatic groups within a crude, which is useful both for correlation and for refinery evaluation purposes.

FIGURE 1

# C<sub>1</sub>-C<sub>7</sub> HYDROCARBONS

WELL 35/3-4



LITHOLOGIES

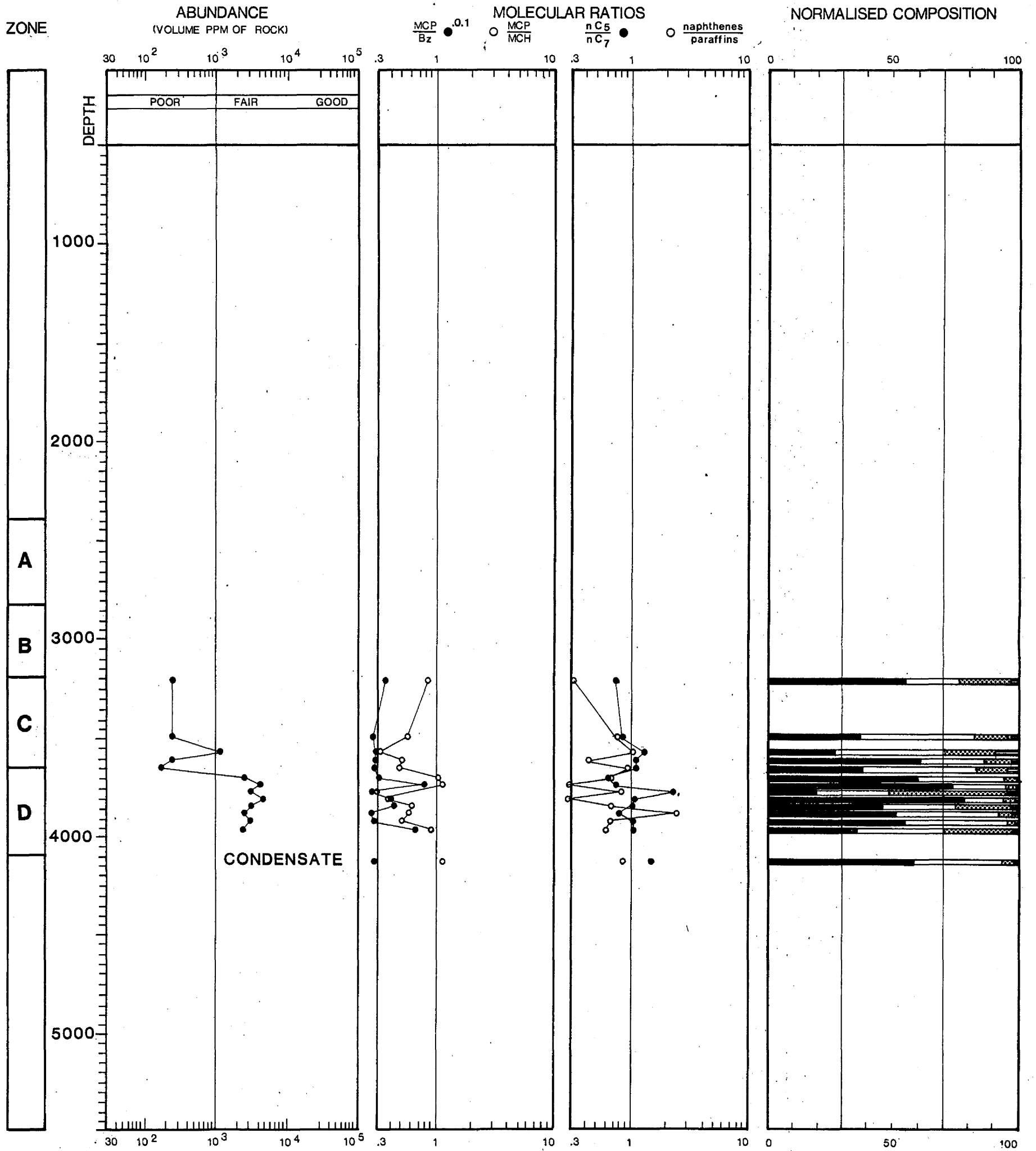
- CARBONATE
- SANDSTONE / SAND
- EVAPORITE
- SHALE / MUDSTONE
- COAL
- LOST CIRCULATION MATERIAL
- SILTSTONE
- IGNEOUS

iC<sub>4</sub> - ISOBUTANE  
nC<sub>4</sub> - NORMAL BUTANE

FIGURE 2

# C<sub>4</sub> - C<sub>7</sub> HYDROCARBONS

WELL 35/3-4



• PPM VALUES EXPRESSED AS VOLUMES  
OF GAS PER MILLION VOLUMES OF SEDIMENT

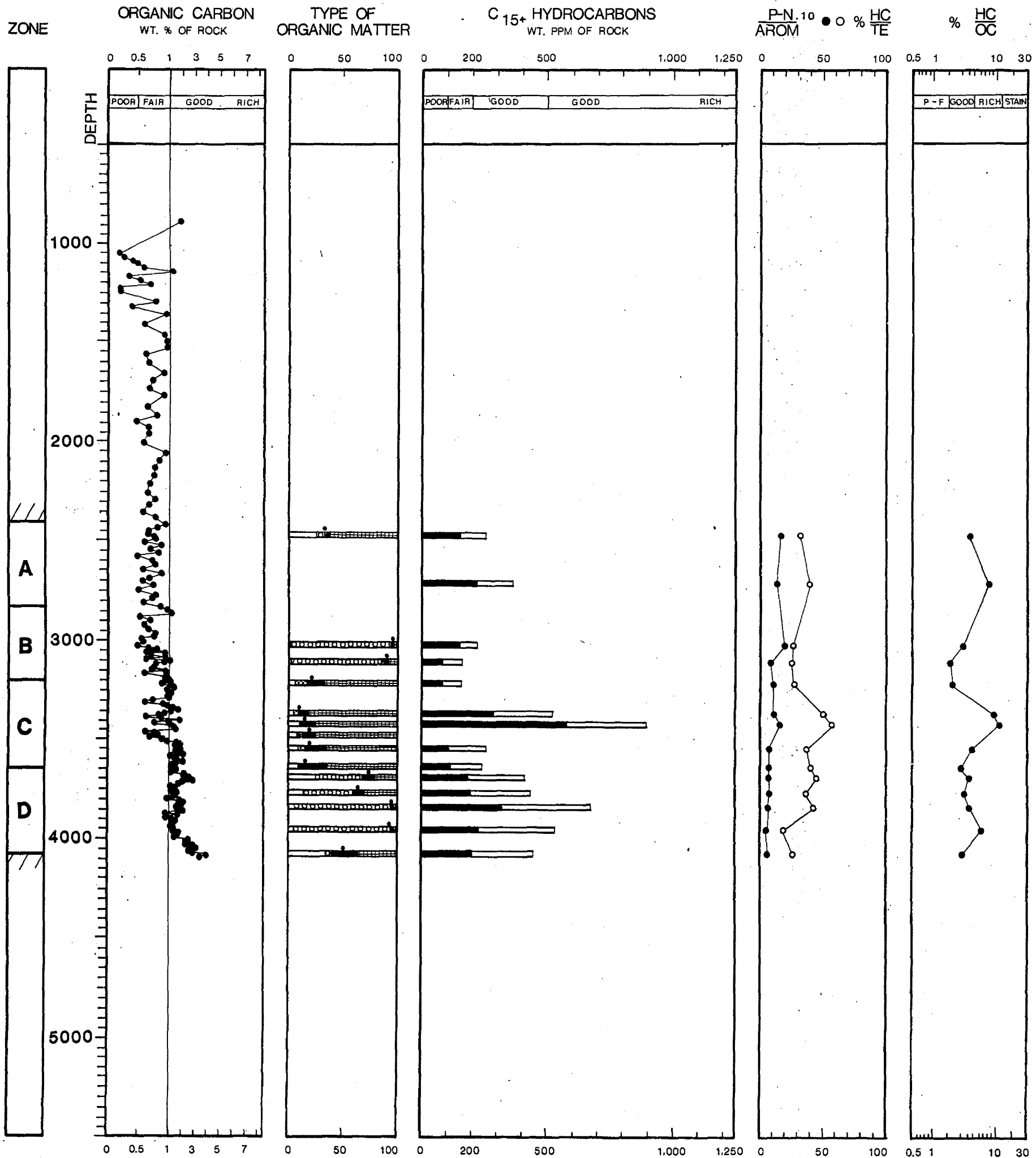
**MCP** = METHYLCYCLOPENTANE    **nC<sub>5</sub>** = NORMAL PENTANE  
**MCH** = METHYLCYCLOHEXANE    **nC<sub>7</sub>** = NORMAL HEPTANE  
**Bz** = BENZENE

■ NORMAL PARAFFINS  
□ ISOPARAFFINS  
▨ NAPHTHENES  
▧ AROMATICS

FIGURE 3

RICHNESS

WELL 35/3-4



● SHALE  
○ OTHER LITHOLOGIES

100% REWORKED ○

ALGAL  
AMORPHOUS  
HERBACEOUS-SPORE, POLLEN, CUTICLE  
RESIN  
WOOD  
INERTINITE ('GOALY')

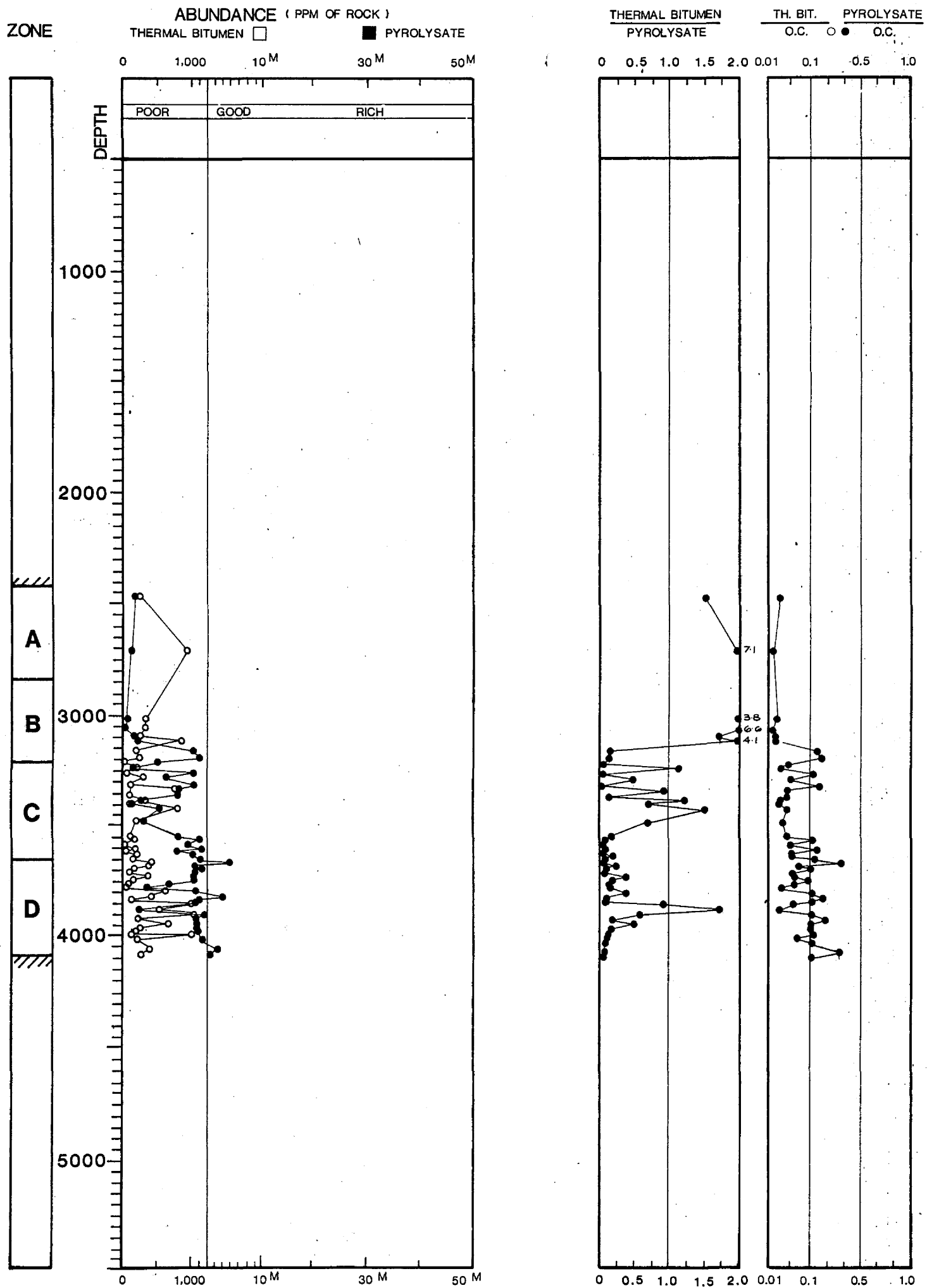
PARAFFIN-NAPHTHENES  
AROMATIC HYDROCARBONS  
FREE ELEMENTAL SULPHUR  
N<sub>2</sub>-S-O<sub>2</sub> BEARING COMPOUNDS  
ASPHALTENES

P-N AROM S NSO ASP  
HC = C<sub>15+</sub> HYDROCARBONS  
OC = ORGANIC CARBON  
TE = TOTAL EXTRACT

FIGURE 4

PYROLYSIS

WELL 35/3-4



M = 10<sup>3</sup>

O.C.=ORGANIC CARBON



FIGURE 5

# C<sub>15+</sub> PARAFFIN - NAPHTHENES

WELL 35/3-4

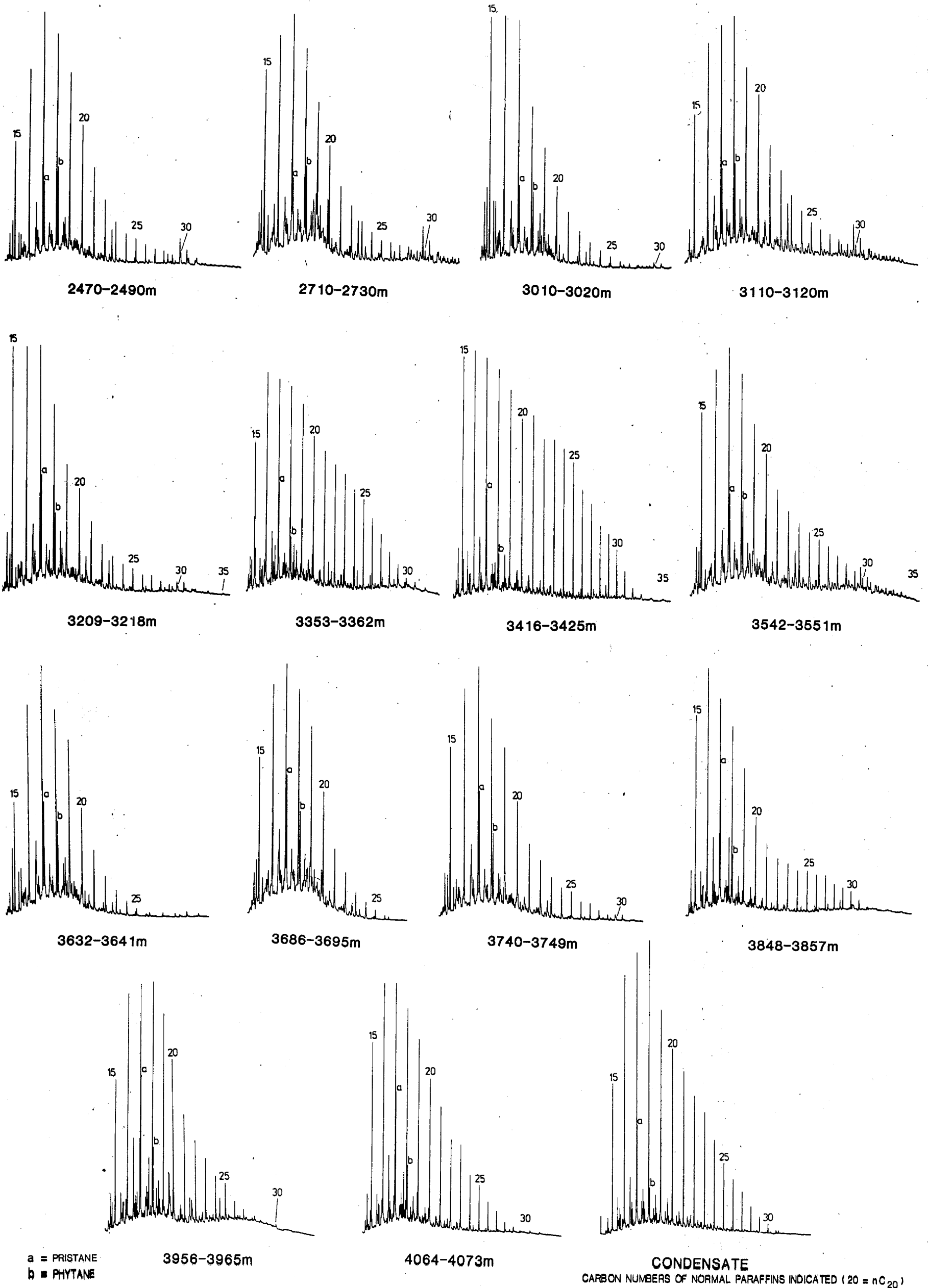
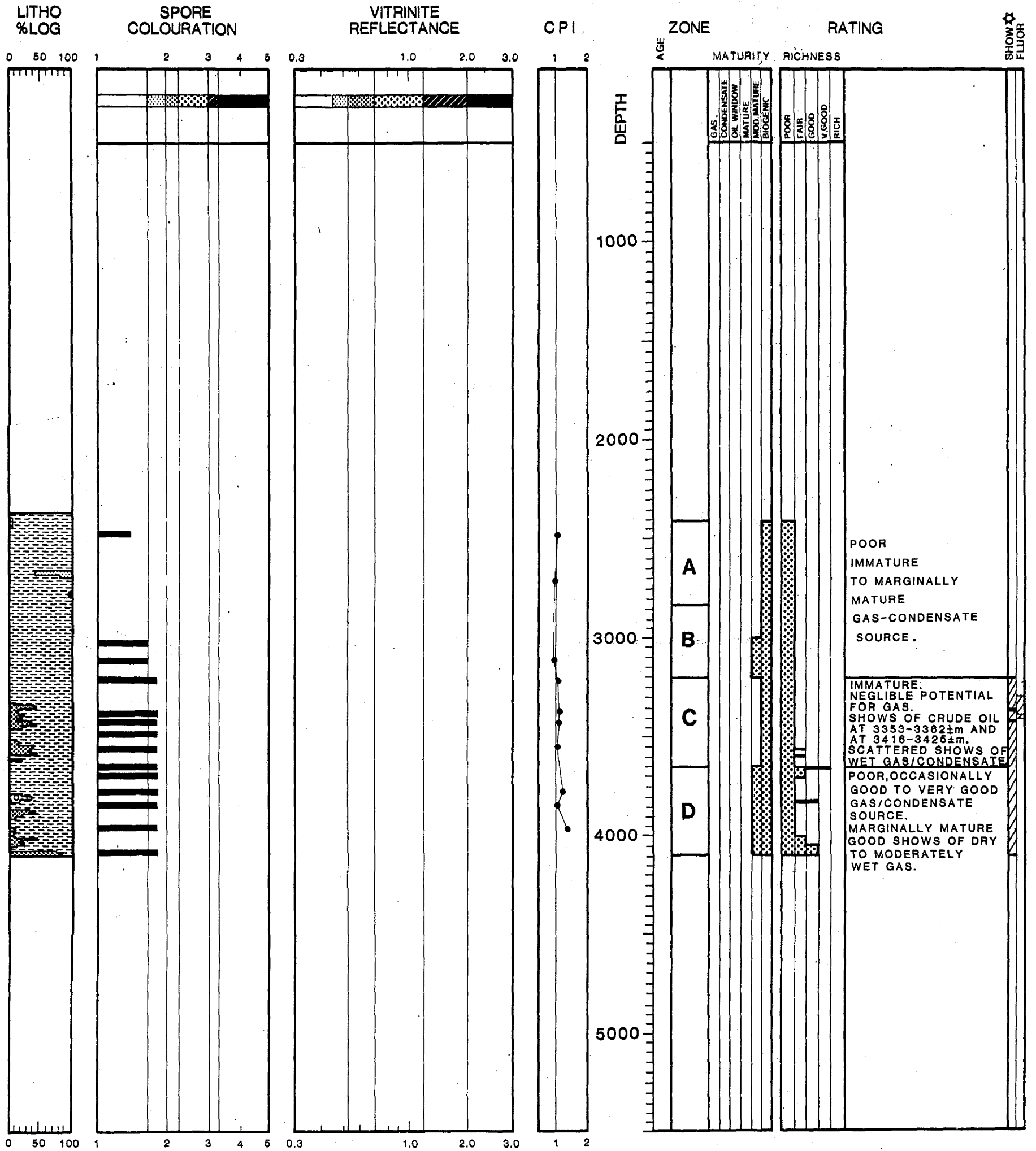


FIGURE 6

INTERPRETATION

WELL 35/3-4



LITHOLOGIES

- CARBONATE
- SAND
- SHALE/MUDSTONE
- COAL
- SILTSTONE
- IGNEOUS
- EVAPORITE
- LOST CIRCULATION MATERIAL

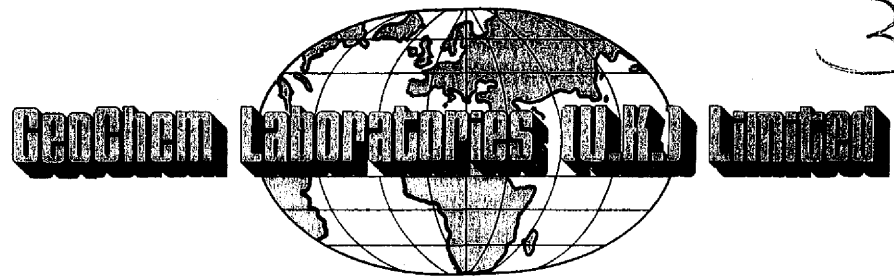
- X RECALCULATED VALUE
- CORE
- PREFERRED TREND

CPI CARBON PREFERENCE INDEX

SPORE COLOURATION

2-	2	2 to 2+	3	3+
IMMATURE	MARG. MATURE	MATURE	OIL WINDOW	COND. EOMETA
REFLECTIVITY	0.59	0.7	1.2	2.0

☆ GEOCHEMICAL



# GEOCHEMICAL SERVICE REPORT

Prepared for  
SAGA PETROLEUM A.S.

GEOCHEMICAL CHARACTERISATION OF THE 35/3-4 DST 2  
CONDENSATE

21 DES 1981  
REGISTRY  
OF COMPANIES

November 1981

CHESTER STREET · CHESTER CH4 8RD · ENGLAND

COMPANY PROPRIETARY

GEOCHEMICAL CHARACTERISATION OF THE 35/3-4 DST 2

CONDENSATE

SUMMARY

Due possibly to the well site sampling technique employed the condensate has an abnormally low GOR of 413 std. cu.ft./barrel. At one atmosphere the liquid has an API gravity of 54° and a sulphur content of less than 0.1%. Nickel and vanadium were not detected.

The light (C<sub>1</sub>-C<sub>7</sub>) hydrocarbons are, consistent with the GOR, depleted in gases although the gasoline (C<sub>4</sub>-C<sub>7</sub>) fraction is normal in other respects and correlates with that of the 35/3-2 fluid. Water washing and biodegradation does not appear to have taken place in the reservoir.

An analysis of the C<sub>15+</sub> hydrocarbons indicates that the condensate is the product of mature source rocks rich in land plant debris. When compared to the corresponding values for the 35/3-2 fluid minor changes in the hydrocarbons and their isotope ratios suggest a minimal increase in the input from marine sediments.



M.J. Sauer

GEOCHEM LABORATORIES (UK) LIMITED

## INTRODUCTION

This report presents a geochemical evaluation and GOR determination of the 35/3-4, DST-2, condensate.

The study based upon the analytical procedures used in the 35/3-2 report (Geochem, June 1981) was designed to characterise the fluid and to determine if possible the nature and maturity of the parent source rocks.

The study was authorised by Mr. T.O. Throndsen, Saga Petroleum A.S., Høvik, Norway.

### A. ANALYTICAL

The condensate sample was assigned the Geochem sample number 553-226.

The sample, in a pressurised steel bottle, was analysed by the scheme proposed by the client for the 35/3-2 study.

To characterise this fluid one GOR determination, one API gravity determination, one sulphur determination, one vanadium and one nickel determination, one light hydrocarbons analysis, one C<sub>4</sub>-C<sub>20</sub> (including detailed C<sub>4</sub>-C<sub>7</sub> analysis) analysis, one chromatographic fractionation, one each high resolution analysis on the paraffin-naphthene, n-paraffin, branched/cyclic and aromatic hydrocarbon fractions and three carbon isotope analyses were performed.

### B. GENERAL INFORMATION

Ten (10) copies of this report have been forward to Mr. T.O. Throndsen, Saga Petroleum A.S., Høvik. A copy has been retained by Geochem for future consultation with authorised Saga personnel.

All of the results and interpretations contained in this report are regarded as highly confidential and are proprietary to Saga Petroleum A.S.

## RESULTS AND DISCUSSION

The 35/3-4 DST-2 condensate sample has been analysed using procedures similar to those adopted for the 35/3-2 fluid. A pressurised bottle containing both gas and liquid phases, at room temperature, was received from the 35/3-4 well. In order to reduce any errors in the GOR measurement minimal quantities of the two phases were withdrawn for the geochemical analyses. For this reason a 20-210°C distillation was not performed although analogous data has been obtained from the C<sub>15+</sub> fraction.

After equilibration at reservoir pressure (5025 PSIG) and temperature (220°F), to obtain a uniform sample, the condensate gave a GOR value of 412.7 std. cu.ft./barrel at 15°C (413.2 std. cu.ft./barrel at 60°F). The stock tank oil gravity was 0.7771 g/ml at 15°C (0.7767 g/ml at 60°F). A GOR of 413 is considerably lower than normal for a condensate; suggesting, in the absence of any other abnormal properties, that the difference is related to the way in which the sample was collected at the wellsite.

The 35/3-4 condensate, equilibrated at room temperature and one atmosphere pressure, has an API gravity of 54°, nickel and vanadium contents of less than 0.25 ppm and contains less than 0.1% sulphur.

The headspace gases consist of methane (1.6%), ethane (3.31%), propane (7.32%), isobutane (9.03%), n butane (14.43%) and a combined C<sub>5</sub>-C<sub>7</sub> fraction (64.30%). A more detailed analysis of the gasoline range (C<sub>4</sub>-C<sub>7</sub>) hydrocarbons shows that the iso and normal butanes, in a pressured sample, amount to over 65% of this fraction. To reproduce the conditions used for the analysis of 35/3-2 condensate a liquid sample (at one atmosphere) was also analysed. The normalised % C<sub>4</sub>-C<sub>7</sub> hydrocarbons, from the C<sub>4</sub>-C<sub>20</sub> chromatogram, are closely similar to those reported for the 35/3-2 fluid.

A small (1-2 ml) portion of the condensate liquid phase was analysed and the proportions of each hydrocarbon type determined from the C<sub>4</sub>-C<sub>20</sub> chromatogram. The C<sub>15</sub>- hydrocarbons (corresponding approximately to the 20-210°C distillation fraction) contain 41.4% n-paraffins, 24.1% isoparaffins, 24.2% naphthenes and 10.6% aromatic hydrocarbons. A further portion of this fluid was evaporated to give a C<sub>15+</sub> fraction, the weight loss (86.4%) is equivalent to the C<sub>15</sub>- fraction. Liquid chromatography was then used to separate the C<sub>15+</sub> fraction into paraffin-naphthene hydrocarbons 74.4%, aromatic hydrocarbons 17.0% and non hydrocarbons 10.6%.

Normal paraffins are dominant in the capillary GC trace of the C<sub>15+</sub> paraffin-naphthene fraction. They extend out to nC<sub>31</sub> and show virtually no carbon preference - suggesting that the condensate is a product of mature source rocks. Pristane is more abundant than phytane and both are more abundant than the corresponding peaks in the equivalent 35/3-2 fraction. The dominance of pristane and phytane is evident in the branched-cyclics chromatogram which also contains minor traces of normal paraffins.

Because the branched and cycloparaffins are sparse beyond the nC<sub>25</sub> position it was necessary to operate the GC-MS at high sensitivity in order to obtain meaningful mass fragmentograms. For this reason the quality of the fragmentograms, as shown by the lack of baseline stability, has deteriorated. This near absence of steranes and triterpanes no doubt accounts for some of the differences between the 35/3-4 and 35/3-2 traces although the groups of peaks A-H formerly identified are still recognisable. Several minor differences are, however, apparent: such as the increased abundance of C<sub>27</sub> tris nor hopanes (group A) and the change in relative abundances of the 17  $\alpha$  C<sub>30</sub> hopanes (group C) at m/e 191 in the 35/3-4 condensate. The stigmastane distribution (group H) at m/e 217 and m/e 259 is also more complex in this fluid than in the 35/3-2 sample. With these exceptions the massfragmentograms from



the two condensates have sufficient in common to suggest that changes in source facies are minimal.

The chromatogram of the C<sub>15+</sub> aromatic hydrocarbons is complex and clearly contains many unresolved components. Several peaks have been identified by GC-MS but, apart from an apparent increase in the abundance of phenanthrene and the substituted phenanthrenes, it is difficult to draw any conclusions from this trace and the corresponding trace for the 35/3-2 fraction.

Carbon isotope  $\delta^{13}\text{C}$  values of  $-27.4^{\circ}/\text{oo}$  and  $-27.0^{\circ}/\text{oo}$  were obtained from the C<sub>15+</sub> paraffin-naphthene and aromatic fractions respectively. They are somewhat heavier than the corresponding figures for the 35/3-2 condensate suggesting, possibly, a slightly greater input from marine facies. Biogenic methane is isotopically light (commonly more negative than  $-60^{\circ}/\text{oo}$ ) so a value of  $-44.6^{\circ}/\text{oo}$  for the methane from this condensate points to a mature, rather than immature (biogenic), source.

#### CONCLUSIONS

The 35/3-4, DST-2, condensate has been analysed using a scheme similar to that adopted for the 35/3-2 fluid. In order to reduce any errors on the GOR measurement minimal volumes of the gas and liquid phases were withdrawn for the geochemical analyses. Since the 20-210°C distillation requires in excess of 100 ml liquid this analysis was not performed. Analogous data from the C<sub>15-</sub> and C<sub>15+</sub> fractions are, however, presented.

The condensate, after equilibration at reservoir conditions (5025 psi and 220°F), gave a GOR of 412.7 std. cu.ft./barrel at 15°C (413.2 std. cu.ft./barrel at 60°F). This low value, for a condensate, is believed to be due to the way in which the sample was taken at the wellsite and not to any abnormal characteristics of the condensate itself.

When equilibrated at one atmosphere the liquid has an API gravity of 54°, contains less than 0.25 ppm nickel and vanadium and less than 0.1% sulphur.

The condensate, at one atmosphere, has a detailed gasoline range (C<sub>4</sub>-C<sub>7</sub>) analysis which is closely comparable to that of the 35/3-2 fluid, benzene and toluene are, again, relatively abundant.

Approximately 86% of the condensate is composed of C<sub>15</sub>-hydrocarbons of which 40% is n-paraffins, 48% branched and cyclo-paraffins and 11% aromatics. Water washing and biodegradation, which results in a loss of the aromatic and n-paraffins, is not suspected.

Paraffin-naphthene and aromatic hydrocarbons amount to 74.4% and 17.0% of the C<sub>15+</sub> fraction. The n-paraffin distribution has a 'front end' bias and extends smoothly out to nC<sub>30</sub>; absence of an odd or even carbon preference indicates a mature source. Pristane and phytane are, due possibly to a source with a slightly more marine character, more abundant than in the 35/3-2 fluid. This conclusion is compatible with the C<sub>15+</sub> carbon isotope values which are somewhat heavier than those for the 35/3-2 condensate.

A methane  $\delta$  value of -44.6‰ is heavier than the normal range of biogenic gases but is compatible with a mature source.

Mass fragmentograms of the steranes and triterpanes differ minimally from those reported for the 35/3-2 condensate. The differences between the two sets of data suggest that a significant change in source facies is unlikely.

TABLE 1  
DETAILED GASOLINE RANGE (C<sub>4</sub> - C<sub>7</sub>) ANALYSIS

GEOCHEM SAMPLE NUMBER	-226	-226
DEPTH	TOTAL CONDENSATE	LIQUID PHASE
isobutane	22.05	1.42
n - butane (nB)	43.01	5.51
isopentane	6.92	4.60
n - pentane (nP)	11.14	7.44
2,2 - dimethylB	0.22	0.36
cyclopentane (CP)	0.74	1.56
2,3 - dimethylB	0.67	0.01
2 - methylIP	1.58	3.52
3 - methylIP	0.78	2.17
n - hexane (nH)	2.33	8.55
methylCP (MCP)	1.36	4.63
2,2 - dimethylIP	0.04	0.34
benzene	1.28	5.33
2,4 - dimethylIP	0.01	0.02
2,2,3 - trimethylB	-	0.02
cyclohexane (CH)	2.25	10.64
3,3 - dimethylIP	-	-
1,1 - dimethylIP	-	-
2 - methylH	0.34	3.31
2,3 - dimethylIP	-	0.19
1,c,3 - dimethylIP	0.07	0.73
3 - methylH	0.19	2.27
1,t,3 - dimethylIP	0.04	0.67
1,t,2 - dimethylIP	0.12	1.36
3 - ethylIP	-	-
n - heptane	0.58	8.25
1,c,2 - dimethylIP	0.03	0.42
methylCH (MCH)	1.20	8.25
toluene	0.74	12.77
ABUNDANCE (ppm)	-	-
MCP/benzene	1.06	0.87
MCP/MCH	1.14	0.33
CH/MCP	1.65	2.30
iP/nP	0.89	0.62
%n - PARAFFINS	57.01	29.75
% ISOPARAFFINS	35.16	18.23
% NAPHTHENES	5.81	33.92
% AROMATICS	2.02	18.10

NORMALISED COMPOSITION

WEIGHT (GRAMMES) OF C<sub>15</sub>+ EXTRACTS AND CHROMATOGRAPHIC FRACTIONS

GEOCHEM SAMPLE NUMBER	INTERVAL	OIL EXTRACTED	TOTAL EXTRACT OBTAINED	TOTAL EXTRACT		nC <sub>5</sub> SOLUBLE FRACTION				
				Preciptd. Asphaltenes	nC <sub>5</sub> soluble	Paraffin – Naphthenes	Aromatics	Eluted NSO's	Non-eluted NSO's	Sulphur
553-226	1	0.1032	0.01325	0.00027	0.01298	0.00986	0.00225	0.00049	0.00038	0.00000

COMPOSITION (NORMALISED %) OF C<sub>15+</sub> MATERIAL EXTRACTED FROM OIL

GEOCHEM SAMPLE NUMBER	INTERVAL	HYDROCARBONS			NON HYDROCARBONS					HC NON HC
		Paraffin -- Naphthenes	Aromatics	$\frac{P-N}{AROM}$	Preciptd. Asphaltenes	Eluted NSO's	Non eluted NSO's	ASPH Sulphur	$\frac{ASPH}{NSO}$	
553-226	1	74.42	16.98	4.38	2.04	3.70	2.87	0.00	0.31	10.62

## BRIEF DESCRIPTION OF THE ANALYSES PERFORMED BY GEOCHEM

"Screen Analyses" are described in sections A, C and D, "Sample Preparation" in section B, "Follow-up Analyses" in sections E through K and "Correlation Studies" in section L. The analyses can be run on either core or cuttings material with the proviso that samples must be canned for the C<sub>1</sub>-C<sub>7</sub> analysis and should be canned (or at least wet) for the C<sub>4</sub>-C<sub>7</sub> analysis. The other analyses can be run on both canned and bagged samples.

### A) C<sub>1</sub>-C<sub>7</sub> LIGHT HYDROCARBON ANALYSIS

The abundance and composition of the C<sub>1</sub>-C<sub>7</sub> hydrocarbons in sediments reflects their source richness, maturity and the character of the hydrocarbons they can yield. Most importantly, it is extremely sensitive to the presence of migrated hydrocarbons and is an excellent method for their detection. As it provides the information on most of the critical parameters and is also economical, this analysis is excellent for screening samples to decide which of them merit further analysis.

During the time which elapses between the collection of the sample at the wellsite and its analysis in the laboratory, a fraction of the total gas passes from the rock to the air space at the top of the can. For this reason, both the air space and the cuttings are analysed.

The analysis involves the gas chromatographic separation of the individual C<sub>1</sub>-C<sub>4</sub> gaseous hydrocarbons (methane, ethane, propane, isobutane and normal butane) and a partial resolution of the C<sub>5</sub>-C<sub>7</sub> gasoline-range hydrocarbons (for their complete resolution see Section E). The ppm abundance of the five gases and of the total C<sub>5</sub>-C<sub>7</sub> hydrocarbons are calculated from their electronically integrated peak areas (not from peak height) by comparison with a standard.

In the report, the following data are tabulated: the abundance and composition of the air space gas, of the cuttings gas and of the combined air space and cuttings gases. The combined results are also presented graphically.

### B) SAMPLE WASHING AND HAND PICKING

All of the analyses described in subsequent sections are run on washed and hand picked samples.

Cuttings are washed to remove the drilling mud, care being taken not to remove soft clays and fine sand during the washing procedure. Using the C<sub>1</sub>-C<sub>7</sub> hydrocarbon data profile of the well, or the organic carbon profile (if this analysis is used for screening), electric logs (if supplied) and the appearance of the cuttings under the binocular microscope, samples are selected to represent the lithological and geochemical zones penetrated by the well. These samples are then carefully hand picked and the lithology of the uncaved material is described. It is these samples which are submitted for further analysis.

Sample material remaining after analysis is retained for six months. Unless instructions are received to the contrary, Geochem Laboratories may then destroy the samples.

Our reports incorporate a gross lithological description of all the samples which have been analysed and litho percentage logs. As screen analyses are recommended at narrow intervals, a complete lithological profile is obtained.

C) ORGANIC CARBON ANALYSIS

The organic carbon content of a rock is a measure of its total organic richness. Combined with the visual kerogen, C<sub>1</sub>-C<sub>7</sub>, C<sub>4</sub>-C<sub>7</sub>, pyrolysis and C<sub>15+</sub> analyses, the organic carbon content is used to evaluate the potential (not necessarily actual) hydrocarbon source richness of the sediment. This analysis is an integral part of a total evaluation and it can also be used as an economical screen analysis for dry samples (when the C<sub>1</sub>-C<sub>7</sub> analysis cannot be used).

Hand picked samples are dried, crushed and then acidised to remove the inorganic calcium and magnesium carbonates. The actual analysis involves combustion in a Leco carbon analyser. Blanks, standards and duplicates are run routinely for purposes of quality control at no extra cost to the client.

The data are tabulated and presented diagrammatically in our reports in a manner which facilitates comparison with the gross lithology (see Section B) of the samples.

D) MINI-PYROLYSIS

An ideal screen analysis which provides a definitive measure of potential source richness upon those samples whose organic carbon contents suggest fair or good source potential. This is described in detail in section K.

E) DETAILED C<sub>4</sub>-C<sub>7</sub> HYDROCARBON ANALYSIS

The abundance and composition of the C<sub>4</sub>-C<sub>7</sub> gasoline-range hydrocarbons in sediments reflects their source quality, level of thermal maturation and organic facies. In addition, the data also reveal the presence of migrated hydrocarbons and can be used for crude oil-parent source rock correlation studies.

This powerful analysis, performed upon hand picked lithologies, is employed as a follow-up to confirm the potential of samples which have been selected using the initial screen analysis. It is used in conjunction with the organic carbon, visual kerogen and C<sub>15+</sub> analyses.

The individual normal paraffins, isoparaffins, naphthenes and aromatics with between four and seven carbon atoms in the molecule (but also including toluene) are resolved by capillary gas chromatography and their peak areas electronically integrated.

Normalised compositions, selected ratios and the ppm abundance of the total gasoline-range fraction are tabulated in the report and also presented graphically.

F) KEROGEN TYPE AND MATURATION

Kerogen is the insoluble organic matter in rocks. Visual examination of the kerogen gives a direct measure of thermal maturity and of the composition of the organic matter (organic facies) and indicates the source quality of the sediment - which is confirmed using the organic carbon, light hydrocarbon, pyrolysis and C<sub>15+</sub> analyses.

The type of hydrocarbon (oil or gas) generated by a source rock is a function of the types and level of thermal maturation of the organic matter which are present. Both of these parameters are measured directly by this method.

Kerogen is separated from the inorganic rock matrix by acid digestion and flotation methods which avoid oxidation of the organic matter. It is then mounted on a glass slide and examined at high and low magnifications with a Leitz microscope. Chemical methods measure the total kerogen population but, with this technique, individual particles can be selected for examination and spurious material identified. This is particularly valuable in reworked, contaminated and turbodrilled sediments.

The following data are generated: the types of organic matter present and their relative abundances, an estimate of the proportion of reworked material, preservation state, the thermal maturity of the non-reworked organic matter using the spore colouration technique.

Our maturation scale has been developed to digitise small but recognisable changes in organic matter colouration resulting from increasing maturity and to place particular emphasis upon the immature to mature transition. In the absence of a universal colouration scale, the most significant points on our scale have been calibrated against equivalent vitrinite reflectance values. The following maturation stages are recognised at the low end of the scale:-

- a) immature; thermal index less than 2- (0.45% Ro)
- b) marginally mature; indices between 2- and 2.  
Minor hydrocarbon generation from amorphous and herbaceous ( $\pm$  algal) organic matter
- c) mature; indices between 2 (0.53% Ro) and 2 to 2+ (0.72% Ro),  
significant generation from amorphous, algal and herbaceous organic matter but wood only marginally mature
- d) oil window; indices of 2 to 2+ (0.72% Ro) through to 3 (1.2% Ro). Peak hydrocarbon generation.

The condensate zone starts at a thermal index of 3 whilst indices of 3+ (2.0% Ro) and higher indicate the eometamorphic dry gas stage.

A total of fourteen types of organic matter are sought based upon the major categories of algal, amorphous, herbaceous (spore, pollen, cuticle), wood, inertinite and resin. This detail is essential for a proper understanding of hydrocarbon source potential as the different sub-groups within each category have different properties.

Upon completion of the study, the kerogen slides are sent to the client.

#### G) VITRINITE REFLECTANCE

Vitrinite reflectance is an alternative/confirmatory method for evaluating thermal maturation which is used in conjunction with the visual kerogen analysis. The reflectivity of vitrinite macerals increases in response to thermal alteration and is used to define maturation levels and, by projection, to predict maturity at depth or the thicknesses of section removed by erosion.

Measurements are made upon kerogen separations in conjunction with polished whole rock samples. In general, this analysis is performed upon the same samples as the visual kerogen analysis, thus facilitating a direct comparison of the two sets of results.

If possible, forty to fifty measurements are taken per sample - unless the sediments are organically lean, vitrinite is sparse or only a single uniform population is present. The data are plotted in a histogram which distinguishes the indigenous vitrinite from possible reworked or caved material. Averages are calculated for each population. Comments upon exinite fluorescence and upon the character of the phytoclasts are noted on the histograms. The reports contain the tabulated data, histograms and the reflectivities plotted against depth.

The vitrinite and visual kerogen techniques provide mutually complementary information upon maturity, organic matter type and diagenesis.



H) C<sub>15+</sub> EXTRACTION, DEASPHALTENING AND CHROMATOGRAPHIC SEPARATION

Sections "A" and "E" dealt with analyses covering the light end of the hydrocarbon spectrum. This section is concerned with the solvent extractable organic material in the rock with more than fourteen carbon atoms in the molecule (i.e. the heavy end). The amount and composition of this extract indicates source richness and type, the level of thermal maturation and the possible presence of migrated hydrocarbons.

These results are integrated with those derived from the pyrolysis, visual kerogen, organic carbon and light hydrocarbon analyses.

The techniques involved in this analysis employ pure solvents and have been designed to give reproducible results. Hand picked samples are ground and then solvent extracted in a soxhlet apparatus, or by blending, with dichloromethane (the solvent system can be adapted to client's specifications). After asphaltene precipitation, the total extract is separated by column chromatography or high pressure liquid chromatography into the following fractions: paraffin-naphthene hydrocarbons, aromatic hydrocarbons, eluted NSO's (nitrogen-, sulphur-, and oxygen- containing non-hydrocarbons) and non-eluted NSO's. Note that the non-hydrocarbons are split into three fractions and not reported as a gross value. These fractions can be submitted for further analyses (carbon isotopes, gas chromatography, high mass spectroscopy) including correlation studies.

For convenience and thoroughness, the data are reported in three formats: the weights of the fractions, ppm abundances and normalised percentage compositions. The data are also presented diagrammatically.

J) GC ANALYSIS OF C<sub>15+</sub> PARAFFIN-NAPHTHENE HYDROCARBONS

The gas chromatographic configurations of the heavy C<sub>15+</sub> paraffin-naphthene hydrocarbons reflect source type, the degree of thermal maturation and the presence and character of migrated hydrocarbons or contamination.

Not only is this analysis an integral part of any source rock study but it also provides a fingerprint for correlation purposes and helps to define the geochemical/palynological environmental character of the source rocks from which crude oils were derived.

The paraffin-naphthene hydrocarbons obtained by column chromatography are separated by high resolution capillary chromatography. Excellent resolution of the individual normal paraffins, isoprenoids and significant individual isoparaffins and naphthenes is achieved. Runs are normally terminated at nC<sub>35</sub>. A powerful in-house microprocessor system is being introduced to correct for the change in response factor with chain length.

The normal paraffin carbon preference indices (C.P.I.) indicate if odd (values in excess of 1) or even (values less than 1) normal paraffins are dominant. Strong odd preferences ( $\pm$  strong pristane peaks) are characteristic of immature land plant organic matter whilst even preferences ( $\pm$  strong phytane peaks) suggest a reducing environment of deposition. With increasing maturity, values approach 1.0 and oils are typically close to 1.0. The indices are calculated using the following formulae:

$$\text{C.P.I.A} = \frac{\text{C}_{21} + \text{C}_{23} + \text{C}_{25} + \text{C}_{27}}{\text{C}_{20} + \text{C}_{22} + \text{C}_{24} + \text{C}_{26}} + \frac{\text{C}_{21} + \text{C}_{23} + \text{C}_{25} + \text{C}_{27}}{\text{C}_{22} + \text{C}_{24} + \text{C}_{26} + \text{C}_{28}}$$

$$\text{C.P.I.B} = \frac{\text{C}_{25} + \text{C}_{27} + \text{C}_{29} + \text{C}_{31}}{\text{C}_{24} + \text{C}_{26} + \text{C}_{28} + \text{C}_{30}} + \frac{\text{C}_{25} + \text{C}_{27} + \text{C}_{29} + \text{C}_{31}}{\text{C}_{26} + \text{C}_{28} + \text{C}_{30} + \text{C}_{32}}$$

Chromatograms are reproduced in the report for use as visual fingerprints and in addition, the following data are tabulated: normalised normal paraffin distributions; proportions of paraffins, isoprenoids and naphthenes in the total paraffin-naphthene fraction; C.P.I<sub>A</sub> and C.P.I<sub>B</sub>; pristane to phytane ratio; pristane to nC<sub>17</sub> ratio.

#### K) PYROLYSIS

The process of thermal maturation can be simulated in the laboratory by pyrolysis, which involves heating the sample under specified conditions and measuring the oil-like material which is freed/generated from the rock. With this analysis, the potential richness of immature sediments can be determined and, by coupling the pyrolysis unit to a gas chromatograph, the liberated material can be characterised. These results are correlated with those obtained from the organic carbon, kerogen and C<sub>15+</sub> analyses.

Small amounts of powdered sample are heated in helium to release the thermal bitumen (up to 340°C) and pyrolysate (340-550°C). The thermal bitumen correlates with the solvent extractable material (see above) whilst the pyrolysate fraction does not exist in a "free" state but is generated from the kerogen, thus simulating maturation in the subsurface. Abundances (weight ppm of rock) are measured with a flame ionisation detector against a standard. Thermal bitumen includes source indigenous, contaminant and migrated hydrocarbons but the pyrolysate abundance is a measure of ultimate source richness. The capillary gas chromatogram of the pyrolysate is used to evaluate the character of the parent organic matter and whether it is oil or gas prone. Peak temperature(s) of pyrolysate evolution is recorded. Carbon dioxide can be measured if requested but is normally ignored as the separation of the organic and inorganic species has been found to be artificial and unreliable.

Pyrolysate yields provide a definitive measure of potential source richness which avoids the ambiguities of the organic carbon data and the problem of contamination. This analysis is also used to evaluate the quality and character of the organic matter and the degree to which it has realised its ultimate hydrocarbon potential. Geochem does not employ the pyrolysis technique to evaluate maturation, preferring the kerogen and vitrinite reflectance analyses which avoid the problem of reworking and hence, are more reliable.

Capillary chromatograms produced for the pyrolysate hydrocarbons range from C<sub>1</sub> (methane) out towards C<sub>35</sub> but exhibit considerable variations. They are used to define whether a source rock will yield oil, condensate or gas. With this new technique, it is now possible to complete the evaluation of a source rock.

The data are tabulated and presented graphically. MINI-PYROLYSIS includes ppm thermal bitumen and ppm pyrolysate. PYROLYSIS also provides the above together with the temperature of peak pyrolysate evolution. The capillary chromatograms of the pyrolysate obtained by PYROLYSIS-GC are reproduced in the report. The Mini-Pyrolysis analysis is recommended as a screening technique.

#### L) CORRELATION STUDY ANALYSES

Oil to oil and oil to parent source rock correlation studies require high resolution analytical techniques. This requirement is satisfied by some of the analyses discussed above but others have been selected specifically for correlation work. Many of these analyses also provide information upon the character of the environment of deposition of the parent source rocks.

- detailed C<sub>4</sub>-C<sub>7</sub> hydrocarbon (gasoline range) analysis. See Section E. Although these hydrocarbons can be affected by migrational/alteration processes, they commonly provide a very useful correlation parameter.
- capillary gas chromatography of the C<sub>15</sub>+ paraffin-naphthenes. See section J. The branched+normal paraffin distributions are used to "fingerprint" the samples.
- capillary chromatograms of whole oils and of the C<sub>8</sub>+ fraction of source rocks.
- capillary gas chromatography of C<sub>15</sub>+ aromatic hydrocarbons. Separate chromatograms of the hydrocarbons and of the sulphur-bearing species are reproduced.
- high pressure liquid chromatograms.
- mass spectrometric carbon isotope analyses of crude oil and rock extract fractions and of kerogen separations. A powerful tool for comparing hydrocarbons and correlating hydrocarbons to organic matter. With this technique the problem of source rock contamination can be avoided. The data are recorded on x-y or Galimov plots.
- mass fragmentograms (mass chromatograms) of fragment ions characteristic of selected hydrocarbon groups such as the steranes and terpanes. The fragmentograms provide a convenient and simple means of presenting detailed mass spectrometric data and are used as a sophisticated fingerprinting technique. This provides the ultimate resolution for correlating hydrocarbons and facilitates the examination of hydrocarbon classes.
- vanadium and nickel contents.

Suites of (rather than single) analyses are employed in correlation studies, the actual selection depending upon the complexity of the problem. See also section N.

#### M) ANALYSES FOR SPECIAL CASES

##### M-1) ELEMENTAL KEROGEN ANALYSIS

This analysis evaluates source quality, whether the sediments are oil or gas prone, the character of the organic matter and its level of thermal maturation. It is the chemical equivalent of the visual kerogen analysis. The pyrolysis analysis is generally preferred to this technique, both methods providing similar information.

##### M-2) SULPHUR ANALYSIS

The abundance of sulphur in source rocks and crude oils.

##### M-3) CARBONATE CONTENT

The mineral carbonate content of sediments is determined by acid treatment. These data are particularly useful when used in conjunction with organic carbon contents as a screening technique.

##### M-4) NORMAL PARAFFIN ANALYSIS

Following the removal of the branched paraffins and naphthenes from the total paraffin-naphthene fraction, a chromatogram of the normal paraffins is obtained. The resulting less complicated chromatogram facilitates the examination of normal paraffin distributions.

M-5) SOLID BITUMEN EVALUATION

Residual solid bitumen after crude oil is generated by three prime processes: the action of waters, gas deasphalting, thermal alteration. Thus it provides a means of determining the reservoir history of a crude and of evaluating whether adjacent traps will or will not be prospective for oil. In carbonate sections, where organic matter is sometimes sparse, this technique is also used to evaluate thermal maturation levels.

The analysis involves the determination of the solubility (in CS<sub>2</sub>) of the solid bitumen and of the atomic hydrogen to carbon ratio of the insoluble fraction.

N) CRUDE OIL ANALYSIS

N-1) API GRAVITY

This can be performed upon large (hydrometer) and small (SG bottle, pycnometer) samples and even upon stains extracted from sediments (refractive index).

N-2) SULPHUR CONTENTS (ASTM E30-47)

N-3) POUR POINT (ASTM D97-66, IP15/67)

N-4) VISCOSITY (ASTM D445-72, IP71/75)

N-5) FRACTIONAL DISTILLATION

Graph of cumulative distillation yield against temperature. Five percent cuts taken for further analysis. Mass spectrometric studies of these fractions provide a detailed picture of the distribution of paraffins and of the various naphthene and aromatic groups within a crude, which is useful both for correlation and for refinery evaluation purposes.