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GEOCHEMICAL ANALYSIS OF THREE COMPOSITE ROCK SAMPLES FROM WELL 11/30-2, UNITED KINGDOM

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RIJSWIJK, THE NETHERLANDS

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SUMMARY

Geochemical analysis has been carried out on extracts of three artificially matured composite samples of well 11/30-2 viz.:

11/30-2 6429 + 6437 + 6449'

11/30-2 6491 + 6496'

11/30-2 6884 + 6888 + 7023'.

It appeared that the organic matter in sample 11/30-2 6429 + 6437 + 6449' consists of sapropelic organic matter with some algal contribution, deposited in a reducing aquatic environment.

The source material of 11/30-2 6491 + 6496' and 11/30-2 6884 + 6888 + 7023' consists of sapropelic organic matter with a considerable algal contribution, deposited in a reducing aquatic environment. The last two samples show a difference in the M2 triangle and in the extract/organic carbon ratio.

Comparison of the extracts of the heated rock samples with the Beatrice crude revealed that the Beatrice crude is related to a source rock of the same type as the sample 11/30-2 6491 + 6496'.

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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 their 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 fractions). 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. 1).

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_{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 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_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. 2). 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. 2). 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 (Fig. 3)

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. 3. Note that the C_{15} diagram 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.

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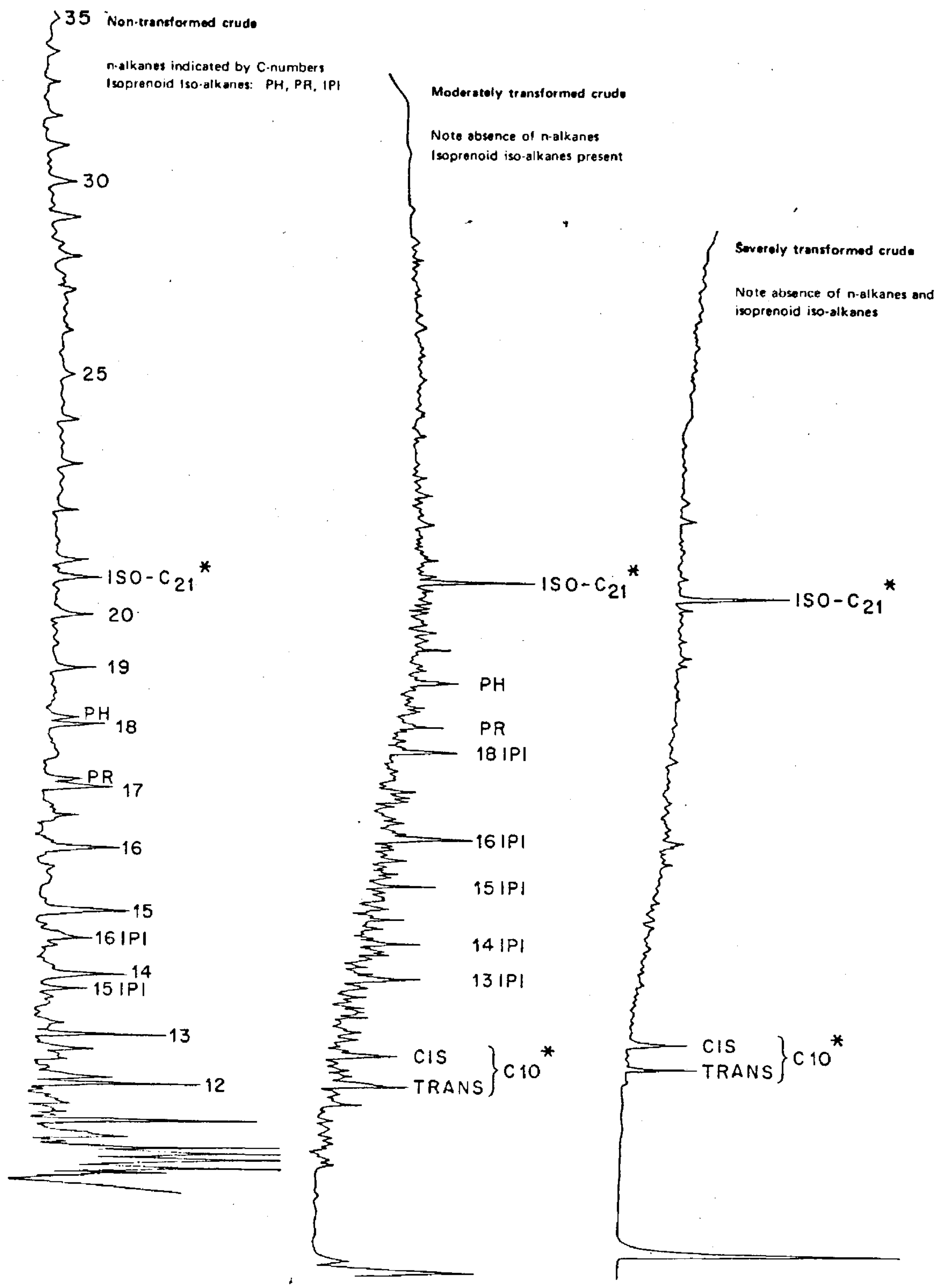
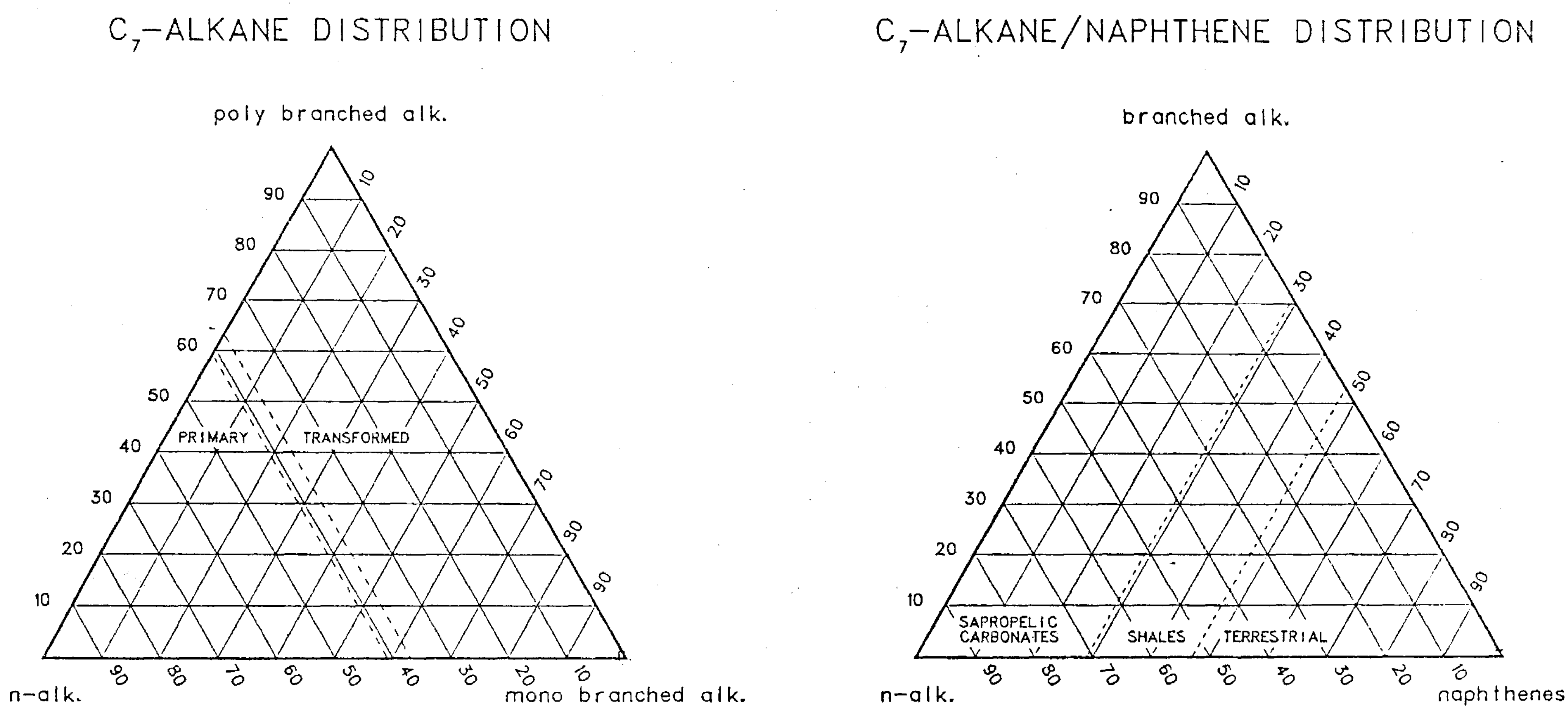


*STANDARD COMPOUNDS ADDED FOR IDENTIFICATION

BACTERIAL DEGRADATION DISPLAYED IN GAS CHROMATOGRAMS OF SATURATED HYDROCARBONS.

FIG: 1.

Draw. no. 25208



C_7 DISTRIBUTION FOR CHARACTERISATION OF RELATED SOURCE MATERIAL.

FIG: 2.

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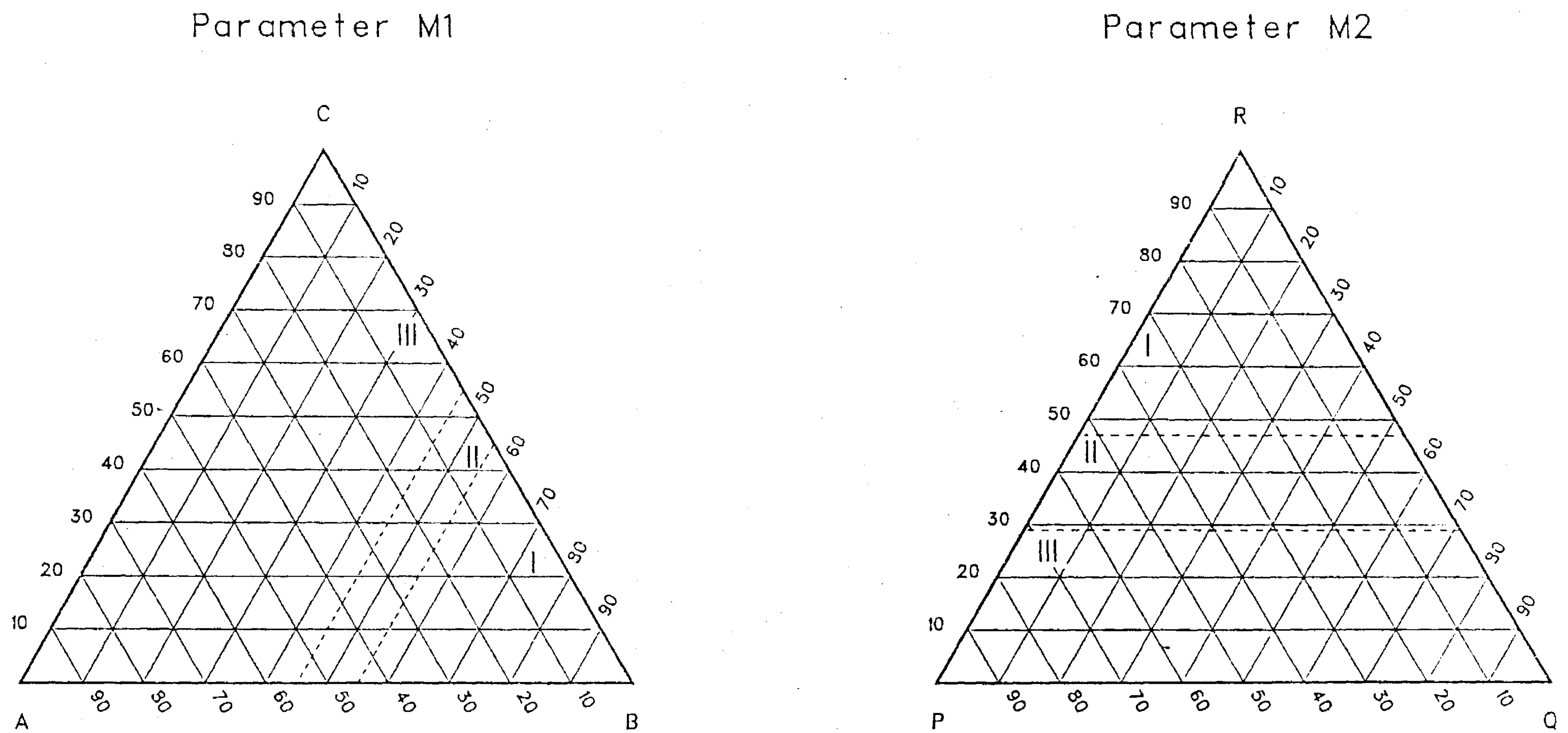


I LANDPLANT-DERIVED CRUDES WITH SUBSTANTIAL RESIN CONTRIBUTION TO SOURCE MATTER

II CRUDES OF MIXED ORIGIN

III CRUDES DERIVED FROM SOM AND/OR ALGAL MATTER

PARAMETERS M1 AND M2 TO TYPE RELATED SOURCE MATERIAL.

FIG.3

3. RESULTS AND DISCUSSION

Three composite rock samples from well 11/30-2* have been artificially matured and analysed, viz.:

11/30-2 6429 + 6437 + 6449'

11/30-2 6491 + 6496'

11/30-2 6884 + 6888 + 7023'.

The results are shown in Table 1 and Figs. 4-8.

Due to the very small sample size no analysis could be carried out on original samples and no sulphur was determined in the matured 11/30-2 6884 + 6888 + 7023' sample.

The extracts are compared with the Beatrice crude, which is interpreted to be related to a shaly source rock, deposited in a reducing environment having organic material mainly consisting of sapropelic organic matter (possibly largely of algal origin).

In Fig. 7 a gaschromatogram of the Beatrice crude is shown.

The shape of the gas chromatogram of the saturated fraction (Figs. 4-6) indicate that the rock samples have reached maturity after heating for 6 days at 330°C.

The M1 and M2 parameters (Fig. 8) point in all three samples to a source material consisting of sapropelic organic matter and/or algal material. The 11/30-2 6884 + 6888 + 7023' sample has a somewhat different position in the M2 triangle compared with the other extracts and the Beatrice crude.

The content of isoprenoids is very low for the 11/30-2 6491 + 6496' and the 11/30-2 6684 + 6888 + 7023' samples (Figs. 5,6), indicating a large algal contribution. This is in agreement with the shape of the n-alkane distribution in the chromatograms.

The relative abundance of isoprenoids in sample 11/30-2 6429 + 6437 + 6449' (Fig. 4) is an indication for more SOM and less algal contribution in the source material.

The pristane/n-C_{17} ratios indicate that he source material of the 6491 + 6496' and the 6884 + 6888 + 7023' sample were deposited in a reducing aquatic environment.

The higher pristane/n-C_{17} ratio in the 6429 + 6437 + 6449' sample indicates a not completely reducing fluviomarine or coastal environment.

* Prepared by F. Vlierboom based on maceral description.

Conclusions

The source material of 11/30-2 6429 + 6437 + 6449' consists of sapropelic organic matter with some algal contribution. It was deposited in a not completely reducing fluviomarine or coastal environment.

The samples 11/30-2 6491 + 6496' and 11/30-2 6884 + 6888 + 7023' seems to be very similar. The organic matter of both samples consists of SOM with a considerable algal contribution, deposited in a reducing aquatic environment. However the samples are different with respect to the position in the M2 triangle and the extract/organic carbon ratios.

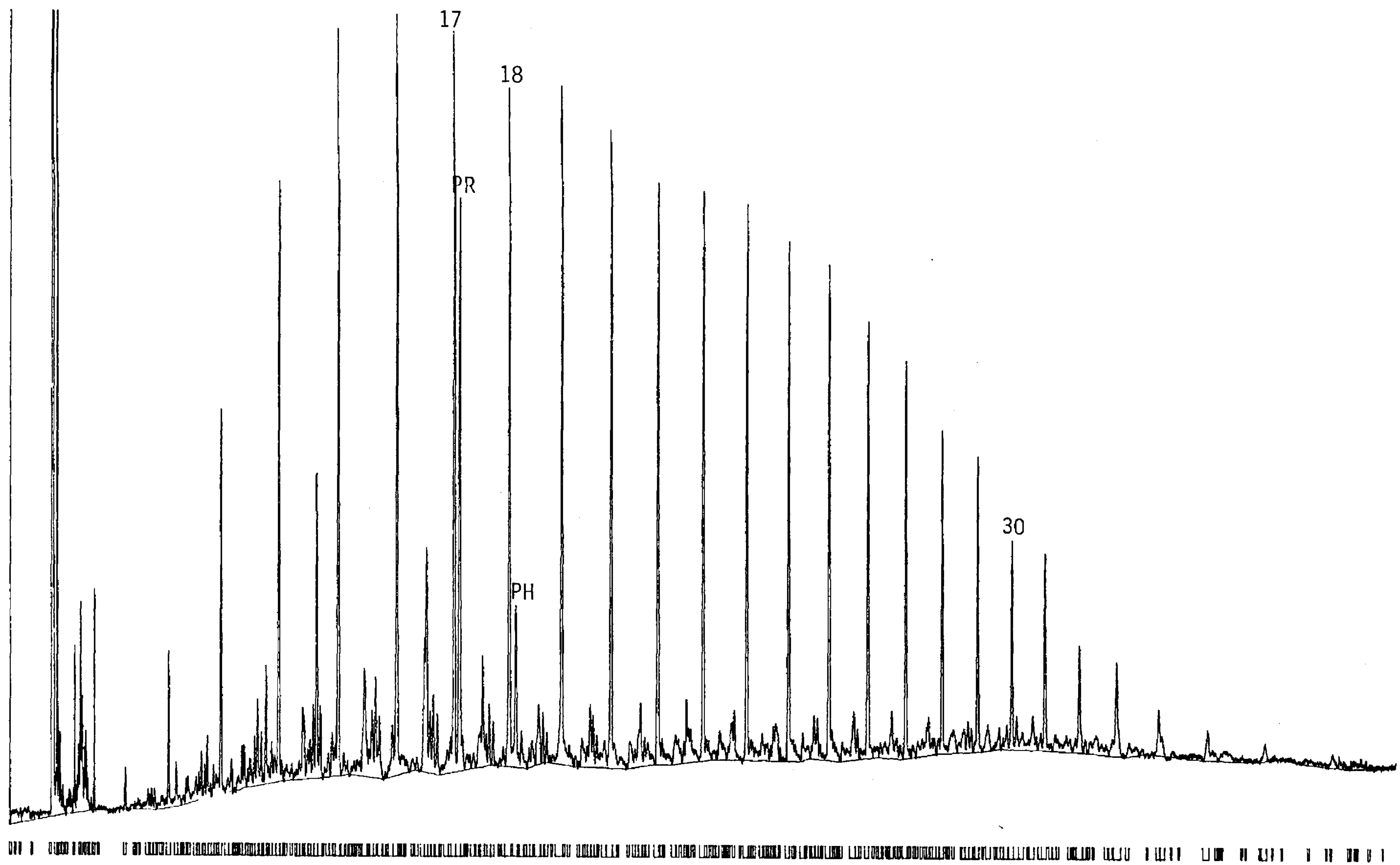
The sample 11/30-2 6491 + 6496' shows a good resemblance with the Beatrice crude. It is likely that the Beatrice crude has been generated from a source rock similar to sample 11/30-2 6491 + 6496'.

Table 1 - Geochemical data of extracts

Sample	11/30-2 6429 + 6437 + 6449'	11/30-2 6491 + 6496'	11/30-2 6884 + 6888 + 7023'
Artificial maturation	6 days 330°C	6 days 330°C	6 days 330°C
% ethyl acetate extract	5.7	9.5	0.8
% organic carbon after extraction	6.8	12.9	4.6
% sulphur	2.0	1.9	
ppm V° porphyrins	<26	<29	< 8
ppm Ni porphyrins	< 1	< 1	< 2
pristane/phytane	2.6	2.1	1.5
pristane/nC_{17}	0.9	0.2	0.2
phytane/nC_{18}	0.4	0.1	0.1
Parameter M1			
A	44	59	66
B	40	27	27
C	16	14	7
Parameter M2			
P	33	29	15
Q	38	42	61
R	29	29	24

Table 2 - Geochemical data of oil

Sample	Beatrice oil
API	39.0
Specific gravity	0.830
% w. boil. < 120 C	10.7
% sulphur	0.2
pristane/phytane	1.9
pristane/nC_{17}	0.2
phytane/nC_{18}	0.1
C_7-distribution	
C_7-alkane	
nC_7	58
monobranched	25
polybranched	17
C_7-alk/naphthene	
nC_7	35
naphthene	40
branched alkanes	25
C_7-alk/naphth/arom	
C_7	59
naphthene	39
aromatic	2
Parameter M1	
A	50
B	40
C	10
Parameter M2	
P	28
Q	40
R	32
Dom of oil	71

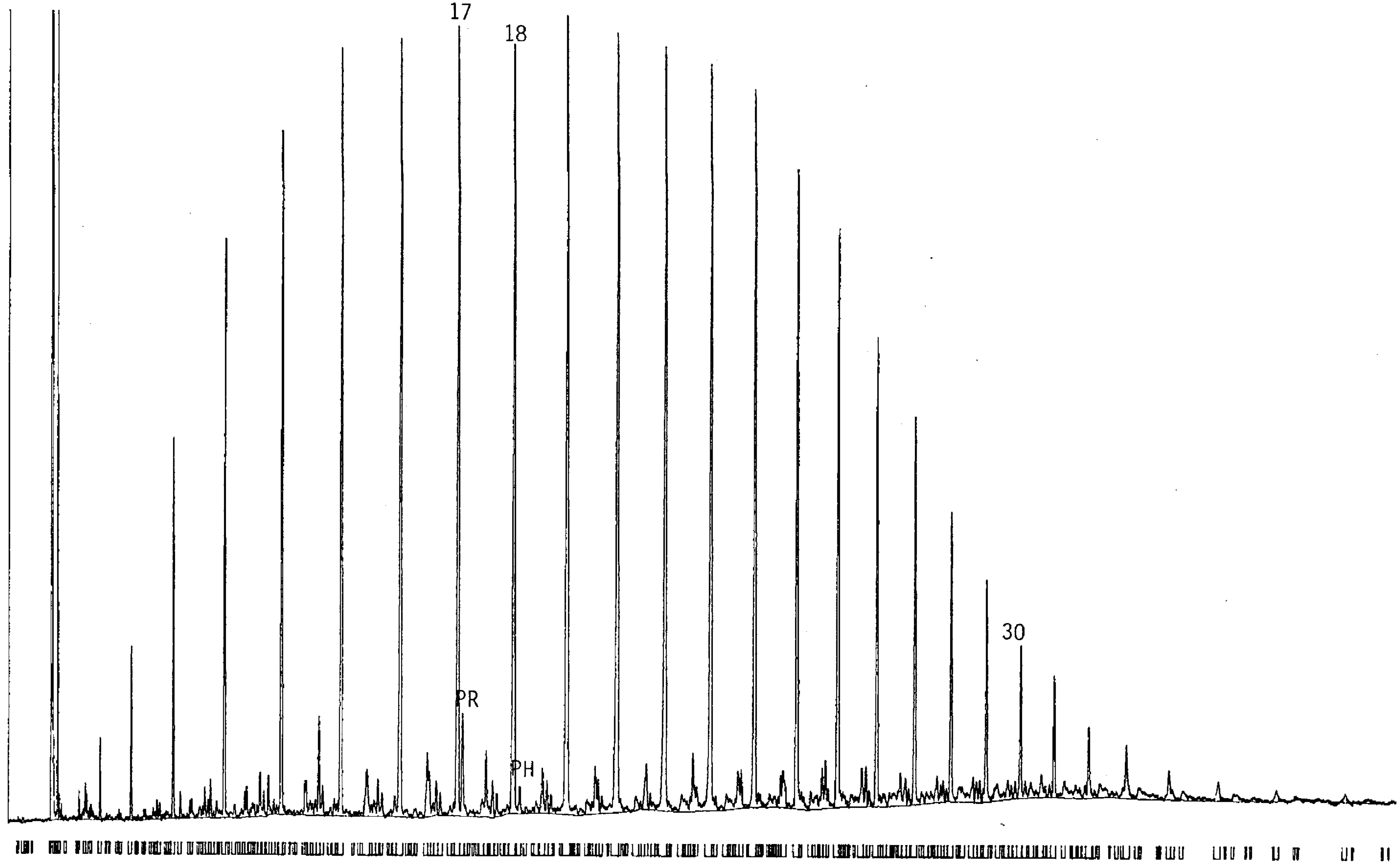


GAS CHROMATOGRAM OF SATURATED HYDROCARBONS

11/30-2
6429+6437+6449 FT
6 DAYS 330 DEGC.

FIG. 4

FIG. 5

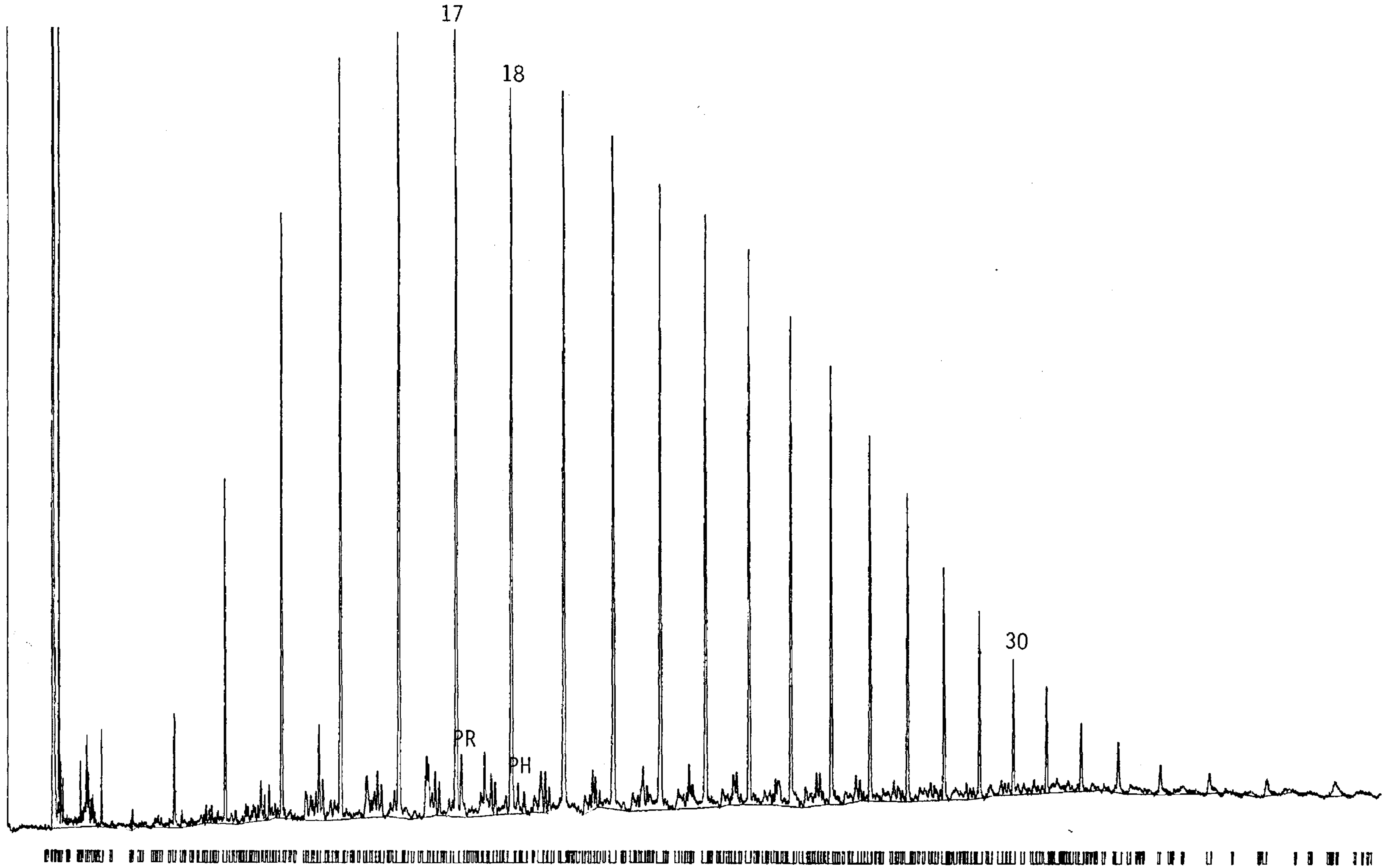


GAS CHROMATOGRAM OF SATURATED HYDROCARBONS

11/30-2

6491+6496 FT

6 DAYS 330 DEGC.



GAS CHROMATOGRAM OF SATURATED HYDROCARBONS

11/30-2
6884+6888+7023 FT
6 DAYS 330 DEGC

FIG. 6

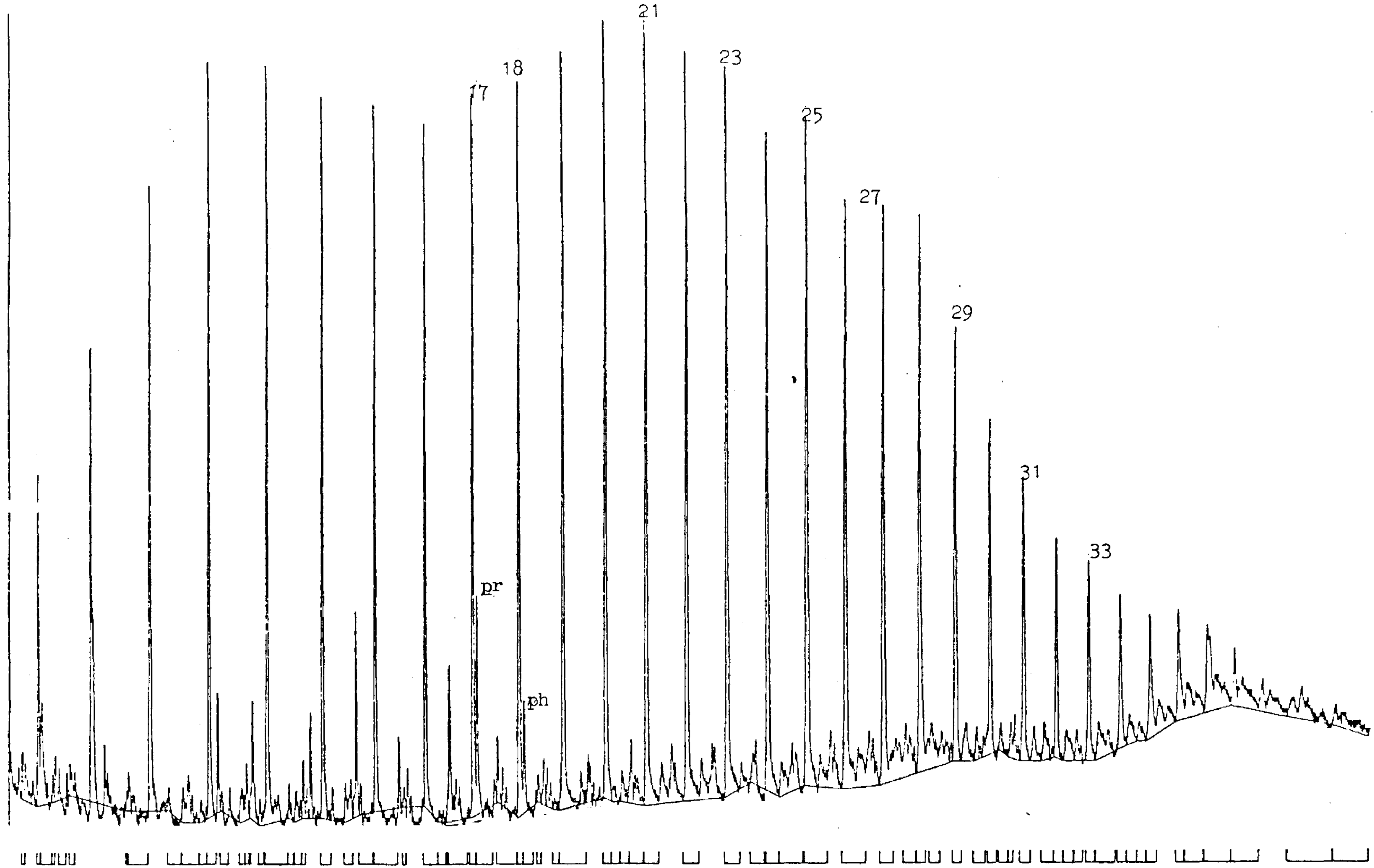
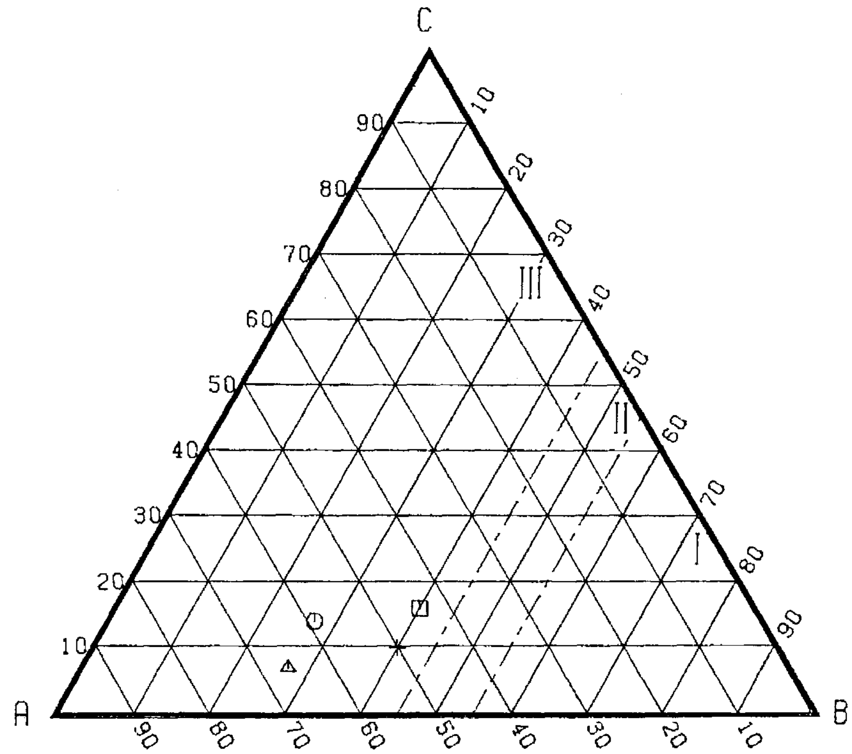


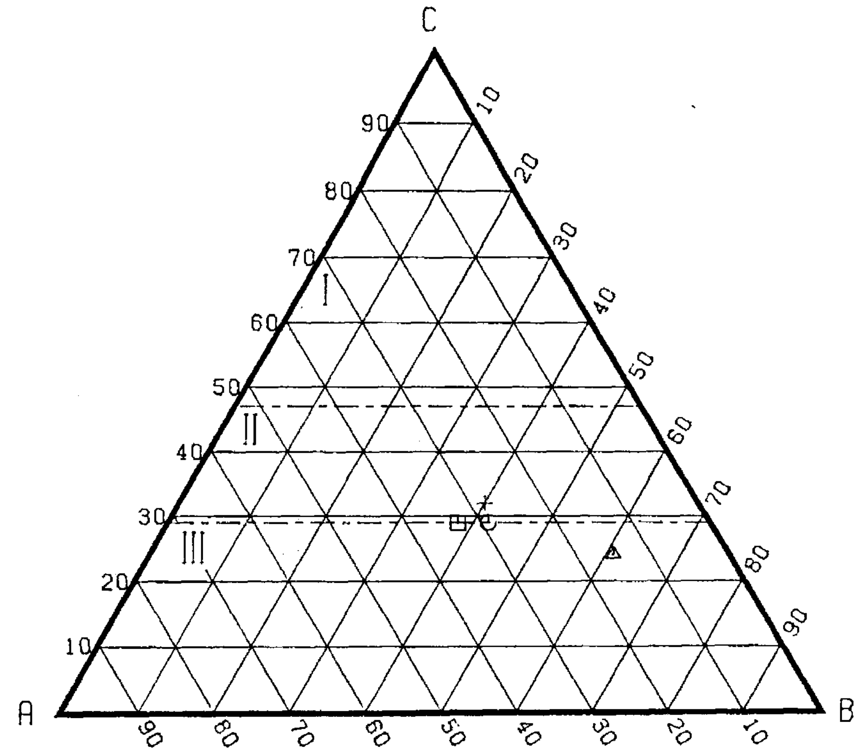
FIG. 7

NAME PENT.EL. UK BEATRICE

PARAMETER M1



PARAMETER M2



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

II CRUDES OF MIXED ORIGIN

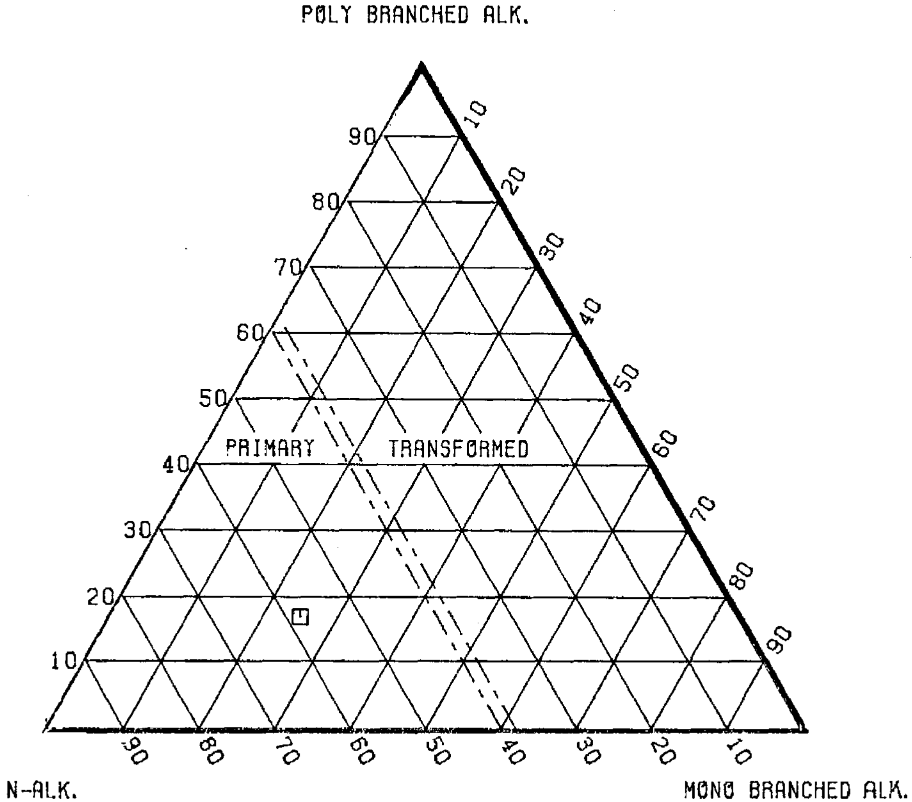
III CRUDES DERIVED FROM SOM AND/OR ALGAL MATTER

LEGEND

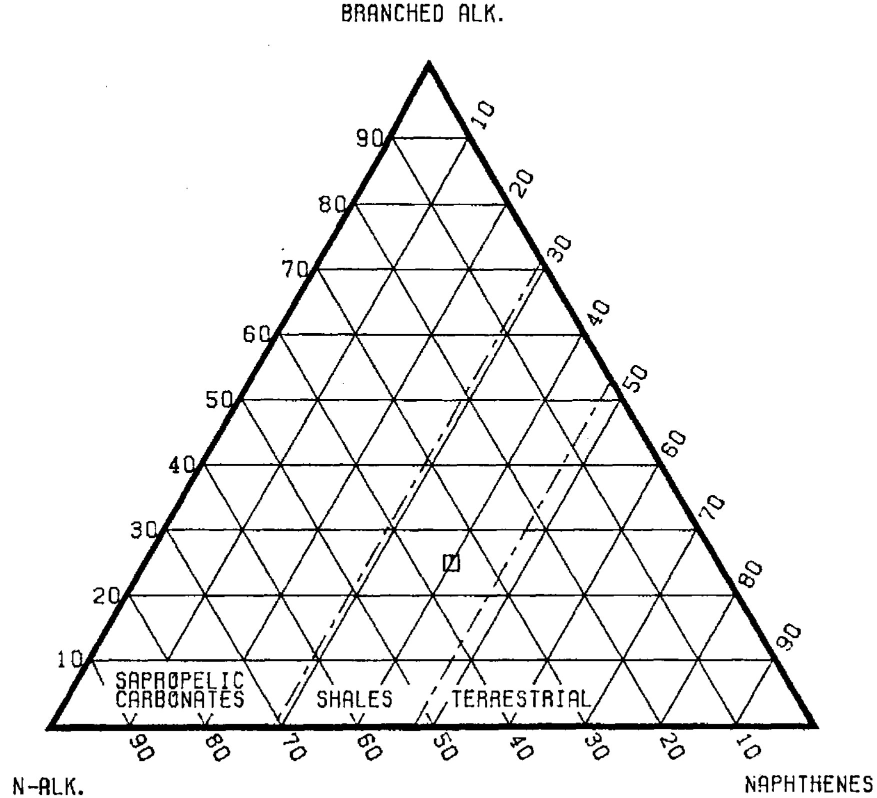
⊞ - 11/30-2	6429+6437+6449	F	6 days 330 C
⊘ - 11/.30-2	6491+6496	F	6 days 330 C
⚠ - 11/30-2	6884+6888+7023	F	6 days 330 C
+ - BEATRICE CRUDE			

FIG. 8

C7-ALKANE DISTRIBUTION



C7-ALKANE/NAPHTHENE DISTRIBUTION



LEGEND

□ - BEATRICE

FIG. 9

INITIAL DISTRIBUTION

3 copies SIPM-EP/12/13

RKER.80.056

SPECIFICATIELIJST van: 80 086

Ex.	Bij/door	Datum	Aan (te)
PG.			
ADDITIONS			~~LOCATION MAP.~~
			TABLE 1-1
			FIG. 1-3 (FIG. BIJ KALKMAN)
			FIG. 4-9.
DISTRIBUTION			~~5 MET KAFT (RINGBAND) - AUSTRALIE~~
			3 U.K.
			3 SIPM (EP/12)
			1 VGG
			1 WIJD
			1 PHA
			1 LIJM
			1 circuleren: DGO,EHT,GRA,GUT,BAAK/MW.KAMSTEEG, SFZ/MW.FABER,VEE,VGG
			1 FILE HTG
			1 BIBLIOTHEEK
			13 x
			Katt 1
			Inv. 912295