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GEOCHEMICAL ANALYSIS OF A KIMMERIDGE CLAY
ROCK SAMPLE AND OF A CRUDE OIL FROM WELL
31/2-2, NORTH SEA

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Investigation 9.12.342.1
9.12.342.2

With Co-operation from
R. Stuifzand and Ms. H. Kampsteeg.

KONINKLIJKE/SHELL EXPLORATIE EN PRODUKTIE LABORATORIUM

RIJSWIJK, THE NETHERLANDS

(Shell Research B.V.)

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SUMMARY

Geochemical analysis of a cored rock sample from the Kimmeridge Clay in well 31/2-2 at 1525-1541 m and of a crude oil sample from a reservoir in the same well at depth 1586.5-1588.5 m have been carried out.

The source rock at 1525-1514 m in well 31/2-2 is very immature. Heating experiments show that the type of organic matter is structureless (bacterially reworked algae) with some contributions from land-plant waxes. The environment of deposition was not completely reducing and in proximately to the land. The sample, when mature, appears to be a good source rock for oil.

The crude oil from the reservoir at 1586.5-1588.5 m in the same well is bacterially degraded. Sterane distributions and the M_2 parameter indicate that it was derived from a source rock containing S.O.M. and that the source rock was mature.

The M_1 and M_2 parameters suggest that there is a correlation between the type of organic matter of the heated source rock and the crude oil.

The investigated source rock itself, being immature, can not have generated the crude oil. However, a mature version of the sample can be considered as a potential source for the crude oil.

GEOCHEMICAL ANALYSIS OF A KIMMERIDGE CLAY ROCK SAMPLE AND OF A CRUDE OIL FROM WELL 31/2-2, 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° 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:
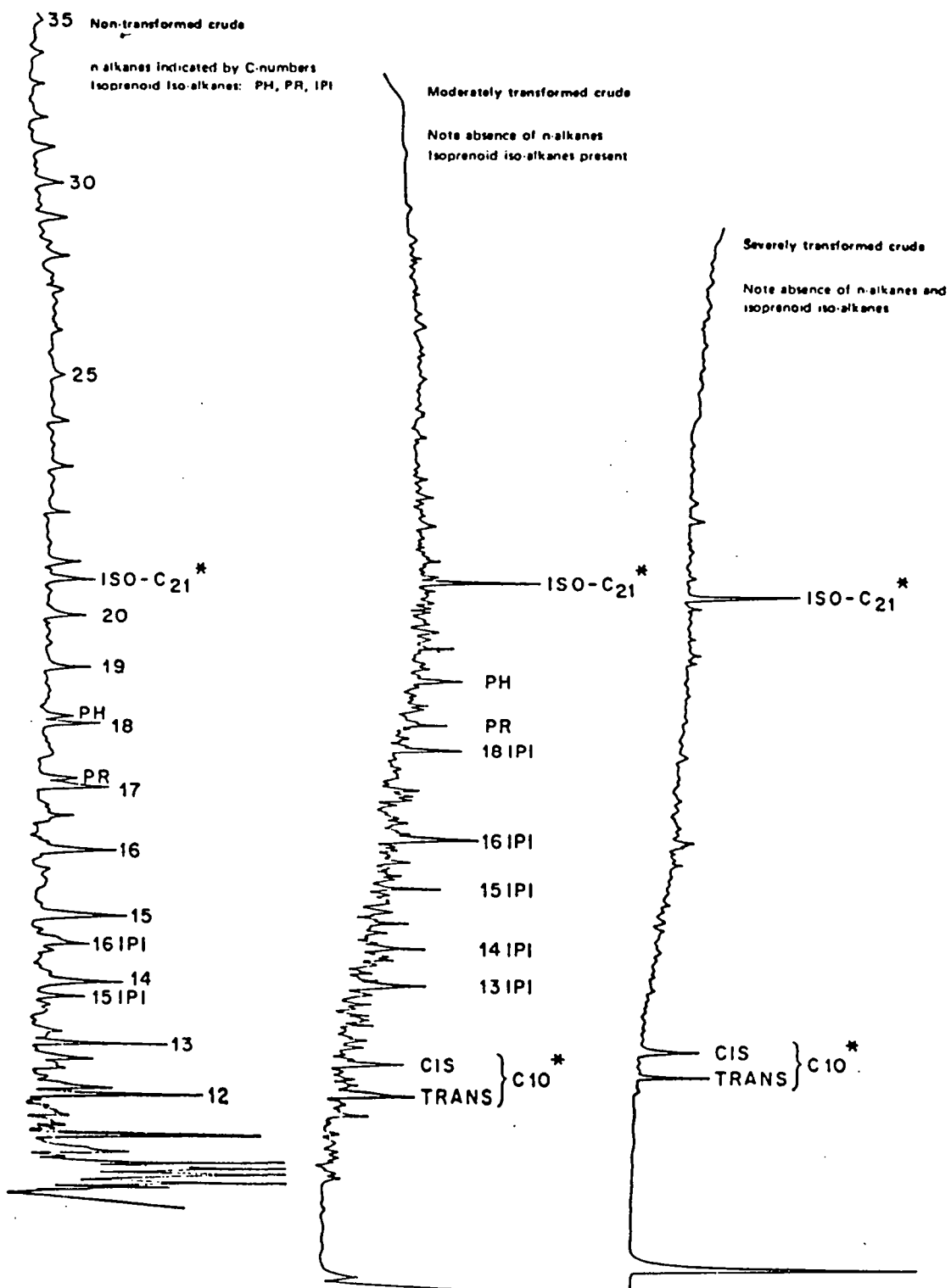
DOM	MATURITY ZONES
<60	Immature
60-75	Mature for oil generation
75-92	Mature for gas generation
	Post mature for oil generation
>92	Post mature for both oil and gas.

Sterane and triterpane parameters

Sterane 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.

35 Non-transformed crude

n alkanes indicated by C-numbers
Isoprenoid Iso-alkanes: PH, PR, IPI

Moderately transformed crude

Note absence of n-alkanes
Isoprenoid iso-alkanes present

Severely transformed crude

Note absence of n-alkanes and
isoprenoid iso-alkanes

30

25

ISO-C$_{21}$*
20
19
PH 18
PR 17
16
15
16 IPI
14
15 IPI
13
12

ISO-C$_{21}$*

PH
PR
18 IPI

16 IPI

15 IPI

14 IPI

13 IPI

ISO-C$_{21}$*

CIS
TRANS } C 10 *

CIS
TRANS } C 10 *

*STANDARD COMPOUNDS ADDED FOR IDENTIFICATION
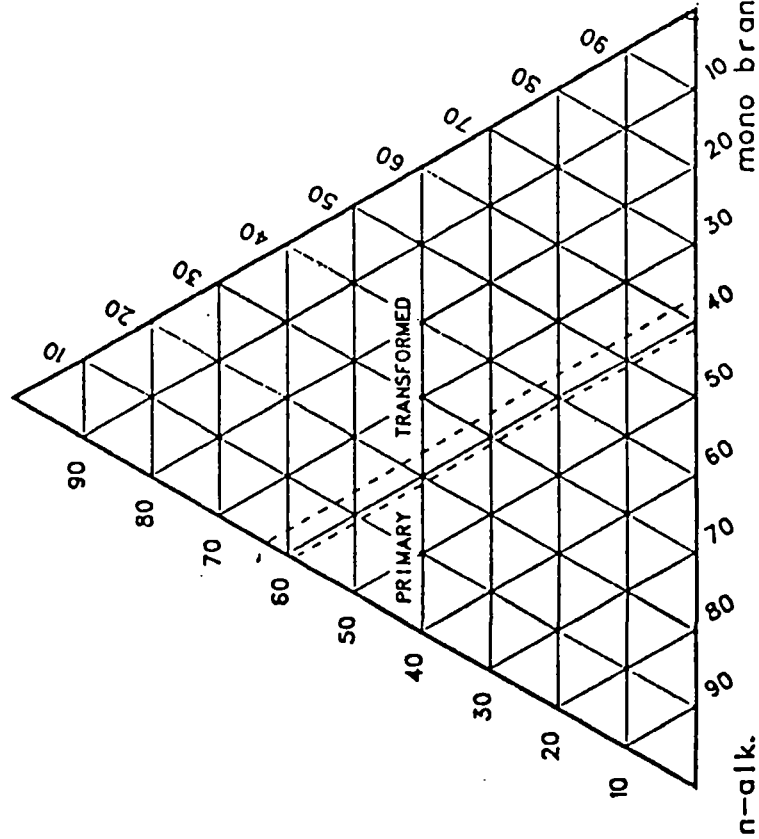
BACTERIAL DEGRADATION DISPLAYED IN GAS CHROMATOGRAMS OF SATURATED HYDROCARBONS.
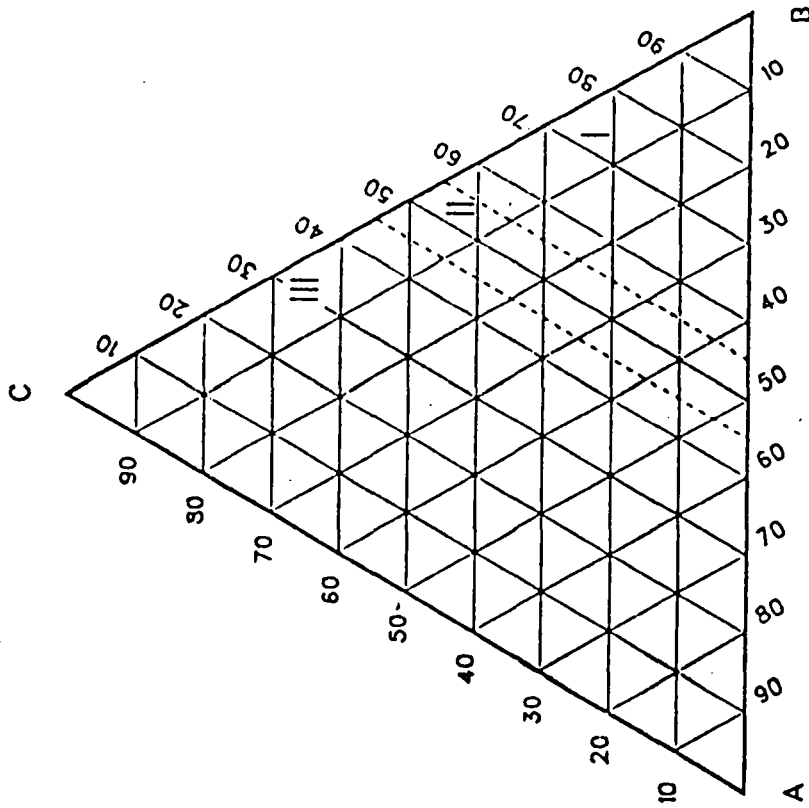
FIG: A

C_7-ALKANE/NAPHTHENE DISTRIBUTION

branched alk.

n-alk.

naphthenes

TERRESTRIAL

SHALES

SAPROPELIC
CARBONATES

C_7-ALKANE DISTRIBUTION

poly branched alk.

n-alk.

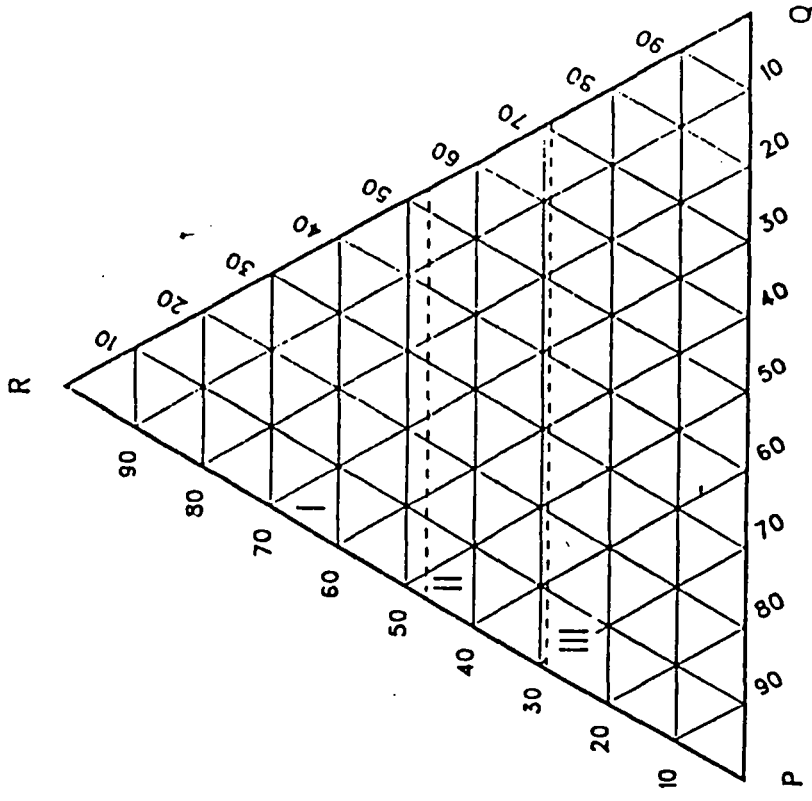mono branched alk.

TRANSFORMED

PRIMARY
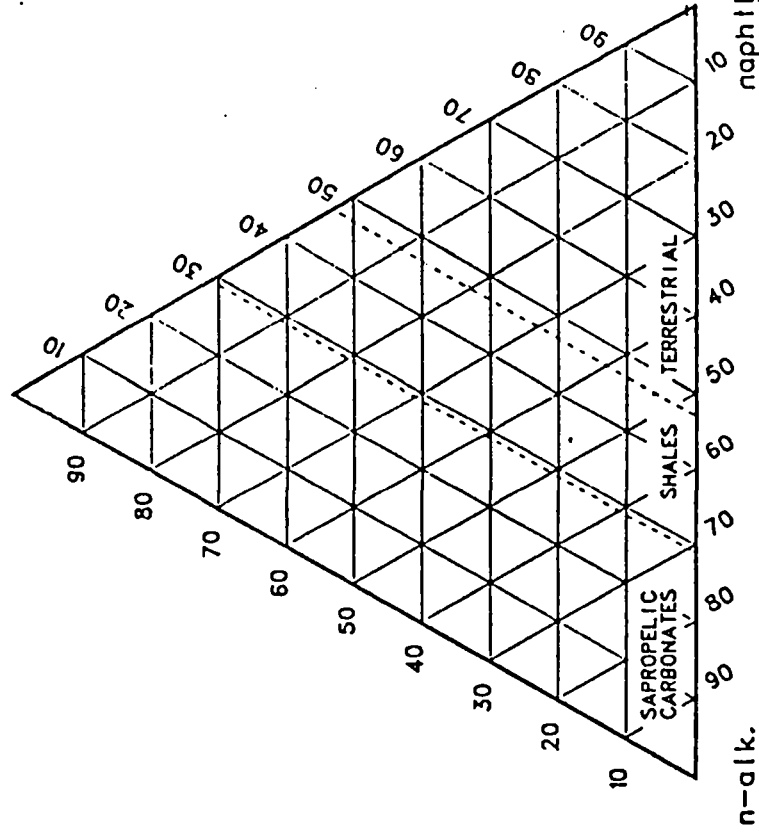
C_7 DISTRIBUTION FOR CHARACTERISATION OF RELATED SOURCE MATERIAL.
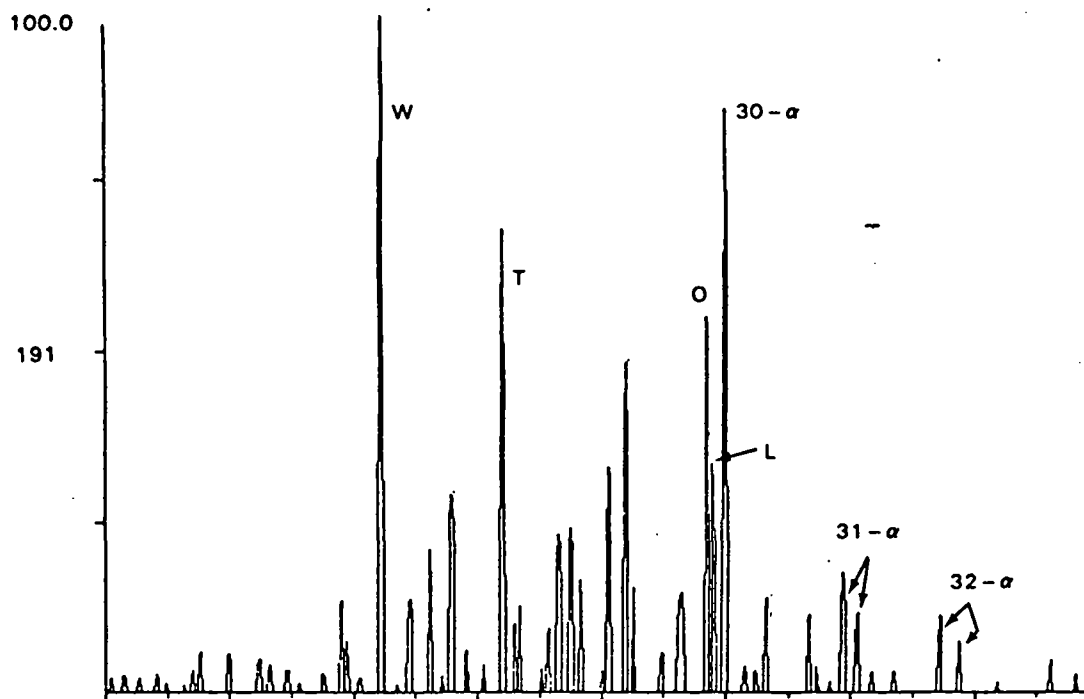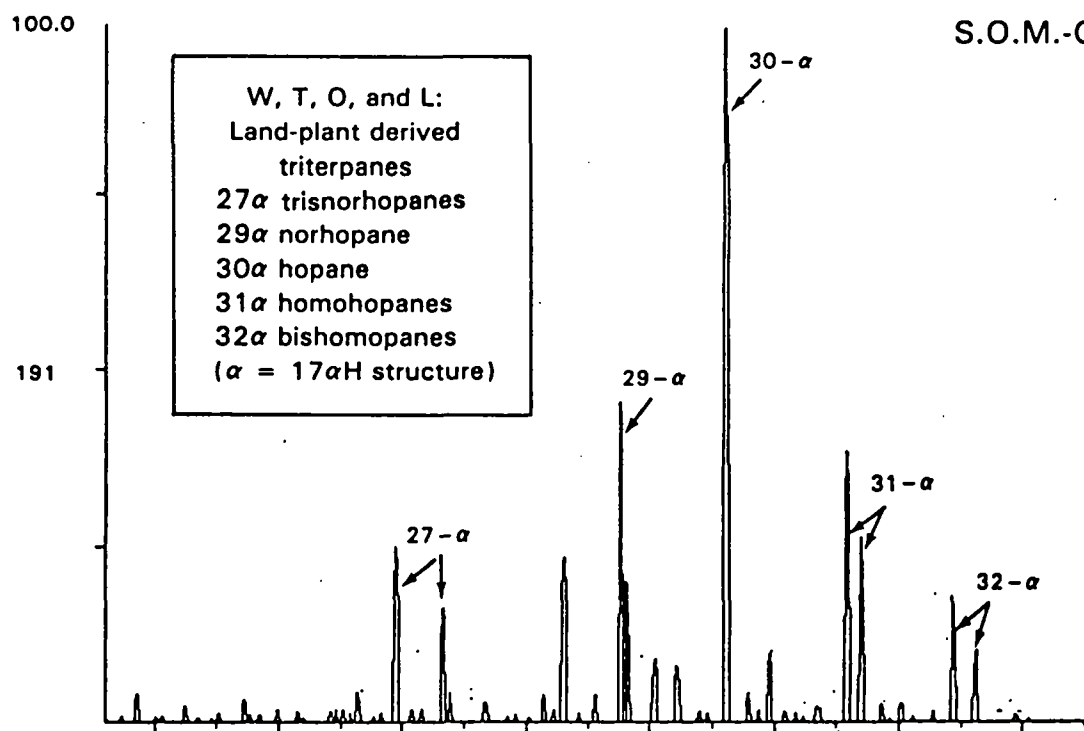
FIG: B

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
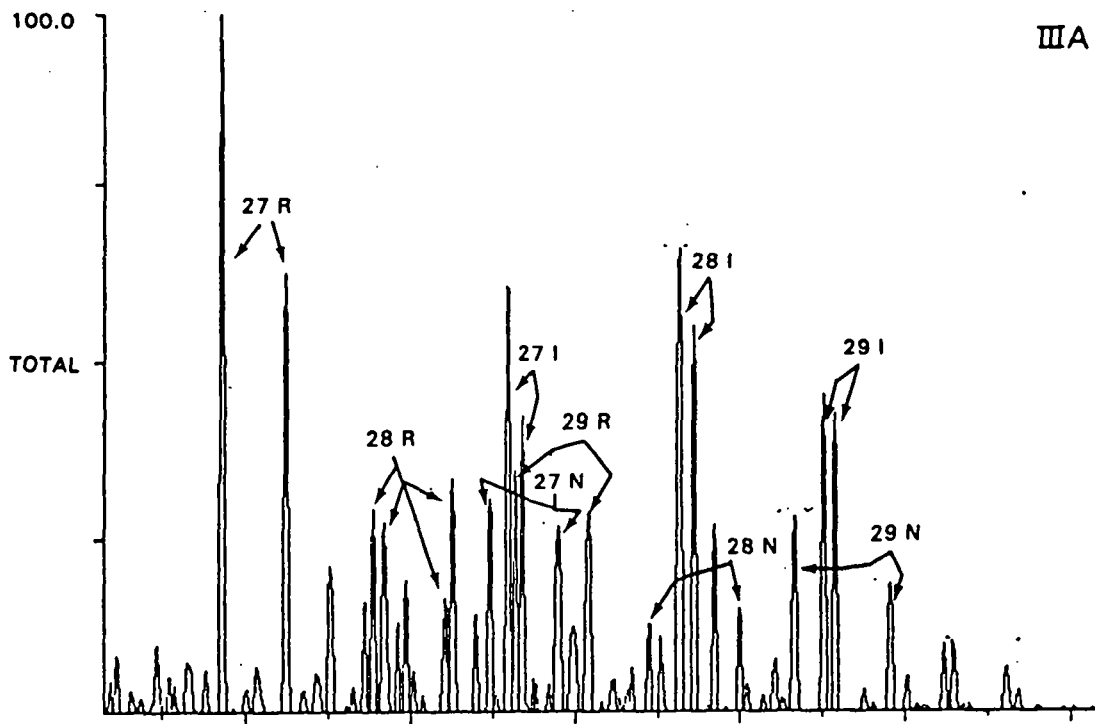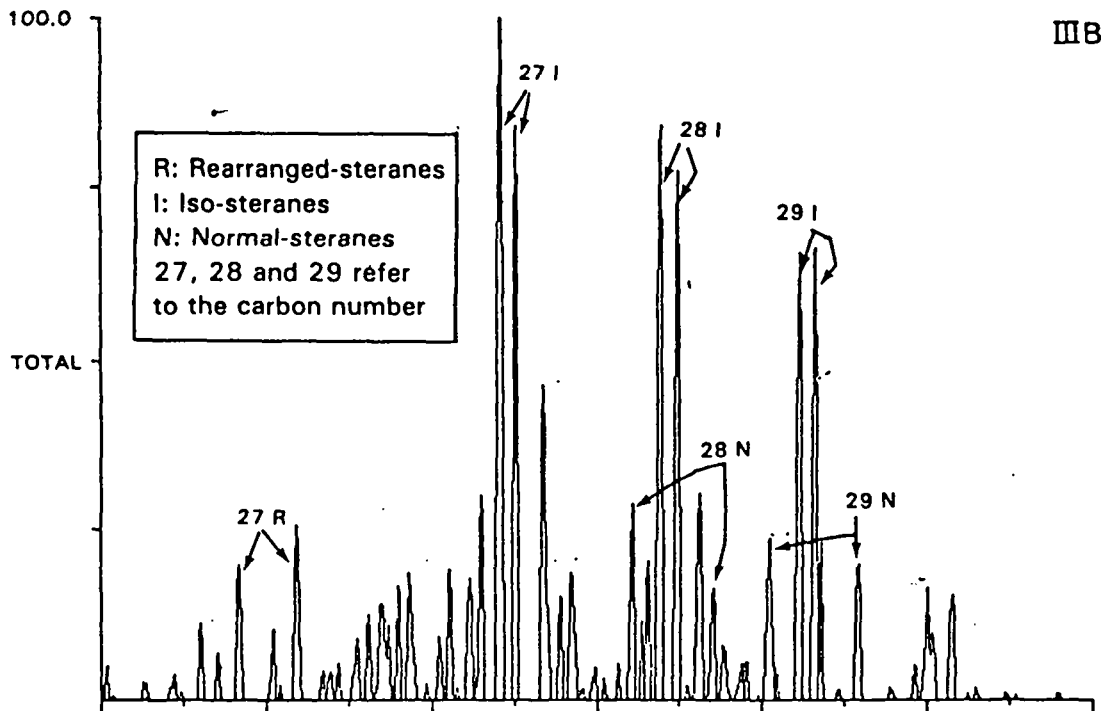
PARAMETERS M1 AND M2 TO TYPE RELATED SOURCE MATERIAL.

FIG C

LAND-PLANT CRUDE

S.O.M.-CRUDE

W, T, O, and L:
Land-plant derived
triterpanes
27α trisnorhopanes
29α norhopane
30α hopane
31α homohopanes
32α bishomopanes
(α = 17αH structure)

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

FIG. D

IIIB

R: Rearranged-steranes
I: Iso-steranes
N: Normal-steranes
27, 28 and 29 refer
to the carbon number

IIIA

STERANE FRAGMENTOGRAMS OF TYPE IIIA AND IIIB CRUDE OILS

FIG. E

3. RESULTS AND DISCUSSION

Geochemical analyses of a cored rock sample from the Kimmeridge Clay in well 31/2-2 at 1525-1514 m. and of a crude oil sample from a reservoir in the same well at depth 1586.5-1588.5 m have been carried out. Analysis of cutting samples from well 31/2-2 at 1867 m has not been undertaken since the source rock indication value was zero.

The results are shown in Tables 1-2 and Figures 1-7.

The gas chromatogram of the saturated hydrocarbons of the rock sample (Fig. 1), the DOM of oil (< 57) and the sterane fragmentogram (Fig. 6), where normal-steranes predominate, indicate that the sample is very immature. Heating experiments have therefore been carried out.

The gas chromatogram of the saturates of the heated sample (Fig. 2) shows a mature distribution which also indicates that the type of organic matter of the sample is structureless. This is further indicated by the M_1 and M_2 distributions of the heated sample (Fig. 5). The shift in the M_2 distribution which occurs on heating indicates that the variety of S.O.M. is bacterially reworked algae. The $C_{27}-C_{29}$ distribution of the sterane fragmnetogram (Fig. 6) indicates that the form of algae is a marine phytoplankton.

The clear presence of an odd/even predominance in the gas chromatogram of the saturates of the unheated sample (Fig. 1) and the persistence of a slight odd/even predominance in that of the heated sample (Fig. 2) indicates contributions of land-plant waxes to the organic matter.

The Pristane /$\underline{n}$-C_{17} ratio of the heated sample (0.7) and the sulphur content (2.3%) indicates that the environment of deposition was not completely reducing. Since nickel porphyrins predominate in the extract of the unheated sample it is probable that the depositional environment was near shore.

The extract/carbon ratios after heating indicate that the sample is a good source rock for oil.

The crude oil from the reservoir at 1586.5-1588.5 m in the same 31/2-2 well is bacterially transformed. This indicated by the gas chromatogram of the saturated hydrocarbons (Fig. 3) and by the C_7 alkrane distribution (Fig. 4). Hence, from the gas chromatogram (Fig. 3) little can be concluded about type or depositional environment.

The sterane fragmentogram (Fig. 7) however, and the C_{30} distribution both unaffected by bacterial degradation, indicate that the type of organic matter of the source rock was structureless and that the crude was expelled from a

mature source rock.

The M_1 and M_2 distributions (Fig. 5) suggests that there may be a correlation between the type of organic matter of the heated source rock and the crude oil.

Since the source rock is clearly very immature, it cannot have generated the crude oil examined. It can only be concluded that a more mature version of the source rock, containing the same type of organic matter, may have generated the crude oil.

4. CONCLUSIONS

The source rock at 1525-1514 m in well 31/2-2 is very immature. Heating experiments show that the type of organic matter is structureless (bacterially reworked algae) with some contributions from land-plant waxes. The environment of deposition was not completely reducing and in proximity to the land. The sample, when mature, appears to be a good source rock for oil.

The crude oil from the reservoir at 1586.5-1588.5 m in the same well is bacterially degraded. Sterane distributions and the M_2 parameter indicate that it was derived from a source rock containing S.O.M. and that the source rock was mature.

The M_1 and M_2 parameters suggests that there is a correlation between the type of organic matter of the heated source rock and the crude oil.

The investigated source rock itself, being immature, can not have generated the crude oil. However a mature version of the sample can be considered as a potential source for the crude oil.
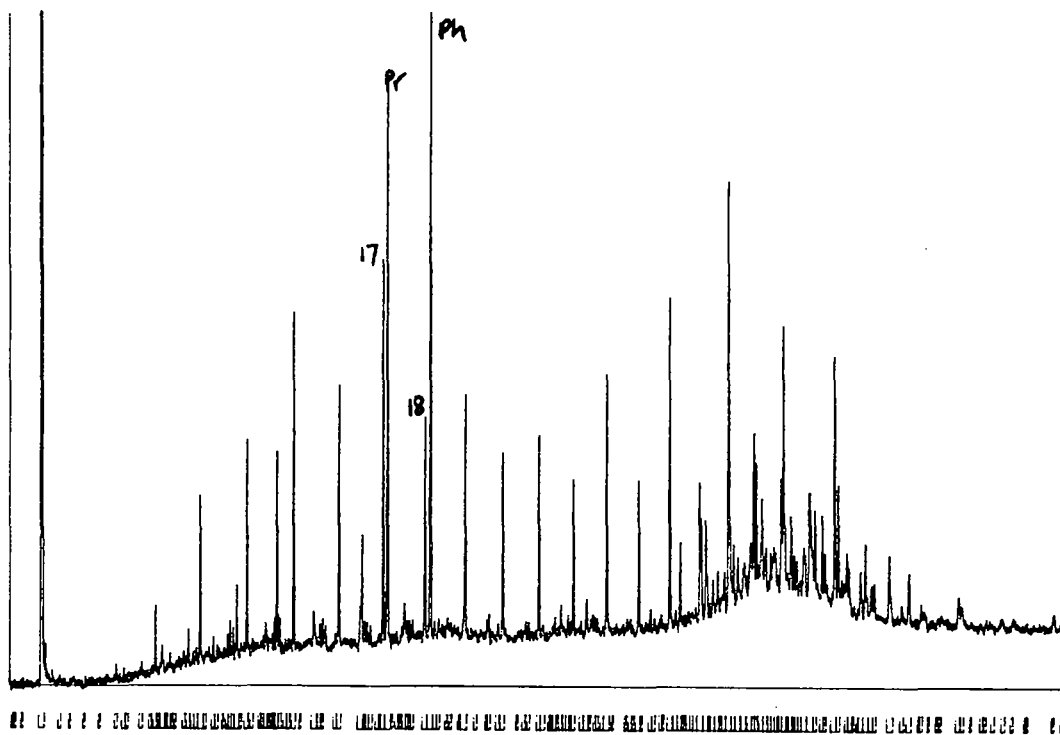
Table 1 - Geochemical data of extracts

Sample	31/2-2 1525-1541 m	31/2-2 1525-1541 m heated
% ethyl acetate extract	0.2	0.9
%organic carbon after extraction	3.3	2.3
% suphur	6.0	2.3
ppm V^O porphyrins	312 (± 10)	
ppm Ni porphyrins	915 (± 11)	
pristane/phytane	0.9	1.8
pristane/nC_{17}	1.5	0.7
phytane/nC_{18}	2.4	0.4
Parameter M_1		
A	30	54
B	39	28
C	31	18
Parameter M_2		
P	5	31
Q	44	37
R	51	32
DOM of oil	< 57	
% saturates	11	10
% aromatics	33	47
% heterocompounds	56	43
Extract/carbon	0.06	0.39
Extract/original carbon	–	0.27

Table 2 – Geochemical data of oil

Sample	31/2-2 1586.5–1588.5 m
API	25.9
Specific gravity	0.899
% W. boil. < 120 C	4.7
% suphur	0.5
ppm V^O porphyrins	b.l.
ppm Ni porphyrins	b.l.
pristane/phytane	1.8
pristane/nC_{17}	1.9
phytane/nC_{18}	1.2
C_7–distribution	
C_7–alkane	
nC_7	1
monobranched	41
polybranched	58
C_7alk/naohthene	
nC_7	–
naphthenes	88
branched alkanes	12
C_7–alk/naphth/arom	
alkanes	12
naphthenes	88
aromatics	–
Parameter M_1	
A	55
B	31
C	14
Parameter M_2	
P	30
Q	44
R	26
DOM of oil	63
% saturates	45
% aromatics	34
% heterocompounds	21

b.l. = below limit of detectability

FIG 1

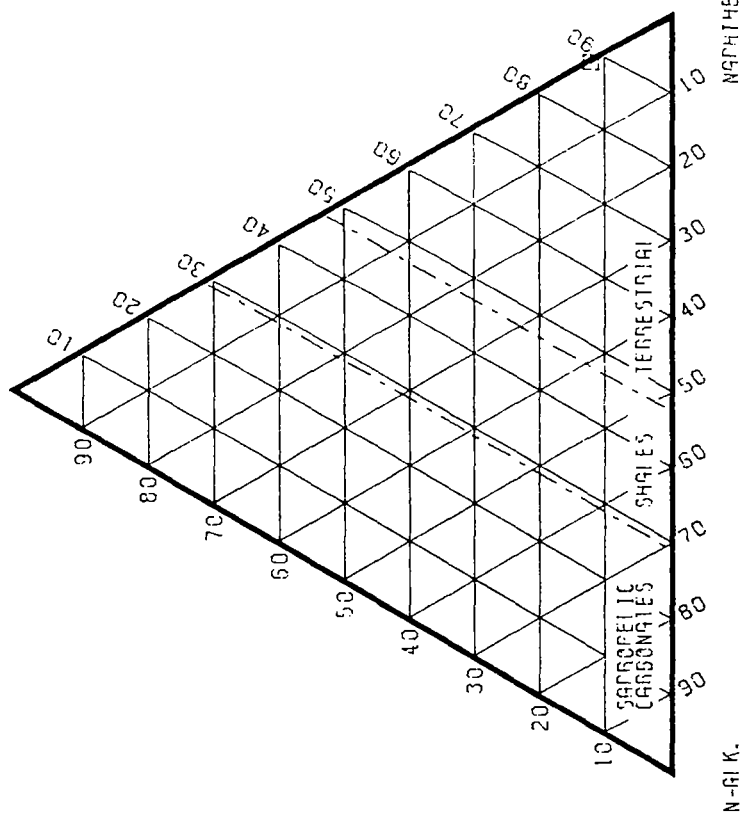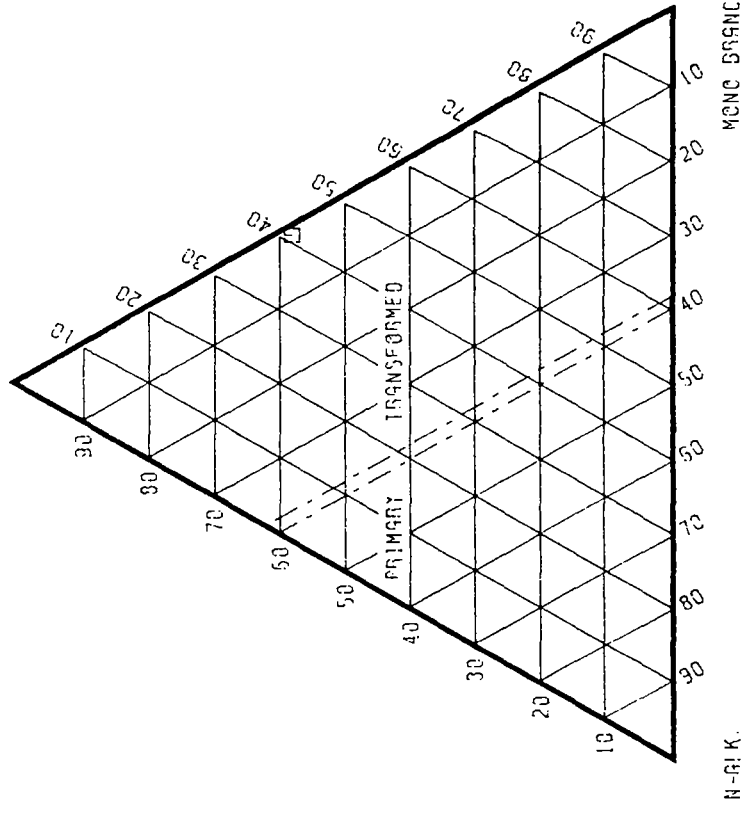GAS CHROMATOGRAM OF SATURATED HYDROCARBONS

NORWAY 31/2-2 1525-1541 M

FIG 2

GAS CHROMATOGRAM OF SATURATED HYDROCARBONS

NORWAY 31/2-2 1525-1541 M HEATED

FIG 3

GAS CHROMATOGRAM OF SATURATED HYDROCARBONS

NORWAY 31/2-2 1586.5-1588.5 M
PROD. TEST-1

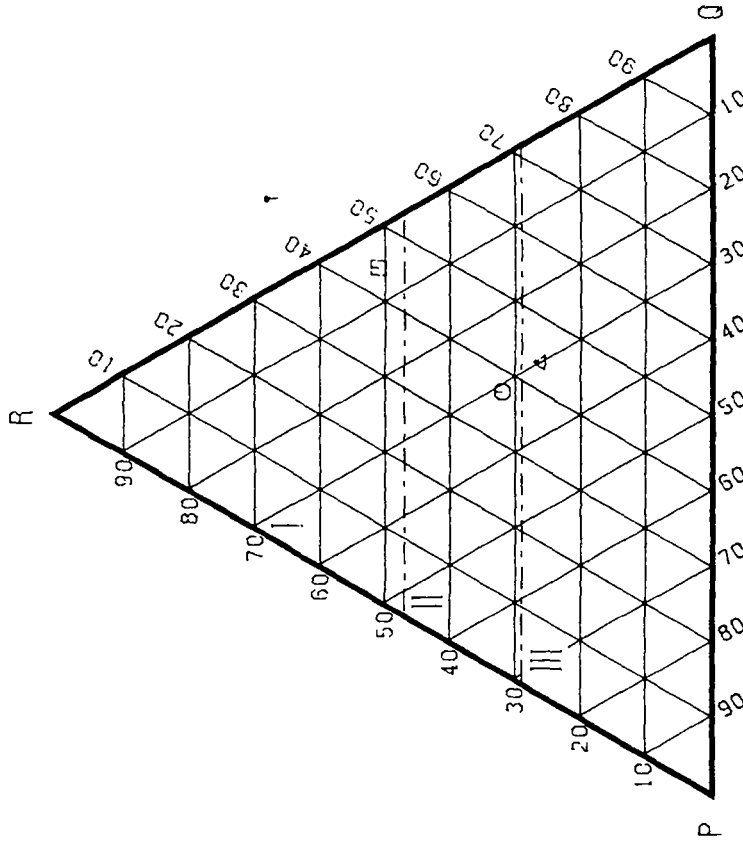C7-ALKANE/NAPHTHENE DISTRIBUTION

C7-ALKANE DISTRIBUTION

LEGEND

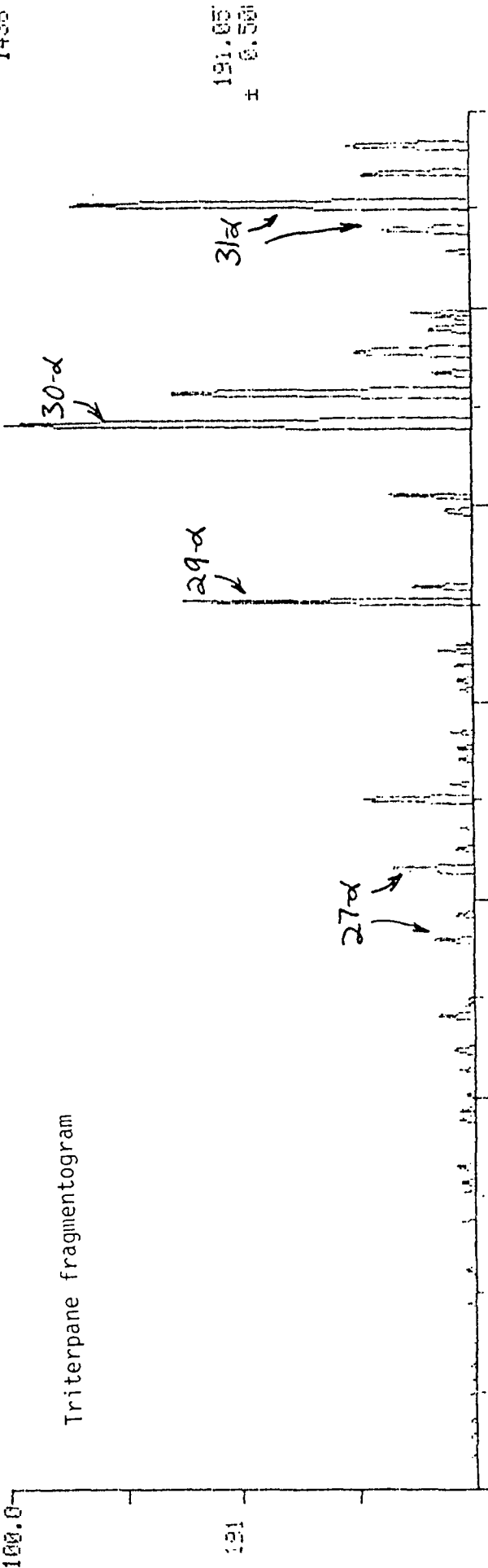G - 3i/2-2 1586.5-1586.5 M

FIG 4
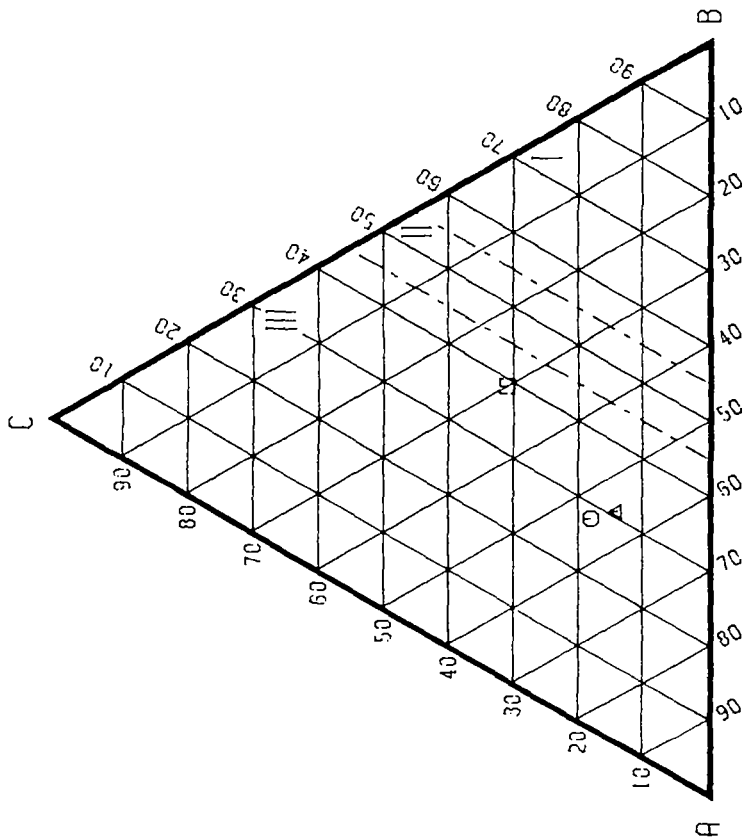
PARAMETER M2

PARAMETER M1

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

II — CRUDES OF MIXED ORIGIN

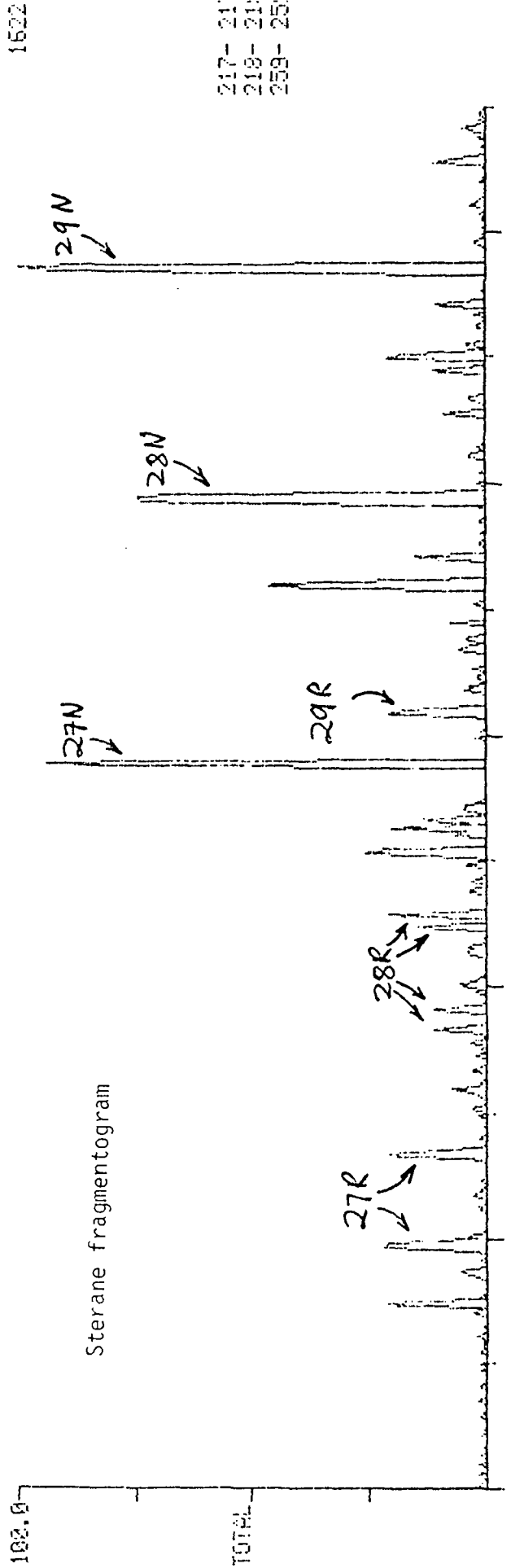III — CRUDES DERIVED FROM SOM AND/OR ALGAL MATTER

LEGEND

□ - 31/2-2 1525-1541 M
⊙ - DITTO HEATED
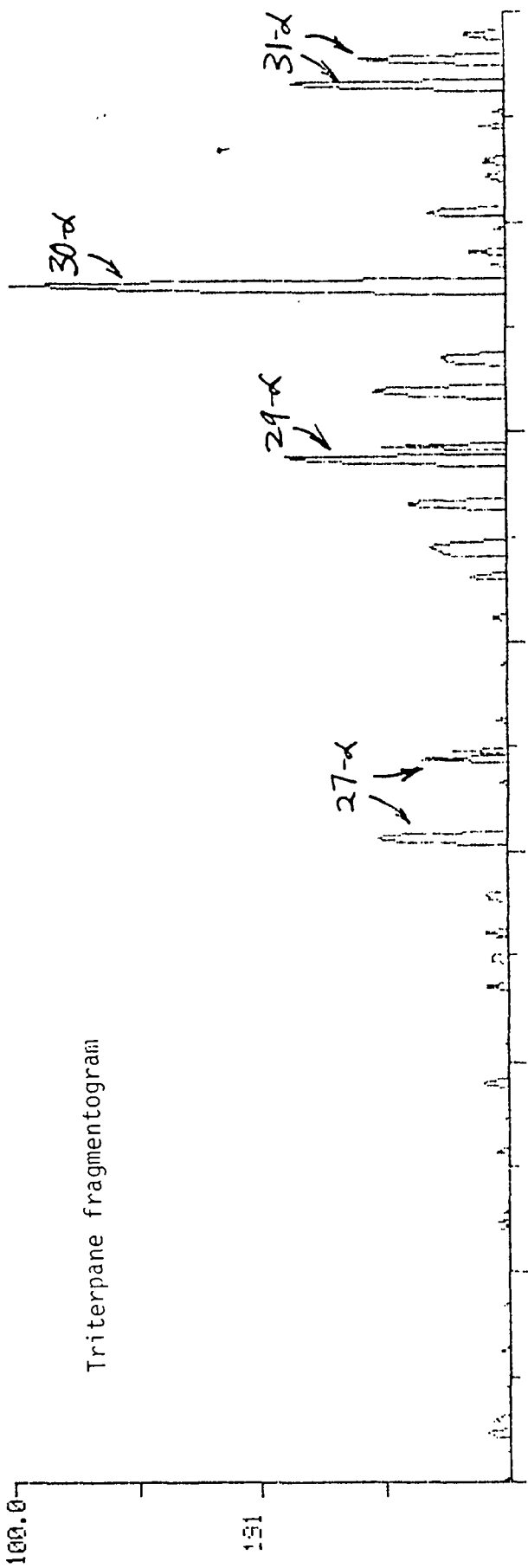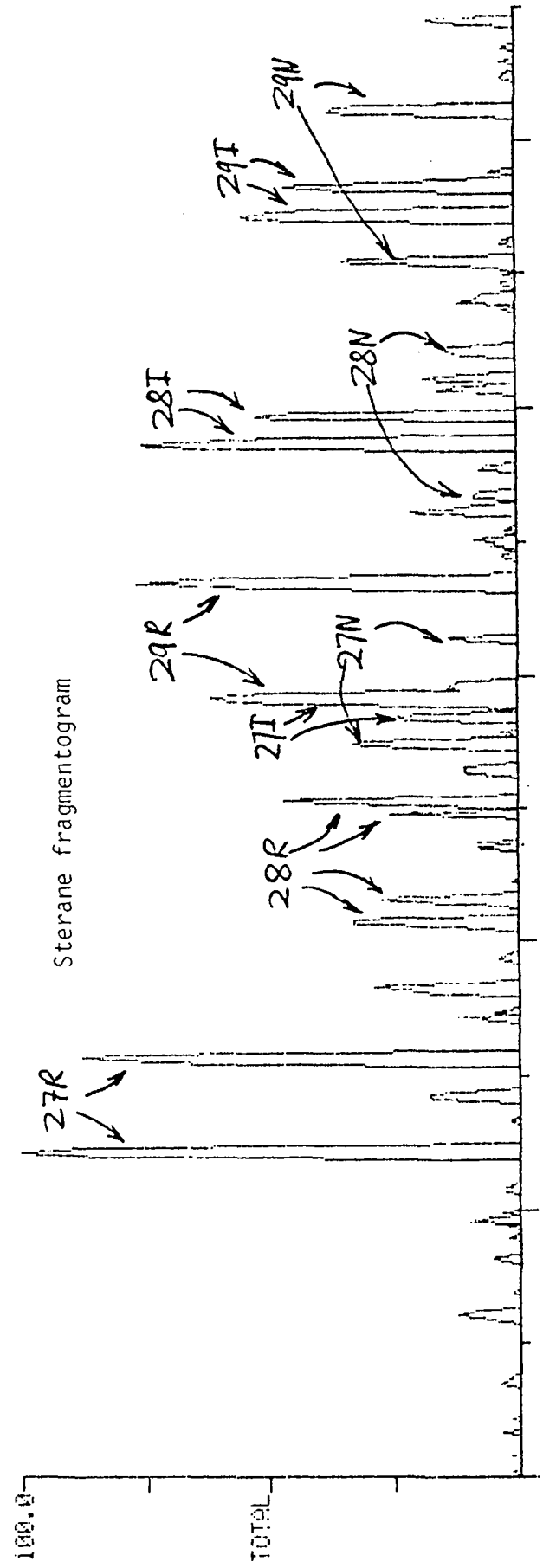△ - 31/2-2 1586.5-1588.5 M OIL

FIG. 5

Triterpane fragmentogram

Sterane fragmentogram

GC-MS analysis 31/2-2 1525-1542 m rock

FIG 6

Triterpane fragmentogram

Sterane fragmentogram

GC-MS analysis 31/2-2 1586.5-1588.5 m oil

FIG 7

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