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# GEOCHEMICAL ANALYSIS OF A CORE FROM WELL 206/5-1 AND OF AN OIL FROM WELL 206/2-1, NORTH SEA

by

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Investigation 9.12.412

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The extract of a core sample from well 206/5-1 contains mature migrated hydrocarbons derived originally from a source rock, the organic matter of which consisted mainly of SOM. There are also indications that this core may contain some tar-like material which may be equivalent to the traces of 'dead oil' reported to be present in the sample. The migrated material differs from the Claire crude oil from well 206/8-1a.

An oil sample and the extract of a mud from well 206/2-1 both resemble diesel oil.

# GEOCHEMICAL NALAYSIS OF A CORE FROM WELL 206/5-1 AND OF AN OIL FROM WELL 206/2-1, NORTH SEA

## 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$^{\circ}$ 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 $C_{25+}$ 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/pytane ratio, pristane/n-$C_{17}$, or phytane/n-$C_{18}$ is mainly an indication of the depositional environment of the source rock. High pristane/phytane and pristane/n-$C_{17}$ ratios are related to a swampy environement of deposition with low bacterial activity. Low ratios are expected in open aquatic conditions (marine or fresh water), where there is abundant bacterial activity.

## $C_7$ 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 $C_7$ hydrocarbon isomers. A triangular plot of straight-chain (normal), monobranched, and polybranched $C_7$ alkanes is used to distinguish slightly bacterially degraded or transformed crudes from their unaltered counterpart (Fig. B). In a plot of n-$C_7$ 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 $C_7$ 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:

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

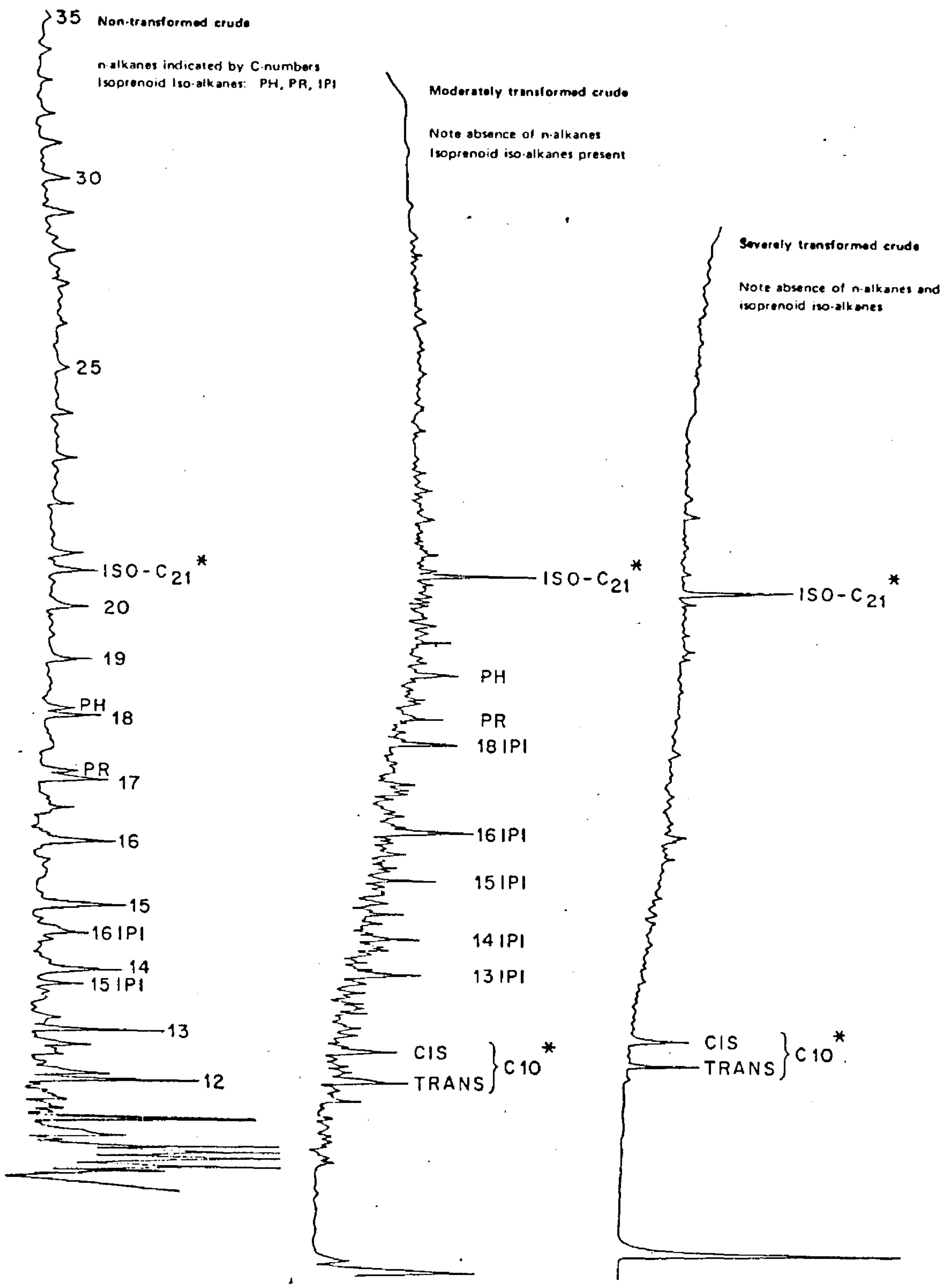
## Sterane and triterpane parameters

Steranes and triterpanes are chemical fossils which can be used in geochemical typing. Combined gas chromatographic-mass spectrometric analysis (GC-MS) of crude oils and rock extracts results in 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.

Draw. no. 25207




*STANDARD COMPOUNDS ADDED FOR IDENTIFICATION

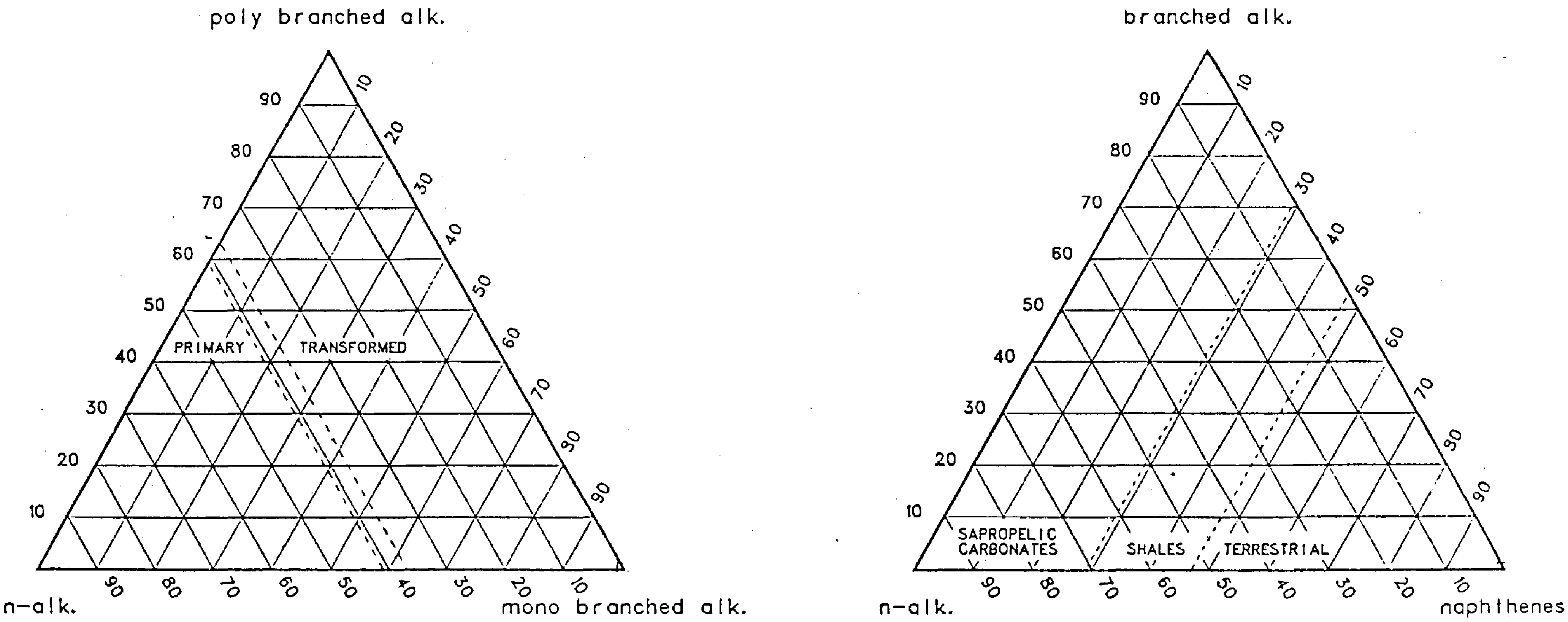
BACTERIAL DEGRADATION DISPLAYED IN GAS CHROMATOGRAMS OF SATURATED HYDROCARBONS.

FIG: A

Draw. no. 25208

## $C_7$-ALKANE DISTRIBUTION

## $C_7$-ALKANE/NAPHTHENE DISTRIBUTION




**$C_7$ DISTRIBUTION FOR CHARACTERISATION OF RELATED SOURCE MATERIAL.**

FIG: B

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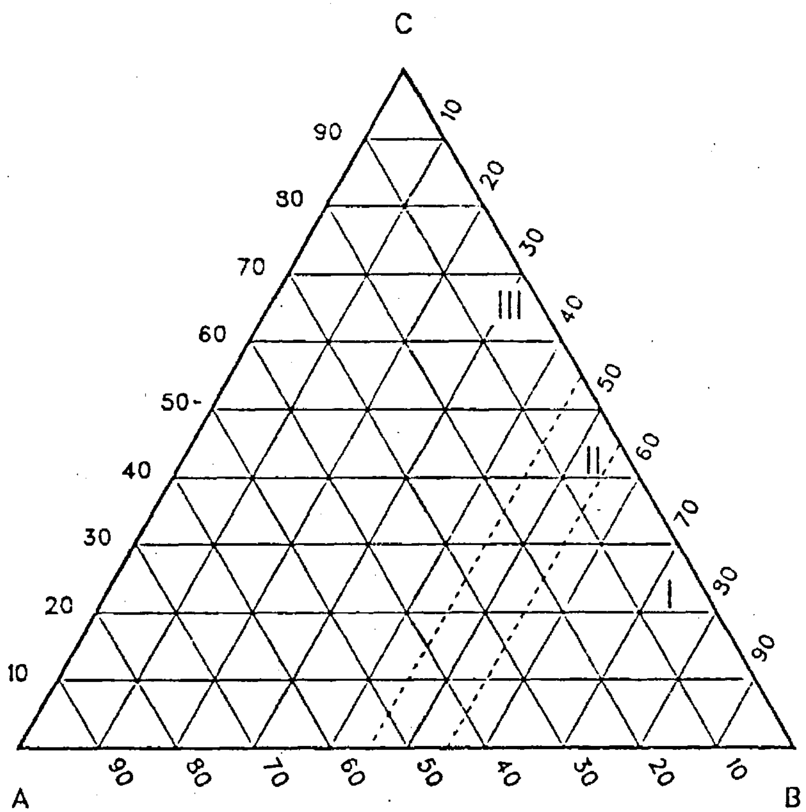
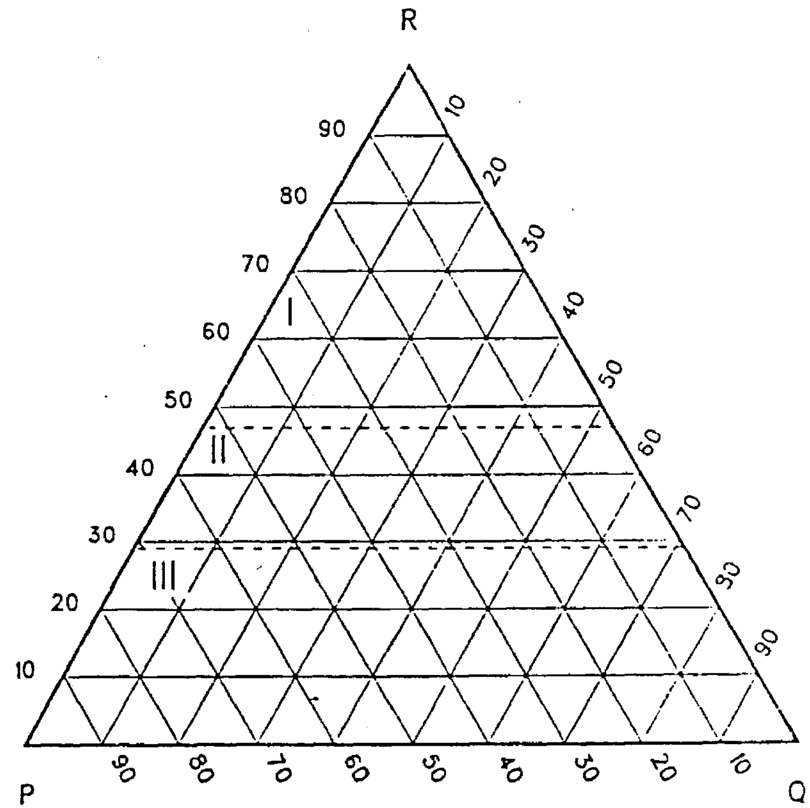
Parameter M1




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.**

FIG C

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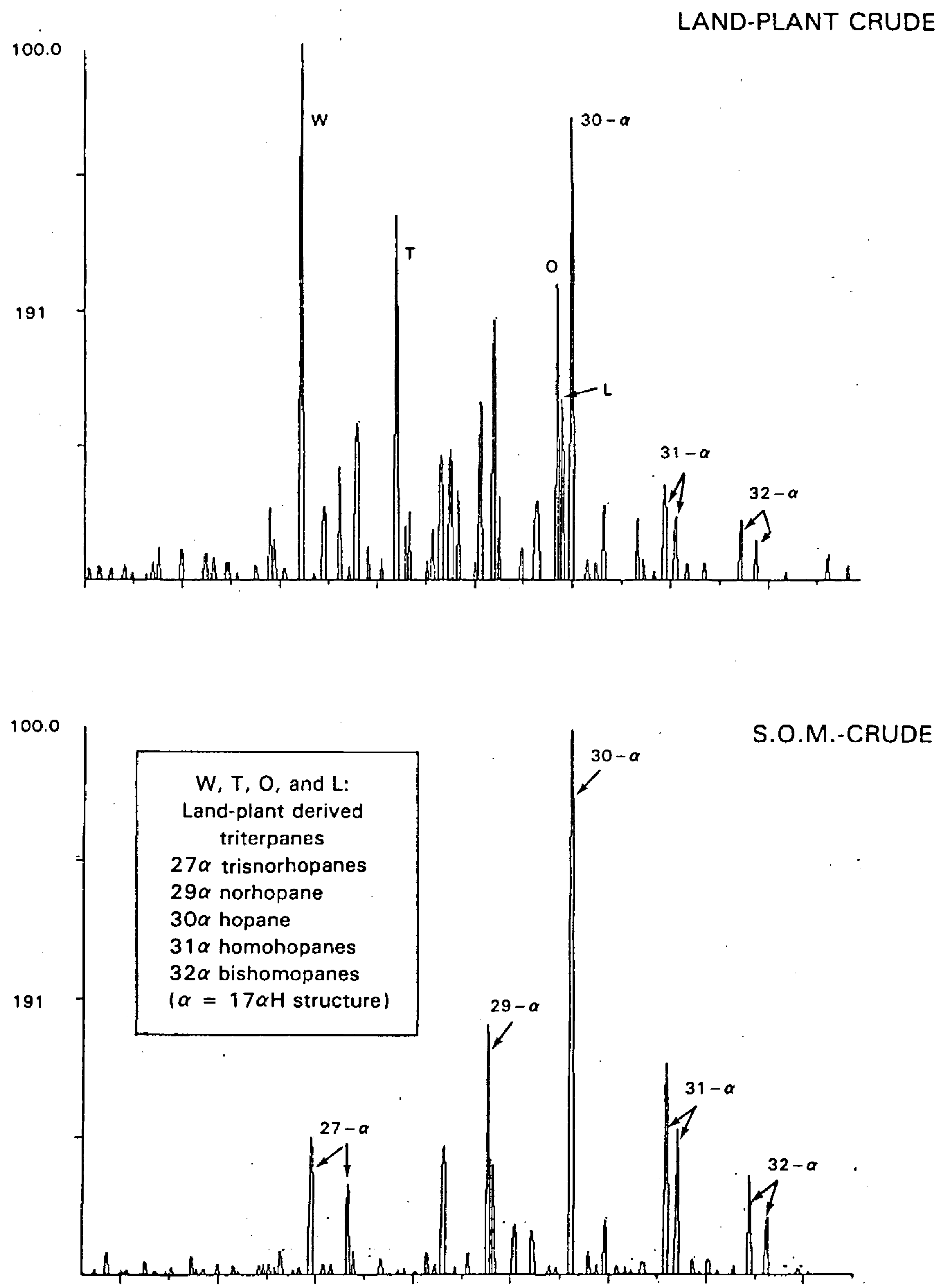
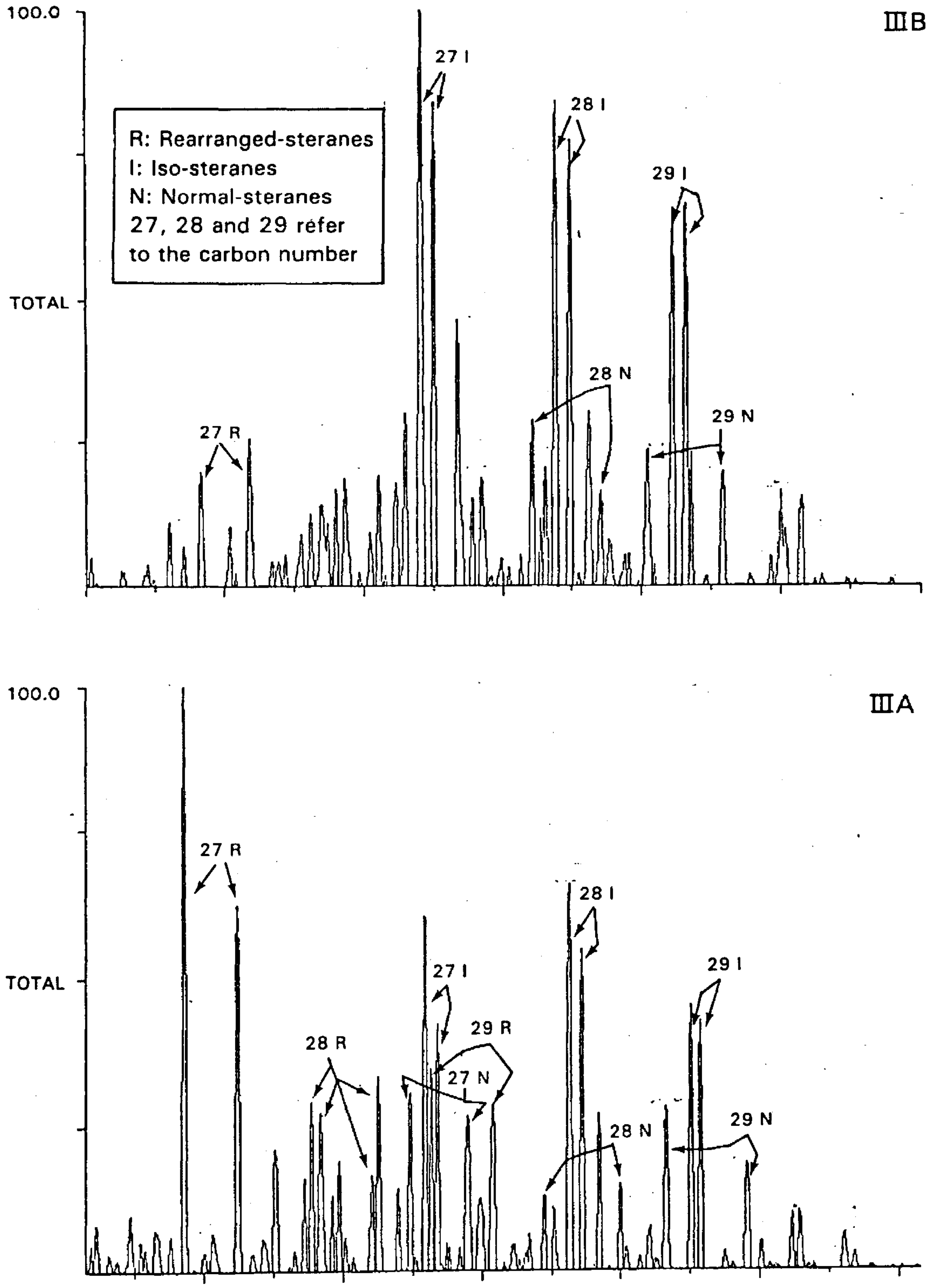



**TRITERPANE FRAGMENTOGRAMS OF CRUDES DERIVED FROM LAND-PLANT AND STRUCTURELESS ORGANIC MATERIAL RESPECIVELY**

FIG. D




STERANE FRAGMENTOGRAMS OF TYPE IIIA AND IIIB CRUDE OILS

FIG. E

## 1. RESULTS AND DISCUSSION

Geochemical analysis of a core (number 4) at depth 12799-12805 ft from well 206/5-1 in the North Sea in which traces of 'dead oil' were reported has been carried out. Also analysed is a sample of presumed diesel oil from the mud of well 206/2-1 and an extract of the mud itself. The results are reported in Table 1 and Figures 1-5.

### 1.1. Core 4, well 206/5-1, 12799-12805 ft

The content of extractable matter in the sample is extremely small (0.02% wt). The extract/carbon ratio (0.2) indicates that the extracted material contains migrated hydrocarbons.

The general shape of the gas chromatogram of the saturated hydrocarbons (Fig. 1), the DOM of oil (67) and the sterane fragmentogram (Fig. 5) all indicate that the migrated material is mature.

The shape of the gas chromatogram indicates that the migrated material was originally derived from a source rock whose organic matter consisted of SOM. The M2 distribution (Fig. 4) confirms derivation from an SOM containing source rock.

The sterane fragmentogram with its $C_{27}$–$C_{29}$ distribution suggests that the variety of SOM is bacterially reworked marine phytoplankton.

Although there are undoubtedly migrated hydrocarbons present in the sample, the rather high sulphur content (3.1%) and the large content of hetero-compounds in the extract (46%) suggests that some heavy, tar-like material may also be present. In view of the small quantities involved this is most likely material left behind by the migrating oil and may be equivalent to the traces of 'dead oil' reported to be present in the sample.

The migrated material is unlike the Claire crude oil (206/8-1a) whose analysis has been reported in RKER.80.010. Firstly, the gas chromatograms of the saturated hydrocarbons of the migrated material (206/5-1) and the Claire crude oil show some dissimilarities. Secondly, the Claire sample is a heavy, rather low-DOM expelled crude and this characteristic is not reflected in the migrated material.

1.2 Oil and mud extract of well 206/2-1

The gas chromatograms of the oil sample from well 206/2-1 (presumed to be a diesel oil) and an extract of the mud from the same well are shown in Figs. 2 and 3. These similar gas chromatograms (which are very alike those of diesel oils), the API gravity of the oil (38), its low sulphur content (0.3%) and its high content of saturates (66%) confirms that the oil and extract of the mud are identical to a diesel oil.

## 2. CONCLUSIONS

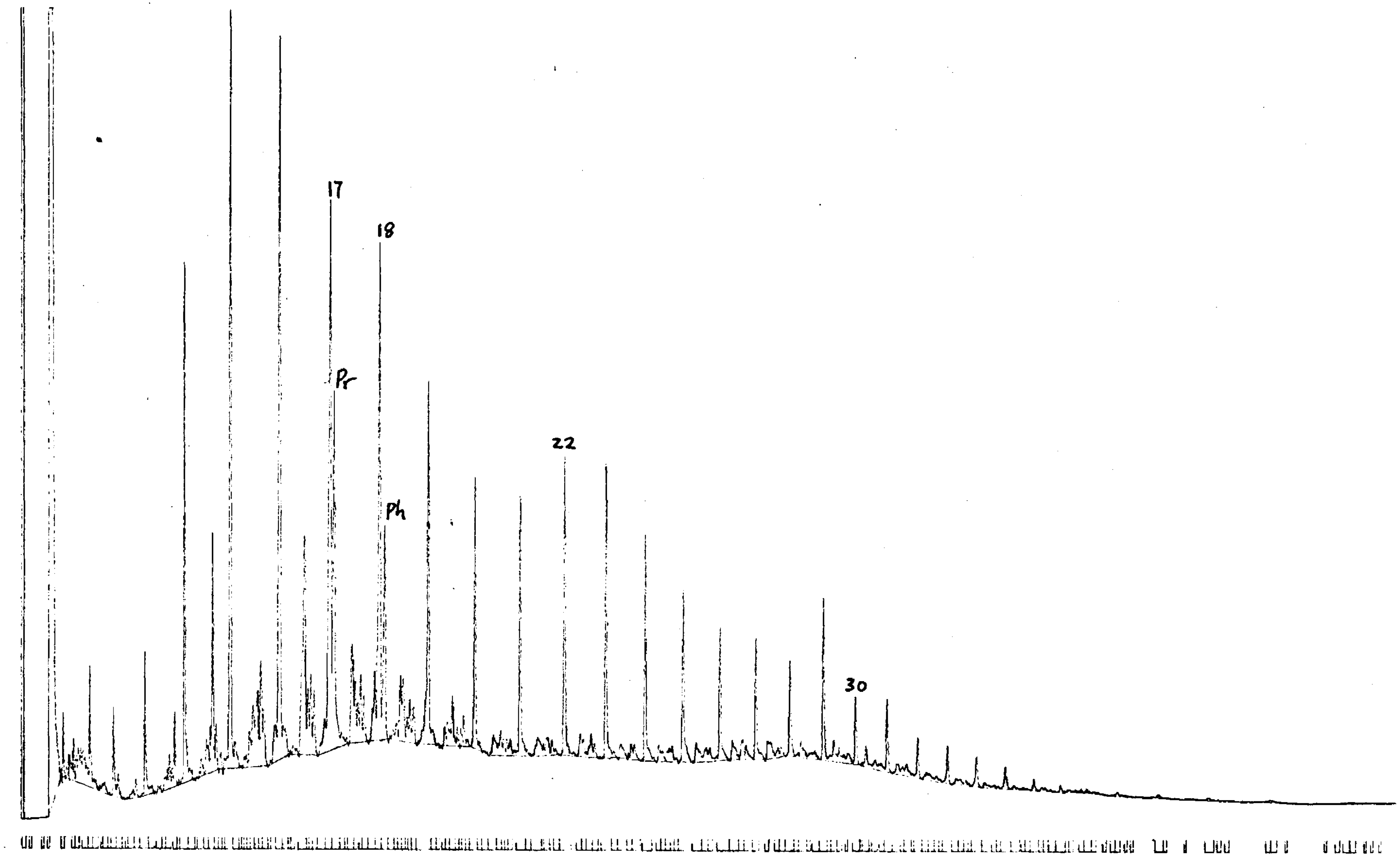
The extract of a core sample from well 206/5-1 contains mature migrated hydrocarbons derived originally from a source rock, the organic matter of which consisted mainly of SOM. There are also indications that this core may contain some tar-like material which may be equivalent to the traces of 'dead oil' reported to be present in the sample. The migrated material differs from the Claire crude oil from well 206/8-1a.

An oil sample and the extract of a mud from well 206/2-1 both resemble diesel oil.

Table 1 Geochemical data of oils and extracts

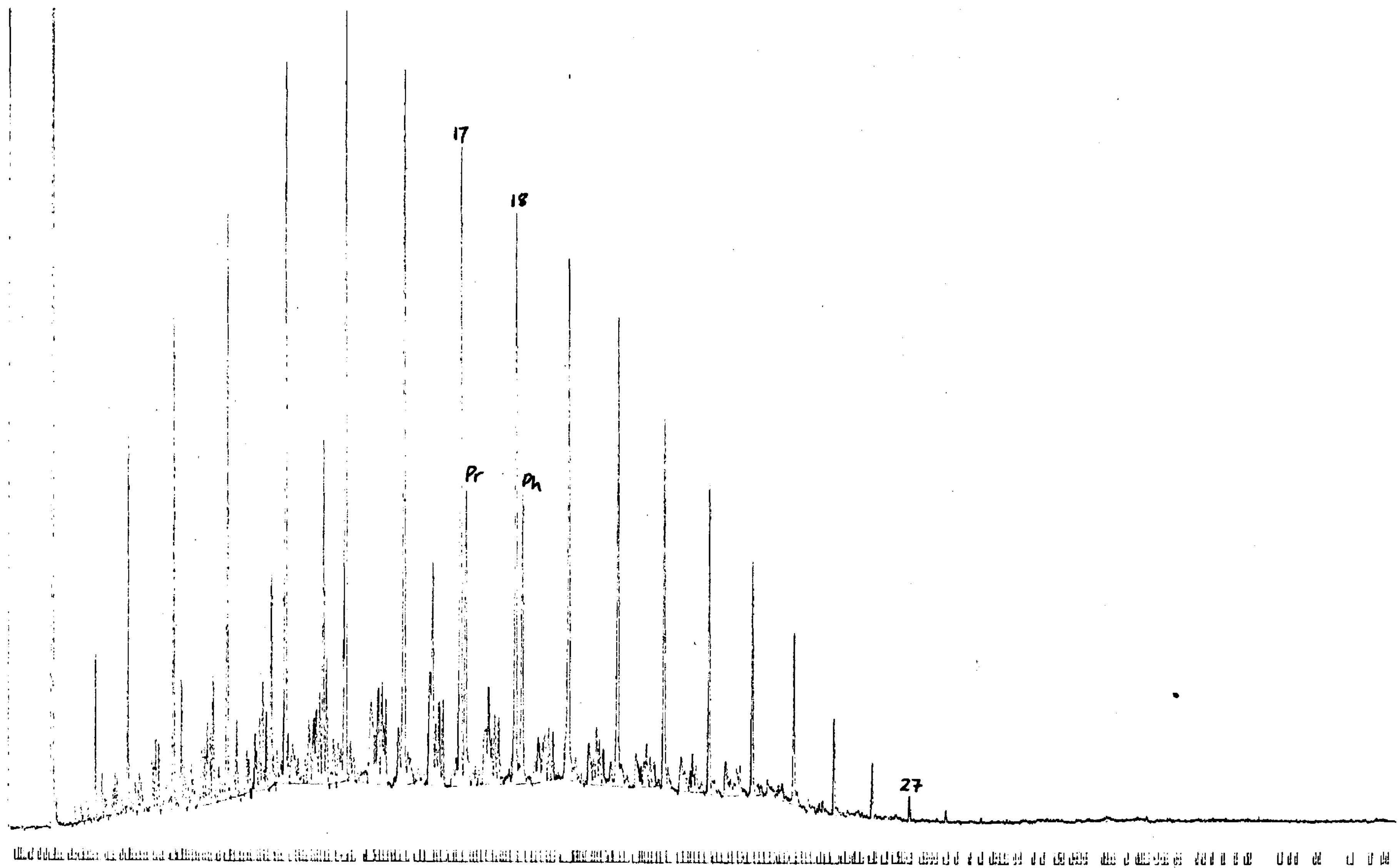
| Sample | Well 206/5-1 Core 4 12799-12805 ft | Well 206/2-1 Oil | Well 206/2-1 Chloroform extract of mud sample |
|---|---|---|---|
| % ethyl acetate extract | 0.02 | | |
| % carbon after extraction | 0.1 | | |
| API | | 37.9 | |
| Specific gravity | | 0.8351 | |
| % sulphur | 3.1 | 0.3 | 0.7 |
| Pristane/phytane | 1.9 | 1.0 | 0.9 |
| Pristane /n-$C_{17}$ | 0.6 | 0.5 | 0.4 |
| Phytane/n-$C_{18}$ | 0.4 | 0.5 | 0.5 |
| $M_1$ distribution | | | |
| A | - | 51 | |
| B | - | 35 | |
| C | - | 14 | |
| $M_2$ distribution | | | |
| P | 24 | 32 | |
| Q | 47 | 44 | |
| R | 29 | 24 | |
| 'DOM of oil' | 67 | 69 | |
| % saturates | 13 | 66 | |
| % aromatics | 41 | 23 | |
| % heterocompounds | 46 | 11 | |
| Extract/carbon | 0.20 | | |

FIG 1




GAS CHROMATOGRAM OF SATURATED HYDROCARBONS

206/5-1, CORE-4 12799-12805 FT




GAS CHROMATOGRAM OF SATURATED HYDROCARBONS

U.K. 206/2-1 OIL

FIG 2

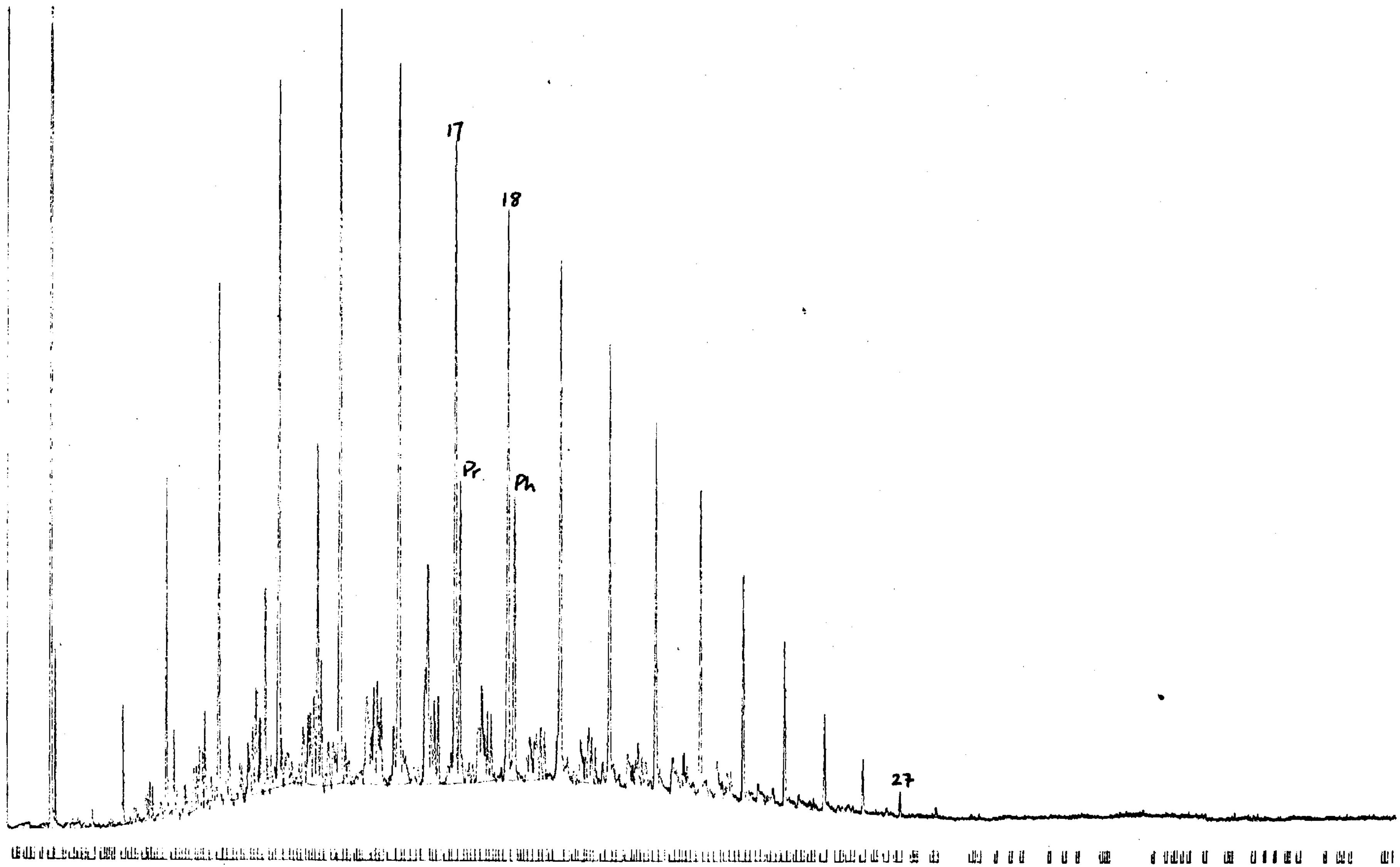
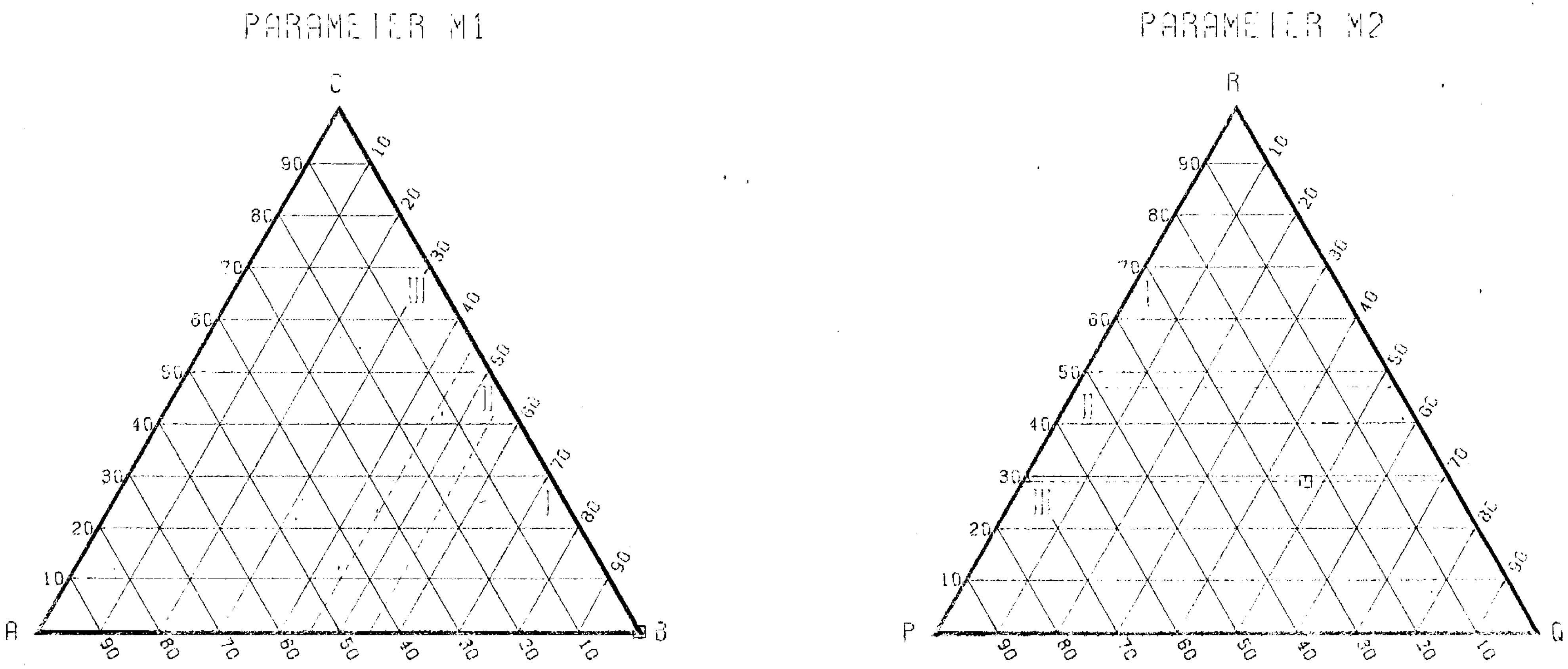



FIG 3

GAS CHROMATOGRAM OF SATURATED HYDROCARBONS

U.K. 206/2-1 (CHCL3 EXTRACT)



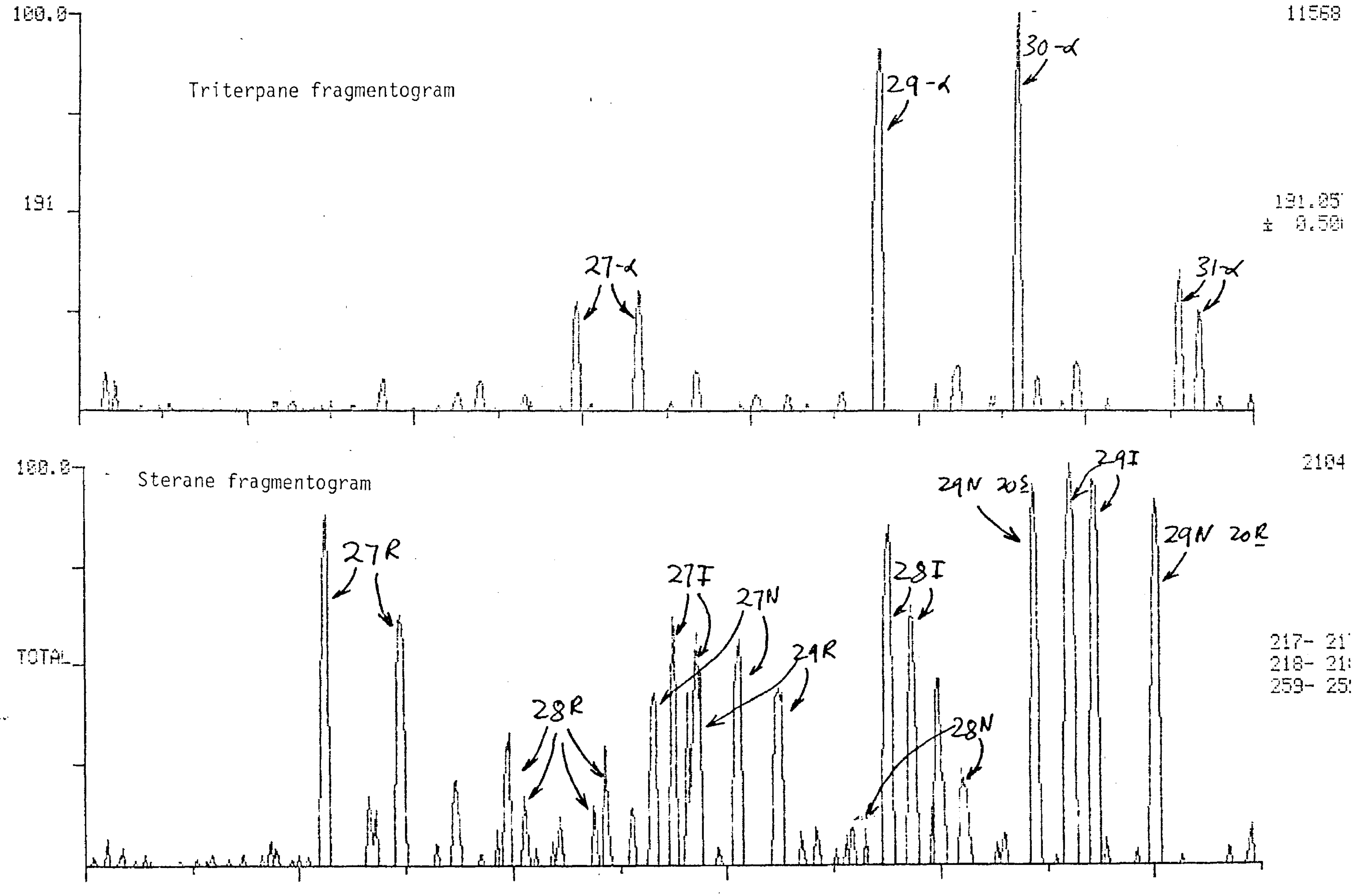

I LANDPLANT-DERIVED CRUDES WITH SUBSTANTIAL RESIN CONTRIBUTION TO SOURCE MATTER

II CRUDES OF MIXED ORIGIN

III CRUDES DERIVED FROM SOM AND/OR ALGAL MATTER

| LEGEND |
|---|
| ⊡ - WELL 208/5-1 12799-12805 FT |

FIG. 4




GC-MS analysis 206/5-1 Core4 12799-12805 ft

FIG 5

INITIAL DISTRIBUTION

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| PG. | | | |
| ADDITIONS | | | ~~LOCATION MAP~~ |
| | | | ~~TABLE 1~~ |
| | | | FIG. A-E (orig. by KALKMAN) ← Cel op met 1-5 |
| | | | FIG. 1-5 |
| DISTRIBUTION | | | ~~3 MET KAFT (RINGBAND) - AUSTRALIA~~ |
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