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GEOCHEMICAL ANALYSIS OF TWO CRUDE OIL SAMPLES  
FROM WYTCH FARM, UNITED KINGDOM

by

J.M.A. Buiskool Toxopeus and J. Posthuma

Investigation 9.12.492

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1. INTRODUCTION

The purpose of geochemical typing of crude oils and rock extracts is to assess oil/oil- and oil/source rock correlation. In this context four objectives are of main interest:

1. to establish the type of source material from which certain crude oils or extracts originated.
2. to find in what type of environment a source rock has been deposited.
3. to estimate the maturity of the source material that has generated a certain oil or rock extract.
4. to determine whether or not a crude has been transformed (altered) after expulsion.

The following notes are intended as a guide to the interpretation of geochemical parameters. They are keyed to the tabulated results of the current study.

2. SYNOPSIS OF INTERPRETATION OF GEOCHEMICAL PARAMETERS

API Gravity

The API gravity scale for oils is related to its specific gravity by the following formula:

$$\text{degrees API} = \frac{141.5}{\text{S.G. at } 60^{\circ} \text{ F}} - 131.5$$

Crude oils commonly range from 10-60° API. The specific gravity is mainly determined by the maturity of the source material at the time of oil expulsion and by the extent of alteration the oil has undergone (e.g. bacterial degradation, physical or thermal transformation).

#### Extract (Ethyl Acetate)

Rock samples are crushed and powdered and subsequently extracted in a soxhlet apparatus using ethylacetate as a solvent. The extract, freed from solvent by evaporation, is used in further analyses.

#### Organic Carbon after Extraction

In the extracted rock sample the organic carbon content is determined using a LECO instrument. It is generally accepted that an organic carbon content of at least 0.5% defines the lower limit for a source rock. However, this is somewhat arbitrary, dependent on the convertibility of the organic matter type into hydrocarbons and on the expulsion capability of the source beds. In this respect only the percentage of pyrolysable organic matter is of interest.

#### Sulphur content

The sulphur content of a crude oil depends on:

1. the kerogen type (high or low sulphur) of the source rock, which is in turn related to its environment of deposition.
2. the level of organic metamorphism of the source rock at the time of expulsion.
3. the degree of transformation (bacterial or physical) of the crude.

The major part of the sulphur in crude oils is present in the heavy ends (higher boiling-point fraction). As bacterial degradation of a crude oil preferentially removes the light ends, the sulphur content of a crude is increased by mere concentration though usually to a not too significant extent. High-sulphur crudes are associated with sulphur-rich source material, deposited in strongly reducing environments (often rich in carbonates or cherts). Sulphur-rich crudes are often heavy, being expelled at a low maturity level. Low sulphur crudes are related to low sulphur source material, deposited either in non-marine environments or in marine siliciclastic sequences. Furthermore oils expelled at a high level of organic metamorphism of the source rock are always low in sulphur, regardless of their original source material.

### Porphyrins

Porphyrins are nitrogen-containing ring components often found in petroleum as nickel or vanadyl complexes. It is generally accepted that the porphyrins are derived from chlorophyll during early diagenesis. A predominance of vanadyl over nickel porphyrins is associated with a deep marine environment of deposition of the source matter, whilst nickel porphyrin predominance is linked with coastal or lagoonal waters with terrestrial influx.

### Normal-Alkane Distribution

The saturated hydrocarbons of an oil (or rock extract) are separated by elution chromatography and then analysed by temperature-programmed gas chromatography. The n-alkane distribution of an oil displayed in the chromatogram provides information on its origin, maturity and possible transformation.

The shape of the n-alkane distribution reflects the original source material. The envelope of the n-alkane distributions of marine crude oils and source rock extracts are, for instance, concave, whereas landplant-related crudes and extracts usually show a convex or even bimodal n-alkane distribution.

Sometimes there is a marked predominance of odd-numbered n-alkanes over the even ones. This odd/even predominance (expressed as a 'carbon preference index') is often used as an index of maturity. However, this can be done in only a few specific cases. Indeed a distinct odd/even predominance in the C<sub>25</sub>+ region is indicative of a landplant wax contribution in the source material while oils and extracts of marine origin do not exhibit such odd/even predominance. Biodegraded oils are characteristically deficient in n-alkanes. Severe bacterial degradation will result in a complete removal of n-alkanes and finally even of the isoprenoids (see Fig. A).

### Isoprenoid isoalkanes

Many crude oils and source-rock extracts contain a series of isoalkanes with structures based on the isoprene unit. They are believed to be derived from phytol, a hydrolysis product of chlorophyll. The most common isoprenoids in crude oil are pristane and phytane. The relative abundances of these two compounds, expressed as pristane/phytane ratio, pristane/n-C<sub>17</sub>, or phytane/n-C<sub>18</sub> is mainly an indication of the depositional environment of the source rock. High pristane/phytane and pristane/n-C<sub>17</sub> ratios are related to a swampy environment of deposition with low bacterial activity. Low ratios are expected in open aquatic conditions (marine or fresh water), where there is abundant bacterial activity.

### C<sub>7</sub> Distribution

Crude oil samples are distilled to obtain the volatile fraction boiling below 120°C. This fraction is subsequently analysed by gas chromatography to obtain a detailed distribution of all C<sub>7</sub> hydrocarbon isomers. A triangular plot of straight-chain (normal), monobranched, and polybranched C<sub>7</sub> alkanes is used to distinguish slightly bacterially degraded or transformed crudes from their unaltered counterpart (Fig. B). In a plot of n-C<sub>7</sub> alkanes - branched alkanes - naphthenes oils of similar origin form clusters, while also some information is obtained from this triangular plot about the environment of deposition of the related source rocks (see Fig. B). Note that this latter plot cannot be used for (even slightly) bacterially degraded crude oils. The relative abundances of C<sub>7</sub> alkanes, naphthenes and aromatics may be used to determine whether waterwashing in the reservoir has occurred.

### Mass spectrometric analysis

#### Parameters M1 and M2

From the mass spectra of crude oils and extracts two parameters M1 and M2 can be derived, which are very useful for oil and source rock characterisation. The positions in these triangular diagrams give information about the original source material as is indicated in Fig. C. Note that parameter M1 cannot be used for bacterially degraded crude oils.

DOM of oils

The maturity of the oil and/or extract can be calculated from mass spectrometric data. The calculated maturity is expressed in DOM (degree of organic metamorphism) units, which cover the following ranges:

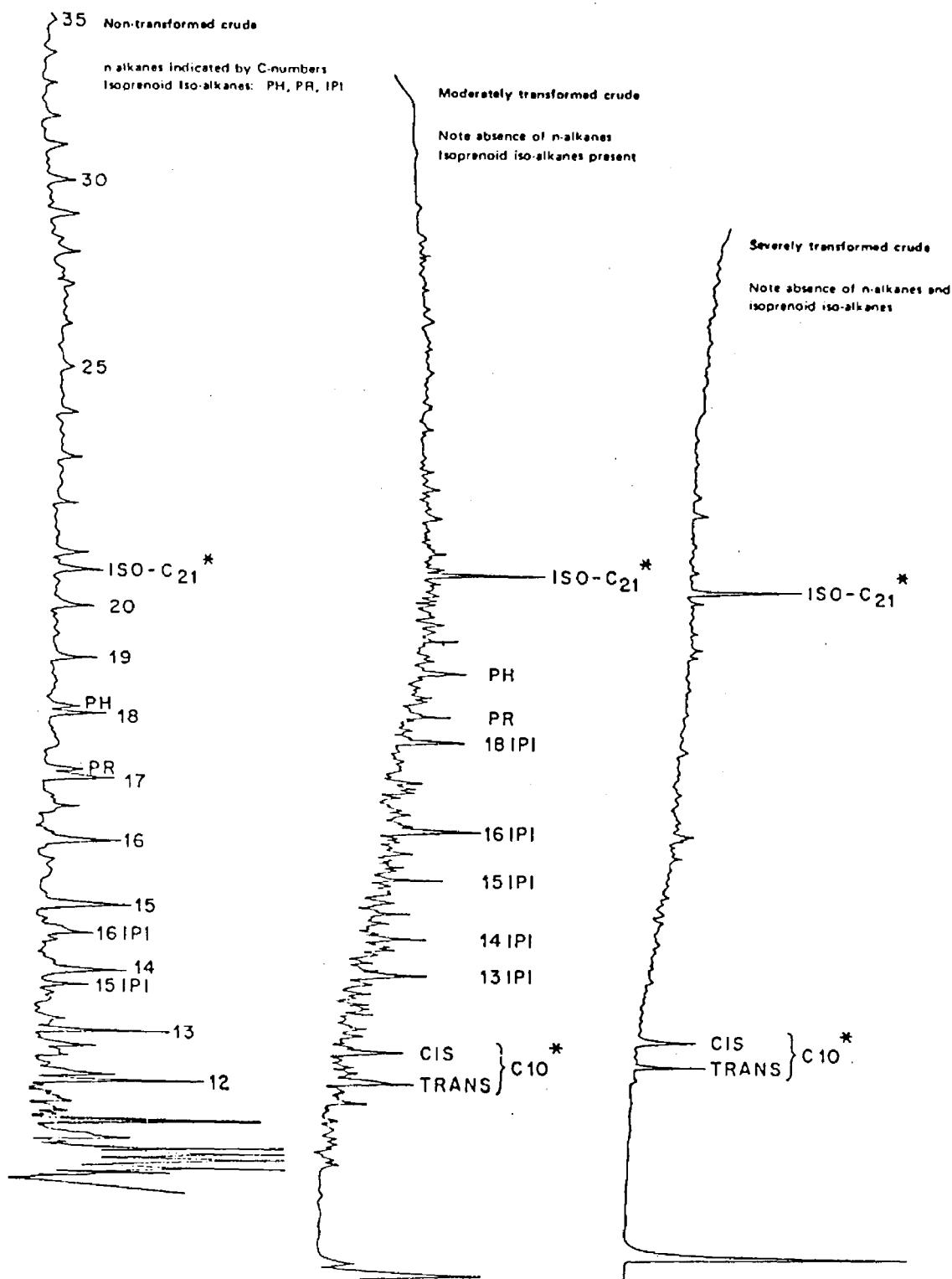
<u>DOM</u>	<u>MATURITY ZONES</u>
<60	Immature
60-75	Mature for oil generation
75-92	Mature for gas generation Post mature for oil generation
>92	Post mature for both oil and gas.

Sterane and triterpane parameters

Steranes and triterpanes are chemical fossils which can be used in geochemical typing. Combined gas chromatographic-mass spectrometric (GC-MS) analysis gives sterane and triterpane fragmentograms. These are gas chromatograms in which all the peaks are those of either steranes or triterpanes. Examples of the triterpane fragmentograms of a land-plant and a marine crude can be seen in Fig. D. Further differentiation between marine crudes can be obtained from sterane fragmentograms (see Fig. E).

From this analysis the organic matter can be classified into material derived from:

- I. resinous land-plant material
- II. mixed land-plant/S.O.M. material or algae
- IIIA reworked marine phytoplankton plus bacteria
- IIIB reworked algae plus bacteria.

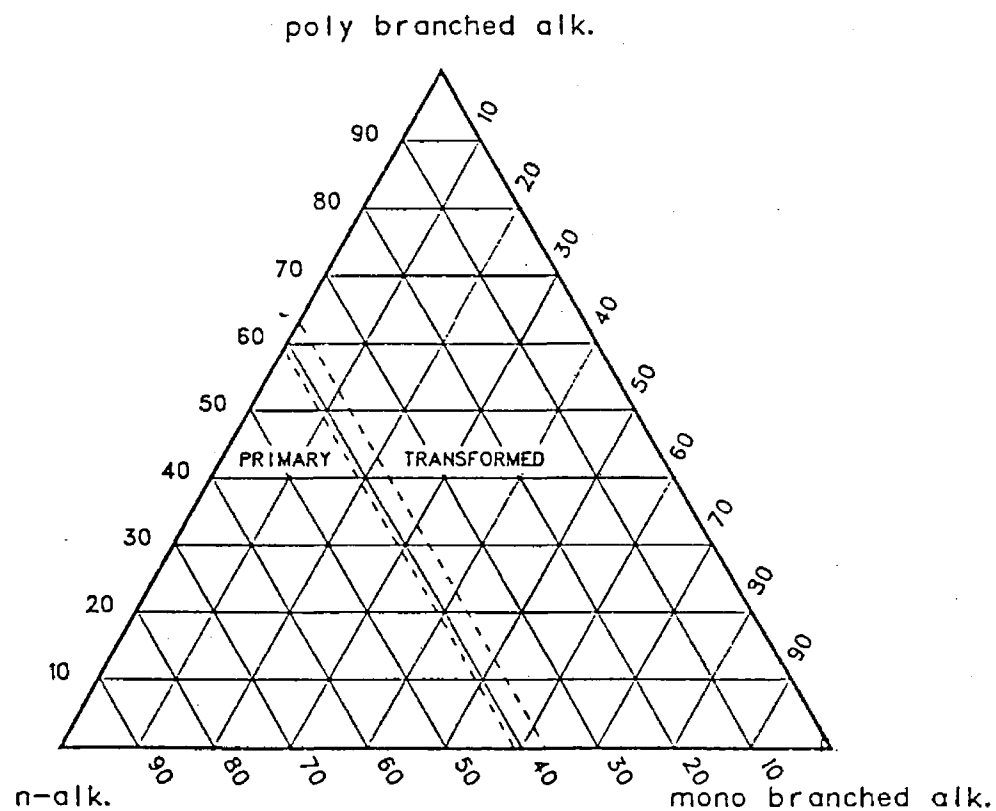


\*STANDARD COMPOUNDS ADDED FOR IDENTIFICATION

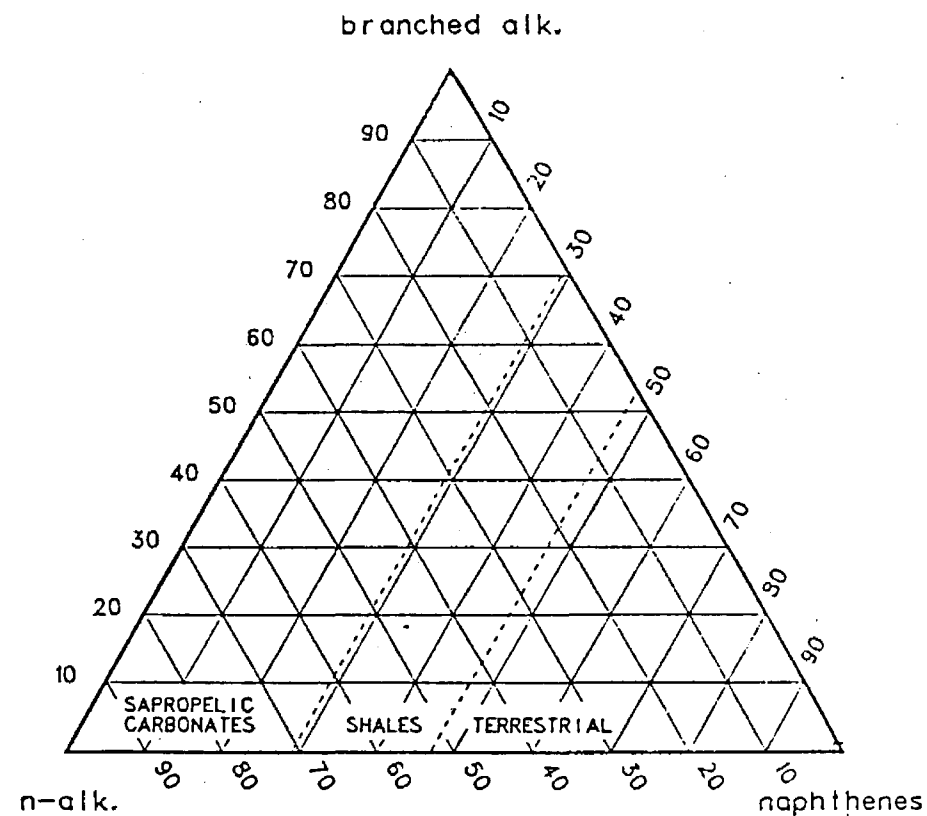
BACTERIAL DEGRADATION DISPLAYED IN GAS CHROMATOGRAMS OF SATURATED HYDROCARBONS.



# C<sub>7</sub>-ALKANE DISTRIBUTION

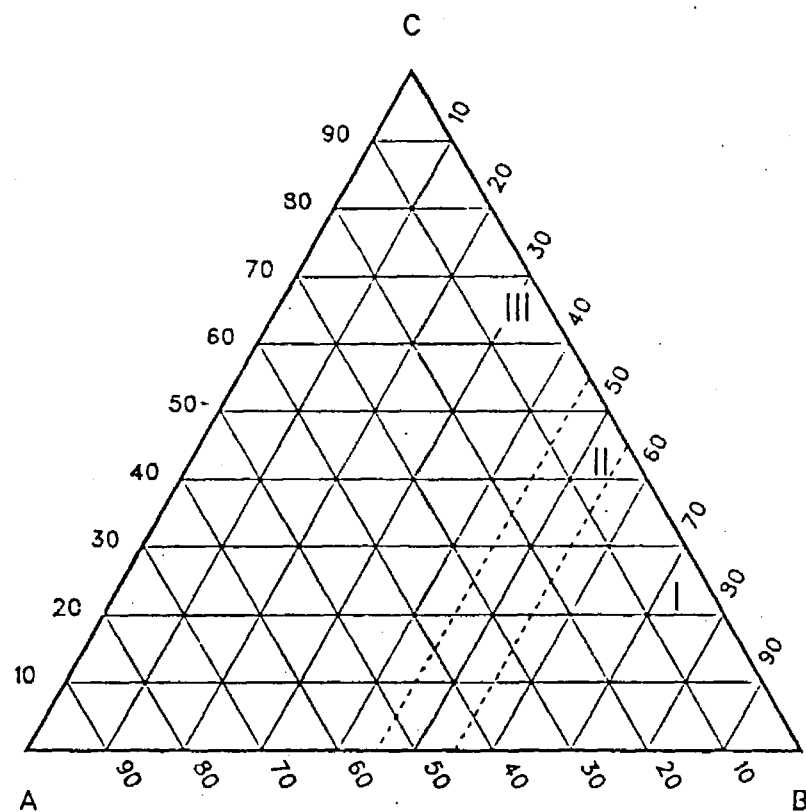


# C<sub>7</sub>-ALKANE/NAPHTHENE DISTRIBUTION

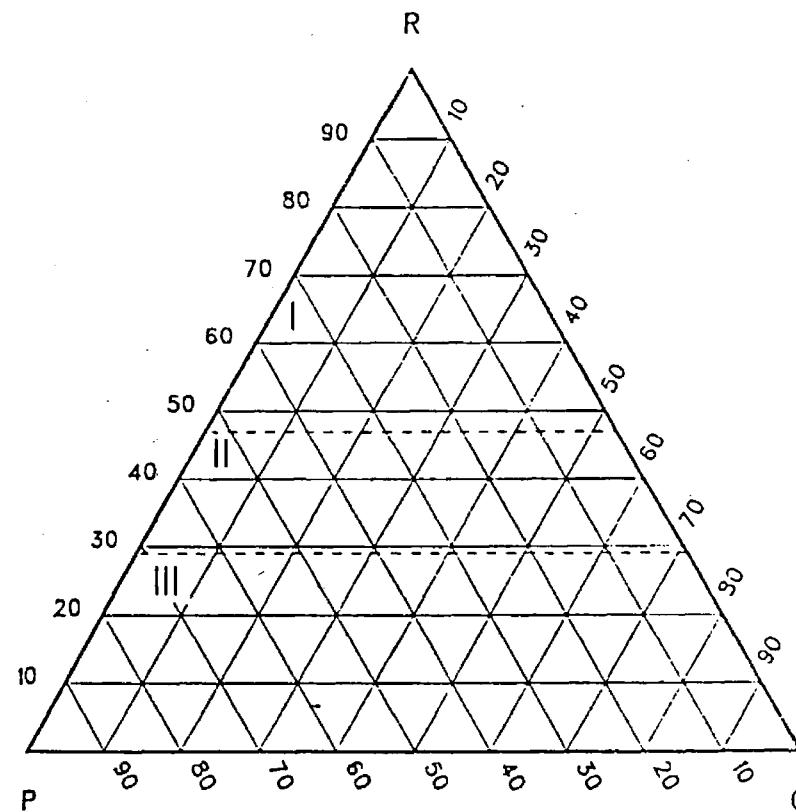


C<sub>7</sub> DISTRIBUTION FOR CHARACTERISATION OF RELATED SOURCE MATERIAL.

Parameter M1

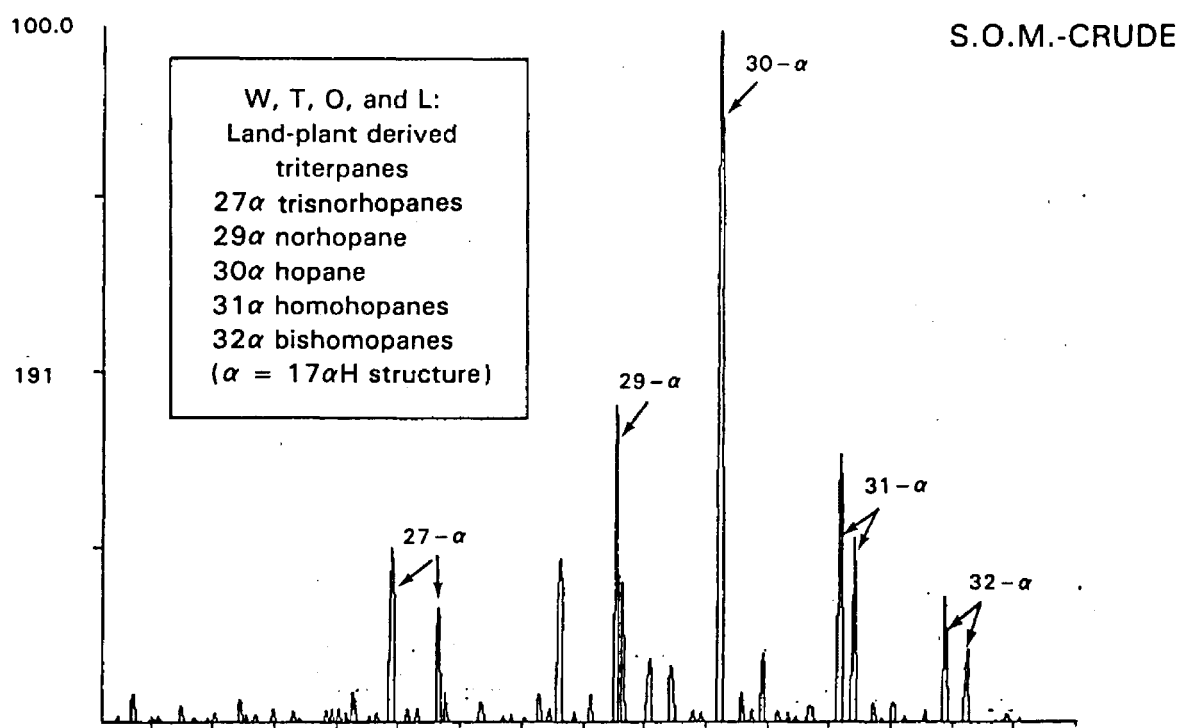
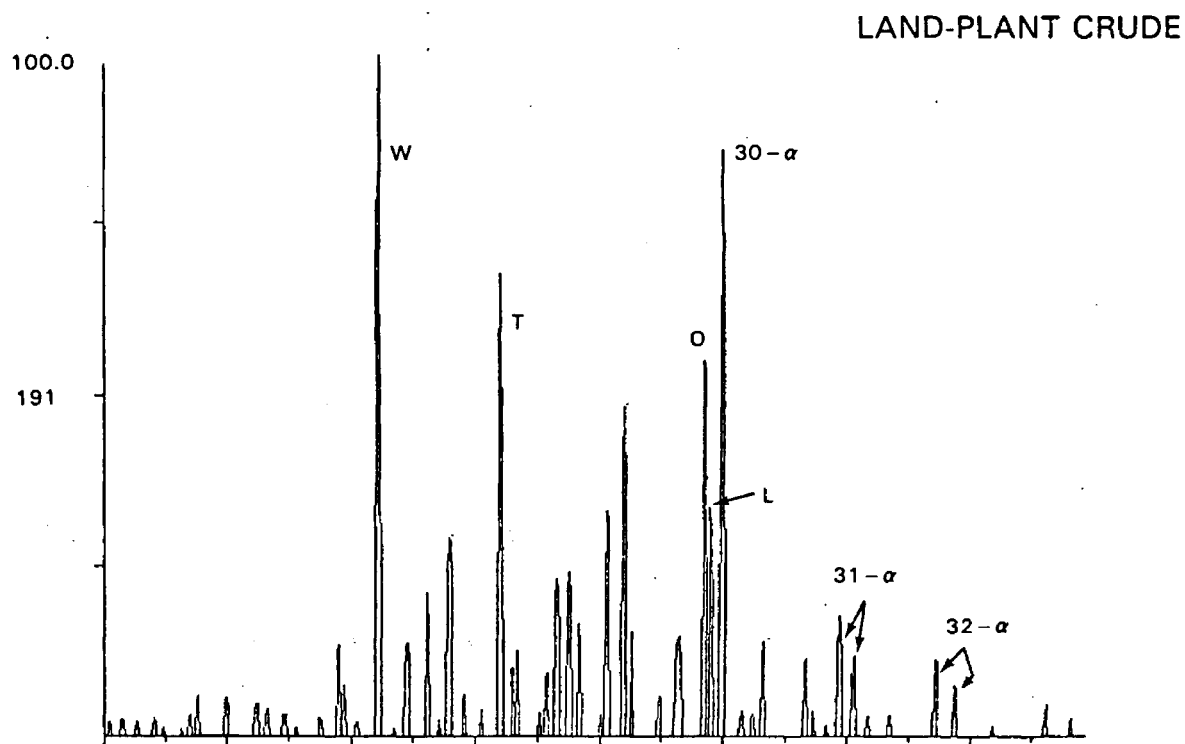


Parameter M2

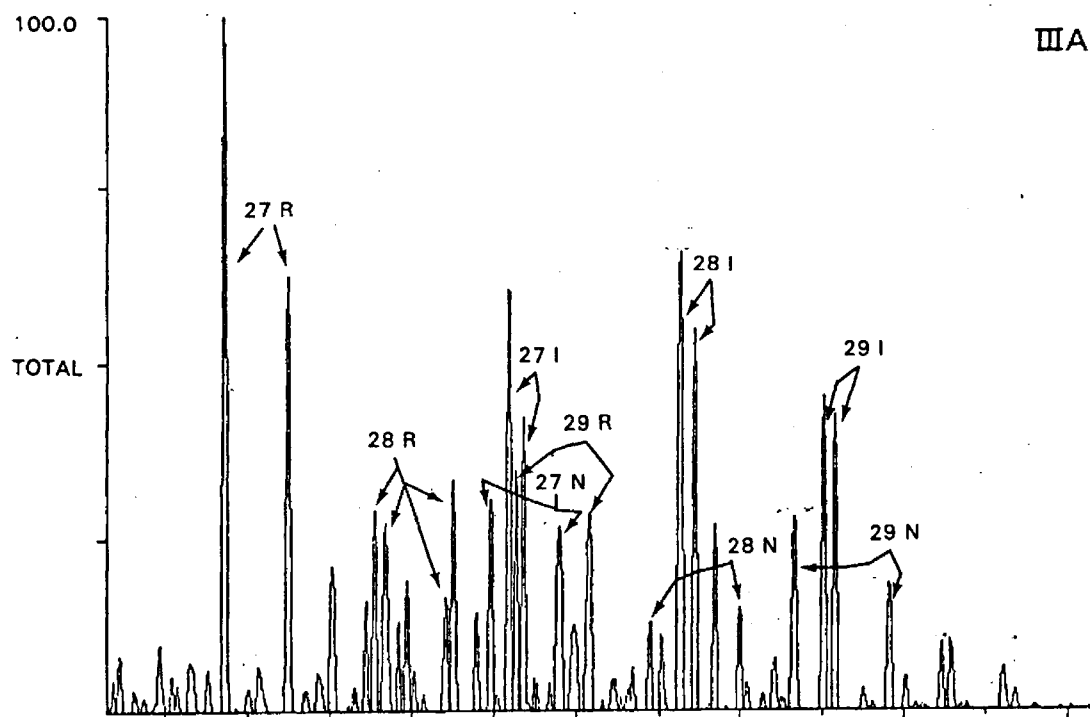
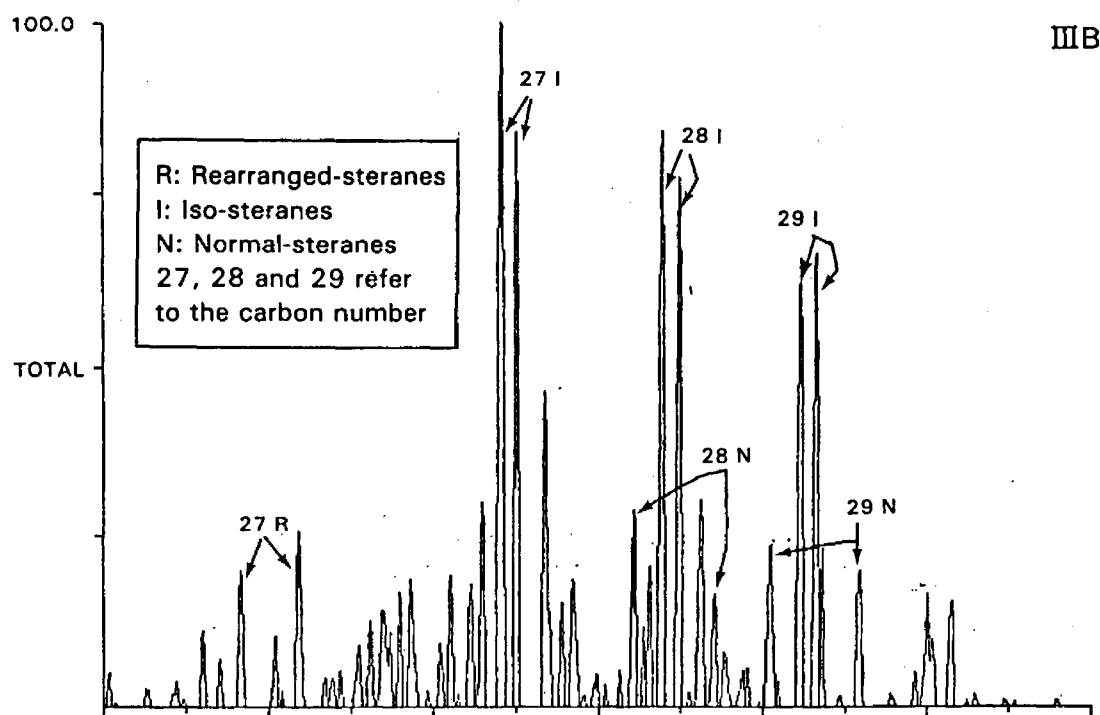


- I LANDPLANT-DERIVED CRUDES WITH SUBSTANTIAL RESIN CONTRIBUTION TO SOURCE MATTER
- II CRUDES OF MIXED ORIGIN
- III CRUDES DERIVED FROM SOM AND/OR ALGAL MATTER

PARAMETERS M1 AND M2 TO TYPE RELATED SOURCE MATERIAL.



TRITERPANE FRAGMENTOGRAMS OF CRUDES DERIVED FROM LAND-PLANT AND STRUCTURELESS ORGANIC MATERIAL RESPECTIVELY



STERANE FRAGMENTOGRAMS OF TYPE III A AND III B CRUDE OILS

### 3. RESULTS AND DISCUSSION

A geochemical analysis has been carried out on two crude oil samples from the Wytch Farm field (Triassic and Lower Jurassic - Bridport sands? - reservoirs). The results are shown in Table 1 and in Figures 1-5. The results indicate the following:

- 3.1 The gas chromatograms of the saturated hydrocarbons (Figs. 1-2) and the C<sub>7</sub>-alkane distribution (Fig. 3) indicate that the crude oils are not bacterially degraded.
- 3.2 The gas chromatograms (Figs. 1-2) show that both crudes were expelled from mature source rocks. The gross compositions and the DOM of oil values (64-68) indicate that the crude from the Lower Jurassic reservoir is less mature than the Triassic crude. The sterane/triterpane fragmentogram (Fig. 5) of the Triassic crude shows a mature character.
- 3.3 The shape of the gas chromatograms (Figs. 1-2) and the parameters M<sub>1</sub> and M<sub>2</sub> (Fig. 4) indicate that the crudes were expelled from source rocks containing structureless organic matter. Due to the low triterpane/sterane concentrations (Fig. 5) no quantitative peak identification was possible. However, the C<sub>27</sub>-C<sub>29</sub> distribution of the sterane fragmentogram indicates that the variety of SOM in the source rock was bacterially-reworked-phytoplankton.
- 3.4 The C<sub>7</sub>-alkane/naphthene distribution (Fig. 3) shows that the environment of deposition of the source rocks was shaly.
- 3.5 Geochemically both crude oils look very similar (gas chromatograms, C<sub>7</sub>-alkanes, gross compositions, parameters M<sub>1</sub> and M<sub>2</sub>, sulphur contents). However, the crude from the Lower Jurassic reservoir is less mature compared with the crude from the Triassic reservoir. Both crude oils resemble closely an average North Sea crude, probably only distinguishable by a lower sulphur content. They were most probably generated from identical source rocks.

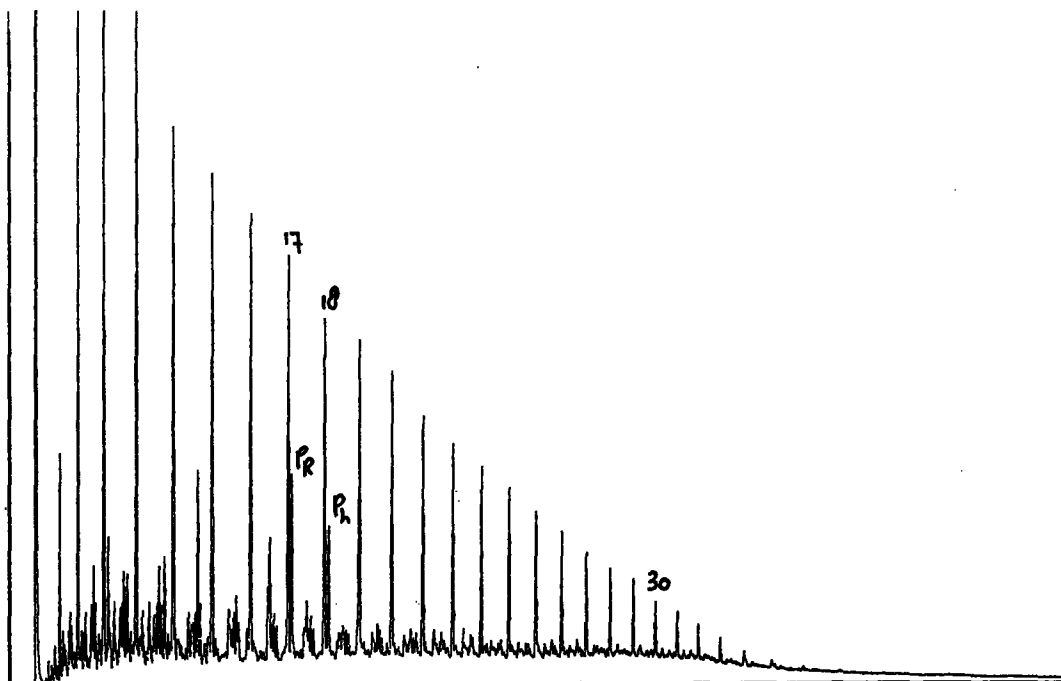
#### 4. CONCLUSIONS

Two crude oils from the Wytch Farm field (Jurassic and Triassic reservoirs) are not bacterially degraded. Both crude oils are mature, although the crude from the Jurassic reservoir shows a slightly less mature character compared with the crude from the Triassic reservoir. Both crudes were generated from shaly source rocks containing structureless organic matter of bacterially-reworked-phytoplanktonic origin. Geochemically both crudes are very similar and were most probably generated from identical source rocks. Both crudes resemble closely an average North Sea crude oil, and are probably only distinguishable by a lower sulphur content.

TABLE 1 - GEOCHEMICAL DATA OF OILS

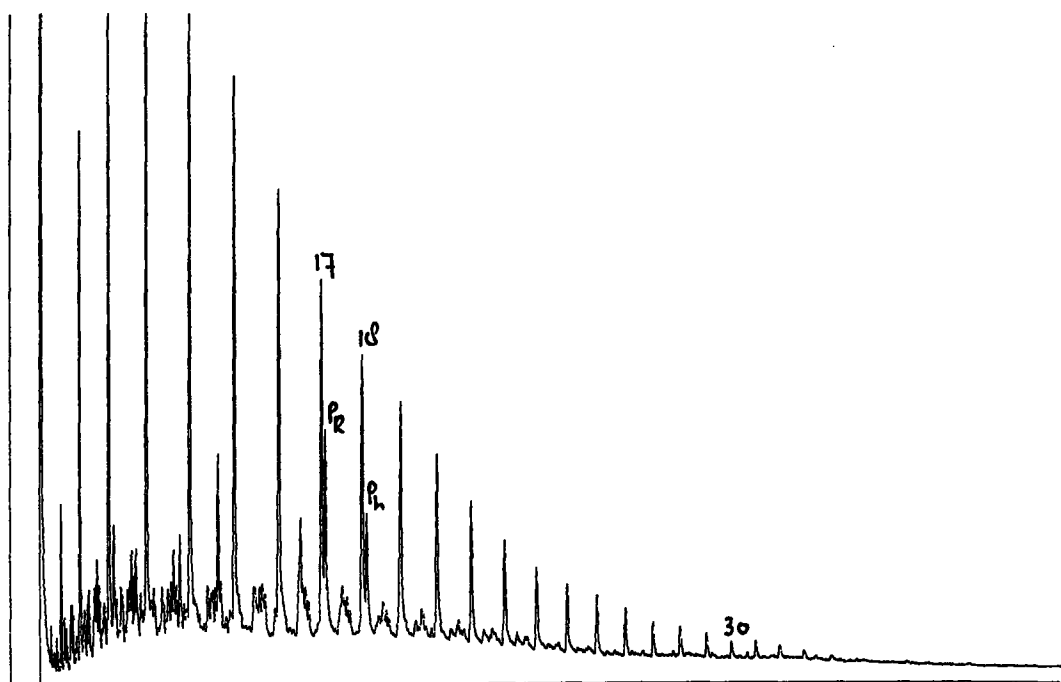
Sample	Wytch Farm* Triassic Reservoir	Wytch Farm* Lower Jurassic Bridport Sands
API	35.7	35.9
specific gravity	0.8459	0.8448
%w. boil. <120°C	10.0	13.0
% sulphur	0.07	0.10
ppm V as metals	0	0
ppm Ni as metals	2	2
pristane/phytane	1.3	1.6
pristane/nC17	0.5	0.7
phytane/nC18	0.4	0.5
C <sub>7</sub> -distribution		
C <sub>7</sub> -alkane		
nC7	49	49
monobranched	40	40
polybranched	11	11
C <sub>7</sub> -alk/naphthene		
nC7	30	28
naphthenes	39	42
branched alkanes	31	30
C <sub>7</sub> -alk/naphth/arom		
nC7	57	55
naphthenes	37	40
aromatics	6	5
Parameter M <sub>1</sub>		
A	58	53
B	29	33
C	13	14
Parameter M <sub>2</sub>		
P	28	24
Q	46	50
R	26	26
DOM of oil	68	64
% asphaltenes	0.2	0.2
% saturates**	52	43
% aromatics	11	20
% heterocompounds	9	6
% rest	28	31
δ <sup>13</sup> C <sup>o</sup> /‰	-29.8	-28.6

\*\* determined by column chromatography



GAS CHROMATOGRAM OF SATURATED HYDROCARBONS

FIG. 1. UNITED KINGDOM WYTH FARM Triassic reservoir

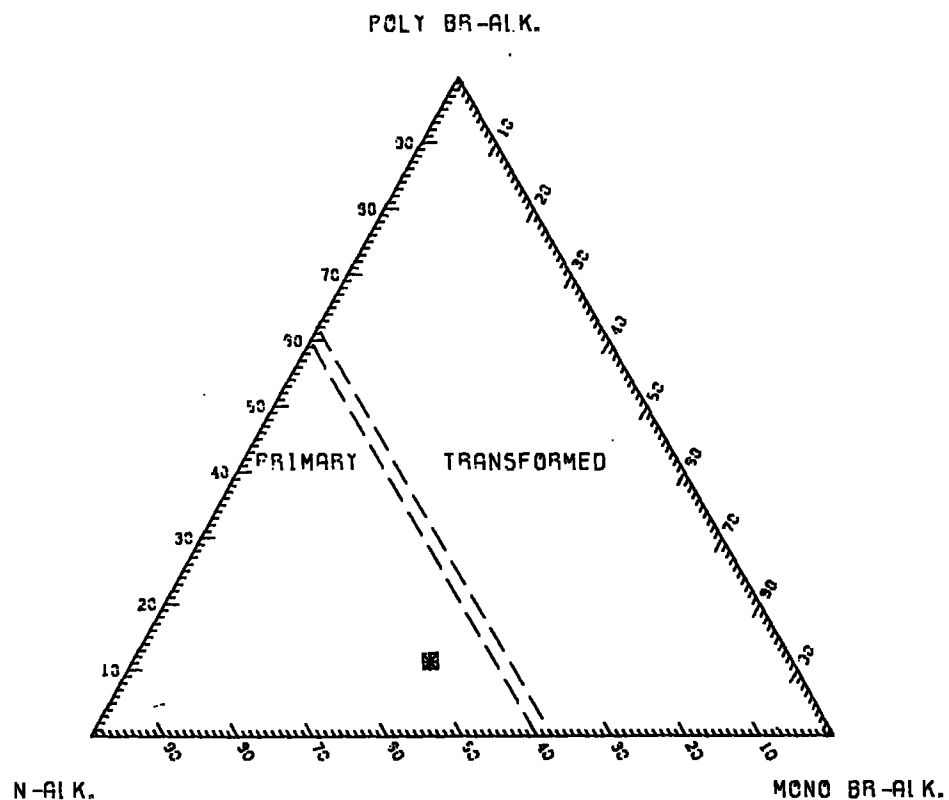


GAS CHROMATOGRAM OF SATURATED HYDROCARBONS

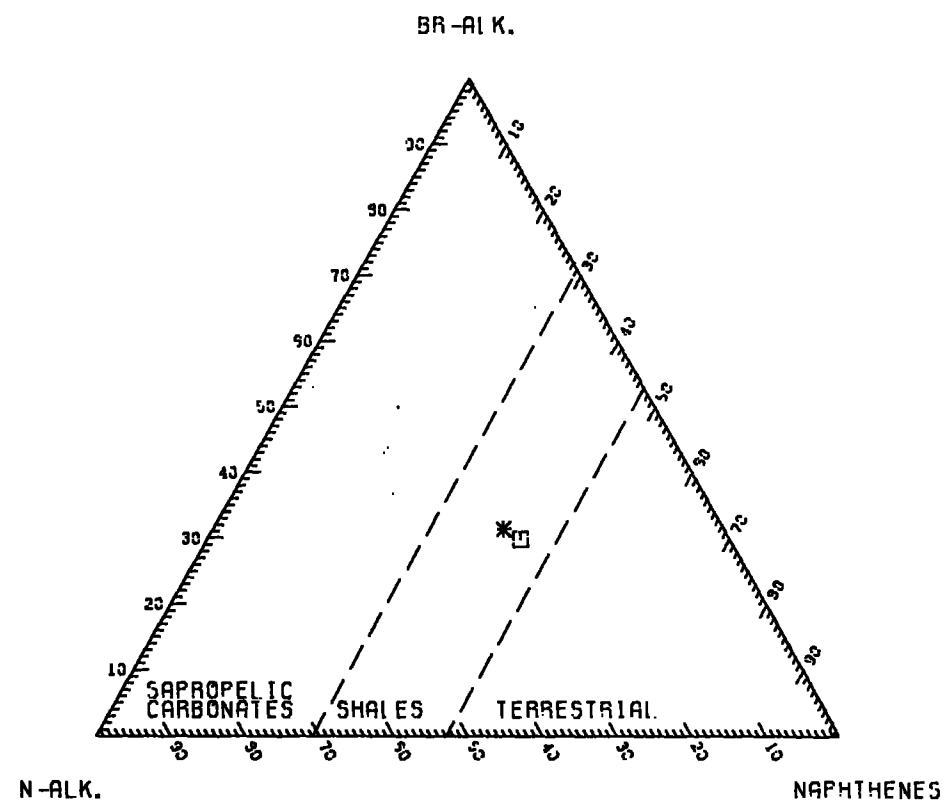
FIG. 2. UNITED KINGDOM WYTH FARM Jurassic reservoir



# C7-ALKANE DISTRIBUTION

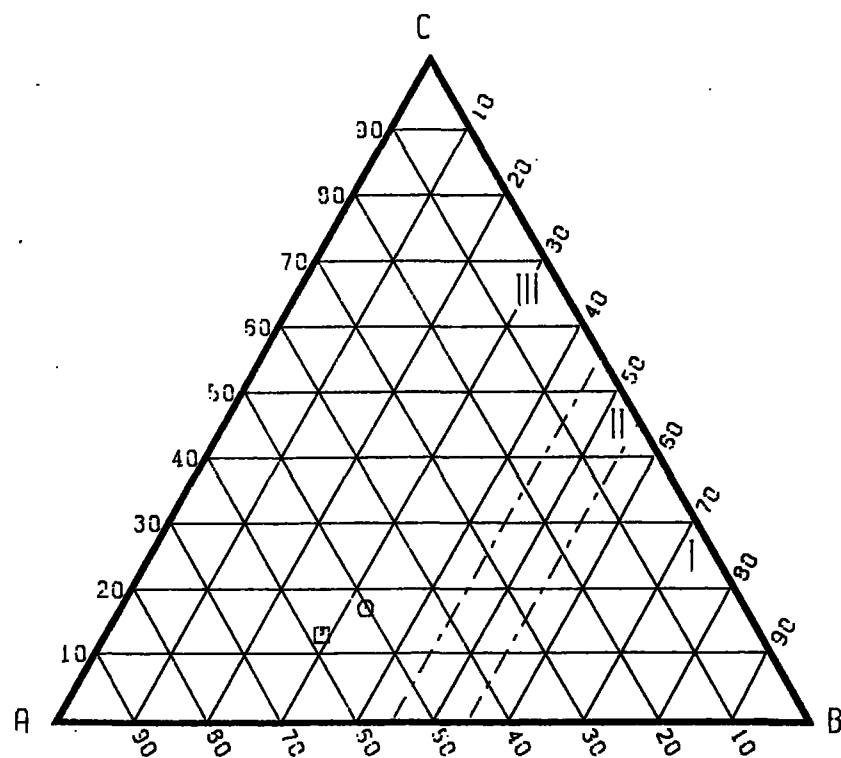


# C7-ALKANE/NAPHTHENE DISTRIBUTION

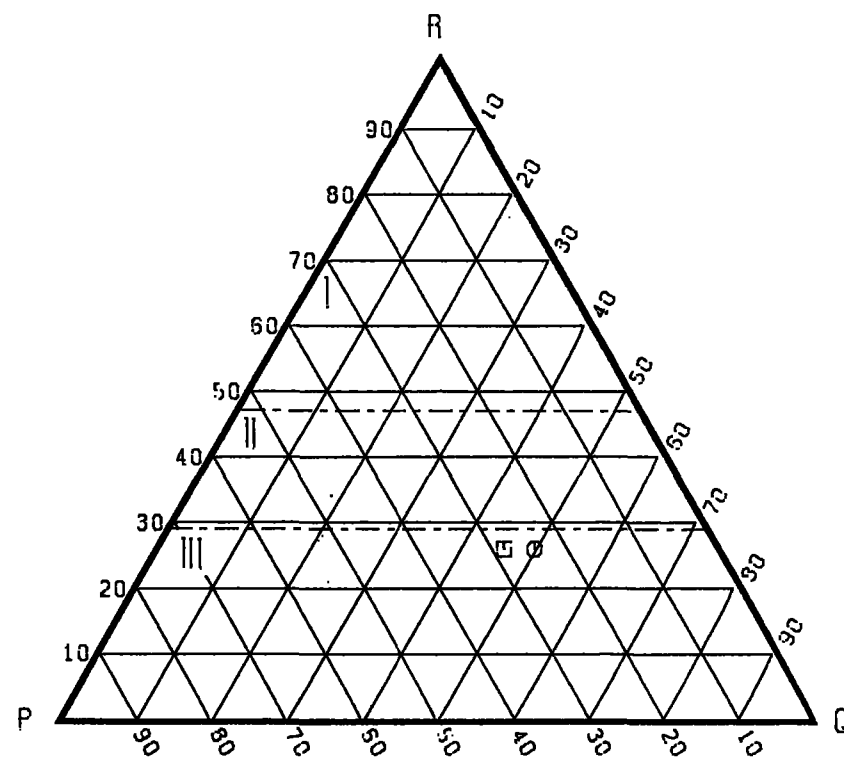


COUNTRY	WELL/OUTCROP	DEPTH/ SAMPLE NR.	
* UNITED KINGDOM	WITCH FARM	UNKNOWN	Triassic reservoir
□ UNITED KINGDOM	WITCH FARM	UNKNOWN	Jurassic reservoir

PARAMETER M1



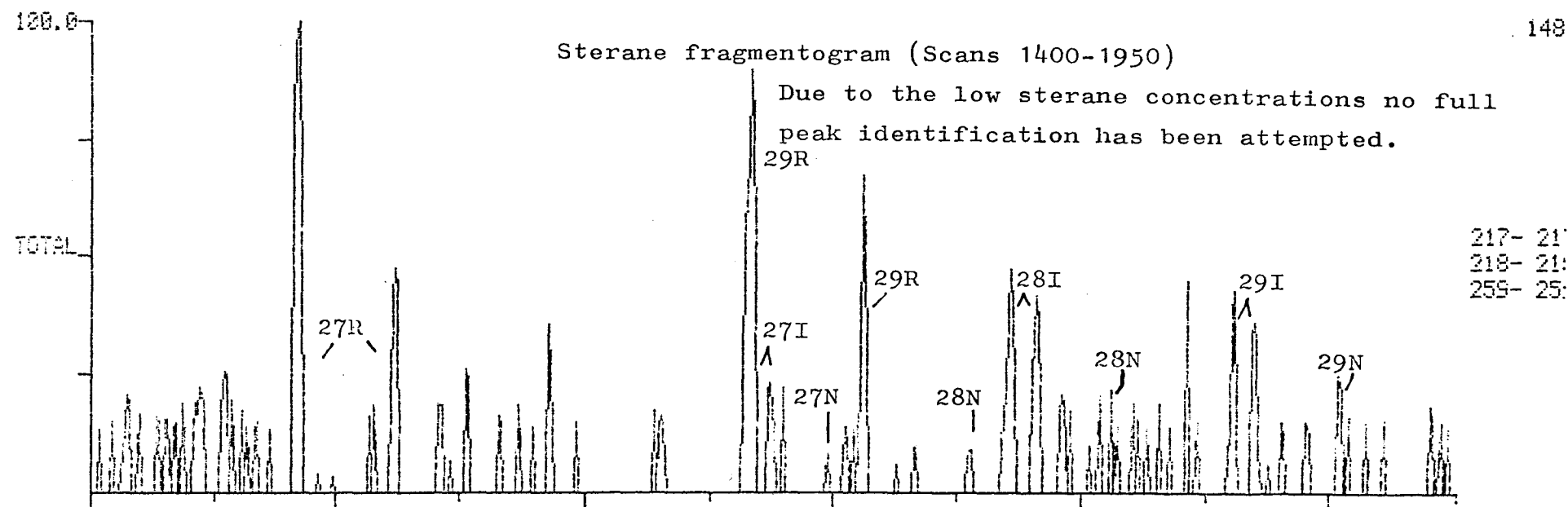
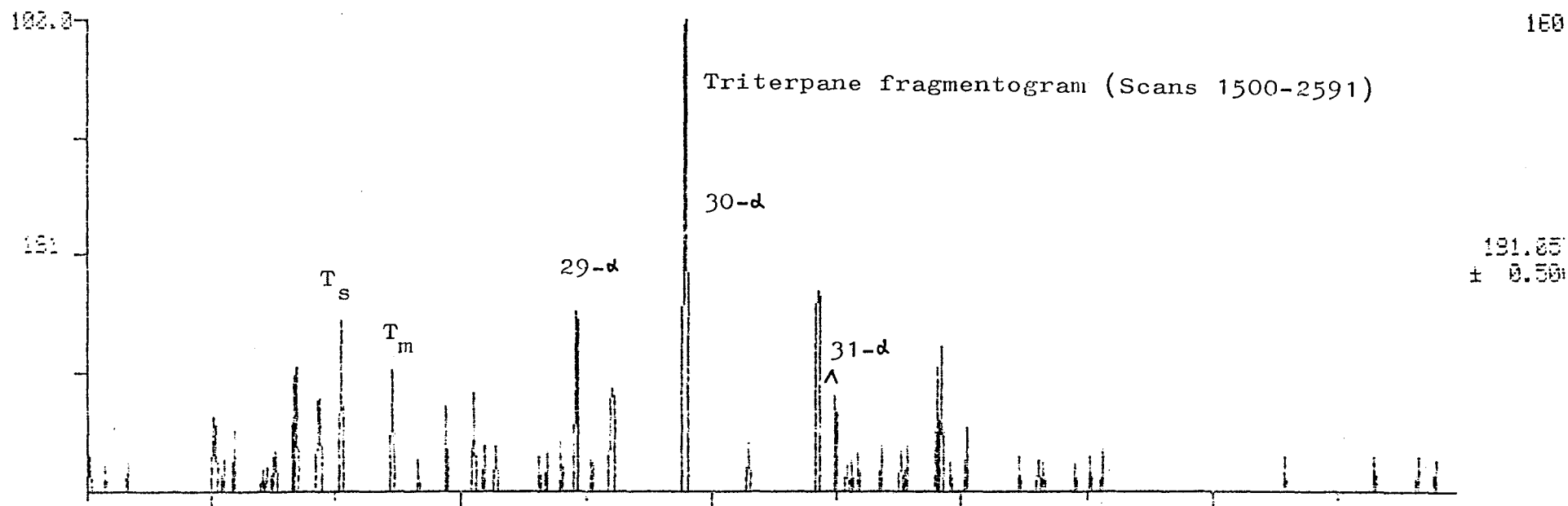
PARAMETER M2



- I LANDPLANT-DERIVED CRUDES WITH SUBSTANTIAL RESIN CONTRIBUTION TO SOURCE MATTER
- II CRUDES OF MIXED ORIGIN
- III CRUDES DERIVED FROM SOM AND/OR ALGAL MATTER

LEGEND	
□ - WITCH FARM	Triassic reservoir
○ - WITCH FARM	Jurassic reservoir

FIG. 5. GC-MS analysis Wythch Farm Triassic reservoir.



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