30-NOR-17α(H)-HOPANES AND THEIR APPLICATIONS IN PETROLEUM GEOCHEMISTRY

by

EDDY ARIYONO SUBROTO

This thesis is presented for the award of the
Degree of Doctor of Philosophy of the
Curtin University of Technology
1990

ABSTRACT

A suite of samples consisting of twenty-two crude oils and eight sedimentary rocks has been analysed for biological marker compounds by GC-MS. The sedimentary rocks are rich in carbonate minerals and the crude oils were reported to have been derived from carbonate source rocks. These samples are from a variety of geographical origins, geological ages and depositional environments. They consistently contain a homologous series of 30-nor-17α(H)-hopanes. Seven homologues (C_{28} - C_{34}) of the 30-nor-17α(H)-hopane series have been identified. These compounds appear to be useful biological markers for samples having carbonate associations.

A series of 25,30-bisnor-17α(H)-hopanes has been observed in a severely biodegraded crude oil of probable carbonate origin. This observation, together with the well-established enrichment of normal hopanes demethylated at position 25 in severely biodegraded crude oils, suggests that the presence of this series of hopanes indicates severe biodegradation of crude oils originating from carbonate-rich source rocks.

Another series of hopanes which was previously unreported, the 2-methyl-30-nor-17α(H)-hopanes, has

also been observed in the carbonate samples. Seven members (C_{29}-C_{35}) of this homologous series have been identified in this study. This series appears to be associated with carbonate rocks deposited under extreme reducing conditions.

The biological marker compounds in another sample suite comprising twelve sediments and three crude oils from the North Sumatra Basin, Indonesia, have also been analysed by GC-MS as part of a correlation study. Sediment samples classified as shales, carbonaceous shales and calcareous shales have been shown to contain very different biomarkers. These distinctive biomarkers have enabled the source characteristics of the crude oils to be inferred. Two crude oils have been recognised with similar biomarker characteristics to the shales and one crude oil has the characteristics of the calcareous shale. The distinctive features of the carbonaceous shale were not observed in the crude oils. This study therefore provides an excellent example of how the 30-nor-17α(H)-hopane compounds can be useful in oil-source rock correlation studies.

ACKNOWLEDGEMENTS

I would like to thank my project supervisors, Professor Robert Alexander and Professor John Scott, for their advice and encouragement during my PhD candidature. I would also like to thank Associate Professor Robert Kagi for his advice and guidance throughout the course of this work.

I am also indebted to the following people and organisations:

Dr Ron Noble (ARCO, Texas) and Dr Michael Strachan (formerly Curtin University), for their advice and assistance at the beginning of this study.

Mr Geoff Chidlow and Mr Nigel West, both of Curtin University, for their expert assistance in GC-MS analysis.

Mrs Gwenda Hart (Analabs), Mr Steve Fisher (Curtin) and Mr Mark Cumbers (SGE, Melbourne), for their assistance in laboratory works.

Dr P L Price (APG Consultant, Brisbane), for several crude oils and a sediment from Seram Basin, Indonesia.

Pertamina (Indonesian Oil Company) and Mobil Oil Indonesia, for a research scholarship and for allowing research to be carried out on their sediments and crude

oils.

PT Geoservices, Bandung, for financial support during the final stage of my study.

Chemistry Centre of the Government of Western Australia for access to their VG TS-250 GC-MS system.

Last but not least, I would like to thank my wife, Emmy, and my son, Rexy, for their support and encouragement throughout our stay in Western Australia.

TABLE OF CONTENTS

CHAPTER ONE

INTRODUCTION

1.1 AIMS AND SIGNIFICANCE OF THIS STUDY

1.1.1 Aims

This thesis reports on a study of crude oils and sediment extracts from carbonate sediments. The aim of this study was to identify biomarkers which characterise hydrocarbons deposited in carbonate-rich sediments. Although a considerable volume of literature is available on biomarkers that occur in carbonate sediments, to date few compounds have been reported that enable ready identification of a carbonate source for crude oils

A second aim of this study was to identify biomarkers characteristic of the main petroleum source rocks of the North Sumatra Basin with the objective of using these compounds to carry out an oil-source correlation study. Because one of the source rocks in the basin is rich in carbonate minerals, the biomarker technology development in the first part of the study has been applied to this problem.

1.1.2 Significance of This Study

A Biomarkers for Carbonate Sourced Crude Oil

Carbonate rocks are often associated with

commercial petroleum accumulations. They can be excellent reservoirs as well as prolific source rocks especially for crude oil (e.g. Mitterer et al., 1988). Their importance can be gauged from the fact that about 40% of the petroleum in major oil fields is in carbonate reservoirs, many of which are completely surrounded by carbonate rocks, indicating that carbonates can be important oil source beds (Oehler, 1984, and references therein). Apart from some bulk chemical characteristics, few definitive molecular indicators have been established which enable ready identification of crude oils from carbonate source rocks.

Some indicators of carbonate depositional environments have been proposed (e.g. Palacas et al., 1984; Moldowan et al., 1985; Mello et al., 1988). However, the present study has revealed a suite of biomarkers that may in future enable carbonate-derived oils to be readily and easily identified. In particular, the 30-nor-17α(H)-hopanes that have been identified in a suite of oils and source rocks from various locations and ages provide evidence that these compounds are potential markers for carbonate environments. In addition, a series of 25,30-bisnor- 17α(H)-hopanes have been investigated which appear to be related to biodegradation effects on carbonate sourced oils.

An additional series of previously unreported

compounds, 2-methyl-30-nor-17α(H)-hopanes, have also been identified. These compounds also appear to be associated with carbonate rocks and have been interpreted as indicators of extreme reducing conditions. They may therefore be biomarkers for highly reducing carbonate environments, conditions that are expected to be very favourable for oil prone source rocks.

B Oil - Source Correlation Study: North Sumatra Basin

The North Sumatra Basin is a major petroleum province of Indonesia. Despite its long history of petroleum production with crude oil first produced in 1893, biomarker studies of the basin are not well documented. In the present study, modern biomarker technology has been applied to twelve sediment samples representing three lithological types and to three crude oils with the aim of establishing the sources of the crude oils. The results demonstrate that the crude oils have been formed from shales and from carbonate source rocks. Both of these source rocks should be therefore regarded as potential sources of crude oil in future exploration programs.

1.2 BIOLOGICAL MARKERS

A biological marker (often shortened as biomarker) is any organic compound detected in the geosphere whose basic carbon skeleton suggests an unambiguous link with a known, contemporary natural product (Mackenzie, 1984). The role of biomarkers in petroleum exploration has greatly increased in the past decade mainly due to the development and ready availability in the mid 1970s of computerised gas chromatography - mass spectrometry systems necessary for routine analysis of crude oils and sediment extracts. The biomarker components of sediments and petroleum have been used for the assessment of the original nature or type of organic matter in sediments and crude oils, indicators for depositional environment and thermal maturation, markers for oil biodegradation and for correlation of oil to oil and oil to source rock (reviewed by Mackenzie, 1984; Philp, 1985a).

1.3 BIOMARKER GEOCHEMISTRY

Biomarkers have played an important role in oil exploration. Biomarkers have been widely used in petroleum geochemical studies for over a decade and several reviews have been published. A comprehensive review of biomarkers and their applications is beyond the scope of this thesis; however, a brief review is presented of biomarker chemistry relevant to the topics discussed in this thesis. Specifically, this review focuses on those aspects of biomarkers which relate to source material type, depositional environment, maturity, and indicators for biodegradation.

1.3.1 Biomarkers and the Source of Organic Matter

Bitumen, the organic material extracted from the rock using a solvent, consists of saturate, aromatic, asphaltene and NSO compounds. The composition of bitumen present in source rocks depends on the nature of the original organic matter. For example, algal material tends to yield predominantly saturated hydrocarbons, whereas a woody-plant contribution will increase the amount of aromatic hydrocarbons (Waples, 1981). The proportions of particular biomarkers in petroleum are very useful for characterising the source of the original organic matter.

Normal alkanes originate from higher alcohols and fatty acids and may therefore be regarded as biomarkers. Different sources give different n-alkane distributions. For instance, higher plants are one source of the higher molecular weight n-alkanes, showing maxima in the n-C_{23}-C_{27} range (reviewed by Philp, 1985a). These alkanes often show a marked predominance of odd carbon numbers in the n-C_{27}-C_{31} region. This feature is usually expressed as a Carbon Preference Index (CPI): in cases where odd carbon numbers predominate the CPI>1. The CPI was originally proposed by Bray and Evans (1961) and was shown to undergo progressive change during maturation. Since then, this index has been widely applied as a maturity parameter. However, its main use is as an indicator of the type of organic matter.

As an indicator for source type, it is generally accepted that an excess of odd-numbered n-alkanes in the C_{23}-C_{31} region means that the petroleum sample contains organic matter derived from higher plant waxes (Bray and Evans, 1961; Philippi, 1965; Scalan and Smith, 1970), whereas an even predominance (CPI<1) is often observed in carbonate-evaporite sediments (Tissot and Welte, 1984; Moldowan et al., 1985). On the other hand, when used as an indicator of thermal maturity, high CPI values (above 1.5) always indicate relatively immature samples, even though low CPI values do not necessarily mean higher maturity, since they may also result from a

lack of higher n-alkanes stemming from higher plant input (Tissot and Welte, 1984). Consequently, in the case of samples containing significant contributions of higher plants the following classification will be used in this thesis:

CPI	Remark
>1.5	Immature (not yet in the oil window)
1.0-1.5	Mature (within oil window)

In the case of samples showing a lack of contribution from higher plants the classification will be :

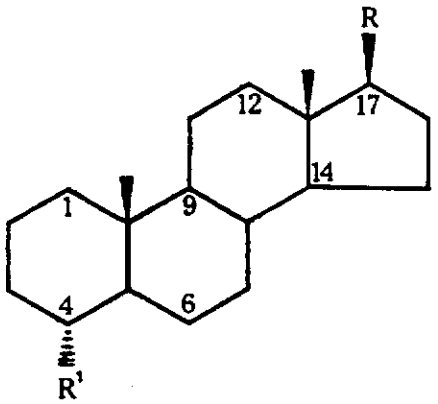
CPI	Remark
>1.2	Immature (not yet in the oil window)
1.0-1.2	Mature (within oil window)
<1.0	Carbonate-evaporite samples; CPI not to be used as maturity indicator

Steranes are an important group of biomarkers. These biomarkers are derived from sterols that can be found in higher plants and microorganisms. The dominant sources of C_{27} sterols are marine organisms (zooplankton), whereas higher plants contain predominantly C_{29} sterols (Huang and Meinschein, 1979). Consequently, the nature of the original source material affects the relative proportion of the C_{27} and C_{29}

steranes (1 and 3, Figure 1.1). C_{28} sterols are abundant in diatoms and the analysis of diatoms suggest that phytoplankton is a probable source of C_{28} sterols in planktonic samples (Huang and Meinschein, 1979 and references therein). C_{30} 4-desmethylsterols occur in marine invertebrates and marine algae (Moldowan et al., 1985 and references therein) and 4-methylsterols are significantly present in dinophyceae (dinoflagellates) (Mackenzie et al., 1982; Moldowan et al., 1985; Summons et al., 1987). 4-Methylsteranes (5) are usually less abundant than 4-desmethylsteranes (1 to 4) in sediments and crude oils, however their presence may provide more information about the type of the organic matter. For example, sediments and crude oils of marine origin may contain high abundances of 4α,23,24-trimethyl-cholestane (dinosterane; 5) whereas lacustrine sediments contain very low abundances of dinosterane (Summons et al., 1987).

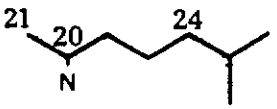
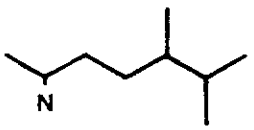
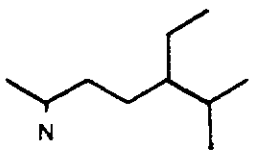
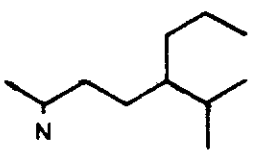
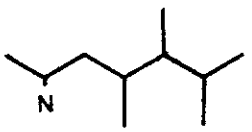
The most widely used parameter is the ratio of cholestane (a C_{27} sterane)/24-ethyl- cholestane (a C_{29} sterane)(e.g. Volkman et al., 1983a). Recently, Volkman (1986) has reviewed the use of this parameter, particularly when used as the sole source indicator, because he has observed that some marine sediments show predominances of C_{29} steranes. Thus, this parameter should be used in association with other source indicators, and interpretations made based upon this

Figure 1.1. The structures and probable precursors of some C_{27}-C_{30} steranes.



STERANE NUCLEUS

(N)

STRUCTURE NUMBER	NUMBER OF CARBONS	R	R^1	PROBABLE PRECURSORS
1	27		H	Marine plankton[a]
2	28		H	Diatoms/phytoplankton[a]
3	29		H	Higher plants[a]
4	30		H	Marine organisms[b]
5	30		CH_3	Dinoflagellates[b,c,d]

a: Huang and Meinschein (1979); b: Moldowan et al. (1985); c: Mackenzie et al. (1982); d: Summons et al. (1987)

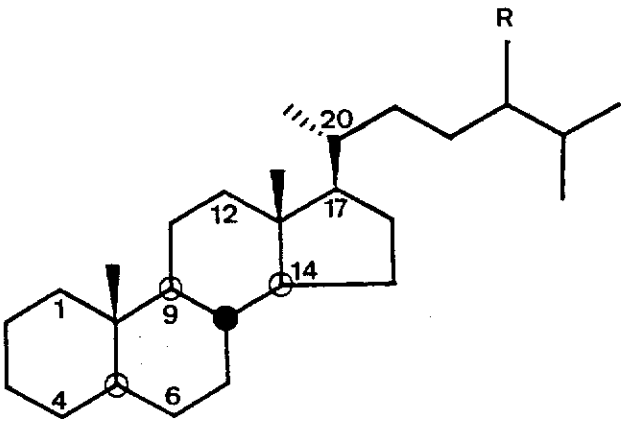
parameter must be consistent with other evidence.

The ratio used in this study is 20R-14α(H),17α(H)-cholestane (6a)/20R-14α(H),17α(H)-24-ethylcholestane (6c, Figure 1.2). Values <1 are interpreted as indicating significant higher plant contributions, and values >1 are taken to indicate high contributions of aquatic organisms.

Another group of polycyclic alkanes which occur widely in sediments and crude oils are the triterpanes. The hopane-type triterpanes (9-13; Figure 1.3 and Figure 1.4) are the group of triterpanes which are most extensively used in biomarker studies. Their precursors are widely distributed among bacteria and the cyanobacteria (blue-green algae) and have also been found in tropical trees, some grasses and lichens, and several ferns (reviewed by Philp, 1985a).

Other triterpanes which are found in petroleum are those having structures other than that of the hopane type. A small number of these triterpanes have been identified and have been employed mainly as source indicators. For example, 18α(H)-oleanane (14; Figure 1.4) has been observed in a number of deltaic sediments (e.g. Ekweozor et al., 1979a; Hoffman et al., 1984; Riva et al., 1986; Mello et al., 1988) and in a number of crude oils mostly related to deltaic sediments (e.g.

Figure 1.2. The structures of some sterane isomers found in sediments.

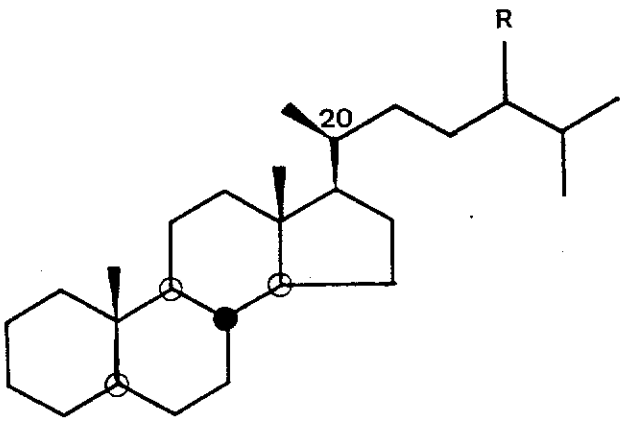


6 (20R)-5α(H),14α(H),17α(H)-STERANES

a R = H ; CHOLESTANE (C_{27})

b R = CH_3 ; METHYLCHOLESTANE (C_{28})

c R = C_2H_5; ETHYLCHOLESTANE (C_{29})

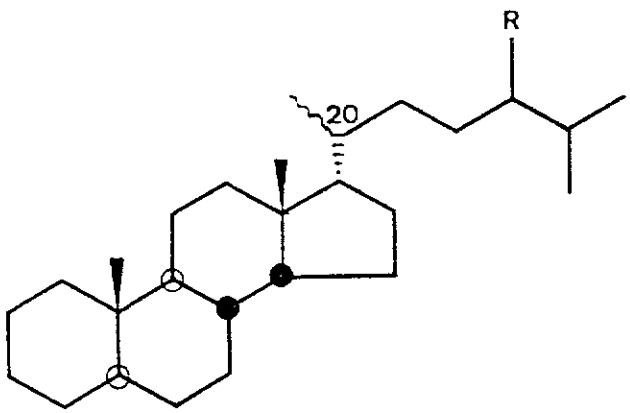


7 (20S)-5α(H),14α(H),17α(H)-STERANES

a R = H ; CHOLESTANE (C_{27})

b R = CH_3 ; METHYLCHOLESTANE (C_{28})

c R = C_2H_5; ETHYLCHOLESTANE (C_{29})



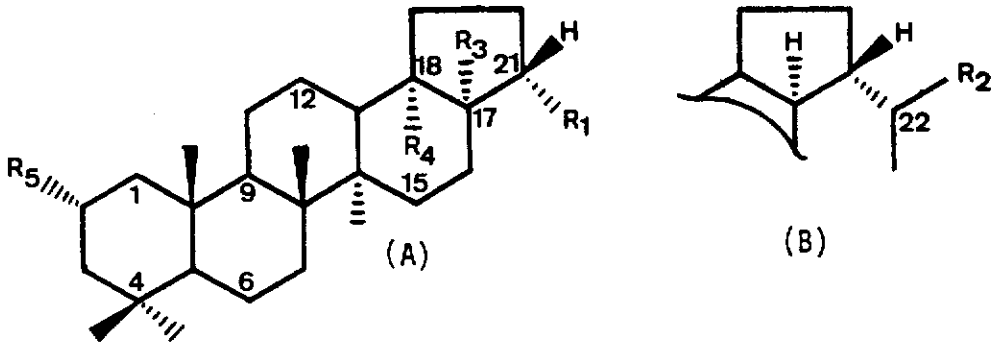
8 5α(H),14β(H),17β(H)-STERANES

a R = H ; CHOLESTANES (C_{27})

b R = CH_3 ; METHYLCHOLESTANES (C_{28})

c R = C_2H_5; ETHYLCHOLESTANES (C_{29})

Figure 1.3. The structures of some hopane-type triterpanes found in sediments. Structures B have a chiral centre at C-22.



9 17α(H),21β(H)-HOPANES

Structure	Carbon Number	Remarks[a]
a	27(Tm)	R_1 = H
b	29	R_2 = H
c	30	R_2 = CH_3
d	31	R_2 = C_2H_5
e	32	R_2 = C_3H_7
f	33	R_2 = C_4H_9
g	34	R_2 = C_5H_{11}
h	35	R_2 = C_6H_{13}

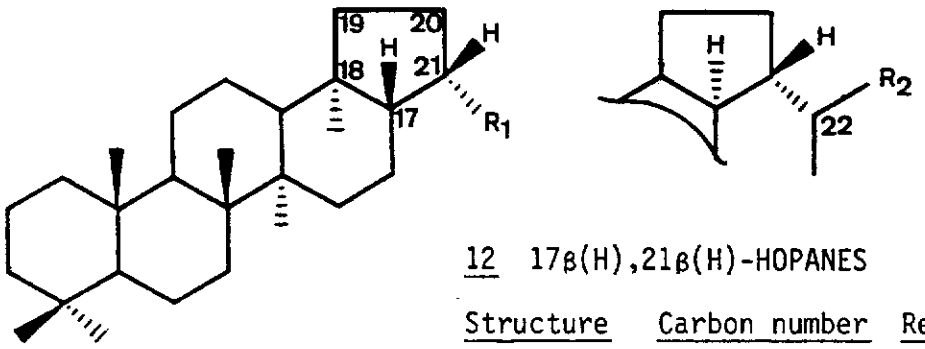
a : All compounds have R_3=R_5=H; R_4=CH_3

10 17α(H)-2α-METHYLHOPANES
(R_3=H; R_4=R_5=CH_3)

11 18α(H)-22,29,30-TRISNORNEOHOPANE (Ts)
(R_1=R_4=R_5=H; R_3=CH_3)

Figure 1.4. The structures of $\beta\beta$ hopanes, moretanes and 18α(H)-oleanane. Structures B have a chiral centre at C-22.

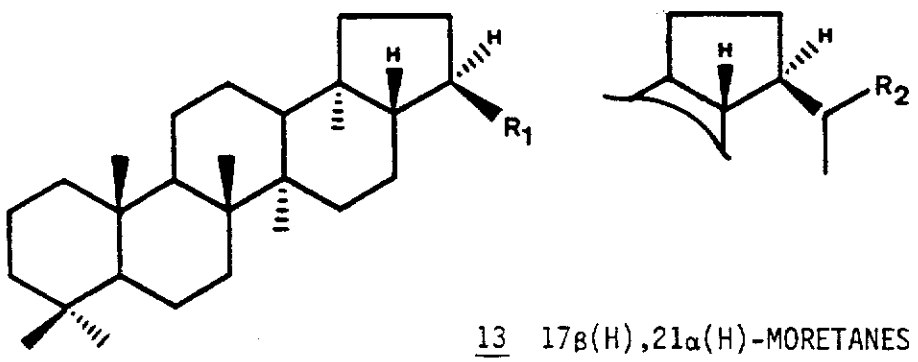
a (A) (B)



12 17β(H),21β(H)-HOPANES

Structure	Carbon number	Remarks
a	27	R_1 = H
b	29	R_2 = H
c	30	R_2 = CH_3
d	31	R_2 = C_2H_5

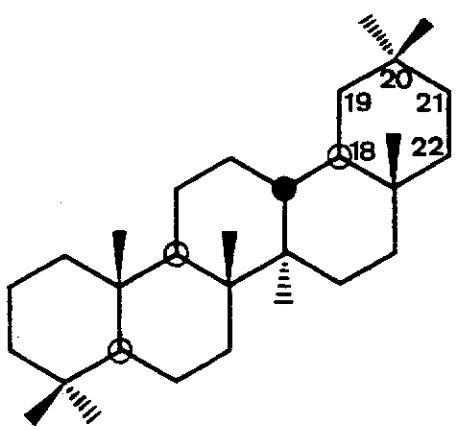
b (A) (B)



13 17β(H),21α(H)-MORETANES

a C_{30} MORETANE (R_2 = CH_3)

c



14 18α(H)-OLEANANE

Whitehead, 1974; Ekweozor et al., 1979b, Grantham et al., 1983, Hoffman et al., 1984; Philp and Gilbert, 1986; Riva et al., 1986; Talukdar et al., 1986; Zumberge, 1987 and references therein; Mello et al., 1988). Recently, Riva et al. (1988) have identified 18α(H)-oleanane and 18β(H)-oleanane, but on most capillary columns these isomers are difficult to separate. The biogenic precursors of oleanane occur in the resins of terrigenous plants, in particular in some angiosperms, flowering plants which have been dominant since the middle of the Cretaceous period (Whitehead, 1974; Ekweozor and Udo, 1988). Furthermore, ten Haven and Rullkotter (1988) have suggested that oleananes are derived from taraxerane. Mello et al. (1988) observed a relationship between the oleanane abundance of some Brazilian sediments and crude oils and their source environments. Using the Oleanane Index defined as a ratio of 18α(H)-oleanane (14) to C_{30} 17α(H)-hopane (9c) x 100, they have found that material deposited in marine deltaic environments has a value for the index between 20 and 40. Oleanane was however not detected in other depositional environments. In addition, this compound is sometimes absent in many terrestrially dominated sediments and crude oils of Tertiary age. This is thought to be due to aromatisation processes which result in conversion of the triterpanes into smaller aromatic molecules such as naphthalenes, particularly in environments which are favourable to coal

formation (Strachan et al., 1988).

1.3.2 Depositional Environments

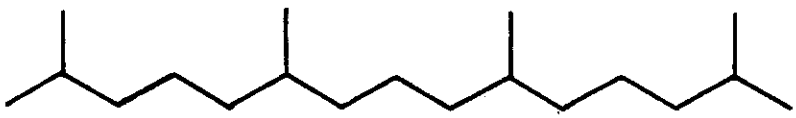
The distributions of n-alkanes and isoprenoids have been used to infer the depositional environment of source rocks. The use of the Carbon Preference Index (CPI) may sometimes indicate a specific depositional environment. For example, an even predominance of the n-alkanes in the C_{20} and C_{30} region is usually assumed to reflect evaporitic facies (Dembicki et al., 1976; Spiro and Aizenshtat, 1977; Sheng et al., 1980; Powell, 1986). In some cases the even n-alkane preference may also reflect marine carbonate environments (Moldowan et al., 1985; Connan et al., 1986) or reducing conditions (Albaiges and Torradas, 1974). A reduction of alcohols, carboxylic acids and esters in the reducing environments has been suggested as a mechanism by which an even n-alkane predominance may arise (Sheng et al., 1980).

Pristane (15, Figure 1.5) and phytane (16) have been widely assumed to be derived from phytol of chlorophyll or from bacterial cell walls (e.g. Brooks et al., 1969), and possibly from other precursors such as tocopherols (Goosens et al., 1984). The ratio of pristane/phytane is usually interpreted to be an

indicator for the degree of oxicity of the environment of deposition (Didyk et al., 1978). In anoxic (highly reducing) conditions, the value of the pristane/phytane ratio is usually less than one as phytane is the predominant product in these environments; in less reducing environments the value is greater than one because in such environments pristane is dominantly formed by bacterial oxidation of phytol (Didyk et al., 1978; Moldowan et al., 1985). Since most of the recent hypersaline environments are characterised by reducing conditions (ten Haven et al., 1985; Sinninghe Damste et al., 1989), the pristane/ phytane ratio, therefore, has also been suggested as an indicator for salinity (ten Haven et al., 1985). Sediments deposited in hypersaline environments are usually characterised by low values (<1) of the pristane/phytane ratio (ten Haven et al., 1987, and references therein). However, these generalisations should be used with caution as the ratio may not always conform to this simplified classification because such a ratio is also influenced by thermal maturity (Mackenzie et al., 1981; Goosens et al., 1984). Moreover, ten Haven et al. (1987) have demonstrated the limitations of the pristane/phytane ratio as an indicator for oxygen levels.

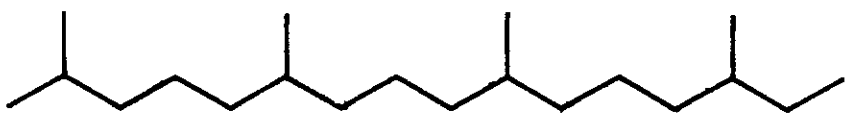
Based on the available literature, the following pristane/phytane ratio boundary values are used to assess the depositional environment :

Figure 1.5. The structures of pristane and phytane.



15

PRISTANE



16

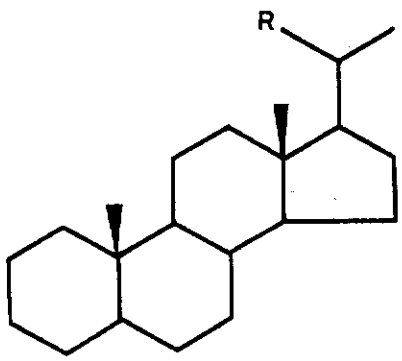
PHYTANE

Pr/Ph	Depositional Environment
>1	Oxic
<1	Anoxic or hypersaline

In the present study, this parameter is used only in conjunction with the other indicators of depositional environment to assess conditions of sedimentation.

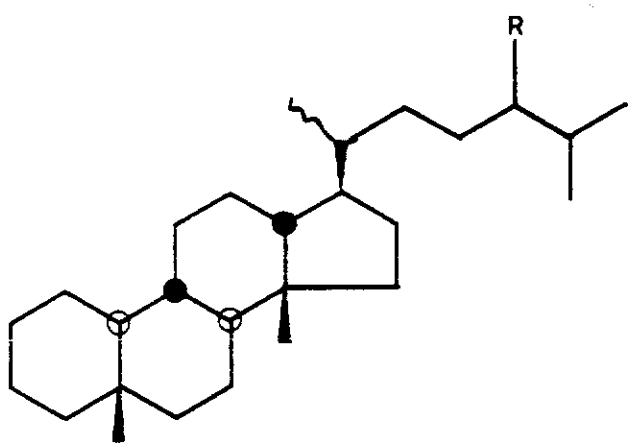
Some of the steranes such as the low molecular weight, C_{21} sterane (pregnane; 17; Figure 1.6) and C_{22} sterane (homopregnane; 18) have been used as palaeoenvironmental indicators. ten Haven et al. (1985) have observed that pregnane and homopregnane are the most abundant compounds in sediments containing gypsum (an evaporite mineral), and therefore suggested that high abundances of these compounds may be the result of a hypersaline environment. These compounds were also reported to be in abundance in saline sediments from the Jianghan Basin, China (Fu et al., 1986). Relatively high abundances of these compounds have also been reported in samples from carbonate environments (Price et al., 1987; Mello et al., 1988), as well as in marine evaporitic and marine deltaic environments (Mello et al., 1988). The precursors of these compounds are still not established (ten Haven et al., 1985), but they might be formed by degradation of the side chain from the cholestanes by certain bacteria (Moldowan et al., 1985).

Figure 1.6. The structures of pregnane, homopregnane and diasteranes.



17 R = H ; PREGNANE

18 R = CH_3; HOMOPREGNANE



19 DIASTERANES

a R = $C_2H_5 \rightarrow C_{29}$

(ETHYLDIACHOLESTANE)

Price et al. (1987) compared the abundances of pregnane and homopregnane to that of 24-ethylcholestanes in crude oils. They reported that in some crude oils deposited in marine deltaic or deeper marine environments the ratio of $(C_{21}+C_{22})/C_{29}$ steranes is usually lower than 0.7, whereas the value in the carbonate-sourced crude oils was usually higher than 0.7. Based on their observations, the following values of the ratio will be used to characterise the depositional environment in this study:

$(C_{21}+C_{22})/C_{29}$ Steranes	Depositional Environment
>0.7	Marine carbonate or hypersaline
<0.7	Marine deltaic, deeper marine

Other steranes which may serve as palaeo-environmental indicators are the rearranged steranes or diasteranes (19, Figure 1.6). Diasteranes occur in most sediments or crude oils, but their abundances are relatively low: they may be absent altogether in samples formed under anoxic or alkaline conditions such as those in hypersaline or carbonate environments (McKirdy et al., 1984; Fu et al., 1986; Price et al., 1987). Such features have been suggested to arise from the absence of acidic clays to catalyse the steroid rearrangement process (Rubinstein et al., 1975). Therefore, the ratio of ethyldiacholestanes (19a)/ethylcholestanes (6c, 7c and

8c) can be used as an indicator of depositional environment. Sediments deposited in alkaline environments have values less than 0.3, whereas those deposited in acidic environments have values greater than 0.3 (Fu et al., 1986; Price et al., 1987).

Pentacyclic triterpanes have also been used as indicators for palaeoenvironments. For example, the occurrence of C_{34} 17α(H),21β(H)-hopanes (9g) and/or C_{35} hopanes (9h) in higher concentrations than the other homohopanes (C_{31}-C_{33}; 9d-f) is a characteristic of many samples from hypersaline environment (Palacas et al., 1984; ten Haven et al., 1985; Connan et al., 1986; Fu et al., 1986; Mello et al., 1988). Structures of these homohopanes are given in Figure 1.3.

Hopanes having an additional methyl substituent in ring A have been reported by a number of authors (e.g. Seifert and Moldowan, 1978; Brassell et al., 1980; Dastillung et al., 1980; Alexander et al., 1984a; McEvoy and Giger, 1986; Hoffman et al., 1987; Price et al., 1987; Summons and Powell, 1987; Summons et al., 1988). It was formerly assumed that these hopanes had an additional methyl at C-3 based on the reported detection of 3-methylhopanes in bacteria (Rohmer and Ourisson, 1976). However, the observation made by Hoffmann et al. (1987) on a sediment having two pseudohomologous series of methylhopanes showed the necessity to establish the

structures of these compounds. Summons and Jahnke (1990a,b) have recently shown that the most commonly reported methylhopanes are 2α-methylhopanes (10; Figure 1.3).

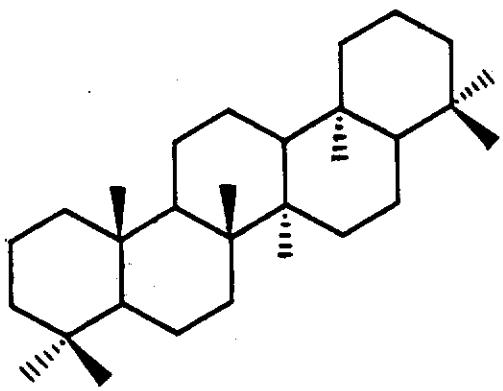
The 2-methylhopane series has been reported to occur in relatively moderate to high abundance in Jurassic crude oils from McKittrick Field, California (Seifert and Moldowan, 1978), in Ordovician - Devonian crude oils from Canning Basin, Australia (Alexander et al., 1984a), in Triassic Serpiano oil shales (McEvoy and Giger, 1986), in numerous Ordovician sediments, particularly those containing Gloeocapsomorpha prisca (Hoffman et al., 1987), in Triassic crude oils from carbonate environments of the Seram Basin, Indonesia (Price et al., 1987), in several Palaeozoic sediments and crude oils from carbonate environments (Summons and Powell, 1987), and in Pre-Cambrian sediments of the McArthur Basin, Australia (Summons et al., 1988). It is noteworthy that most of the samples were deposited in carbonate and/or hypersaline environments. However, because some of the occurrences are in clastic sediments it is likely that some feature of the depositional environments other than the presence of carbonate minerals, promotes the formation of the 2-methylhopanes.

Another pentacyclic triterpane which has often been used as an indicator for salinity is gammacerane (20,

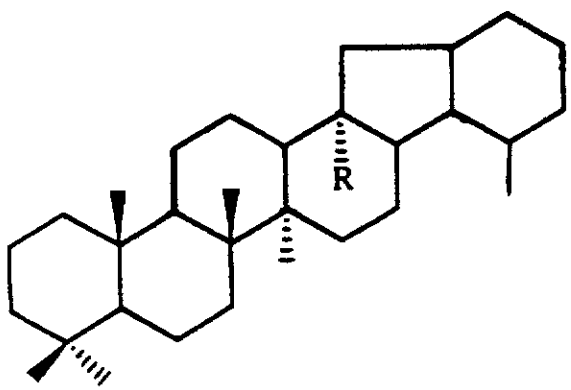
Figure 1.7). Tetrahymanol (gammaceran-3β-ol) is the only known potential biological precursor of gammacerane. Tetrahymanol has been observed in the protozoan Tetrahymena (Mallory et al., 1963), in a fern (Zander et al., 1969) and in cultures of the anaerobic rumen fungus Piromonas communis (Kemp et al., 1984). ten Haven et al. (1989) point out that an origin from land plants as suggested by Zander et al. (1969) appears unlikely, since gammacerane was also detected in Late Proterozoic sediments by Summons et al. (1988) which predate the first appearance of land plants. On the other hand, tetrahymanol has been observed to commonly occur in various marine sediments suggesting that protozoa of the genus Tetrahymena are probably the source organisms of this compound (ten Haven et al., 1989; Venkatesan, 1989).

Gammacerane was first identified in the Green River shale (Hills et al., 1966) and was therefore suggested as a biomarker for nonmarine environments. However, more recent studies have shown gammacerane to be present, even though sometimes in very low concentrations, in many samples from various environments (Moldowan et al., 1985; ten Haven et al., 1988; Mello et al., 1988). Nevertheless, it has been suggested that a high relative abundance of gammacerane usually relates to hypersaline depositional conditions (ten Haven et al., 1985, 1988; Moldowan et al., 1985; Fu et al., 1986; Mello et al., 1988). Thus, the use of gammacerane as a biomarker for

Figure 1.7. The structures of gammacerane and hexacyclic hopanoid alkanes.

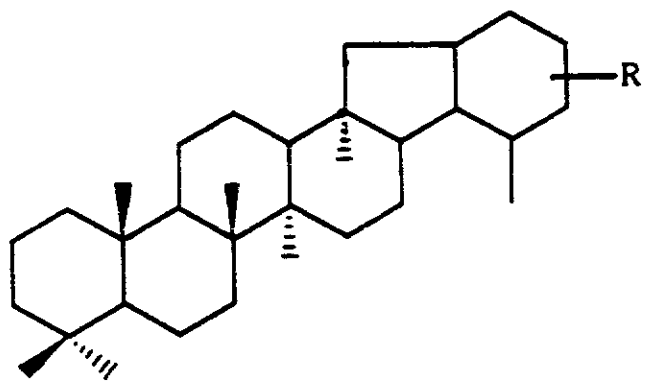


20 GAMMACERANE



HEXACYCLIC HOPANOID ALKANES

Structure Number	R	Carbon Number
21	CH_3	32
25	H	31



22	CH_3	33
23	C_2H_5	34
24	C_3H_7	35

salinity is not based on its occurrence, but rather on its relative abundance. In this study the abundance of gammacerane has been expressed as the Gammacerane Index and is defined in Section 2.4.2. It appears that the boundary between hypersaline and non-hypersaline environments lies on the index value of 20 (Fu et al., 1986; Mello et al., 1988).

Connan and Dessort (1987) have used C_{32}-C_{35} hexacyclic hopanoid alkanes (21-24; Figure 1.7) as indicators for anoxic palaeoenvironments, in particular sabkha-type deposits. In addition, Rinaldi et al. (1988) have tentatively identified the C_{31} member of these hexacyclic hopanoid alkanes (25). The C_{31} homologue occurs more widely than the other four members ($C_{32/6}$-$C_{35/6}$), but its occurrence is restricted to samples from anoxic environments (Connan and Dessort, 1987; Rinaldi et al., 1988). These authors have suggested that the hexacyclic hopanoid alkanes were derived from bacteriohopanetetrol (C_{35}) precursors through cyclisation of the side chain of extended hopanoids during early diagenesis.

1.3.3 Maturation of Organic Matter

Biomarker maturity determinations are generally based upon changes in steranes and triterpanes (Mackenzie, 1984). One of the maturity parameters based upon steranes is the proportion of the two diastereomeric forms (20R and 20S) of steranes (6) and (7). The 20R isomer (6) is derived from natural product steroid precursors and therefore it dominates the sterane distributions of immature sediments. With increasing maturity the relative proportion of 20S isomer (7) increases until a steady state value is reached in the oil window. The steady state value is approximately 1.1 if expressed as 20S/20R or 0.55 if expressed as 20S/(20S+20R) (Mackenzie, 1984). Thus the majority of crude oils have ratios near this value. However, the report of 20S/(20S+20R) values as low as 0.18 in some Tertiary crude oils (Grantham, 1986) is a notable exception to this pattern and was interpreted as a very unusual sediment heating rate effect.

Strachan et al. (1989) have investigated this phenomenon using a kinetic approach. Two sedimentary sequences were examined: one sequence was a shale containing predominantly type II kerogen, and the other contained mainly type III kerogen in the form of thin coal seams and dispersed particles. They concluded that the rate at which the sterane isomer ratio changes depends upon the type of rock matrix and the sediment

heating rate. Sediments which contain type III organic matter in the form of dispersed coals as the dominant source of hydrocarbons would produce petroleum with anomalously low sterane epimer ratios if they had experienced a high heating rate as a result of high geothermal gradients and/or high burial rates. Therefore caution should be exercised in interpreting the values for the sterane ratio when assessing the maturity of sediments, as it is a function of both the rock matrix and the sedimentary heating rate. In this study the ratio of 20S/20R diastereomers was used only in conjunction with other maturity parameters. Values were obtained from measurements on the C_{29} steranes, which are least susceptible to coelution problems.

The 14α(H),17α(H)-sterane skeletons which are produced biologically and appear as hydrocarbons when sediments mature are believed to be converted into the thermodynamically more stable compounds, 14β(H),17β(H)-steranes (8) with increase in sediment maturity (Seifert and Moldowan, 1979; Mackenzie et al., 1980;1982). Thus, the proportion of these two species has also been used as a maturity indicator. It is usually expressed as either the ratio $\beta\beta/\alpha\alpha$ or $\beta\beta/(\beta\beta+\alpha\alpha)$. However, there are some warnings concerning the use of this indicator (e.g. Mackenzie, 1984; ten Haven et al., 1986). These warnings have recently been confirmed by Peakman et al. (1989) who

point out that the 14β(H),17β(H)-steranes in immature sediments can also be derived from Δ^7 and $\Delta^{8(14)}$ 5α(H)-sterols. This situation can occur in hypersaline environments, even though other environments cannot be excluded (Peakman et al., 1989 and references therein). In the present study this parameter is expressed as $\beta\beta/(\beta\beta+\alpha\alpha)$. Using this expression an apparent equilibrium is reached at the value of 0.6-0.7 (Seifert and Moldowan, 1986).

The hopane stereoisomers also change with increasing thermal maturation. The natural products which are the precursors of the sedimentary hopanes have the 17β(H),21β(H) stereochemistry (12; Figure 1.4). The hydrocarbons with this stereochemistry are abundant in immature sediments (Ourisson et al., 1979). Diagenesis and maturation result in a relative increase in the more stable 17α(H),21β(H) and 17β(H),21α(H) compounds (9 and 13, respectively) (Ensminger et al., 1977). The relative proportions of 17β(H),21α(H)-hopanes (13), often termed moretanes, also decrease at higher levels of maturity (Seifert and Moldowan, 1980). The equilibrium ratio for $\beta\alpha$ to $\alpha\beta$ configurations is approximately 0.1 which is achieved at an early stage of oil generation (Mackenzie, 1984). When R_1 in Figure 1.3 and Figure 1.4 is greater than $-CH_3$, that is for extended hopanes and moretanes ($\geq C_{31}$), then a chiral centre exists at position C-22 and therefore 22S and 22R epimers are

possible. The hopanoid natural products have the 22R configuration, but increase in maturity leads to a mixture of 22R and 22S epimers whose equilibrium ratio is approximately 60:40 (Ensminger et al., 1974; Seifert and Moldowan, 1980).

Another maturity parameter based on a hopane-type triterpane is the ratio between C_{27} 17α(H)-hopane or Tm (9a) and C_{27} 18α(H)-hopane or Ts (11). Seifert and Moldowan (1978) have observed that Ts is more resistant to thermal degradation than Tm and consequently the ratio of Tm/Ts decreases systematically with increasing maturity. However, the abundances of these compounds are partly dependent on source input as well as maturity (Palacas et al, 1984). Therefore, the Tm/Ts ratio, as an indicator of maturity, must be used with caution.

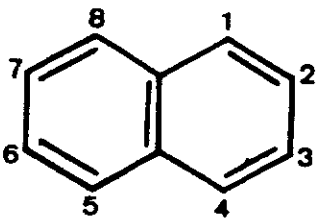
The use of aromatic hydrocarbons as maturity indicators has attracted much attention (e.g. Radke et al., 1982a,b; Radke and Welte, 1983; Mackenzie and McKenzie, 1983; Alexander et al., 1984b;1985;1986;1988; Radke, 1987;1988). The aromatic maturity indicators that have been used are based upon naphthalene (26; Figure 1.8) and phenanthrene (27) ring systems with two (di-) or three (tri-) methyl groups attached. It has been observed that in the more mature sediments the relative proportions of $\alpha\alpha$ isomers in dimethylnaphthalenes

(DMN) are lower than the $\alpha\beta$ and the $\beta\beta$ isomers and the proportions of the $\alpha\alpha\beta$ isomers in trimethylnaphthalenes (TMN) are lower than those of the $\alpha\beta\beta$ isomers (Alexander et al., 1985). These phenomena have been attributed to maturation effects; that is, the less stable α-substituted isomers are continuously depleted relative to the more stable β-substituted isomers (Radke et al., 1982b; Alexander et al., 1985). Based on investigations of alkyl naphthalenes and alkyl phenanthrenes, a number of potential maturity indicators have been proposed (Radke et al., 1982b; Radke and Welte, 1983; Alexander et al., 1985; Radke, 1988). For definitions of parameters used in this study see Section 2.4.2.

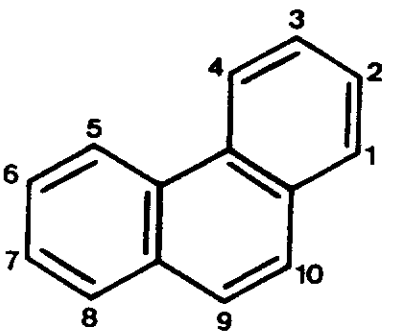
1.3.4 Assessment of Biodegradation

The initial composition of a crude oil is mainly dependent on the nature of the organic matter in the source rock, but it may be substantially altered during migration (e.g. Leythaeuser et al, 1984; England et al., 1987) or in the reservoir by processes such as biodegradation and water washing (Seifert and Moldowan, 1979; Goodwin et al., 1983; Palmer, 1984; Lafargue and Barker, 1988). Biodegradation of crude oil results from the utilisation of petroleum hydrocarbon mainly by the aerobic bacteria which obtain the oxygen and nutrients

Figure 1.8. The structures of naphthalene and phenanthrene.



26 NAPHTHALENE



27 PHENANTHRENE

they need from meteoric waters (Bailey et al., 1973; Connan, 1984). Such waters will remove the more soluble components from the oil so that water washing generally co-occurs with biodegradation (Lafargue and Barker, 1988). It should be noted that the effects of bacterial degradation become less important as temperature increases. Extensive biodegradation of crude oils occurs in reservoirs with a temperature range from 20 to 75°C (Connan, 1984).

It has been reported that aerobic bacteria attack crude oils preferentially removing n-alkanes, isoalkanes, cycloalkanes, and aromatic hydrocarbons (Bailey et al., 1973; Seifert and Moldowan, 1979; Volkman et al., 1983b; Connan, 1984). Volkman et al. (1983b) have proposed a numerical classification scale to describe the major changes to the composition of a typical paraffinic oil with increasing extent of biodegradation, starting from 1 for undegraded to 9 for oil showing extreme biodegradation. However, since biodegradation is made up of a number of complex processes involving different types and populations of bacteria and environmental factors such as oxygen availability, crude oil degradation may not always follow the same sequence of steps (Volkman et al., 1983b). For example, McKirdy et al. (1983) reported that non-rearranged and rearranged steranes were degraded before hopanes in a group of heavily biodegraded crude oils from South Australia,

however the opposite order of depletion was observed in some biodegraded crude oils from the U.S. Gulf Coast and Western Greece (Seifert and Moldowan, 1979; Seifert et al., 1984).

1.4 SOURCE ROCK - CRUDE OIL CORRELATION

The main objective in source rock - crude oil correlation is to identify the source rock of a given oil. The principal subjects of study for correlation are the kerogen of a source rock, the bitumen extractable from the source rock and the oil which is possibly derived from the source rock. Correlation between oil and source rock is usually more difficult than oil - oil correlation (e.g. Hunt, 1979; Tissot and Welte, 1984). Oil has accumulated through the processes of primary and secondary migration, thus there are compositional differences between the bitumen left behind in a source rock and the fraction of bitumen which accumulated in a reservoir. For example, crude oils are commonly enriched in saturated fractions and depleted in resin and asphaltene compounds when compared to the source rock bitumen.

The differences which occur in biomarker composition between crude oils and their source rocks are caused by at least two factors, namely variations in biomarker distributions with the state of kerogen maturation and migration effects. It has been reported by Eglinton and Douglas (1988) that the biomarker distributions in bitumens may differ from that in kerogen generation products. Noble *et al*. (1985) in their

pyrolysis experiments on some Western Australian shales have demonstrated such differences. In the rock extract they identified 25-desmethylhopane compounds in addition to the common hopane and moretane series, but in contrast pyrolysates of solvent-extracted sediments contained only the common hopanes and moretane series. These differences were attributed to the occurrence of one compound class mainly as free hydrocarbon whereas the other occurred mainly in the bound state. Thus it is apparent that biomarker compositions in kerogen and in bitumen may differ substantialy so that the biomarker composition of the bitumen may vary according to the amount of kerogen that has been cracked.

Migration of hydrocarbons, particularly at the stage of expulsion, may influence biomarker distributions. Leythaeuser et al. (1984) have observed that during expulsion the lower carbon number n-alkanes are expelled preferentially. This leads to an absolute enrichment of the lower carbon number n-alkanes in the migrating fluids and a relative enrichment of the higher molecular weight n-alkanes in the residual hydrocarbon mixture in the source rock. Following the same principle, some other parameters such as the odd/even predominance of the high carbon number n-alkanes, the Carbon Preference Index (CPI) and the pristane/n-heptadecane ratio are also claimed to be influenced by migration processes (Leythaeuser et al., 1984; Leythaeuser and

Schwarzkoff, 1986). In addition, Jiang et al. (1988) have observed that gammacerane is a late expulsion product and pointed out that oils with low concentrations of gammacerane may be derived from source rocks with higher concentrations of this component. It is apparent that migration processes affect the biomarker composition in crude oils and in source rocks and such processes may sometimes make the correlation between the crude oils and their source rocks difficult.

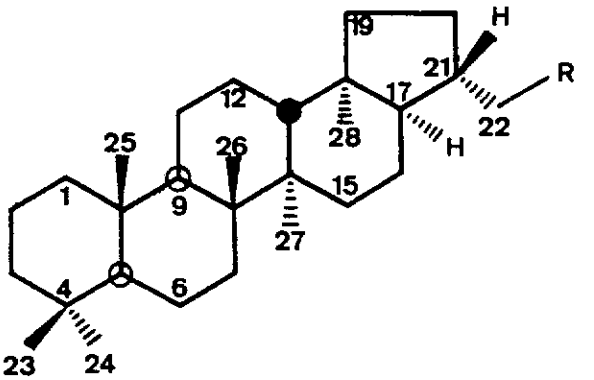
Geochemical correlation between oil and source rock is generally based upon recognition of compositional similarities. Such similarities are established on relative distribution patterns of certain compounds and not on absolute concentration values (e.g. Tissot and Welte, 1984; Eglinton and Douglas, 1988). Therefore, any group of compounds selected for correlation should be similar in their physicochemical properties.

1.5 30-NOR-17α(H)-HOPANES IN CRUDE OILS AND SEDIMENTS

Pentacyclic triterpanes of the hopane structural type are ubiquitous constituents of sedimentary organic matter (Ries-Kautt and Albrecht, 1989). The hopanes are apparently derived from a C_{35} hopanetetrol synthesised by bacteria, which is subsequently defunctionalised and degraded to yield a series of saturated compounds with carbon numbers from 27 to 35 (Ourisson et al., 1979; 1984). Crude oils and mature sediments usually contain a predominance of hopanes with the 17α(H),21β(H) skeletal configurations (Seifert and Moldowan, 1980), commonly referred to as 17α(H)-hopanes. The following section describes the literature associated with a particular novel series of hopanes namely the 30-nor-17α(H)-hopanes (28; Figure 1.9), in which the methyl group found at C-22 in normal 17α(H)-hopanes is absent.

Seifert et al. (1984) reported on the occurrence of a related but less common group of hopanes in oil seep samples from Greece. Five compounds (C_{28}, C_{30}, C_{31}, C_{32} and C_{33}) were tentatively identified as a series of 17α(H)-hopanes with n-alkyl side chains. More recently, Moldowan et al. (1989) have confirmed the identity of the C_{28}, C_{30} and C_{34} members in crude oils by comparison with synthetic standards. All of the

Figure 1.9. The structure and numbering system of 30-nor-17α(H)-hopanes.



28 30-NOR-17α(H)-HOPANES

compounds that were synthesised had identical stereochemistry to the common 17α(H)-hopanes as shown in structure 28. They also have shown that the distribution of the 30-nor-17α(H)-homohopanes (C_{30} - C_{34}) closely reflects that of the common 17α(H)-homohopanes (C_{31} - C_{35}). They then concluded that the 30-nor-17α(H)-hopanes are produced from similar bacterial precursor compound(s) except for the presence or absence of a C-30 methyl group, and that the geochemistry of the two series is similar.

The occurrence of some members of the 30-nor-17α(H)-hopane series has been reported by other authors. For example, the C_{28} member has been observed to occur in oil-stained dolomites from the Camargue Basin, South France (Connan and Dessort, 1987); in the Zama oil from Canada (Summons and Powell, 1987); in the Barney Creek sediments from Australia and in Siberian oil (Summons et al., 1988). In addition, Price et al. (1987) have reported the presence of both the C_{28} and C_{30} homologues in some crude oils from the Seram Basin, Indonesia. Interestingly, all the samples containing the 30-nor-17α(H)-hopanes were carbonates, or, in the case of crude oils, sourced from carbonate source rocks. These compounds have been reported to occur in biodegraded as well as in non-biodegraded crude oils and in sediments.

CHAPTER TWO

EXPERIMENTAL

2.1 MATERIALS

2.1.1 Solvents

Benzene : Ajax laboratory grade benzene was fractionally distilled (b.p.=80-81^{o}C). The solvent was stored over activated 5 A BDH molecular sieves.

Dichloromethane : Ajax laboratory grade dichloromethane was fractonally distilled (b.p.=40-41^{o}C).

Diethyl Ether : Ajax laboratory grade diethyl ether was fractionally distilled (b.p.=35^{o}C).

n-Hexane : Mallinckrodt analytical grade n-hexane (b.p.= 68.7^{o}C) was fractionally distilled.

Methanol : Laboratory grade methanol (BP Australia) was purified by adding concentrated sulfuric acid (5% by volume), refluxing for 2 hours, followed by fractional distillation (b.p.=65^{o}C).

n-Pentane : Ajax laboratory grade pentane (b.p.=36^{o}C) was fractionally distilled.

2.1.2 Miscellaneous

Aluminium Oxide : Merck 60G neutral (type E) aluminium oxide for thin layer chromatography.

Basic Aluminium Oxide : Woelm basic activity grade I for chromatography.

Copper (precipitated) : Ajax technical copper powder was activated with 1-2M hydrochloric acid. It was then rinsed with deionized water, ethanol then acetone and dichloromethane, and then stored under dichloromethane at 5°C.

Molecular Sieves : 5 A calcium aluminium silicate molecular sieves (BDH) were heated for 12 hours under vacuum (0.5 mm Hg) at 160°C in a Gallenkamp drying pistol. Reactivation prior to each usage was necessary.

Silica Gel : 100-200 um silica gel (Ajax Chemicals).

Silicic Acid : 100 um AR grade silicic acid (Mallinckrodt) was heated for at least 24 hours at 250°C then placed in a vacuum desiccator. Weekly reactivation was necessary.

2.2 GEOCHEMICAL TECHNIQUES

2.2.1 Sample Preparation

Dry cuttings and/or sidewall cores were crushed in a N.V. Tema grinder to a particle size of approximately 150 um.

2.2.2 Extraction of Soluble Organic Matter from Sediments

Crushed sediment (7-30 g) was placed in a 250 mL conical flask and then extracted with 200 mL of dichloromethane using a high speed blender for about 20 minutes. The solvent was separated from the sediment by filtering through a large Buchner system. Approximately 100 mg of activated copper (precipitated) was added to the solvent to remove any elemental sulfur and then the mixture was extracted again using a high speed blender for 5 minutes. The mixture was then gravity filtered to obtain a sediment (and copper) free solution. The dichloromethane solvent was removed from the filtrate by fractional distillation using a 15 cm column packed with Raschig rings. Finally, the organic residue was quantitatively transferred to a tared sample vial. The weight of the extract organic residue was used to calculate the percentage of soluble organic matter (% SOM).

2.2.3 Fractionation of Crude Oils and Rock Extracts by Column Chromatography

Sediment extract and crude oil samples were separated into saturate, aromatic and NSO (asphaltenes and resins) fractions by liquid chromatography. Glass columns (40 cm x 1.2 cm ID) sealed by packed cotton wool at the base were then filled with activated silicic acid (2.5 g) in n-pentane (30 mL) as a slurry. The sample (crude oil or SOM) was introduced to the column as a solution in n-pentane. Firstly, n-pentane (50 mL) was used to elute saturated hydrocarbons. Secondly, a mixture of n-pentane and diethyl ether with a 9:1 ratio (50 mL) was used to elute aromatic hydrocarbons, and finally a 9:1 mixture of dichloromethane and methanol (50 mL) was used to elute NSO compounds. The neat fractions were recovered by complete removal of solvent using a 15 cm column packed with Raschig rings. The saturate fractions were analysed by gas chromatography prior to the complete removal of solvent as this step might cause severe effects upon the distribution of the lower molecular weight components. The weight of each fraction was used to calculate the percentage of each component group in the sediment or crude oil.

2.2.4 Isolation of Branched and Cyclic Alkanes

Approximately 20 g of molecular sieves were placed

in a 50 mL round bottom flask and benzene (20 mL) was added. The saturate fraction residue obtained from the previous step (5-10 mg) was dissolved in the benzene and warmed under gentle reflux for at least 24 hours. After being cooled to room temperature, the benzene solution was decanted from the molecular sieves. The solvent was then removed using a rotary evaporator. The residue was taken up in n-pentane and filtered through a short silicic acid column using n-pentane to elute the saturated hydrocarbons. Removal of the solvent afforded the branched and cyclic alkane fraction.

2.2.5 Isolation of Aromatic Fractions

Analytical thin layer chromatography (TLC) was used for isolation of dimethylnaphthalenes, trimethyl-naphthalenes, phenanthrene and methylphenanthrene fractions. The aromatic fraction was spread on a TLC alumina plate (0.6 mm thick), activated at 120-140^{o}C for at least 12 hours. The plate was developed with n-hexane, and the required band (Rf=0.3-0.7), comprising dinuclear and trinuclear aromatics, was located using short wavelength UV light. This band was scraped off with blade and extracted with dichloromethane (20 mL) and then m-chloroperoxy- benzoic acid 80-85% (approximately 2 mg) was added to oxidise any sulphur-containing compounds. All but approximately 1-2 mL of the dichloromethane was

removed by heating on a sand bath. The residue was filtered through a short alumina column using n-pentane to remove the resultant sulphones and residual acidic material. The solution was then quantitatively transferred to a tared sample vial.

2.2.6 Hydrous Pyrolysis of Extracted Sediments

Hydrous pyrolysis experiments were performed in stainless steel tube reactors with a 20 mL capacity (ID=12.5 mm). The extracted crushed sample (1-2 g) was put in the reactor with 6 mL deionised water. The reactor was heated for 72 hours at 330^{o}C. After the reactor cooled to room temperature, the pyrolysate was transferred to a 50 mL glass vial and was then dried in an oven for 24 hours at 50^{o}C. Dry sediment pyrolysate was then treated in a similar manner to crushed sediment sample as described above. For the 'blank experiments', crude oil (100 mg) was mixed with a sample (1-2 g) of sediment that had previously been pyrolysed and extracted so as to remove all pyrolysable material, and added to the reactor together with water (6 mL).

2.3 ANALYTICAL METHODS AND INSTRUMENTATION

2.3.1 Total Organic Carbon (TOC) Determination

Crushed sample (1 g) was treated with hot dilute HCl (3M) mixed with ferrous chloride (2%) for one hour to remove carbonate minerals then washed with deionised water to remove exess acid. To obtain TOC value, the residue was heated to 1700^{o}C in Leco Induction Furnace in an atmosphere of pure oxygen. The carbon dioxide produced was collected on a 'Carbosorb' and weighed. The TOC value was calculated as percent of carbon in the sediment.

2.3.2 Rock-Eval Pyrolysis

Rock-Eval pyrolysis was carried out on both the crushed, untreated sediment and crushed, carbonate-mineral free (Espitalie et al., 1977) using a Rock-Eval II. Both kinds of samples were analysed to obtain the most reliable data. Approximately 100 mg of both sediment samples were analysed using the following cycle :

Stage 1 : Sample purged with helium for 3.5 minutes outside the furnace.

Stage 2 : Sample heated rapidly to 300^{o}C and held for 3 minutes to liberate free bitumen (S_1 peak).

Stage 3 : Sample heated from 300 to 550^{o}C at 25^{o}C/ minute to produce hydrocarbons from kerogen (S_2

peak). The furnace is then held at 550°C for one minute. The carbon dioxide produced before the furnace reaches 390°C is trapped on a column. The temperature reached in the maxima of S_2 peak is determined as Tmax.

Stage 4 : During the cool down period the carbon dioxide trapped on column is measured (S_3 peak).

The units used for Rock-Eval data are kg/tonne or mg/g of rock and °C for Tmax.

2.3.3 Gas Chromatography (GC)

The GC analysis of saturate and branched/cyclic fractions was carried out using Hewlett-Packard (HP) chromatographs, either an HP 5880A or an HP 5890. They were fitted with 50 m WCOT column (0.2 mm ID) coated with crosslinked methyl silicone when used to analyse saturate fractions, or coated with 5% crosslinked phenylmethyl silicone when used to analyse aromatic fractions. Hydrogen was used as carrier gas at a linear velocity of 28 cm/sec. Detector (FID) and injector temperatures were 300°C and 280°C, respectively. The oven was temperature programmed from 65 to 280°C at 4°C/min for saturate fraction analyses. For aromatic fraction analyses the temperature was programmed from 70 to 300°C at 2°C/min.

2.3.4 Gas Chromatography - Mass Spectrometry (GC-MS)

GC-MS analyses for saturate fractions were mainly performed using either an HP 5985B or an HP 5987 capillary GC-quadrupole MS, and analyses for aromatic fractions were performed using an HP 5970 Mass Selective Detector (GC-MSD). The GC-MS was fitted with a 50 m x 0.2 mm ID WCOT fused silica crosslinked methylsilicone column (DB-1) when used for saturated hydrocarbon analyses, or fitted with a 50 m x 0.2 mm ID fused silica column coated with 5% crosslinked phenylmethyl silicone (BP-5, SGE) when used for aromatic hydrocarbon analyses. Some samples were analysed in the multiple reaction monitoring (MRM) mode using a VG-TS250 GC-MS system fitted with the BP-5 column described above.

The temperature programs used are dependent on the purpose of the study and they generally can be grouped into 6 programs :

Program 1 : was used to analyse most of the saturated hydrocarbon samples The temperature program was from 50 to 274^{o}C at a rate of 8^{o}C/minute and then from 274 to 300^{o}C at 1^{o}C/minute.

Program 2 : was used for isothermal analysis. The temperature program was 50 to 280^{o}C at 15^{o}C/ minute, then isothermal at 280^{o}C.

Program 3 : was used for injection hold time experiment. The oven was temperature programmed from 50 to 130^{o}C at 20^{o}C/minute. It was then held for 60

hours. The temperature was then programmed from 130 to 300°C at a rate of 2°C/minute.

Program 4: was used for aromatic hydrocarbon analysis. Injection temperature was 70°C (on column). Temperature program was 70 to 300°C at 2°C/ minute.

Program 5 : was used in the multiple reaction monitoring (MRM) mode. Injection temperature was 70°C (evaporated). Temperature program was 70 to 274°C at 10°C/minute and then from 274 to 300°C at 1°C/minute.

Program 6 : was used to obtain data for the retention time plot using MRM system. Temperature program was 70 to 300°C at a rate of 4°C/minute.

Program 1 to Program 3 were performed on either the HP 5985B or the HP 5987 GC-MS system, Program 4 was performed on the HP 5970 GC-MSD, and Program 5 and Program 6 were performed on the VG-TS250 GC-MS data system. Mass chromatographic information for Program 1 to Program 4 was collected in either the selected ion monitoring (SIM), using dwell times of 40 msec for each ion monitored, or the full data acquisition mode by scanning from 50 to 500 amu. Typical MS operating conditions were: EM voltage 2200 V; ionization energy 70 eV; source temperature 250°C. Hydrogen was used as carrier gas at a linear velocity of 28 cm/sec.

2.4 IDENTIFICATION OF BIOLOGICAL MARKER COMPOUNDS

2.4.1 GC and GC-MS Peak Assignments

The acyclic isoprenoids used in this study, pristane and phytane (15 and 16, respectively; Figure 1.5), were assigned from their GC retention times. For analysis performed with apolar capillary columns, pristane elutes just after n-C_{17}, and phytane elutes after n-C_{18} (e.g. Gassemann, 1981).

Tricyclic, tetracyclic, pentacyclic and hexacyclic terpanes were assigned by comparing their mass spectra with those reported for the authentic compounds, and from the GC elution order. For tricyclic terpanes, see Aquino Neto et al. (1983); Ekweozor and Strausz (1983); Alexander et al. (1984c); Philp (1985b); Noble (1986); for 17α(H)-hopanes, see Allan et al. (1977); Seifert and Moldowan (1980); Philp (1985a,b); for 25-norhopanes, see Rullkotter and Wendisch (1982); Volkman et al. (1983b,c); for oleananes, see Hoffman et al. (1984); Ekweozor and Udo (1988); for 2-methylhopanes, see Seifert and Moldowan (1978); Alexander et al. (1984a); Hoffman et al. (1987) Price et al. (1987); Summons and Jahnke (1990a); for 30-nor-17α(H)-hopanes, see Seifert et al. (1984); Summons and Powell (1987); and for hexacyclic hopanoid alkanes, see Connan and Dessort (1987); Rinaldi et al. (1988).

Steranes, which include non-rearranged and rearranged steranes were also identified by comparison of their chromatograms and mass spectra with those in the published literature (see Wardroper et al., 1977; Ensminger et al., 1978; Seifert and Moldowan, 1979; Mackenzie et al., 1980; Philp, 1985a,b).

2.4.2 Quantification and Errors

This section describes methods of calculation, abbreviations and the error associated with the methods used in this thesis.

(i) Parameters measured from peak areas of capillary gas chromatograms of the saturated hydrocarbon fractions were :

Pr/Ph = Pristane/phytane

CPI = Carbon Preference Index

$$= \frac{(C_{23}+C_{25}+C_{27}+C_{29})+(C_{25}+C_{27}+C_{29}+C_{31})}{2(C_{24}+C_{26}+C_{28}+C_{30})}$$

(ii) Parameter involving sterane biomarkers were measured by GC-MS using m/z 217 mass chromatograms:

$(C_{21}+C_{22})/C_{29}$ = (Pregnane + Homopregnane)/[(20S+20R) 14α(H),17α(H)-24-ethylcholestanes + (20S+20R) 14β(H),17β(H)-24-ethylcholestanes]

$C_{27}\alpha\alpha R/C_{29}\alpha\alpha R$ = (20R) 14α(H),17α(H)-

cholestane/(20R) 14α(H),17α(H)-24-ethylcholestane

$C_{29}\alpha\alpha$ 20S/20R = (20S) 14α(H),17α(H)-24-ethyl-cholestane/(20R) 14α(H),17α(H)-24-ethylcholestane

C_{29} [ββ/(ββ+αα)] = (20R+20S) 14β(H),17β(H)-24-ethylcholestanes/[(20R+20S) 14β(H),17β(H)-24-ethylcholestanes + (20S+20R) 14α(H),17α(H)-24-ethylcholestanes]

C_{29} DIAS/STE = (20S+20R) 13β(H),17α(H)-24-ethyl-diacholestanes/[(20S+20R) 14α(H),17α(H)-24-ethyl-cholestanes + (20R+20S) 14β(H),17β(H)-24-ethyl-cholestanes]

(iii) Parameters involving tricyclic and pentacyclic terpanes were measured by GC-MS using m/z 191 mass chromatograms:

DOM TRIC = Dominant tricyclic terpane

IP/DOM TRIC = Ratio of isopimarane to dominant tricyclic terpane

Tm/Ts = 17α(H)-22,29,30-trisnorhopane/18α(H)-22,29,30-trisnorneohopane

C_{30} M/H = 17β(H),21α(H)-moretane/17α(H),21β(H)-hopane

Oleanane Index = [18α(H)-oleanane/17α(H)-hopane]x100

Gammacerane Index = [Gammacerane/17α(H)-hopane]x100

33H/30H = (22S+22R)-17α(H)-trishomohopanes/17α(H)-hopane

34H/30H = (22S+22R)-17α(H)-tetrakishomohopanes/17α(H)-hopane

35H/30H = (22S+22R)-17α(H)-pentakishomohopanes/17α(H)-hopane

30-Norhopane Index = [30-nor-17α(H)-hopane/17α(H)-hopane] x 100

(iv) Parameters involving aromatic hydrocarbons were measured from peak areas of capillary gas chromatograms and/or by GC-MS using m/z 156 (dimethylnaphthalenes), m/z 170 (trimethylnaphthalenes), m/z 178 (phenanthrene), and m/z 192 (methylphenanthrenes):

$$\text{MPI-1} = \frac{1.5(2\text{-MP} + 3\text{-MP})}{\text{P} + 1\text{-MP} + 9\text{-MP}}$$

$\%R_c$ = 0.60 MPI-1 + 0.40 (for R_m <1.35%)

$\%R_c$ = -0.60 MPI-1 + 2.30 (for R_m >1.35%)

(P = Phenanthrene; MP = methylphenanthrene)

If using the GC-MS data, to get to MPI-1 and $\%R_c$ these values have to be corrected for response factors.

Replicate analyses on selected samples showed that the values for reported parameters were subject to approximately ± 5% error.

CHAPTER THREE

IDENTIFICATION OF 30-NOR-17α(H)-HOPANES AND THEIR APPLICATION AS INDICATORS FOR A CARBONATE DEPOSITIONAL ENVIRONMENT

3.1 GEOLOGICAL DESCRIPTION OF THE CARBONATE SAMPLES

A suite of carbonate samples comprising twenty-two crude oils and eight sediments from several countries were used in this study. The sediment samples generally comprise material obtained from oil exploration drilling operations. The crude oil samples consist of those obtained from commercial reservoirs, as well as those obtained from drill-stem tests from exploration wells.

3.1.1 Crude Oils

Geological information related to the twenty two crude oil samples is shown in Table 3.1. These crude oils were reported to have originated from carbonate source rocks (see references in Table 3.1). Most of these crude oils have been investigated in the present study to obtain the data, however previously published information has been used for four samples (see footnotes of Tables 3.3 - 3.5). Thus, the data regarding such samples were obtained by examining gas chromatograms and/or mass chromatograms published in the literature.

Table 3.1. Crude oil details.

NO	SAMPLE	SEDIMENTARY BASIN	COUNTRY	SOURCE ROCK AGE	REF[a]
C1	Well A	NA	Northern Arabian Gulf	Miocene	1
C2	Well B	NA		Cretaceous	1
C3	Well C	NA		Cretaceous	1
C4	Maracaibo	Maracaibo	Venezuela	Cretaceous	2
C5	Sunniland (11,600ft)	South Florida	USA	Cretaceous	3
C6	Well X	Northern Zagros	N.Arabian Gulf	Jurassic	1
C7	Safaniya	NA	Saudi Arabia	Jurassic[b]	4,5
C8	Sana#1-390	Seram	Indonesia	Triassic	6
C9	Sana#1-414	Seram	Indonesia	Triassic	6
C10	Bula Tin#2-230	Seram	Indonesia	Triassic	6
C11	Bula Tin#2-280	Seram	Indonesia	Triassic	6
C12	Bula 44X-1A	Seram	Indonesia	Triassic	6
C13	Bula 89X-1	Seram	Indonesia	Triassic	6
C14	BT 2X-8	Seram	Indonesia	Triassic	6
C15	BT 13X-8	Seram	Indonesia	Triassic	6
C16	BT 100X-5	Seram	Indonesia	Triassic	6
C17	Delik River Seep	Seram	Indonesia	Triassic	6
C18	Buton Asphalt	South East Sulawesi	Indonesia	?Triassic	6
C19	Baoussi	NA	Greece	NA	7
C20	Neiber Dome	Big Horn	USA	Carboni-ferous[b]	4,8
C21	Etosha	Etosha	Namibia	Pre Cambrian	9
C22	Siberian Platform	NA	USSR	Pre Cambrian	10,11

a : References: (1) J. Scott (1989, personal commun.); (2) Talukdar et al. (1986); (3) Palacas et al. (1984); (4) Noble (1986); (5) Tissot and Welte (1984); (6) Price et al. (1987); (7) Seifert et al. (1984); (8) Orr (1977); (9) McKirdy et al. (1983); (10) Summons et al. (1988); (11) Fowler and Douglas (1987).

b : Reservoir age NA : Not available

3.1.2 Sedimentary Rocks

Details of the sediment samples are shown in Table 3.2. These sediments were reported to be rich in carbonate minerals (see references in Table 3.2). Data for two of the sediments, that is Ste Cecile and Barney Creek, were taken from the published literature, while the others were obtained from analyses carried out as part of this study. One very immature sediment, Seram, was used for hydrous pyrolysis experiments.

Table 3.2. Sediment sample details.

NO	SAMPLE	DEPTH (m)	SEDIMENTARY BASIN	COUNTRY	GEOLOGICAL AGE	REF[a]
S1	Ste Cecile#1	2340	Camargue	France	Oligocene	1
S2	Lu#6	1185	Songliao	China	Cretaceous	2
S3	Well X	3548	N. Zagros	N.Arabian Gulf	Jurassic	3
S4	Well X	3911	N. Zagros	N.Arabian Gulf	Jurassic	3
S5	Mardi#1	219	Carnarvon	Australia	Devonian	4
S6	Peedamullah	1068	Carnarvon	Australia	Devonian	4
S7	Barney Creek	39	McArthur	Australia	Pre Cambrian	5,6
S8	Seram[b]	NA	Seram	Indonesia	Triassic	7

a : References: (1) Connan and Dessort (1987); (2) Yang et al. (1985); (3) J. Scott (1989, personal commun.); (4) Thomas and Smith (1974); (5) Summons et al. (1988); (6) Jackson et al. (1988); (7) Price et al. (1987).

b : Very immature sample; for hydrous pyrolysis experiment

NA : Not available

3.2 GEOCHEMICAL CHARACTERISTICS OF THE CARBONATE SAMPLES

3.2.1 Crude Oils

A Biodegradation

Table 3.3 shows the biodegradation level of the crude oils according to the scheme proposed by Volkman et al. (1983b). Two samples had been severely biodegraded as shown by alteration of their steranes, and were classified as level 8 biodegraded oils. Eight samples were found to have been moderately altered and were assigned biodegradation levels between 3 and 5. Seven samples had been slightly altered, and were classified as level 2 biodegraded oils. Four samples showed no signs of biodegradation and were classified as level 1. No gas chromatography data was available for one sample and thus its biodegradation level could not be assessed.

B Source Type

Table 3.3 also shows source type data for the crude oils. In terms of the distribution of n-alkanes, most of the crude oils are similar. Several of the crude oils show some degree of biodegradation, but where the crude oils are not degraded their n-alkane distributions show maxima in the C_9-C_{16} region, suggesting contributions

Table 3.3. Level of biodegradation and biomarker indicators of source type for the crude oil samples.

SAMPLE NO	LEVEL OF BIODEG[a]	N-ALKANES[b]		STERANES[b]
		MAXIMA	CPI	$\frac{C_{27}\alpha\alpha R}{C_{29}\alpha\alpha R}$
C1	3	B	B	0.9
C2	2	C_{22}[c]	0.92	1.0
C3	2	C_{22}[c]	0.95	0.9
C4	1	C_9	0.98	1.9
C5[d]	1	C_{16}	0.90	0.8
C6	4	B	B	0.5
C7	1	C_9	0.95	0.8
C8	2	C_{18}[c]	1.00	1.3
C9	2	C_{18}[c]	0.98	0.7
C10	5	B	B	0.9
C11	3	B	B	0.8
C12	5	B	B	0.8
C13	5	B	B	0.8
C14	2	C_{16}[c]	1.00	0.9
C15	4	B	B	1.0
C16	2	C_{14}[c]	0.90	0.9
C17	5	B	B	0.8
C18	8	B	B	B
C19[d]	8	B	B	B
C20	1	C_9	0.97	1.8
C21[d]	2	C_{21}[c]	ND	ND
C22[d]	ND	ND	ND	0.4

a : Based on classification by Volkman et al. (1983b)
b : Refer to Section 2.4.2 for definition of abbreviations and methods of calculation
c : Light n-alkanes depleted
d : From literature data
B : Biodegraded samples
ND : No data

of marine algal material. The relatively low CPI (≤ 1) is characteristic of carbonate crude oils.

Figure 3.1 shows m/z 217 mass chromatogram patterns representative of sterane distributions of the crude oils. In general terms the C_{29} sterane concentrations exceed or are equivalent to the C_{27} sterane concentrations except for three crude oils (Table 3.3). This phenomenon might suggest some terrestrial plant input, but such an interpretation should be regarded with extreme caution (Volkman, 1986), particularly because such phenomena are very common in carbonate-evaporite oils (Palacas et al., 1984; Price et al., 1987). Palacas et al. (1984) have suggested that special conditions in a carbonate-evaporite environment such as intense microbiologic activity and highly preserving saline conditions could lead to a greater production of the C_{29} steranes. In addition, all the available geological and other geochemical evidence indicates that these crude oils have a marine origin.

C Depositional Environment

Table 3.4 gives the biomarker data for the crude oils. By comparing the biomarker data with the geological data concerning depositional environment obtained from literature (see the list of references in Table 3.1) it

Figure 3.1. Partial m/z 217 mass chromatograms illustrating typical sterane distributions in carbonate oils. Numbers denote carbon numbers. GC conditions were Program 1 (Section 2.3.4).

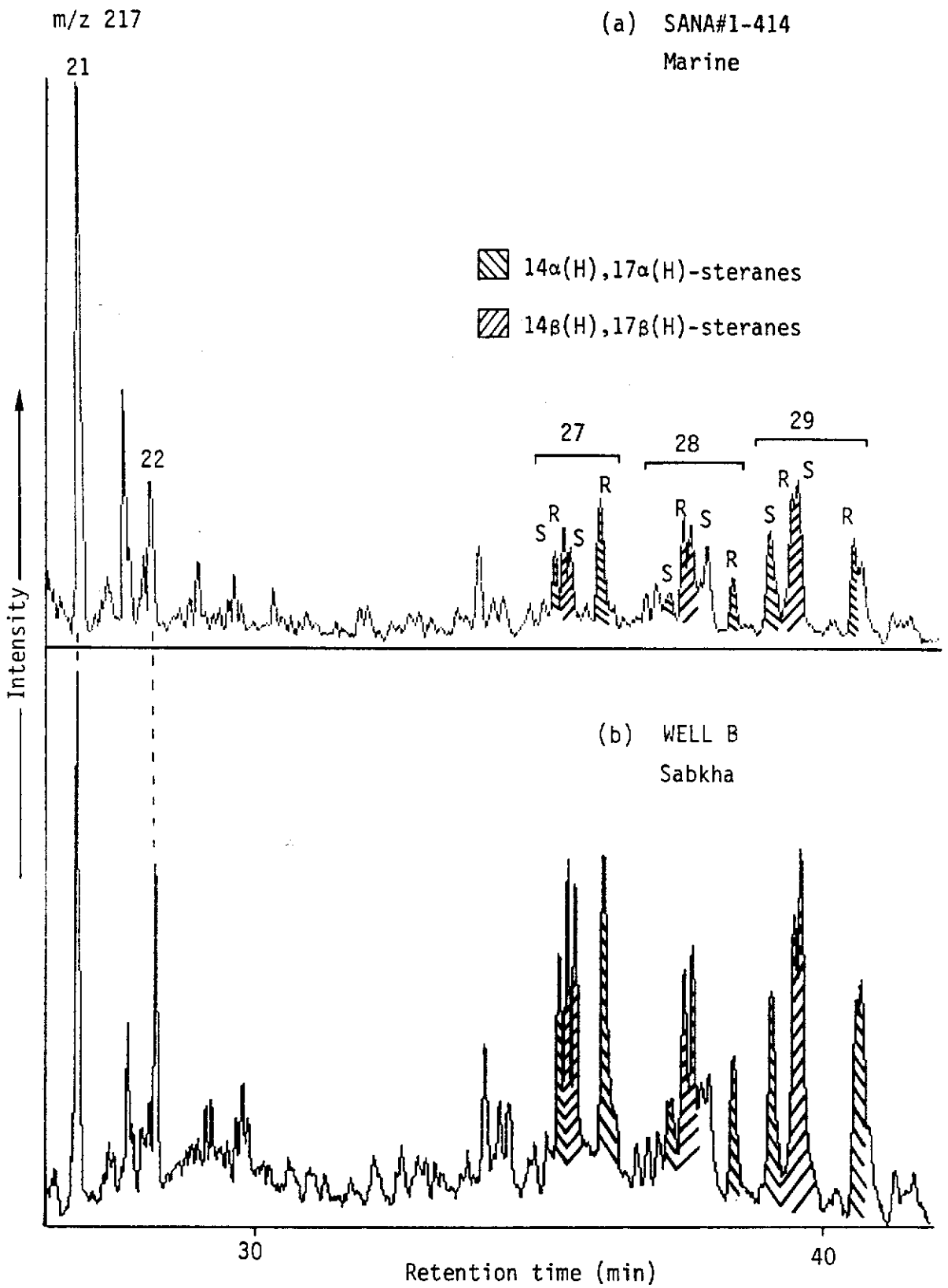


Table 3.4. Biomarker characteristics of crude oils resulting from differences in depositional environment.

NO	STERANES[a]			TERPANES[a]					DEPOSITIONAL ENVIRONMENT
	Pr/Ph	$\frac{C_{21}+C_{22}}{C_{29}}$	$\frac{C_{29}\ DIAS}{STE}$	GI	33H 30H	34H 30H	35H 30H	31-35 HEXAC[b]	
C1	0.4	1.1	<0.1	25	0.2	0.1	0.2	+	Sabkha
C2	0.3	1.0	<0.1	22	0.3	0.1	0.2	+	Sabkha
C3	0.4	0.8	0.1	20	0.3	0.1	0.2	+	Sabkha
C4	0.8	1.5	0.1	10	0.5	0.2	0.2	-	Marine
C5[c]	0.6	ND	0.2	ND	0.2	0.1	0.1	ND	Marine
C6	B	0.8	<0.1	30	0.3	0.3	0.4	+	Sabkha
C7	0.6	1.4	<0.1	<5	0.3	0.2	0.2	-	Marine
C8	0.6	1.7	<0.1	5	0.2	0.2	0.1	31[d]	Marine
C9	0.7	1.6	<0.1	5	0.2	0.2	0.2	31[d]	Marine
C10	B	2.6	<0.1	7	0.2	0.2	0.1	-	Marine
C11	B	2.1	<0.1	6	0.2	0.1	0.1	-	Marine
C12	B	2.3	<0.1	<5	0.2	0.1	0.1	-	Marine
C13	B	1.8	<0.1	<5	0.2	0.2	0.2	-	Marine
C14	5.9	1.9	<0.1	<5	-	-	-	-	Marine
C15	B	2.3	<0.1	5	-	-	-	-	Marine
C16	0.6	2.1	<0.1	<5	0.2	-	-	-	Marine
C17	B	2.4	<0.1	<5	-	-	-	-	Marine
C18	B	B	B	10	0.3	0.1	-	-	Marine
C19[c]	B	B	B	L	ND	ND	ND	ND	Marine
C20	0.7	1.3	<0.1	10	0.5	0.3	0.2	-	Marine
C21[c]	0.5	ND	ND	ND	0.4	0.3	0.3	ND	Marine
C22[c]	ND	ND	ND	ND	ND	ND	ND	ND	Marine

a : Refer to Section 2.4.2 for methods of calculation and definition of abbreviations
b : Hexacyclic hopanoid alkanes
c : From literature data
d : Only C_{31} member observed
B : Biodegraded sample
L : Large, no C_{30} hopane present
GI : Gammacerane Index
+ : Present (all members)
- : Not detected
ND : No data

was found that the crude oils could be classified chemically according to the environment in which their organic matter was deposited. In general, the crude oils form two groups, namely those deposited in marine environments and those deposited in sabkha-type environments.

The crude oils deposited in marine environments have relatively higher pristane/phytane ratios ($\geq$0.5), even though these values are still relatively low compared with non-carbonate oils. Sample no. C14 (BT 2X-8) is an exception as it has a high pristane/phytane ratio (5.9). The marine crude oils also show relatively higher $(C_{21}+C_{22})/C_{29}$ sterane ratios ($\geq$1.3), low Gammacerane Index values ($\leq$10), and normal extended hopane distributions in that their concentrations generally decrease with increasing carbon numbers (see ratios of C_{33}-C_{35} hopanes/C_{30} hopane in Table 3.4). The hexacyclic hopanoid alkanes are absent from all except two crude oils (Sana#1-390 and 414) where the C_{31} member of the series was observed.

The crude oils deposited in sabkha-type environments are characterised by very low pristane/phytane ratios (<0.5), low $(C_{21}+C_{22})/C_{29}$ sterane ratios (between 0.8 and 1.1), and high Gammacerane Index values ($\geq$20). These crude oils are also characterised by the presence of the C_{31}-C_{36} hexacyclic hopanoid

alkanes and an abnormally high level of the C_{35} extended hopanes (see ratios C_{33}-C_{35} hopanes/C_{30} hopane in Table 3.4). A comparison of the triterpane distributions between the crude oils deposited in marine and in sabkha-type environments is shown in Figure 3.2, and a summary of biomarker characteristics which characterise each depositional environment is given in Table 3.5.

In addition, these sabkha and marine crude oils show very low C_{29} diasterane to sterane ratios suggesting anoxic or alkaline depositional environments (Price et al., 1987).

D Thermal Maturation

Thermal maturation data for the crude oil samples is given in Table 3.6. On the basis of the sterane maturity parameters and C_{30} moretane to hopane ratio (Mackenzie, 1984), it is apparent that the crude oils are considered as mature to very mature (see also Figure 3.1 and Figure 3.2). In contrast, the high values (>1) of the Tm/Ts ratios suggest that the crude oils are immature. Such a phenomenon is, in fact, very common in carbonate crude oils (Palacas et al., 1984; Price et al, 1987). Thus, this ratio should only be used with extreme caution, as a maturity indicator, particularly in

Figure 3.2. Partial m/z 191 mass chromatograms showing a comparison of triterpane distributions between marine carbonate oil (a) and sabkha carbonate oil (b). Numbers denote carbon numbers. G = gammacerane. GC conditions were Program 1 (Section 2.3.4).

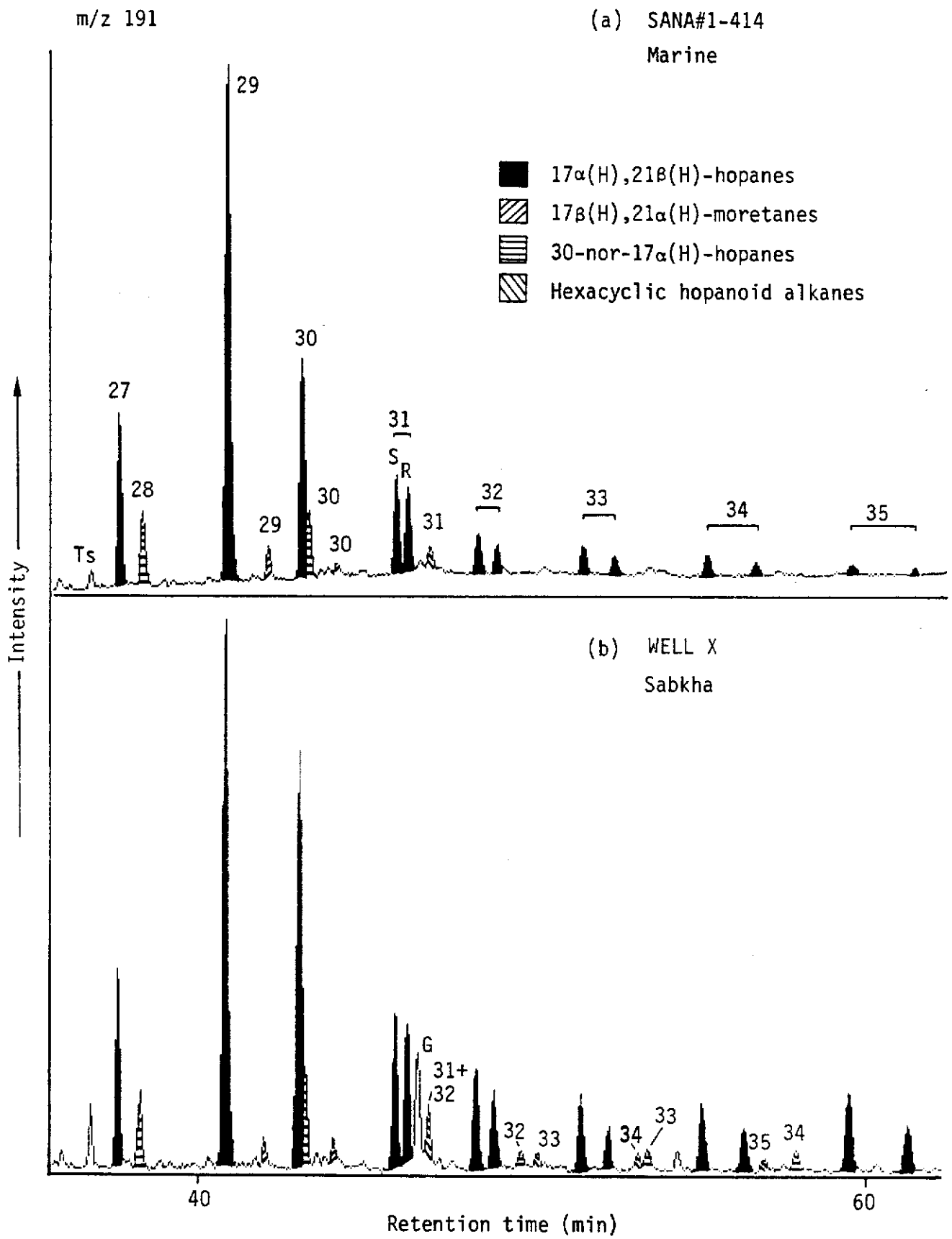


Table 3.5. Parameters which characterise depositional environments for the crude oils.

PARAMETERS	DEPOSITIONAL ENVIRONMENT	
	MARINE	SABKHA
Pristane/phytane	≥ 0.5	≤ 0.4
$(C_{21}+C_{22})/C_{29}$ Steranes	>1.2	≤ 1.1
Gammacerane Index	≤ 10	≥ 20
Hopanes: $C_{35}>C_{34}$	-	+
Hexacyclic hopanoid alkanes	-[a]	+

a : C_{31} member was observed in some marine samples
\+ : Observed
\- : Not observed

Table 3.6. Biomarker thermal maturity indicators for the crude oils.

SAMPLE	STERANES[a]		HOPANES[a]	
NO	$C_{29}^{\alpha\alpha}$ 20S/20R	C_{29} $\frac{\beta\beta}{\beta\beta+\alpha\alpha}$	C_{30} M/H	Tm/Ts
C1	1.0	0.5	<0.1	5.4
C2	1.1	0.5	<0.1	5.8
C3	1.0	0.5	<0.1	3.5
C4	0.9	0.6	0.1	2.0
C5[b]	0.9	0.5	0.1	3.0
C6	1.0	0.6	<0.1	3.1
C7	0.9	0.6	0.1	2.6
C8	1.0	0.6	<0.1	9.1
C9	1.0	0.6	0.1	8.0
C10	1.2	0.6	0.1	4.5
C11	1.1	0.6	<0.1	5.0
C12	1.2	0.6	0.1	3.9
C13	1.1	0.6	<0.1	4.0
C14	1.0	0.6	0.2	3.6
C15	1.1	0.6	0.2	7.7
C16	1.1	0.6	0.1	7.7
C17	1.1	0.6	0.2	5.0
C18	B	B	0.1	3.7
C19[b]	B	B	ND	5.0
C20	1.0	0.6	0.1	1.6
C21[b]	ND	ND	0.1	2.9
C22[b]	1.1	0.6	ND	1.3

a : Refer to Section 2.4.2 for methods of calculation and definition of abbreviations
b : From literature data ND : No data
B : Biodegraded samples

carbonate samples, since values for this ratio are also partly dependent on organic facies (Palacas et al., 1984).

3.2.2 Sedimentary Rocks

A Source Type

Table 3.7 gives the source type data for the sediment samples, and Figure 3.3 shows the sterane distributions of extracts from three of the sediments. The n-alkane distributions of the sediments are remarkably similar, showing maxima in the C_{16}-C_{19} region, which is indicative of marine algal contribution (Philp, 1985). This is supported by the observation of relatively high C_{27}/C_{29} sterane ratios (>1). The CPI values range between 0.81 and 1.20. In this case, such values may indicate maturity rather than the source type.

B Depositional Environment

Table 3.8 shows the analytical data relative to depositional environment of the sediment samples. According to the available geological information (see references in Table 3.2), the sediments could be classified into three groups in terms of their depositional environments. In addition to that, some

Table 3.7. Biomarker indicators of source type for the sediment samples.

SAMPLE	N-ALKANES[a]		STERANES[a]
NO	MAXIMA	CPI	$\frac{C_{27\alpha\alpha R}}{C_{29\alpha\alpha R}}$
S1[b]	C_{16}	0.81	ND
S2	C_{17}	1.10	1.3
S3	C_{17}	1.10	1.2
S4	C_{17}	0.90	1.3
S5	C_{18}	1.30	1.1
S6	C_{19}	1.20	1.5
S7[b]	C_{17}	0.98	1.6

a : Refer to Section 2.4.2 for methods of calculation and definition of abbreviations

b : From literature data

Figure 3.3. Partial m/z 217 mass chromatograms showing sterane distributions in three types of carbonate sediments. Numbers denote carbon numbers. Refer to Program 1 (Section 2.3.4) for GC conditions.

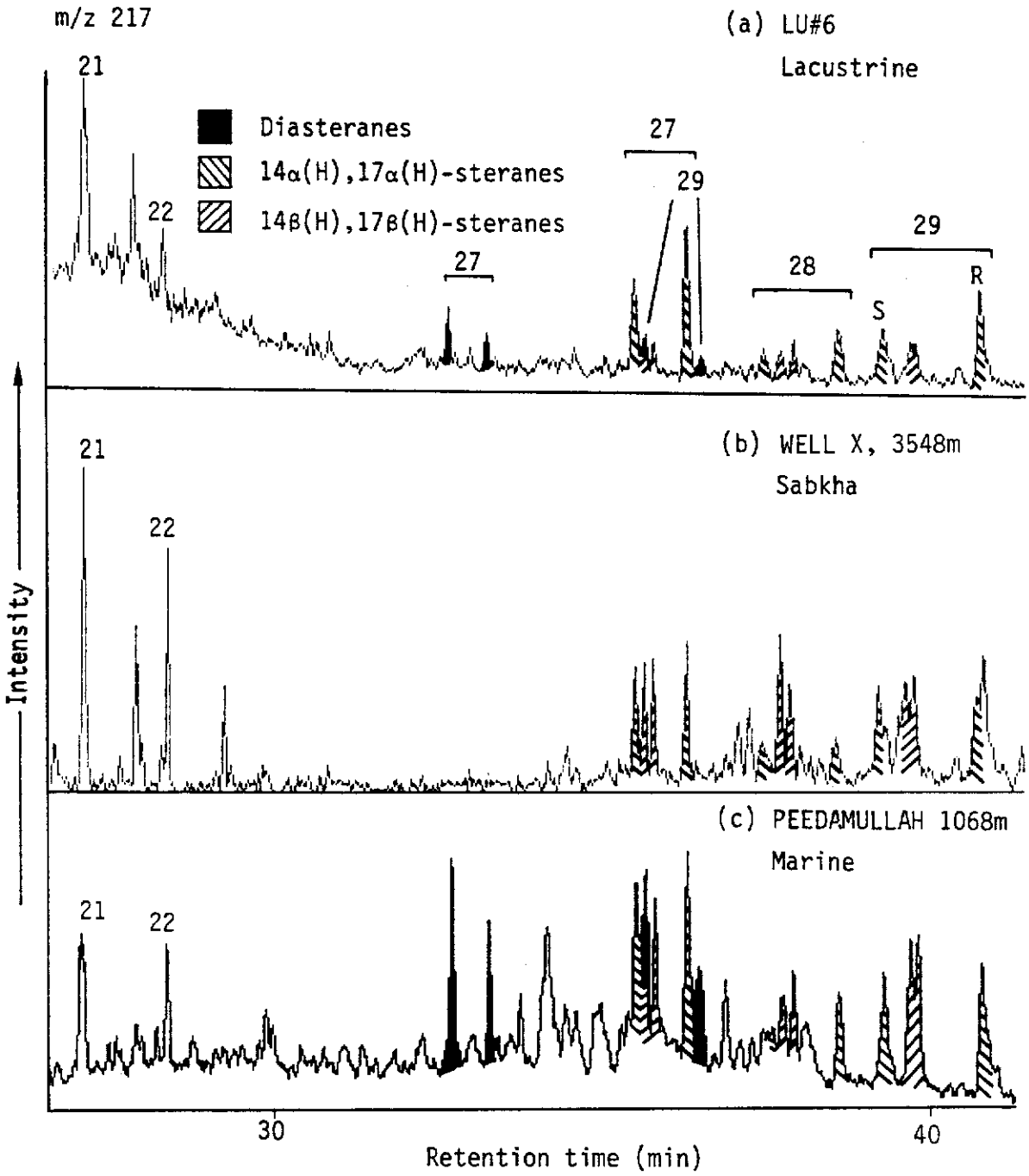


Table 3.8. Biomarker indicators of depositional environment: sediments.

NO	STERANES[a]			TERPANES[a]					DEPOSITIONAL ENVIRONMENT
	Pr/Ph	$\frac{C_{21}+C_{22}}{C_{29}}$	$\frac{C_{29}\ DIAS}{STE}$	GI	33H/30H	34H/30H	35H/30H	31-35 HEXAC[b]	
S1[c]	0.5	ND	ND	40	0.1	0.1	0.2	+	Sabkha
S2	0.6	1.7	<0.1	20	0.2	0.2	0.2	-	Lacustrine
S3	1.0	0.8	<0.1	30	0.3	0.2	0.3	+	Sabkha
S4	0.8	1.5	<0.1	30	0.2	0.1	0.2	+	Sabkha
S5	0.8	1.1	0.4	<5	0.4	0.3	0.2	-	Marine
S6	0.8	0.9	0.4	<5	0.3	0.2	0.1	-	Marine
S7[c]	ND	ND	ND	ND	ND	ND	ND	ND	Lacustrine or lagoonal

a : Refer to Section 2.4.2 for methods of calculation and definition of abbreviations
b : Hexacyclic hopanoid alkanes
c : From literature data
+ : Present
- : Not detected
GI : Gammacerane Index
ND : No data

geochemical parameters such as Gammacerane Index, C_{29} diasteranes to steranes ratio, the extended hopane distributions and the occurrence of the hexacyclic hopanoid alkanes appear to be specific for each environment. Sediments deposited in sabkha-type environments are characterised by high Gammacerane Index values ($\geq$30), low diasteranes (trace), relatively higher concentration of the C_{35} hopanes than the C_{34} members, and occurrences of the hexacyclic hopanoid alkanes. In contrast, the sediments deposited in marine environments show no significant gammacerane, high diasterane to sterane ratios (0.4), normal extended hopane distributions, and no hexacyclic hopanes. Such features may reflect differences in salinity, oxicity and alkalinity. The lacustrine sediments were represented by two samples. Unfortunately, no such data was available for sample no. S7 (Barney Creek) which was taken from the literature (Summons et al., 1988). Nevertheless, the only other lacustrine sediment shows a relatively high Gammacerane Index value (20), low diasteranes, abnormal extended hopane distributions, the C_{33} to C_{35} members have relatively similar concentrations, and no hexacyclic hopanes could be detected. Such phenomena are characteristic of some Chinese sediments deposited in lacustrine saline depositional environments (Fan and Zhang, 1988). A comparison of triterpane distributions for the three groups of sediments is given in Figure 3.4, and a summary of the biomarkers characterising each

Figure 3.4. Partial m/z 191 mass fragmentograms showing a comparison of triterpane distributions in the lacustrine (a), sabkha (b), and marine (c) carbonate sediments. Numbers denote carbon numbers. G = gammacerane. Refer to Program 1 (Section 2.3.4) for GC conditions.

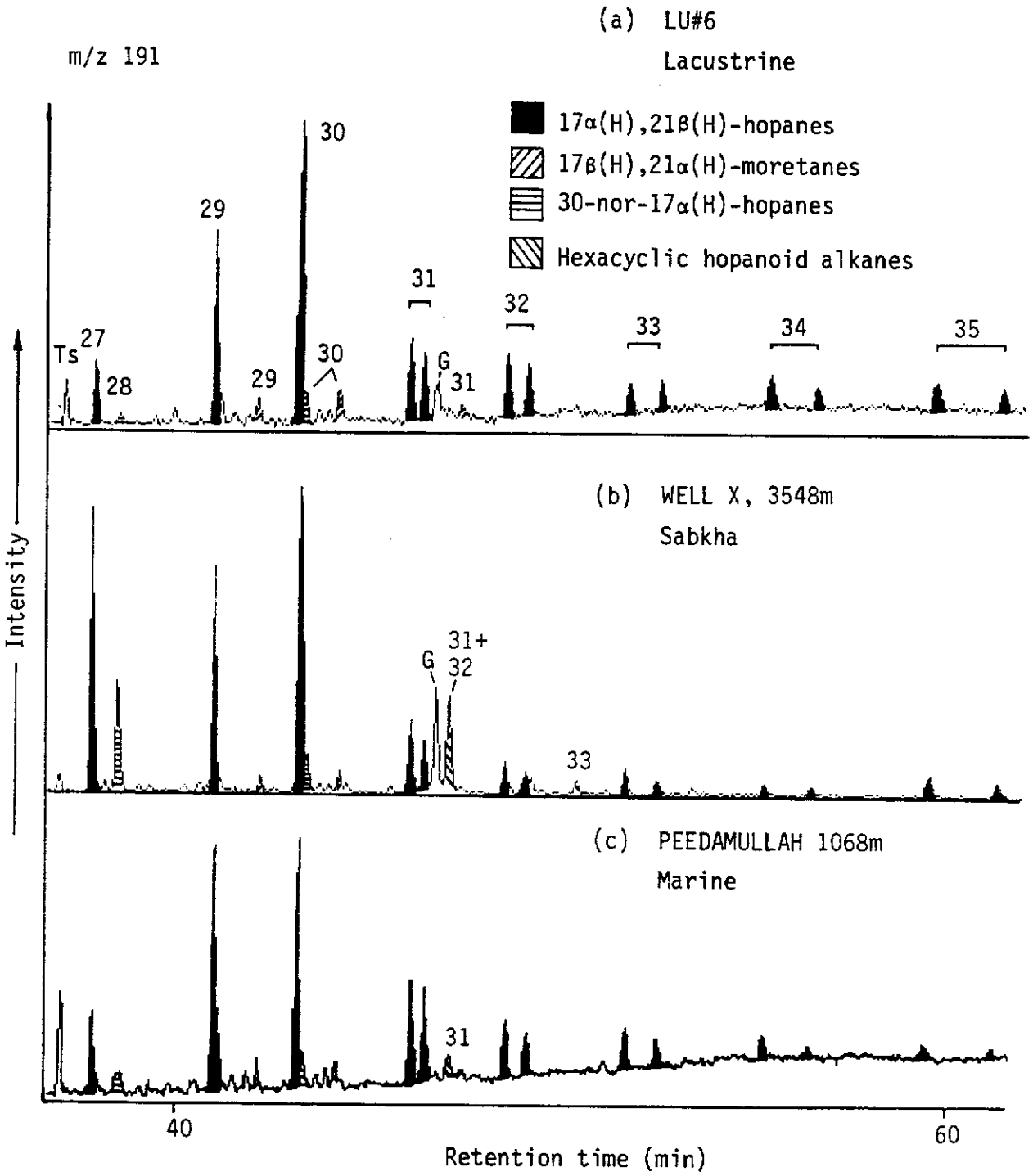


Table 3.9. Parameters which characterise depositional environments of the sedimentary rocks.

PARAMETERS	DEPOSITIONAL ENVIRONMENT		
	LACUSTRINE	MARINE	SABKHA
C_{29} Diasteranes/steranes	<0.1	0.4	<0.1
Gammacerane Index	20	<5	≥30
Hopanes: $C_{35} > C_{34}$	=[a]	-	+
Hexacyclic hopanoid alkanes	-	-	+

a : Consentration of C_{35} $\alpha\beta$ hopanes = C_{34} $\alpha\beta$ hopanes

\+ : Observed

\- : Not observed

depositional environment is given in Table 3.9.

The other parameters, pristane to phytane ratio and $(C_{21}+C_{22})/C_{29}$ steranes ratio for the sediments are inconsistent compared with those in the crude oils. However, pristane/phytane ratios for all group members are relatively low (≤ 1) and $(C_{21}+C_{22})/C_{29}$ sterane ratios are relatively high (≥ 0.8). These parameters, particularly the pristane/ phytane ratio, are probably influenced by thermal maturation.

C Thermal Maturation

Table 3.10 gives the thermal maturation data for the sediments. According to these maturity parameters (except Tm/Ts), the sediments may be considered as marginally mature to mature. Again, the Tm/Ts ratios are inconsistent as maturity indicators; however, as was the case with the crude oil samples, most of the Tm/Ts values are greater than 1.0 with only one sample having a value of 0.8.

Table 3.10. Thermal maturation data for the sediment samples.

SAMPLE NO	STERANES[a]		HOPANES[a]	
	$C_{29}^{\alpha\alpha}$ 20S/20R	C_{29} $\frac{\beta\beta}{\beta\beta+\alpha\alpha}$	C_{30} M/H	Tm/Ts
S1[b]	0.5	0.6	<0.1	ND
S2	0.6	0.4	0.1	1.5
S3	0.8	0.4	0.1	5.0
S4	0.9	0.5	0.1	14.0
S5	0.8	0.6	0.1	1.1
S6	0.7	0.5	<0.1	0.8
S7[b]	0.8	0.5	0.1	1.7

a : Refer to Section 2.4.2 for methods of calculation and definition of abbreviations

b : From literature data

ND : No data

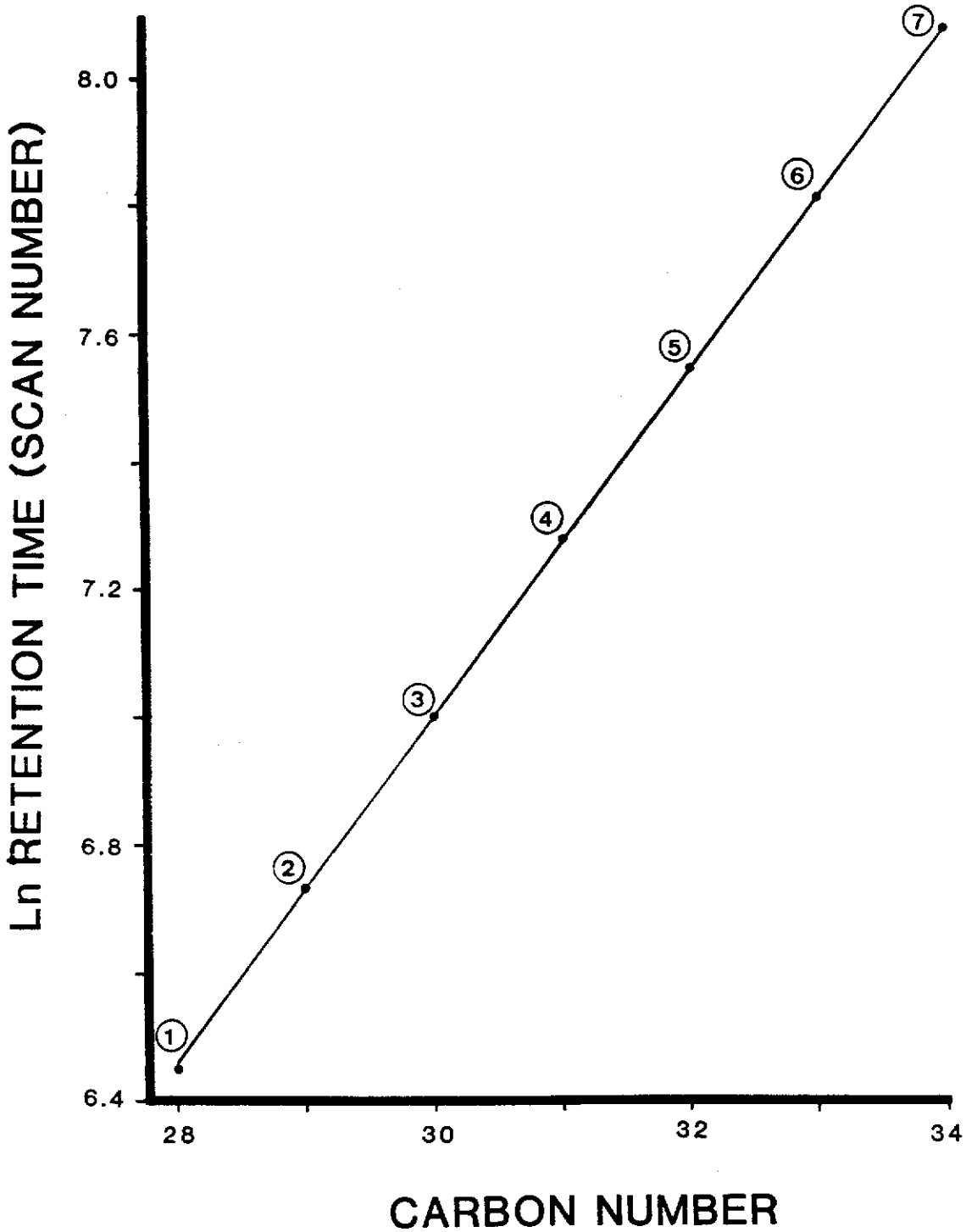
3.3 IDENTIFICATION OF 30-NOR-17α(H)-HOPANES

3.3.1 Evidence for a Homologous Series of 30-Nor-17α(H)-hopanes

It has been recognised that specific structural features such as addition or removal of a methyl group on a ring system will give a predictable effect on the retention times. Thus, plots of the logarithm of the retention times against carbon number usually yield a straight line for members of a homologous series when analysis is performed isothermally (e.g. Rullkotter and Philp, 1981; Larcher et al., 1987). Figure 3.5 shows a plot of retention time data obtained from an m/z 191 mass chromatogram of the branched and cyclic fraction of the Well X oil using isothermal GC conditions (Program 2, Section 2.3.4). The linear relationship observed between the logarithm of the retention times and carbon numbers strongly suggests that the compounds are members of a homologous series.

The C_{32}-C_{34} members of the series have retention times which are very close to those of the extended moretanes. However, they are certainly not moretanes because the C_{32}-C_{34} members of the series have slightly different retention times to those of the C_{32}-C_{34} moretanes. This was confirmed by cochromatography of the Well X oil with the branched and

Figure 3.5. A plot of the natural logarithms of the retention times of a homologous series of 30-norhopanes against their carbon numbers. The data was obtained from GC-MS analysis of the Well X oil using isothermal GC-conditions (Program 2, Section 2.3.4). Refer to Table 3.11 for identification of the circled numbers.



cyclic fraction of Mercury#1, 3650m rock extract which contains relatively high abundance of extended moretane compounds (Larcher et al., 1987). Figure 3.6 shows a comparison of the m/z 191 mass chromatograms between Well X oil and Mercury#1, 3650m sediment. It is apparent that elution positions of the extended 30-nor-17α(H)-hopanes and those of the extended moretanes (shown by arrows) are slightly different. This is supported by the coinjection experiment of the two samples (Figure 3.7). It should be noted that concentrations of the extended moretanes gradually decrease with increasing carbon numbers (Figure 3.6b). The Well X oil is very mature (see Section 3.2.1), hence the presence of the C_{32}-C_{34} moretanes with greater intensities than that of the C_{31} homologue (Figure 3.6a) is very unlikely.

For 17α(H)-hopanes, the relative intensities of the A/B ring fragment ions (fragment A, Figure 3.8) are greater than those of the D/E ring fragment ions (fragment B), whereas for moretanes this relationship is usually reversed (van Dorsselaer et al., 1974; Ensminger et al., 1974; Philp, 1985a,b; Larcher et al., 1987). In the case of 30-nor-17α(H)-hopane, the relative intensities of the A/B ring fragment ions (m/z 191) are always greater than those of the D/E rings (Figure 3.9). Furthermore, the mass spectra shown in Figure 3.9 are very similar to those of the 30-nor-17α(H)-hopanes in the Greek oils reported by Seifert et al. (1984). The

Figure 3.6. Partial m/z 191 mass chromatograms showing a comparison between a sample containing extended 30-norhopanes (a) and a sample containing extended moretanes (b). Arrows mark the elution positions of extended moretanes. H = normal hopanes. G = gammacerane. GC conditions were Program 1 (Section 2.3.4).

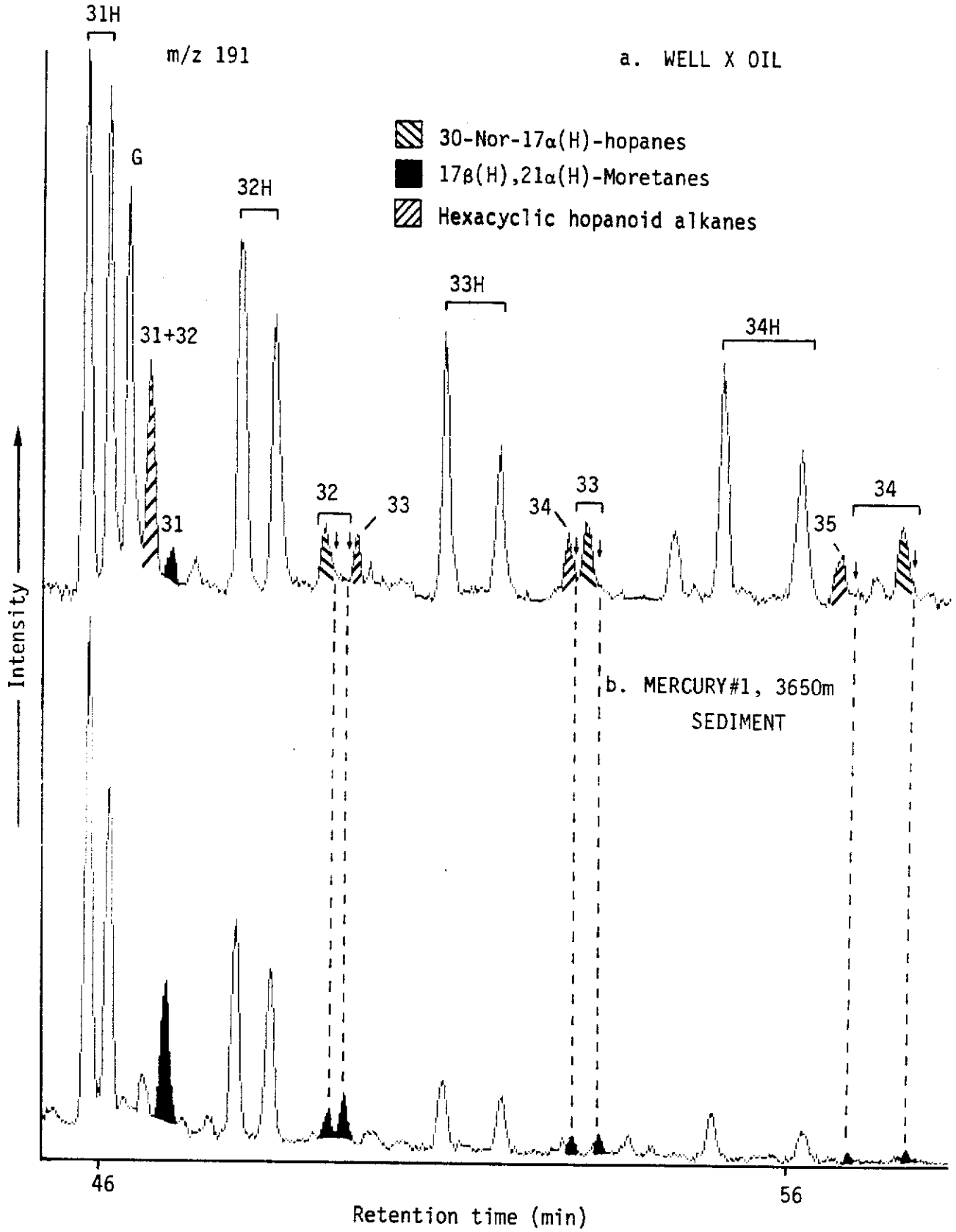


Figure 3.7. Mass chromatograms showing the distribution of pentacyclic triterpanes of a coinjection between Well X oil and Mercury#1, 3650m. M/z 191 corresponds to mass spectral fragment A; other chromatograms reflect fragment B ions (Figure 3.8). GC conditions were Program 1 (Section 2.3.4). Arrows mark the elution positions of the extended moretanes.

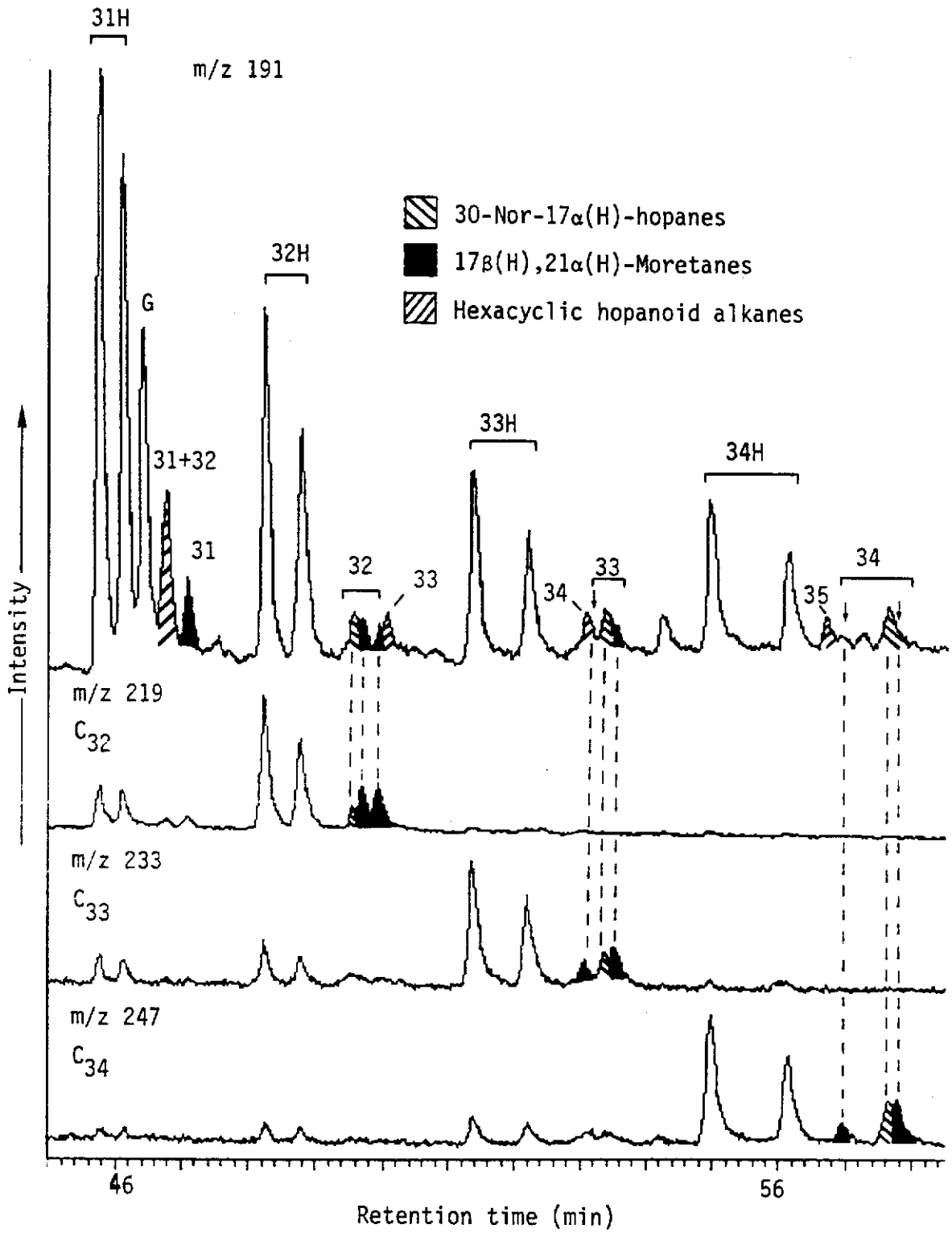
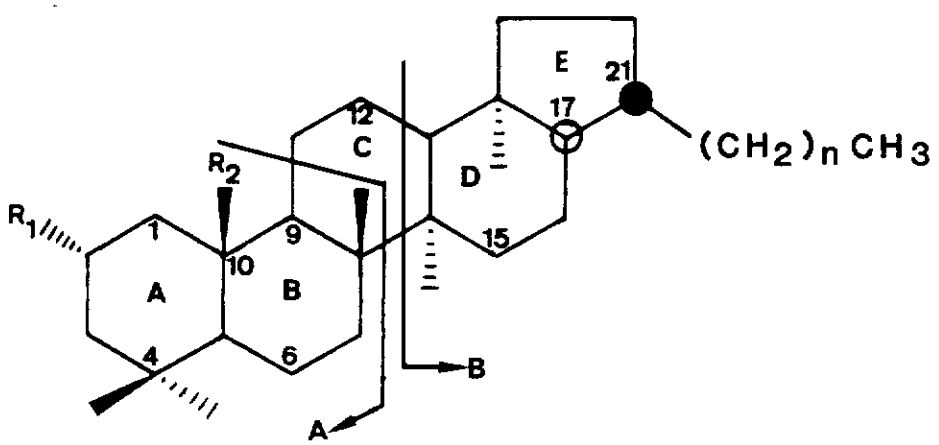


Figure 3.8. The structures of 30-norhopanes, 25,30-bisnorhopanes and 2-methyl-30-nor-hopanes.



29 30-NOR-17α(H)-HOPANES (R_1=H; R_2=CH_3; fragment A = 191)

30 25,30-BISNOR-17α(H)-HOPANES (R_1=H; R_2=H; fragment A = 177)

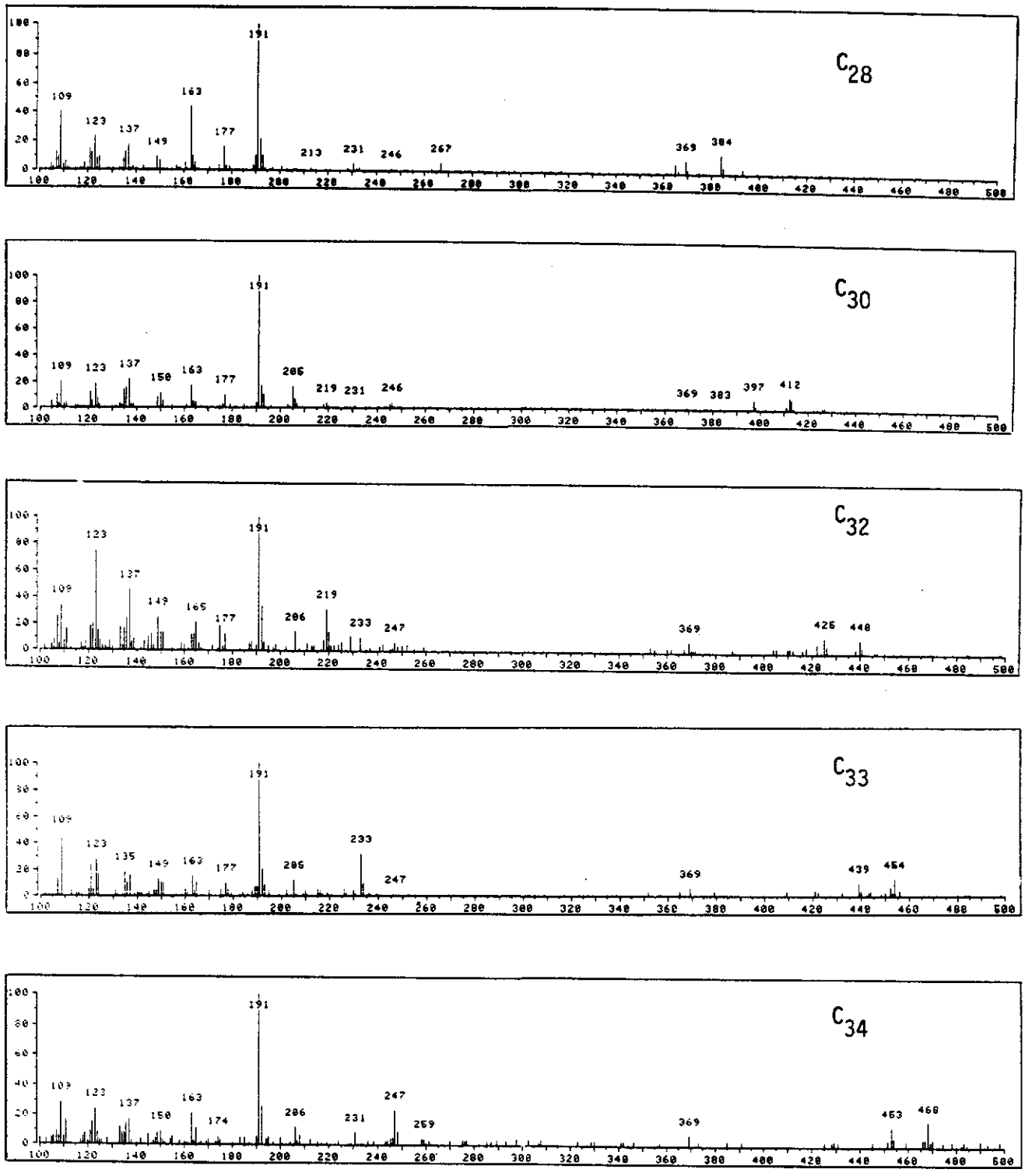
31 2-METHYL-30-NOR-17α(H)-HOPANES (R_1=CH_3; R_2=CH_3; fragment A = 205)

Table 3.11. Mass spectral data and peak assignments for 30-nor-17α(H)-hopanes.

PEAK NO[a]	COMPOUND NAME	n STRUCTURE 29 (FIG.3.8)	CARBON NUMBER	ION OBSERVED PARENT	MRM DAUGHTER A^b	MRM DAUGHTER B^b
1	29,30-Bisnor-17α(H)-hopane	0	28	384	191	163
2	30-Nor-17α(H)-hopane	1	29	398	191	177
3	30-Nor-29-homo-17α(H)-hopane	2	30	412	191	191
4	30-Nor-29,31-bishomo-17α(H)-hopane	3	31	426	191	205
5	30-Nor-29,31,32-trishomo-17α(H)-hopane	4	32	440	191	219
6	30-Nor-29,31,32,33-tetrakishomo-17-α(H)-hopane	5	33	454	191	233
7	30-Nor-29,31,32,33,34-pentakishomo-17α(H)-hopane	6	34	468	191	247

a: Refers to Fig. 3.10; b: Refers to Structure 29 (Fig. 3.8)

Figure 3.9. Mass spectra of the 30-nor-17α(H)-hopanes.

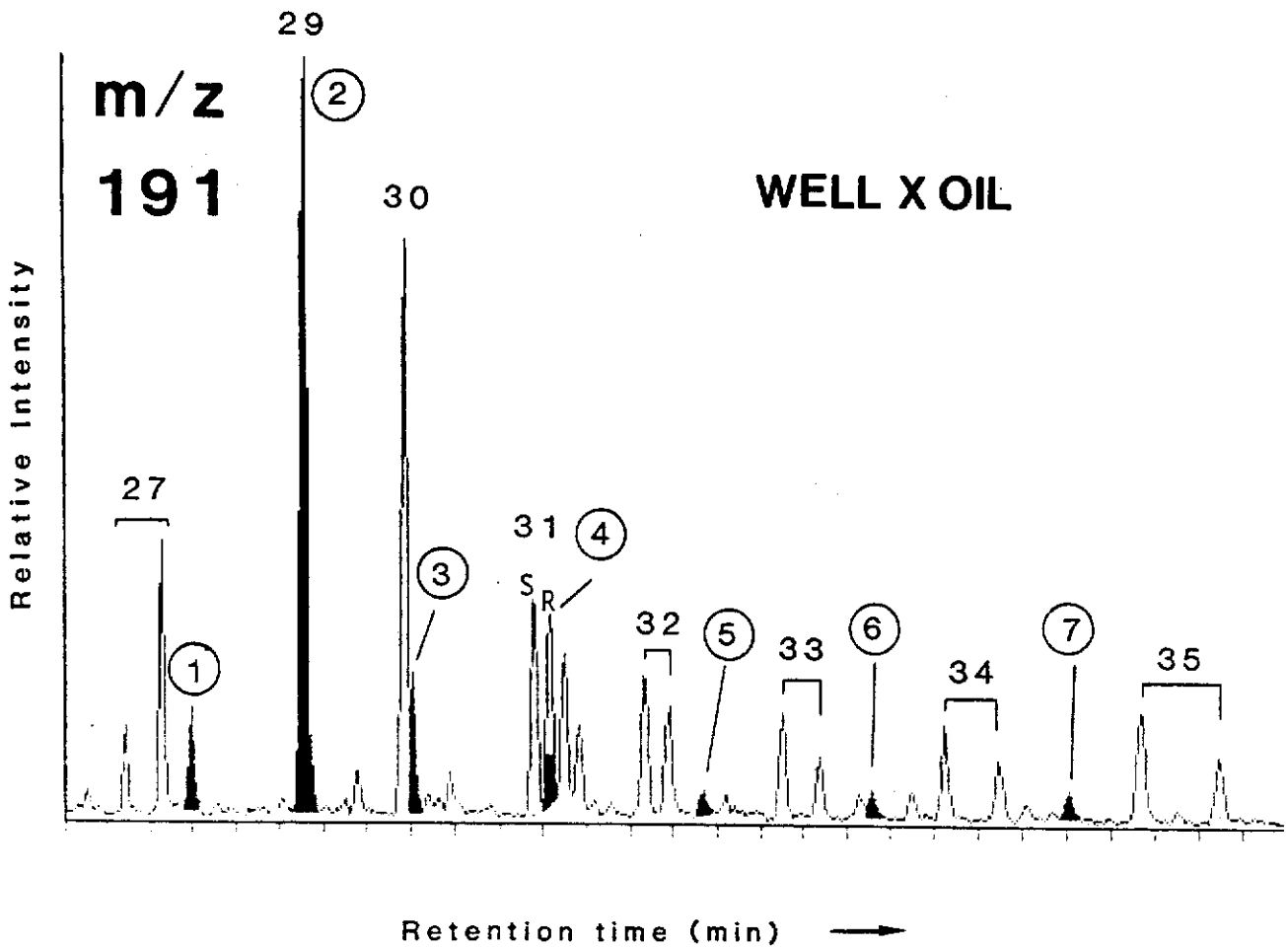


extended 30-nor-17α(H)-hopanes have a single peak because they have normal alkyl side chains, whereas the 22S and 22R diastereomers of the extended moretanes produce doublets (Mackenzie, 1984; Larcher et al., 1987).

Further evidence that each of the compounds was a member of the 30-nor-17α(H)-hopane series was obtained using temperature-programmed gas chromatography (Program 1, Section 2.3.4) combined with metastable reaction monitoring (MRM) mass spectrometry (Program 5, Section 2.3.4). Figure 3.10 shows the m/z 191 mass chromatogram for the Well X oil. Table 3.11 shows the parent ions and the MRM daughter ions obtained from decomposition of each of the parent ions together with the peak assignments. This evidence, together with the similarities in retention behaviour and mass spectra of these compounds with those previously reported (Seifert et al., 1984) suggest that these compounds are a homologous series of 30-nor-17α(H)-hopanes.

It should be noted that the C_{30} member elutes immediately after the C_{30} normal 17α(H)-hopane, and this compound coeluted with the C_{31} 2-methylhopane when the sample was analysed using Program 1 (Section 2.3.4). However, when it was analysed using Program 3, in an injection hold time experiment (Gallegos and Moldowan, 1989), the two peaks could be resolved (Figure 3.11). The C_{29} member of the 30-nor-17α(H)-hopane series is

Figure 3.10. Mass chromatogram (m/z 191) showing peaks assigned to 30-norhopanes (circled numbers; refer to Table 3.11 for identifications). Other numbers denote carbon numbers of normal hopanes. GC conditions were Program 1 (Section 2.3.4).



the same compound as the C_{29} normal 17α(H)-hopane. The C_{31} member could not be separated from the 22R-17α(H)-homohopane, and coelution occurred under temperature programmed and isothermal analyses. The last two features make recognition of the presence of 30-nor-17α(H)-hopanes from routine m/z 191 mass fragmentograms relatively simple, because when these compounds are present in mature samples the peak from C_{29} 17α(H)-hopane is appreciably larger than that of the C_{30} 17α(H)-hopane and the 22S:22R 17α(H)-homohopane value is less than the corresponding values from higher homologues. Coelution between the C_{31} 30-nor-17α(H)-hopane and the 22R-17α(H)-homohopane, however, could be separated under hold-time analysis (Program 3, Section 2.3.4). Figure 3.11 shows separation between these two compounds (note that the 22S:22R ratio of the 17α(H)-homohopanes is higher than the corresponding value in Figure 3.10).

3.3.2 Distribution of 30-Nor-17α(H)-hopanes

Table 3.12 shows the data regarding the 30-nor-17α(H)-hopanes in the crude oils and sediments. In all of the samples the 30-nor-17α(H)-hopane series could be detected. The C_{28} member is present in all samples and the C_{30} in most. In cases where the

Table 3.12. Ratios of C_{28}, C_{29} and C_{30} 30-nor-17α(H)-hopanes over C_{30} 17α(H)-hopane and extended 30-nor-17α(H)-hopane contents of sediments and oil samples.

SAMPLE NO.	28N/30H	29N/30H	30N/30H	C_{31}-C_{34}N
C1	0.26	2.1	0.37	+
C2	0.23	1.9	0.35	+
C3	0.18	1.4	0.27	+
C4	0.16	1.1	0.14	-
C5[a]	0.12	1.1	0.13	ND
C6	0.19	1.3	0.24	+
C7	0.28	1.5	0.25	-
C8	0.38	2.0	0.29	-
C9	0.41	2.6	0.38	-
C10	0.34	2.2	0.29	-
C11	0.34	2.0	0.27	-
C12	0.38	2.4	0.27	-
C13	0.36	2.3	0.27	-
C14	0.33	2.3	0.30	-
C15	0.32	2.6	0.32	-
C16	0.43	2.3	0.39	-
C17	0.33	2.3	0.33	-
C18	0.22	1.4	0.23	-
C19[a]	L[b]	L[b]	L[b]	+
C20	0.29	1.4	0.24	-
C21[a]	0.19	1.5	0.22	ND
C22[a]	0.19	0.9	ND	ND
S1[a]	0.12	0.59	0.07	ND
S2	0.10	0.70	0.05	-
S3	0.10	0.63	0.09	-
S4	0.38	0.79	0.11	+
S5	0.21	1.1	0.20	-
S6	0.10	1.0	0.13	-
S7[a]	0.10	0.80	ND	ND

a : From literature data
b : Large, no C_{30}H present
ND: No data

+ : Present
- : Not detected

30-nor-17α(H)-hopanes are moderately abundant, the value for the ratio 30-nor-17α(H)-hopane/17α(H)-hopane (29N/30H) exceeds one. The C_{31}-C_{34} members of the series could only be unequivocally identified in five crude oils (C1-C3, C6 and C19) and in one sediment (S4). In this sample set the 30-nor-17α(H)-hopanes do not occur at such high relative abundances in sediments and crude oils from non-carbonate origins in accordance with the observation of Price et al. (1987). Typical values of ratio 30-nor-17α(H)-hopane to 17α(H)-hopane for non carbonate derived oils are less than 0.05.

The presence of 30-nor-17α(H)-hopanes in samples from a range of locations, a variety of apparent maturities and differing depositional regimes, but with a common carbonate mineral facies (see Section 3.1 and Section 3.2) suggests that these compounds are useful biomarkers for petroleum from carbonate source rocks.

3.4 OCCURRENCE OF 30-NOR-17α(H)-HOPANES

3.4.1 Relative Abundance of 30-Nor-17α(H)-hopanes with Change in Maturity

Figure 3.12 shows a plot of the ratio of the C_{30} 30-nor-17α(H)-hopane/C_{30} 17α(H)-hopane against the common 20S/20R C_{29} sterane diastereomer ratio used to indicate maturity. Samples used to construct this plot include both crude oils and sediments. It is apparent from the plot that the crude oil samples usually have higher values for both parameters than do the sediments. It should be noted however, that some of the crude oils have been severely biodegraded and the very high values (above 1.1) for the sterane parameter may be due, in part, to selective depletion of the 20R diastereomer by microorganisms. Notwithstanding this effect, a general trend towards higher relative abundances of 30-nor-17α(H)-hopanes is apparent with increased maturity in the sample suite.

One explanation for this observation is that the 30-nor-17α(H)-hopanes are bonded to kerogen and are released as kerogen cracking proceeds with enhanced sediment maturity. Evidence that the 30-nor-17α(H)-hopanes were bonded to kerogen was obtained from the hydrous pyrolysis experiments. Figure 3.13 shows partial m/z 191 mass fragmentograms obtained from the Seram

Figure 3.12. A plot of sterane maturity parameter (20S/20R) against ratio of C_{30} 30-nor-17α(H)-hopane/C_{30} 17α(H)-hopane. * Shows samples with biodegradation level ≥3. Numbers denote sample numbers (see Table 3.1 and Table 3.2).

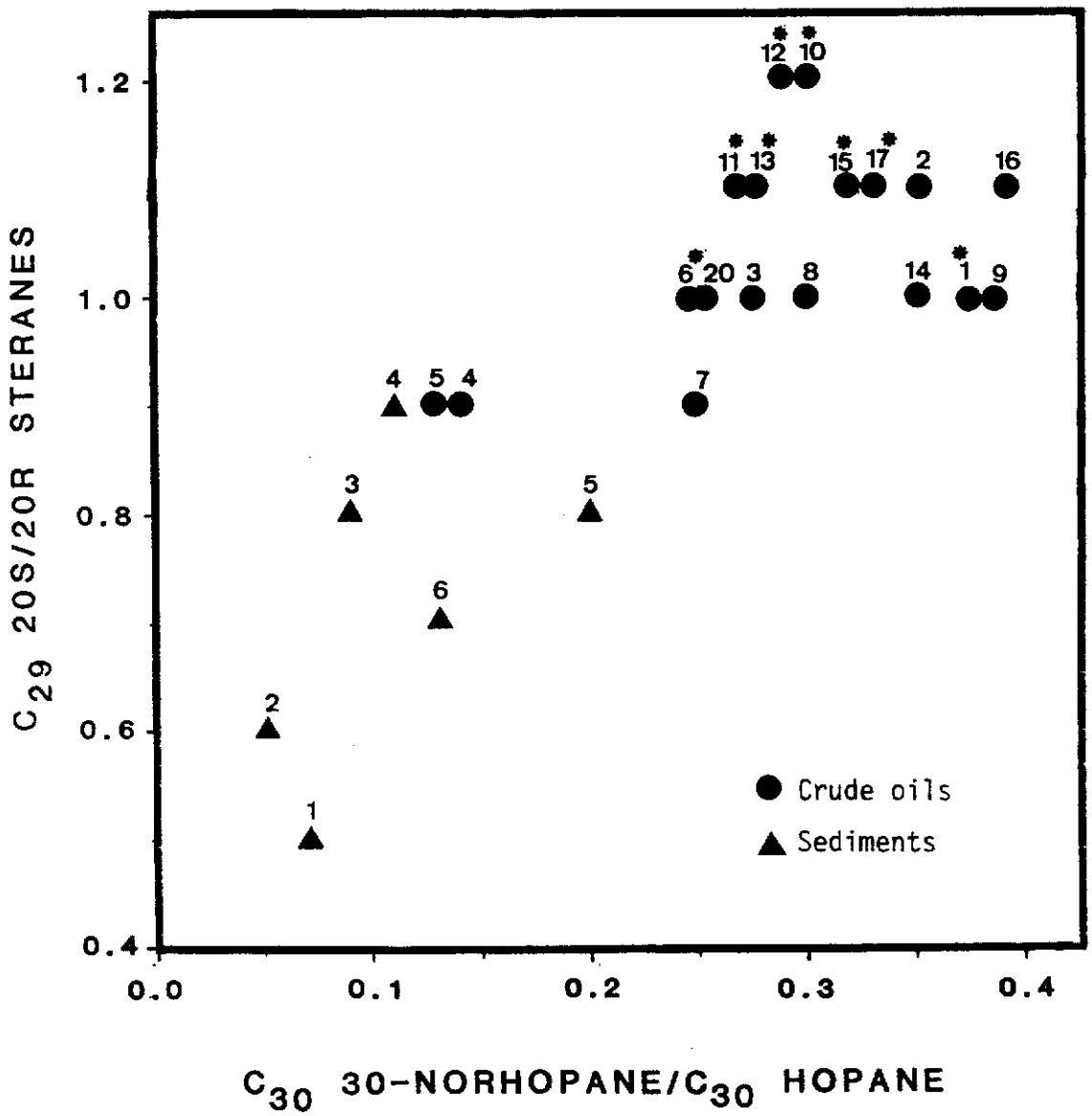
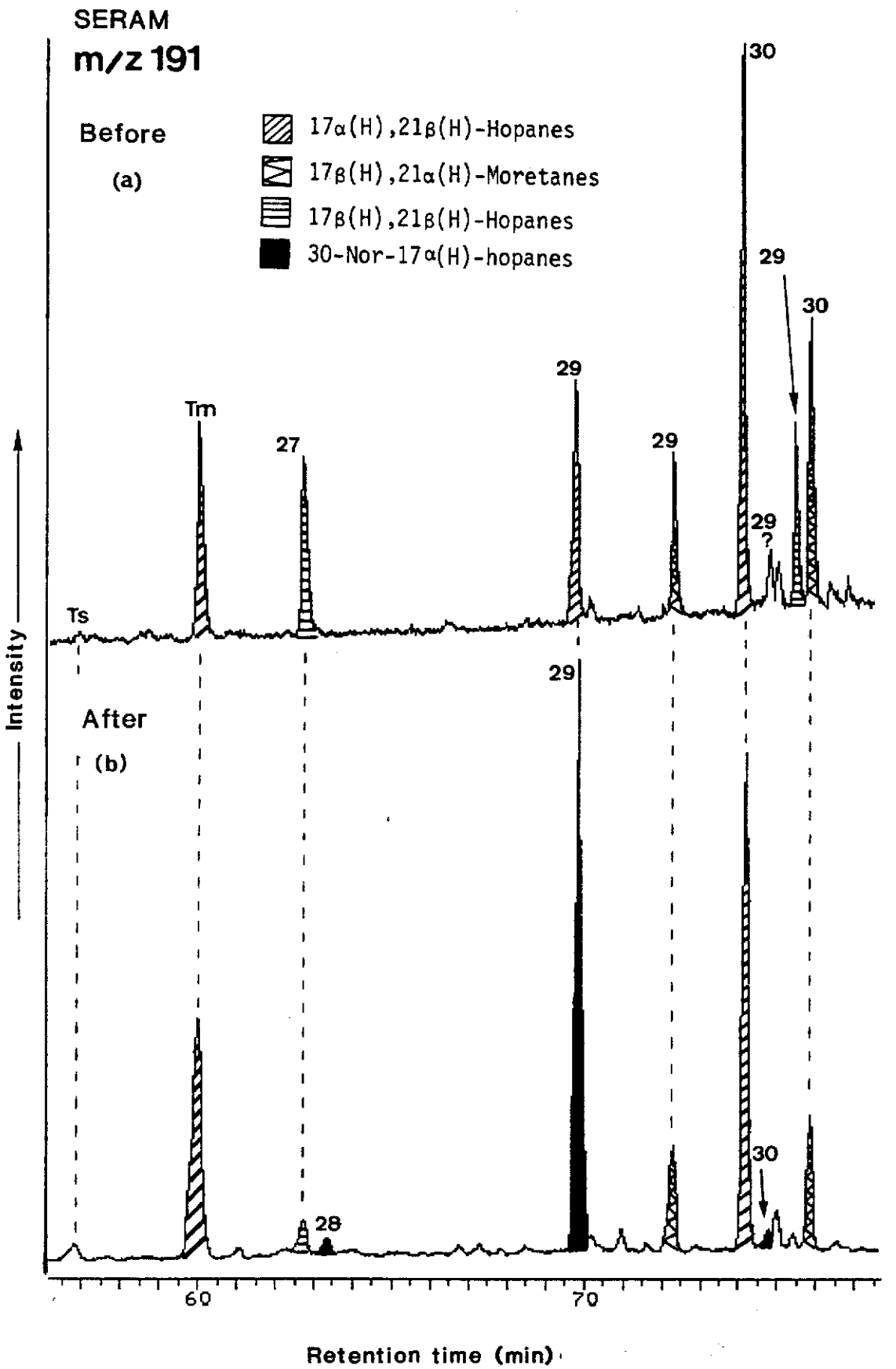
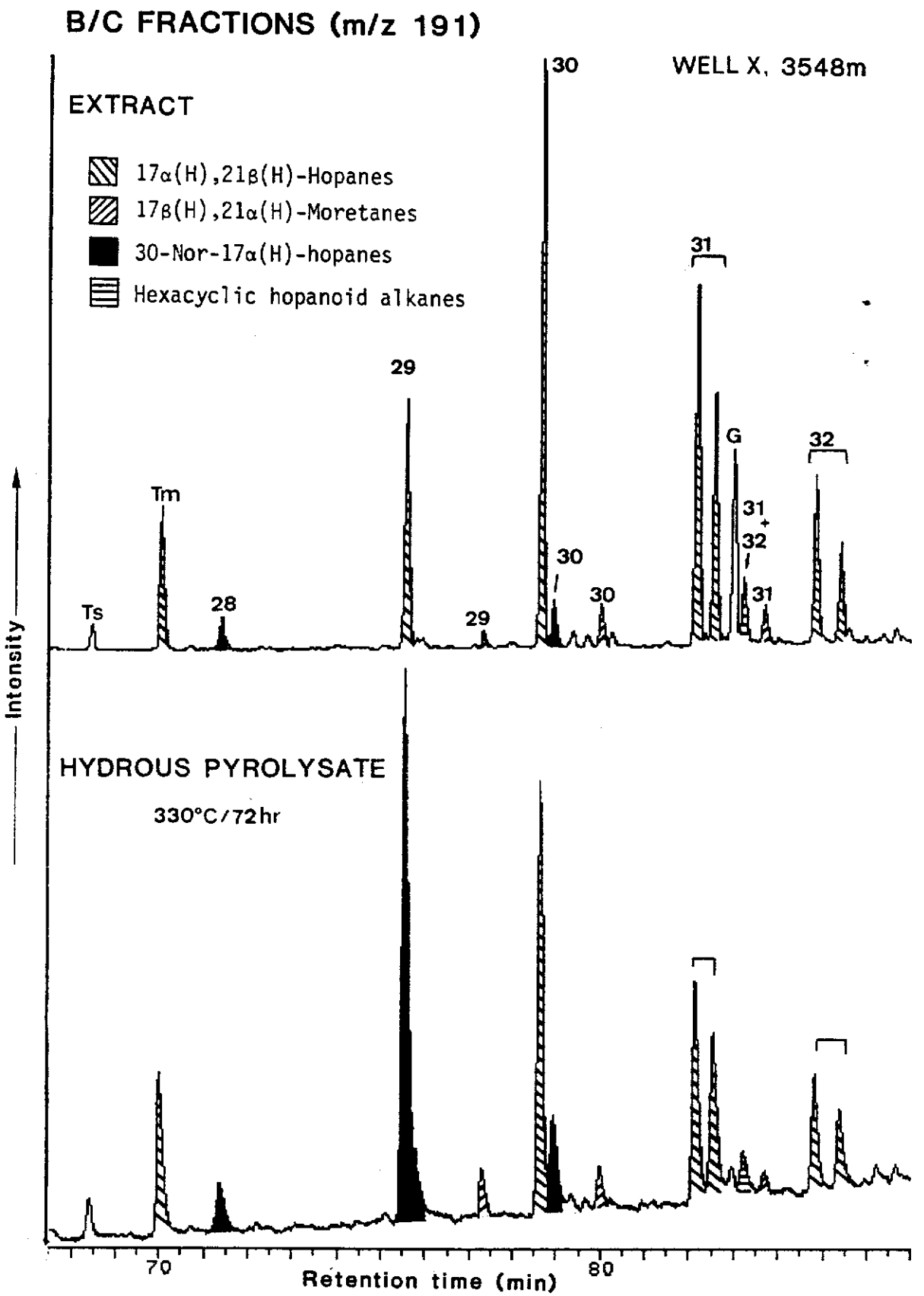


Figure 3.13. Partial m/z 191 mass chromatograms of the Seram rock extracts (a) before and (b) after hydrous pyrolysis. H = normal hopane. ? = unknown compound. Numbers denote carbon numbers. GC conditions were Program 3 (Section 2.3.4).



sediment extracted before and after hydrous pyrolysis (Lewan and Williams, 1987). The mass fragmentogram (a) obtained from the rock extract before the hydrous pyrolysis shows that the sample is immature [17β(H),21β(H)-hopanes and 17β(H),21α(H)-moretanes in relatively high concentrations]. The mass chromatogram (b) of the hydrous pyrolysate shows that the sample has become relatively more mature and the C_{28} and C_{30} members of the 30-nor-17α(H)-hopanes have appeared. These compounds are present only in relatively low concentrations in the pyrolysate, however in the rock extract these compounds are totally absent within the limits of analytical sensitivity. Further evidence was obtained from the Well X, 3548m sediment. Figure 3.14 shows a comparison of the triterpane distributions in the rock extract and hydrous pyrolysate of the sediment. It is apparent that concentrations of the C_{28} - C_{30} members of the 30-nor-17α(H)-hopanes are enhanced relative to those of the normal 17α(H)-hopanes in the hydrous pyrolysate. Thus, these two sets of experiments prove that 30-nor-17α(H)-hopanes are more abundant in the pyrolysates than in the soluble organic matter. Aside from the possibility that the 30-nor-17α(H)-hopanes are more tightly bound in the sediments than the normal 17α(H)-hopanes it is also possible that the 30-nor-17α(H)-hopanes are more stable than 17α(H)-hopanes and hence assume greater relative abundance after pyrolysis or maturation because of

Figure 3.14. Partial m/z 191 mass fragmentograms of the Well X, 3548m sediment showing a comparison of the triterpane distributions in the rock extract and hydrous pyrolysate. Numbers denote carbon numbers. GC conditions were Program 3 (Section 2.3.4).



selective loss of the 17α(H)-hopanes. To test the latter hypothesis a blank experiment was performed to examine if any selective depletion of 17α(H)-hopanes relative to the C_{28}, C_{29} or C_{30} 30-nor-17α(H)-hopanes occurred during hydrous pyrolysis (Section 2.2.6). Figure 3.15 displays the triterpane distributions of the Safaniya oil before and after pyrolysis. It is apparent that concentrations of the C_{28}, C_{29} and C_{30} 30-nor-17α(H)-hopanes relative to those of the ordinary hopanes in the crude oil before and after hydrous pyrolysis are approximately constant. These observations lead to the conclusion that the 30-nor-17α(H)-hopanes are preferentially bonded to kerogen and are released during hydrous pyrolysis.

During the hydrous pyrolysis experiments appreciable changes occurred in the distributions of steranes. Figure 3.16 shows the sterane distributions in the rock extract and the hydrous pyrolysate of the Well X, 3548m sediment. Maturity assessment on the basis of the 20S/20R sterane ratio shows no difference between the rock extract and the hydrous pyrolysate. However, relative concentrations of the ββ steranes are appreciably enhanced in the hydrous pyrolysate, a very common feature in carbonate crude oils or mature sediments (e.g. Palacas et al., 1984). Again in the case of the Safaniya crude oil significant changes were observed. Figure 3.17 shows a comparison of the sterane

Figure 3.15. Partial m/z 191 mass chromatograms of the Safaniya oil showing a comparison of the triterpane distributions (a) before and (b) after hydrous pyrolysis. Numbers denote carbon numbers. H = normal hopanes. GC conditions were Program 1 (Section 2.3.4).

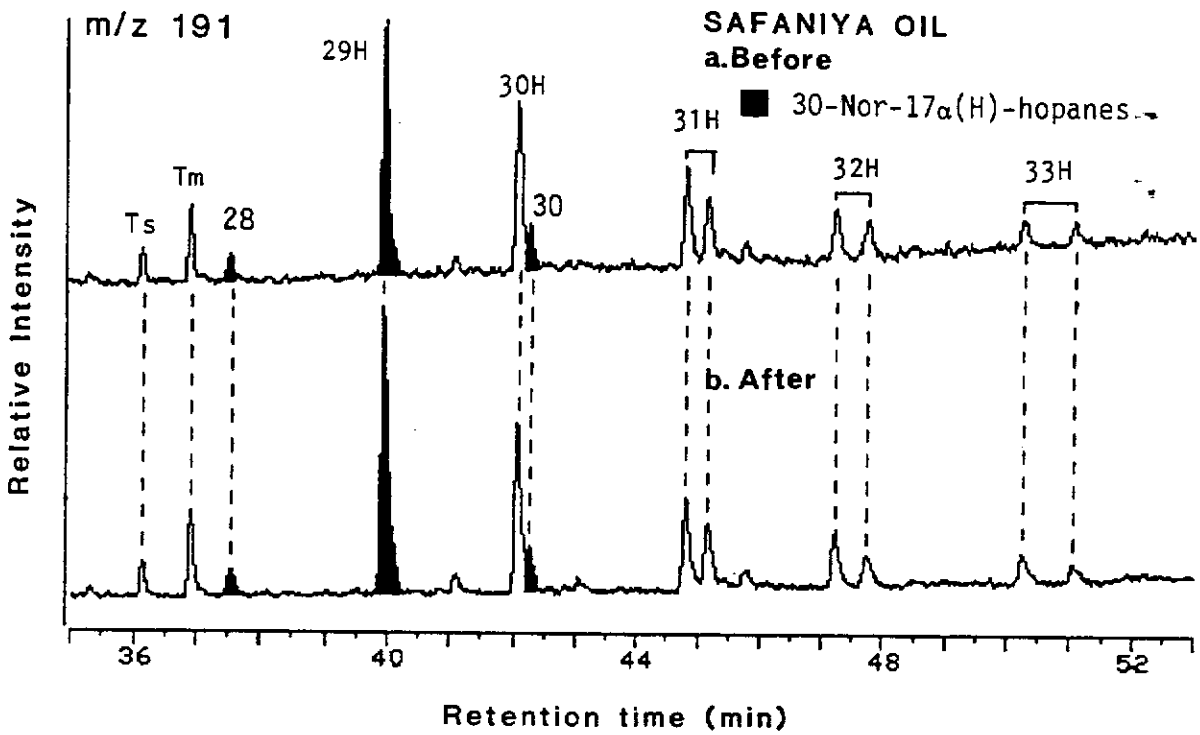
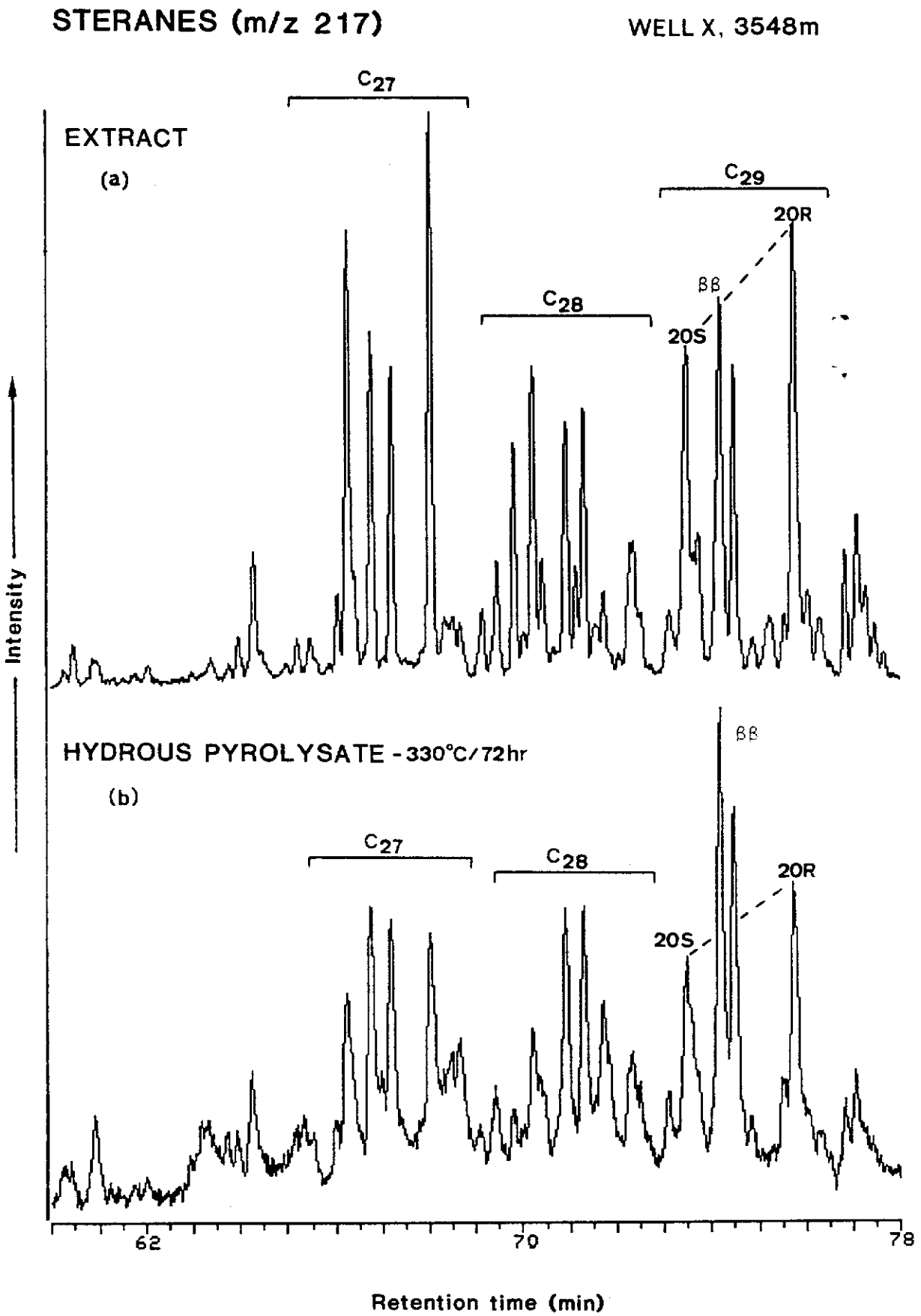


Figure 3.16. Partial m/z 217 mass chromatograms of the Well X, 2548m sediment showing comparison of the sterane distribution in the rock extract (a) and hydrous pyrolysate (b). GC conditions were Program 3 (Section 2.3.4).

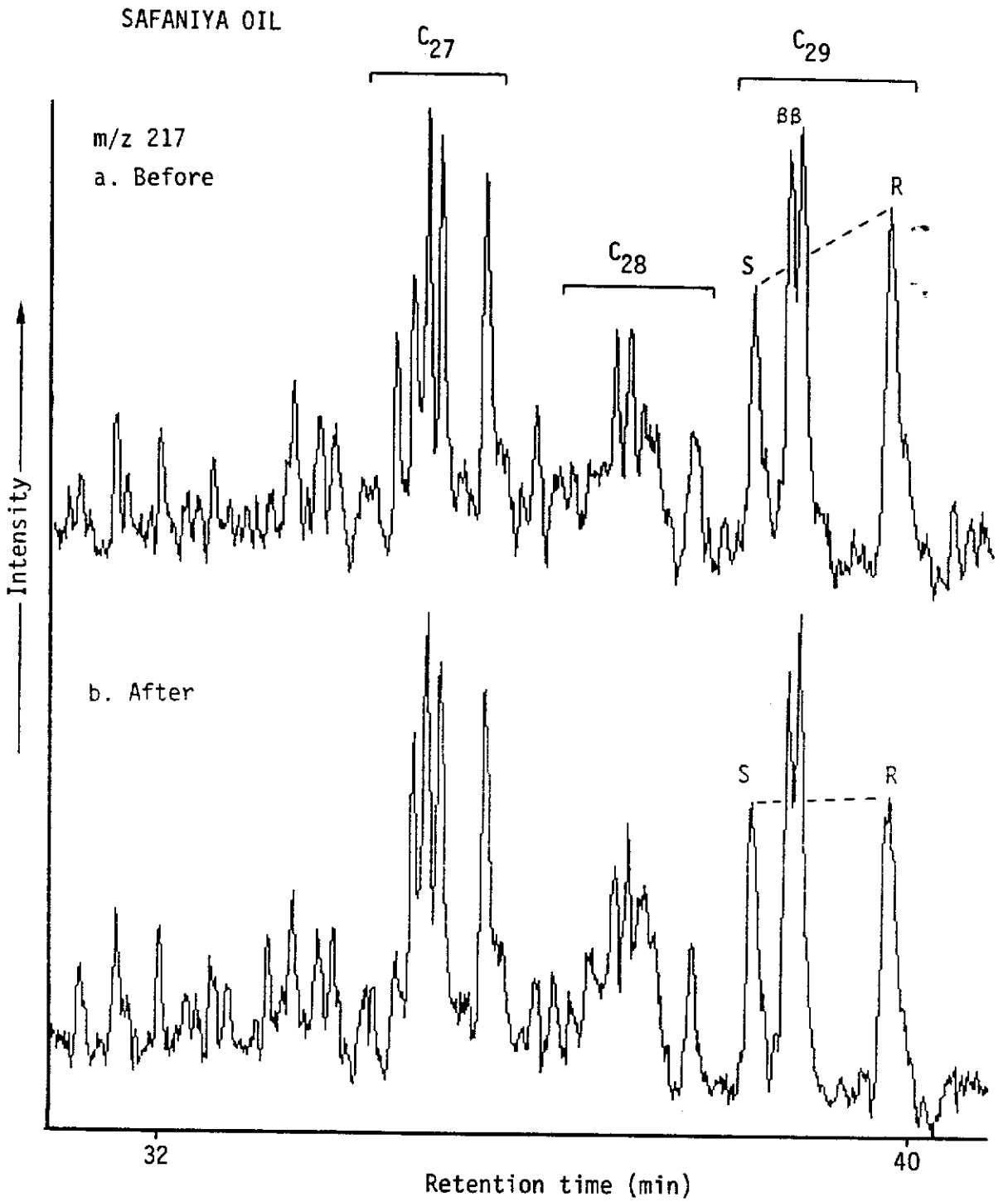


distributions in the Safaniya oil before and after hydrous pyrolysis. It is apparent that after hydrous pyrolysis the Safaniya oil appears to be more mature than the oil before hydrous pyrolysis (see ratio C_{29} 20S sterane relative to C_{29} 20R sterane and ratio of C_{29} $\beta\beta$ to $\alpha\alpha$ steranes). These phenomena are similar to those previously reported during hydrous pyrolysis (e.g. Lewan et al., 1986).

3.4.2 Origin of 30-Nor-17α(H)-hopanes

Seifert et al. (1984) suggested two possibilities for the formation of 30-nor-17α(H)-hopanes. They suggested that these compounds may be formed during the processes of biodegradation, or may become unmasked by removal of the dominant series of 17α(H)-hopanes during biodegradation. However, in the present study, because these compounds were found in sediments as well as in non-biodegraded crude oils, and moreover, because the hydrous pyrolysis experiments proved that these compounds are more tightly bound to kerogen than the normal hopanes, one must conclude that they are formed directly from biological precursor(s) and their presence is not related to reservoir biodegradation processes. More recently, Moldowan et al. (1989) have suggested that both the 17α(H)-hopanes and the 30-nor-17α(H)-hopanes are produced from similar bacterial precursor

Figure 3.17. Partial m/z 217 mass chromatograms of the Safaniya oil showing a comparison of the sterane distributions (a) before and (b) after hydrous pyrolysis. GC conditions were Program 1 (Section 2.3.4).



compound(s) based on the fact that the relative proportion of each of the 30-norhopanes (C_{30}-C_{34}) in a sample closely reflects the relative distribution of the common extended 17α(H)-hopanes (C_{31}-C_{35}). The data obtained in the present study appears to be in agreement with their suggestion of a bacterial origin. The compounds were observed in samples having a great range of geological ages (the oldest samples are Pre Cambrian; Table 3.1 and Table 3.2) indicating that they must have been produced by very primitive and widespread organisms such as bacteria.

3.5 IDENTIFICATION OF 25,30-BISNOR-17α(H)-HOPANES IN CRUDE OILS

3.5.1 Evidence for a Series of 25,30-Bisnor-17α(H)-hopanes

Figure 3.18 shows mass chromatograms obtained in the analysis of a severely biodegraded crude oil, the Buton Asphalt, using the mass spectrometer operating in the MRM mode. Table 3.13 gives peak assignments for the triterpanes present in Figure 3.18. Members of the 30-nor-17α(H)-hopane series are shown in the m/z 191 mass chromatogram indicated with circled numbers (Figure 3.18a; 191 -> 191). It is apparent from these results that peaks occur in the m/z 177 mass chromatogram (177 -> 177; Figure 3.18b) which represent compounds whose metastable ion transitions are consistent with 30-nor-17α(H)-hopanes which have been demethylated in fragment A (30, Figure 3.8). The reported similarity of the geochemistry of the 30-nor-17α(H)-hopanes with that of the 17α(H)-hopanes (Moldowan et al., 1989), suggests that in common with the 17α(H)-hopanes the 30-nor-17α(H)-hopanes also occur with structures which are demethylated at C-10. By analogy, these compounds are probably 25,30-bisnor-17α(H)-hopanes.

Additional evidence that these compounds were members of a homologous series and that members of this

Figure 3.18. Metastable reaction chromatograms of Buton Asphalt showing the distribution of 25,30-bisnorhopanes and other demethylated hopanes. Refer to Table 3.13 for peak identifications. A and B ring fragments refer to Structure 30 (Figure 3.8). GC conditions were Program 6 (Section 2.3.4).

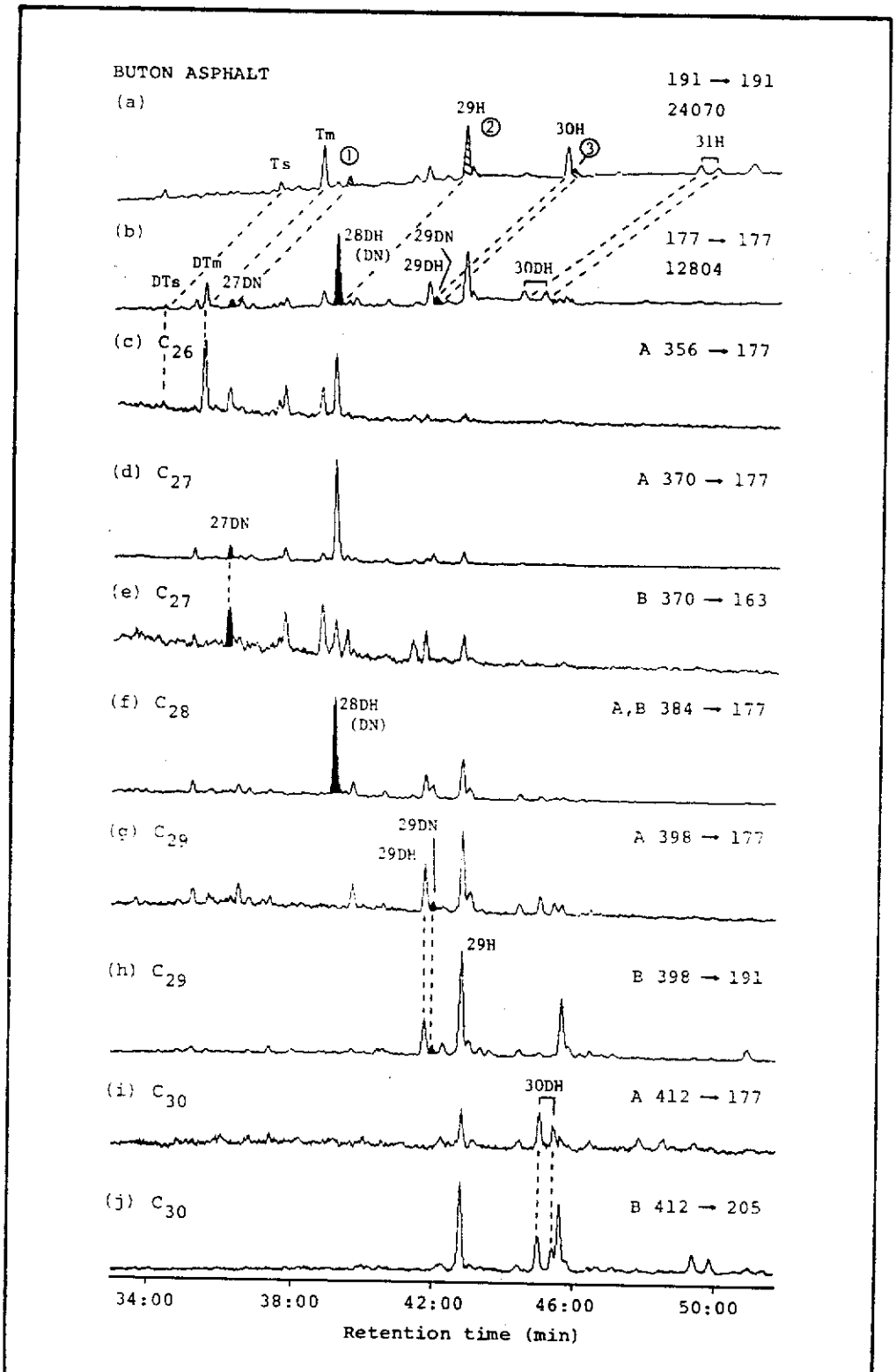


Table 3.13. Peak assignments for triterpanes present in Figure 3.18.

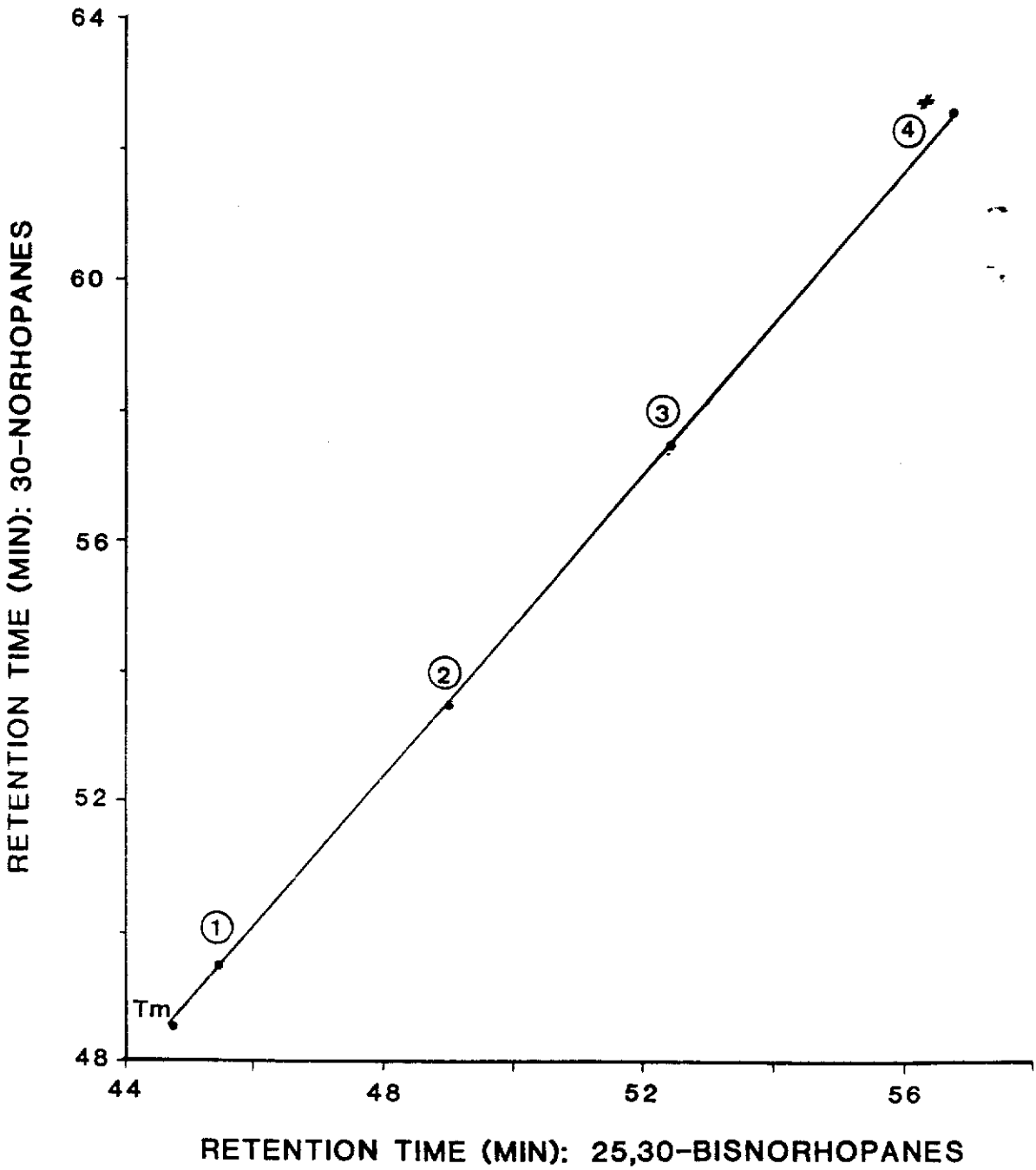
PEAK	COMPOUND NAME	CARBON NUMBER
DTs	18α(H)-22,25,29,30-Tetrakisnor-neohopane	26
DTm	17α(H)-22,25,29,30-Tetrakisnor-hopane	26
27DN	25,29,30-Trisnor-17α(H)-hopane	27
Ts	18α(H)-22,29,30-Trisnorneohopane	27
Tm	17α(H)-22,29,30-Trisnorhopane	27
28DH(DN)	25,30-Bisnor-17α(H)-hopane	28
1	29,30-Bisnor-17α(H)-hopane	28
29DH	17α(H)-25-Norhopane	29
29DN	25,30-Bisnor-17α(H)-29-homo-hopane	29
29H (2)	17α(H)-30-Norhopane	29
30DH	(22S+22R)-17α(H)-25-Nor-29-homohopanes	30
30H	17α(H)-Hopane	30
3	30-Nor-17α(H)-29-homohopane	30
31H	(22S+22R)-17α(H)-29-Homo-hopanes	31

series were structurally related to members of the 30-nor-17α(H)-hopane series was obtained from GC retention data. Figure 3.19 shows a plot of the retention times for the 30-nor-17α(H)-hopanes against the retention times for the compounds identified in Figure 3.18 as 25,30-bisnor-17α(H)-hopanes in the Buton Asphalt. A good linear relationship is apparent suggesting that the parent member, Tm, without a side chain, along with C_{28}-C_{31} 30-nor-17α(H)-hopanes all have analogues with a common structural feature (Volkman et al., 1983b), namely the absence of a methyl group, probably from C-10. In constructing this plot the retention time of the 22R-17α(H)-homohopane was used for that of the C_{31} 30-nor-17α(H)-hopane since the 30-nor-17α(H)-hopanes cannot be resolved.

3.5.2 25,30-Bisnor-17α(H)-hopanes as Indicators of Biodegraded Carbonate Crude Oils

The presence of 25,30-bisnor-17α(H)-hopanes in a crude oil sample which contains appreciable concentrations of 30-nor-17α(H)-hopanes suggests that just as other aspects of their geochemistry parallels that of the 17α(H)-hopanes (Moldowan et al., 1989), biodegradation effects are also similar in the two series. The question as to whether the 25-norhopanes, which are present in source rocks at low concentrations

Figure 3.19. A plot of the retention times of 30-norhopanes against the retention times of the corresponding 25,30-bisnorhopanes. The data was obtained from MRM GC-MS analysis of the Buton Asphalt using linear temperature programmed conditions (Program 6, Section 2.3.4). # = Retention time of 22R-homohopane was used for this plot. Refer to Table 3.11 for identification of circled numbers.



relative to the common hopanes, are enriched during severe biodegradation because they are more resistant to bacterial attack than the common hopanes, or, are biotransformation products of the hopanes, is equivocal. Certainly, the 25-nor-17α(H)-hopanes with extended side-chains have been reported in high relative abundance in severely biodegraded crude oils (Seifert et al., 1984; Moldowan et al., 1989). However irrespective of the mechanism by which these compounds become enriched in severely biodegraded crude oils, it appears that they are useful indicators for severely biodegraded crude oils. It is therefore proposed that the 25,30-bisnor-17α(H)-hopanes are biomarkers for severely biodegraded crude oils that originated from carbonate source rocks.

3.6 IDENTIFICATION OF 2-METHYL-30-NOR-17α(H)-HOPANES

3.6.1 Evidence for a Series of 2-Methyl-30-nor-17α(H)-hopanes

Figure 3.20 and Figure 3.21 show results obtained from the Well X oil using GC-MS injection hold time techniques (Program 3, Section 2.3.4). Table 3.14 and Table 3.15 give the assignment of peaks in these figures. The shaded peaks show strong responses in m/z 205 mass chromatograms (see also their mass spectra in Figure 3.22) and consistently elute after the 30-nor-17α(H)-hopanes suggesting an additional methyl substituent in the A/B ring fragment of the 30-nor-17α(H)-hopanes. Hopanoids having an additional methyl substituent in ring A have been reported by numerous authors (e.g. Seifert and Moldowan, 1978; Brassell et al., 1980; Dastillung et al., 1980; Alexander et al., 1984a; McEvoy and Giger, 1986; Hoffman et al., 1987; Price et al., 1987; Summons and Powell, 1987; Summons et al., 1988). Hoffman et al. (1987) reported the occurrence of two homologous series of methylhopanes. On a non-polar phase, they observed that one series of methylhopanes eluted immediately after the 17α(H)-hopanes with one less carbon atom, and the other eluted much later. The series eluting just after the 17α(H)-hopanes with one less carbon atom has been identified by Summons and Jahnke (1990a,b) as the 2α-methylhopanes, whereas the later eluting series

Figure 3.20. Mass chromatograms for m/z 191, 205 and parent ions m/z 384, 398, 412 and 426 for Well X oil. Numbers denote carbon numbers. H = normal hopanes. GC conditions were Program 3 (Section 2.3.4).

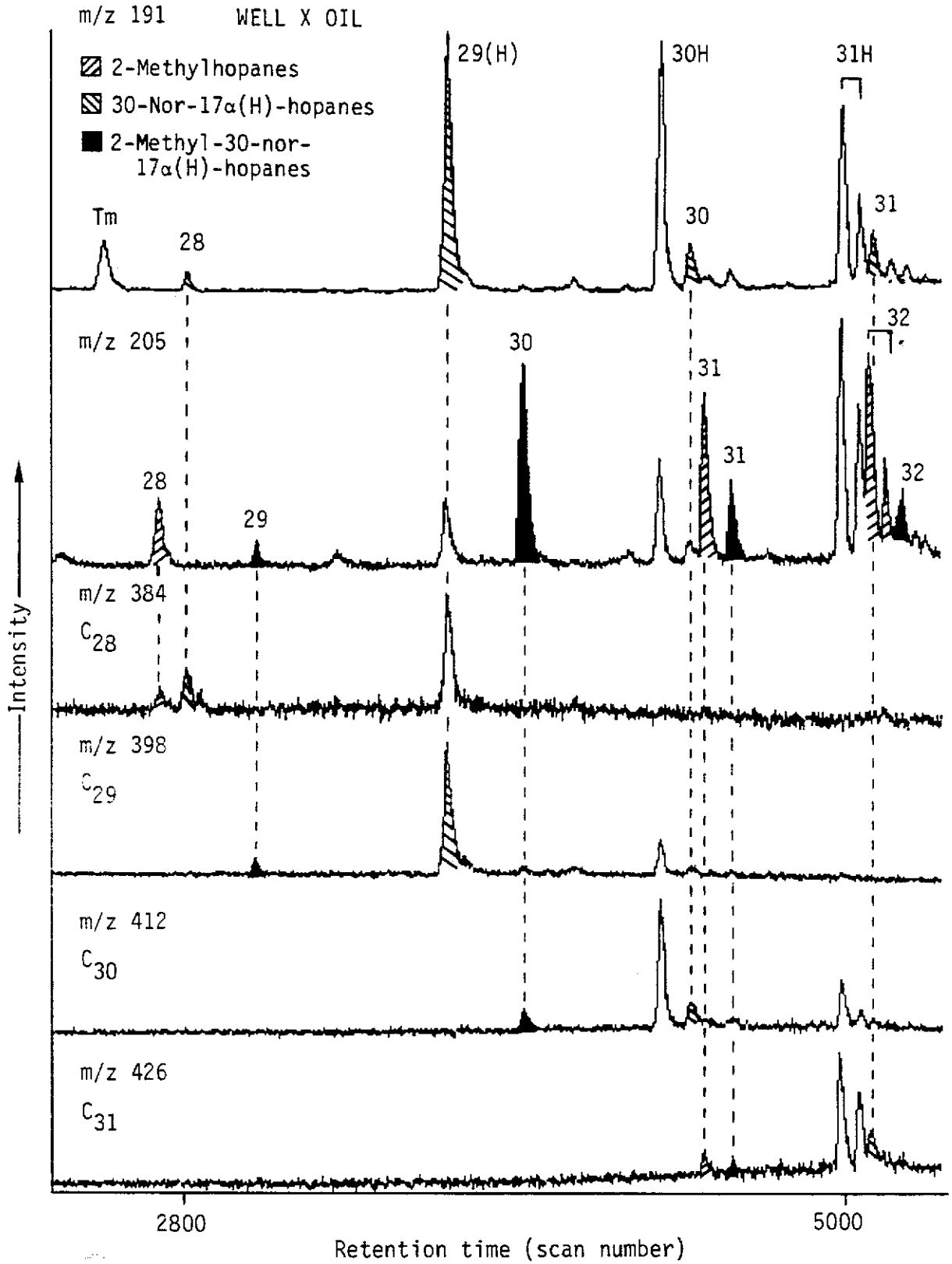


Figure 3.21. Mass chromatograms for m/z 191, 205 and parent ions m/z 440, 454, 468 and 482 for Well X oil. Numbers denote carbon numbers. H = normal hopanes. Refer to Program 3 (Section 2.3.4) for GC conditions.

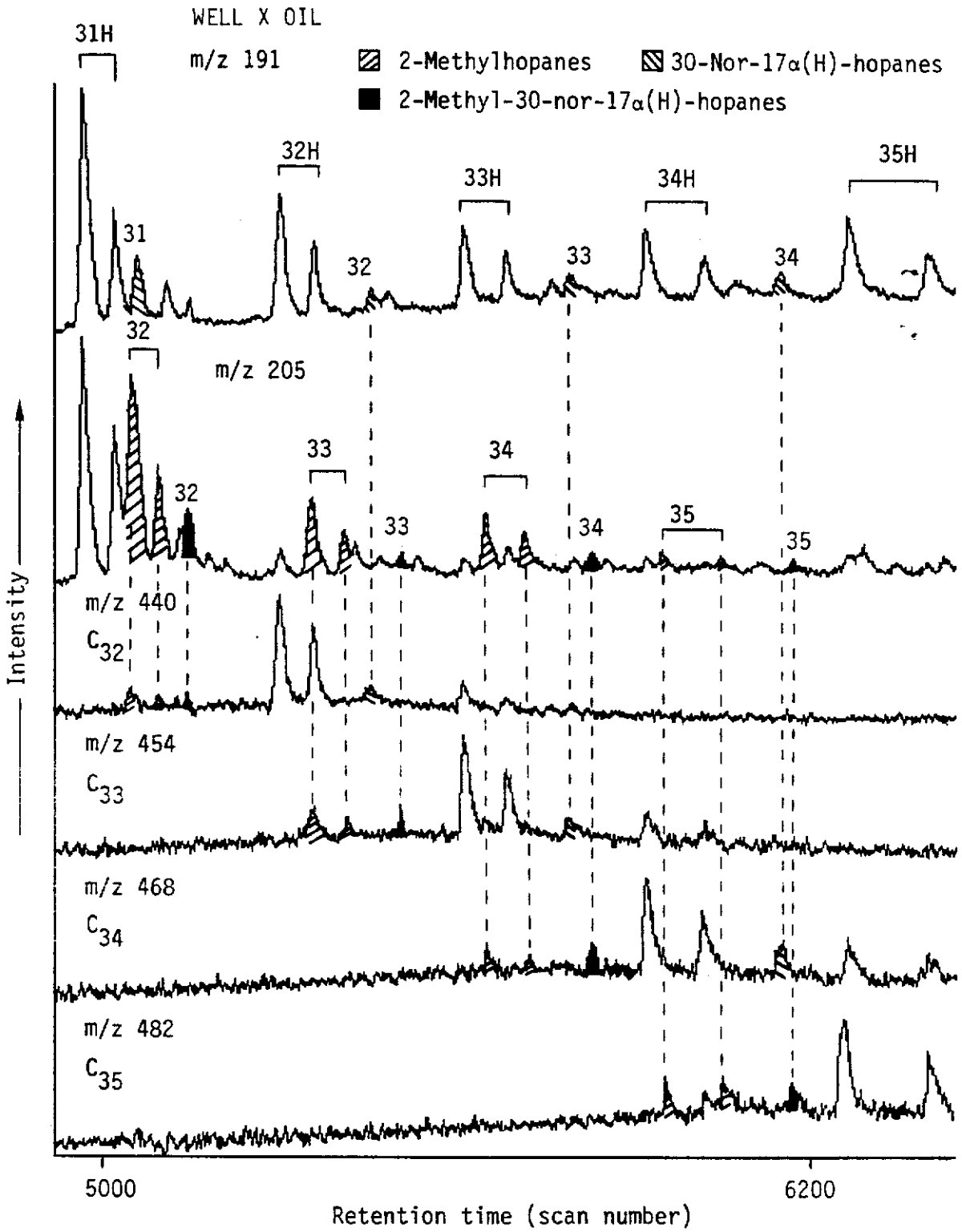


Figure 3.22. Mass spectra of 2-methyl-30-nor-17α(H)-hopanes.

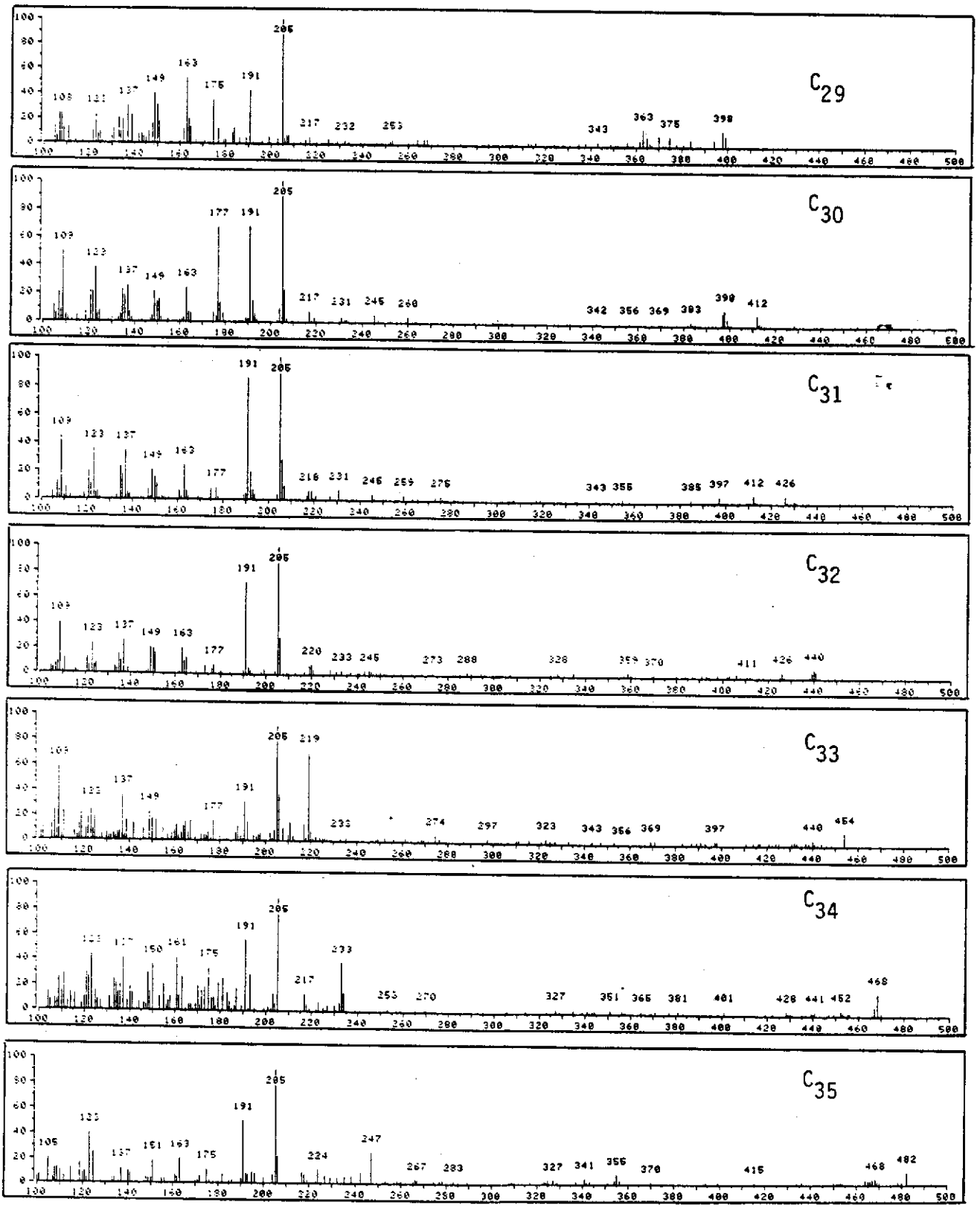


Table 3.14. Peak assignments for 17α(H)-hopanes and their corresponding 2-methylhopanes in Figure 3.20 and Figure 3.21.

CARBON NUMBER	COMPOUND NAME	SCAN NUMBER
17α(H)-hopanes		
27	22,29,30-Trisnorhopane (Tm)	2291
29	30-Norhopane	3913
30	Hopane	4497
31	22S-29-Homohopane	4983
31	22R-29-Homohopane	5035
32	22S-29,31-Bishomohopane	5308
32	22R-29,31-Bishomohopane	5360
33	22S-29,31,32-Trishomohopane	5607
33	22R-29,31,32-Trishomohopane	5690
34	22S-29,31,32,33-Tetrakishomohopane	5913
34	22R-29,31,32,33-Tetrakishomohopane	6012
2-Methylhopanes		
28	2-Methyl-22,29,30-trisnorhopane	2657
30	2-Methyl-30-norhopane	4130
31	2-Methylhopane	4615
32	22S-2-Methyl-29-homohopane	5060
32	22R-2-Methyl-29-homohopane	5113
33	22S-2-Methyl-29,31-bishomohopane	5254
33	22R-2-Methyl-29,31-bishomohopane	5403
34	22S-2-Methyl-29,31,32-trishomohopane	5650
34	22R-2-Methyl-29,31,32-trishomohopane	5710
35	22S-2-Methyl-29,31,32,33-tetrakishomohopane	5938
35	22R-2-Methyl-29,31,32,33-tetrakishomohopane	6037

Table 3.15. Peak assignments for 30-nor-17α(H)-hopanes and their corresponding 2-methyl compounds in Figure 3.20 and Figure 3.21.

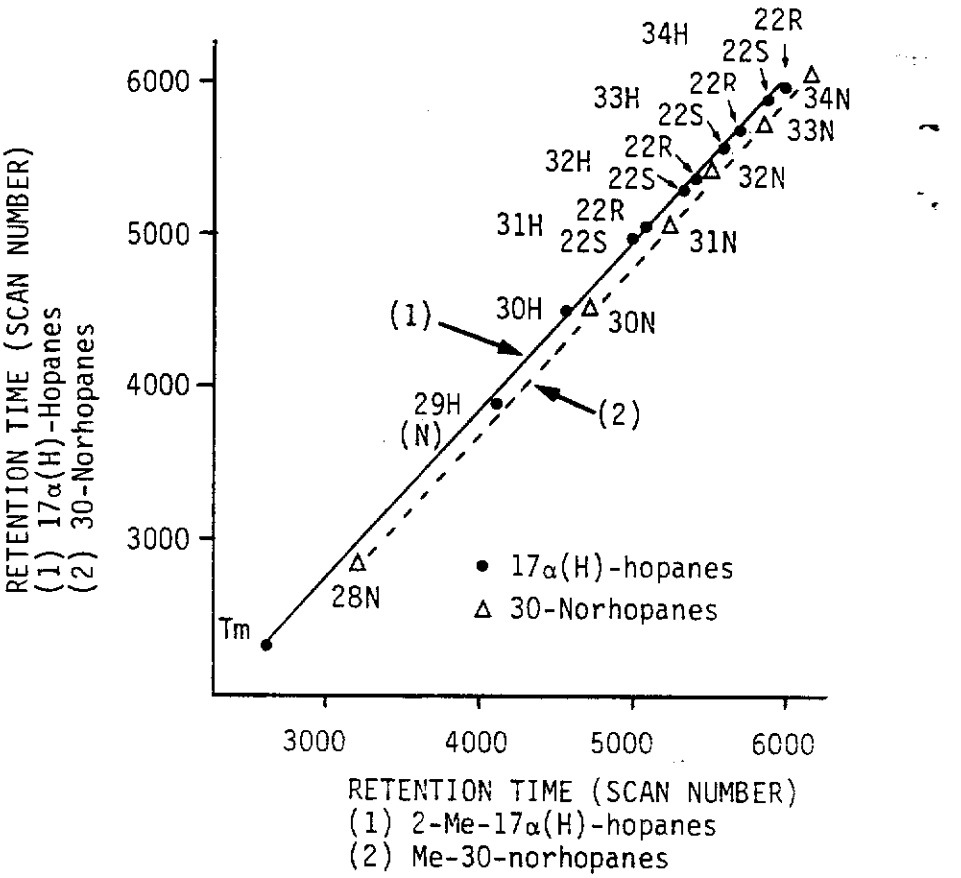
CARBON NUMBER	COMPOUND NAME	SCAN NUMBER
30-Nor-17α(H)-hopanes		
28	29,30-Bisnor-17α(H)-hopane	2802
29	30-Nor-17α(H)-hopane	3913
30	30-Nor-29-homo-17α(H)-hopane	4568
31	30-Nor-29,31-bishomo-17α(H)-hopane	5035
32	30-Nor-29,31,32-trishomo-17α(H)-hopane	5461
33	30-Nor-29,31,32,33-tetrakishomo-17α(H)-hopane	5772
34	30-Nor-29,31,32,33,34-pentakishomo-17α(H)-hopane	6125
2-Methyl-30-nor-17α(H)-hopanes		
29	2-Methyl-29,30-bisnor-17α(H)-hopane	3205
30	2-Methyl-30-nor-17α(H)-hopane	4130
31	2-Methyl-30-nor-29-homo-17α(H)-hopane	4694
32	2-Methyl-30-nor-29,31-bishomo-17α(H)-hopane	5113
33	2-Methyl-30-nor-29,31,32-trishomo-17α(H)-hopane	5500
34	2-Methyl-30-nor-29,31,32,33-tetrakishomo-17α(H)-hopane	5846
35	2-Methyl-30-nor-29,31,32,33,34-pentakishomo-17α(H)-hopane	6152

has been identified by Summons and Jahnke (1990a,b) as the 3β-methylhopanes.

From Figure 3.20 and Figure 3.21 it is apparent from the m/z 205 mass chromatograms that a series of compounds with an additional methyl group in the A/B ring moiety elutes after the corresponding 30-nor-17α(H)-hopanes (m/z 191). These compounds have carbon numbers of 29 to 35. Figure 3.22 shows the mass spectra of these compounds. The mass spectra of the C_{29}, C_{31} and C_{32} compounds are similar to those of the C_{28}, C_{30} and C_{31} of the 30-nor-17α(H)-hopanes reported by Seifert et al. (1984) except that the major fragmentations are increased by 14 Daltons.

Figure 3.23 shows a plot (1) of the retention times of 17α(H)-hopanes against the retention times of the 2α-methyl-17α(H)-hopanes together with the corresponding plot (2) for the retention times of 30-nor-17α(H)-hopanes and the new series of methyl-30-nor-17α(H)-hopanes. Since the two lines are parallel it can be concluded that addition of a 2α-methyl group to 17α(H)-hopanes has the same affect on retention behaviour as addition of the methyl group to 30-nor-17α(H)-hopanes. This result suggests that the additional methyl group in the 30-nor-17α(H)-hopanes is also 2α.

Figure 3.23. A plot of GC-MS retention times (scan number) of normal hopanes and 30-norhopanes against the retention times of 2-methylhopanes and methyl-30-norhopanes, respectively. The data was obtained from GC-MS analysis of the Well X oil using an injection hold time and linear temperature programmed techniques (Program 3, Section 2.3.4). Numbers (28-34) denote carbon numbers. H = hopane; N = 30-norhopane.

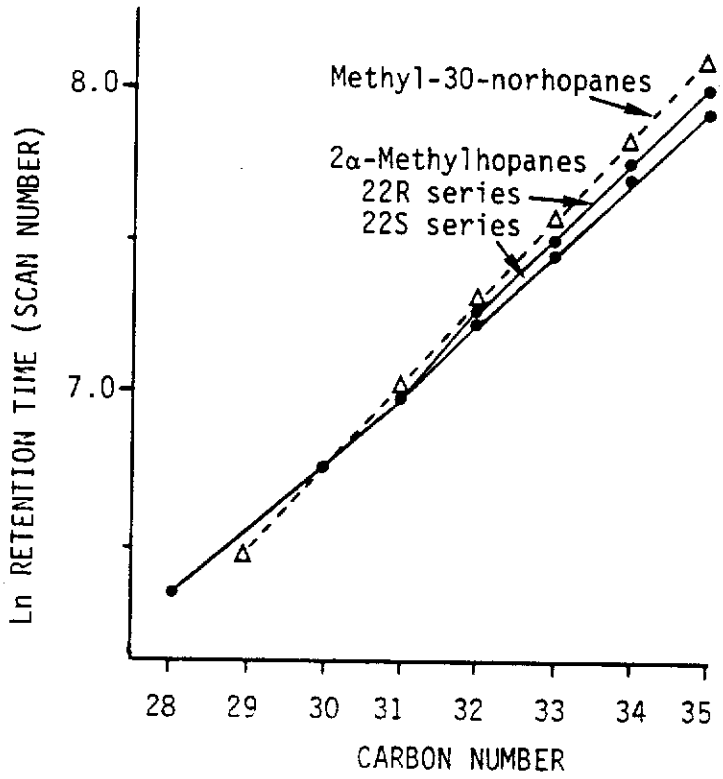


Further evidence that the methyl group in the methyl-30-nor-17α(H)-hopanes is 2α was obtained by establishing that 2α-methyl-17α(H)-hopane, a member of the 2α-methyl-17α(H)-hopane homologous series, whose structures have been established by synthesis (Summons and Jahnke, 1990a,b), was also a member of the new series of methyl-30-nor-17α(H)-hopanes. Figure 3.24 shows plots of the retention times, expressed as natural logarithms, against carbon number for members of the 2α-methyl-17α(H)-hopane series and for the new series of methyl-30-nor-17α(H)-hopanes. These data were obtained from isothermal GC-MS analysis (Program 2, Section 2.3.4) of the Well X crude oil. It is apparent from these plots that the C_{30} member is common to both series of compounds. This result shows that the new series of compounds are in fact 2α-methyl-30-nor-17α(H)-hopanes (31, Figure 3.8).

3.6.2 2-Methyl-30-nor-17α(H)-hopanes as Biomarkers

The precise conditions that facilitate methylation of hopanes in sediments is currently unclear. 2-Methylhopanes have been reported to occur in samples derived from carbonate and/or evaporitic depositional environments (e.g. Alexander et al., 1984a; Hoffman et al., 1987; Price et al., 1987; Summons and Powell, 1987; Summons et al., 1988) and in clastic sediments from

Figure 3.24. A plot of the natural logarithms of the retention times (scan numbers) of a homologous series of methyl-30-norhopanes and the 22S and 22R epimers of homologous series of 2-methylhopanes for the Well X oil sample.



shallow marine environments (McEvoy and Giger, 1986). McEvoy and Giger (1986) pointed out the high relative abundance of 2-methylhopanes in samples of the Serpiano oil shale which was deposited in extremely reducing conditions. If these conditions were in fact those that were conducive to methylation processes on a wider scale, then the presence of 2-methyl-30-nor-17α(H)-hopanes may be the result of methylation of 30-nor-17α(H)-hopanes. The 2-methyl-30-nor-17α(H)-hopanes may therefore indicate a specific depositional environment where carbonates have been deposited in very reducing conditions. They may therefore be indicators of conditions very favourable for the formation of crude oil source rocks.

3.7 CONCLUSIONS

1. Members of the homologous series of 30-nor-17α(H)-hopanes have been shown to be widely distributed in crude oils derived from carbonate source rocks.

2. The 30-nor-17α(H)-hopanes have been shown to increase in concentration relative to the common 17α(H)-hopanes with increase in hydrocarbon maturity and with increased kerogen cracking in laboratory hydrous pyrolysis experiments suggesting that they occur in sediments in a kerogen-bound form and not just as the free hydrocarbons.

3. Using GC-MS techniques, a series of 25,30-bisnor-17α(H)-hopanes have been identified in severely biodegraded crude oil. These compounds are suggested as biomarkers for severely biodegraded crude oils originating from carbonates.

4. Seven 2-methyl-30-nor-17α(H)-hopanes have also been identified using GC-MS techniques. Retention time correlations show that these compounds are members of a homologous series with members from C_{29} to C_{35}. They appear to be associated with carbonate source rocks and may indicate extreme reducing conditions during deposition.

CHAPTER FOUR

PETROLEUM GEOCHEMISTRY OF THE NORTH SUMATRA BASIN (INDONESIA)

4.1 GEOLOGIC SETTING

4.1.1 Location

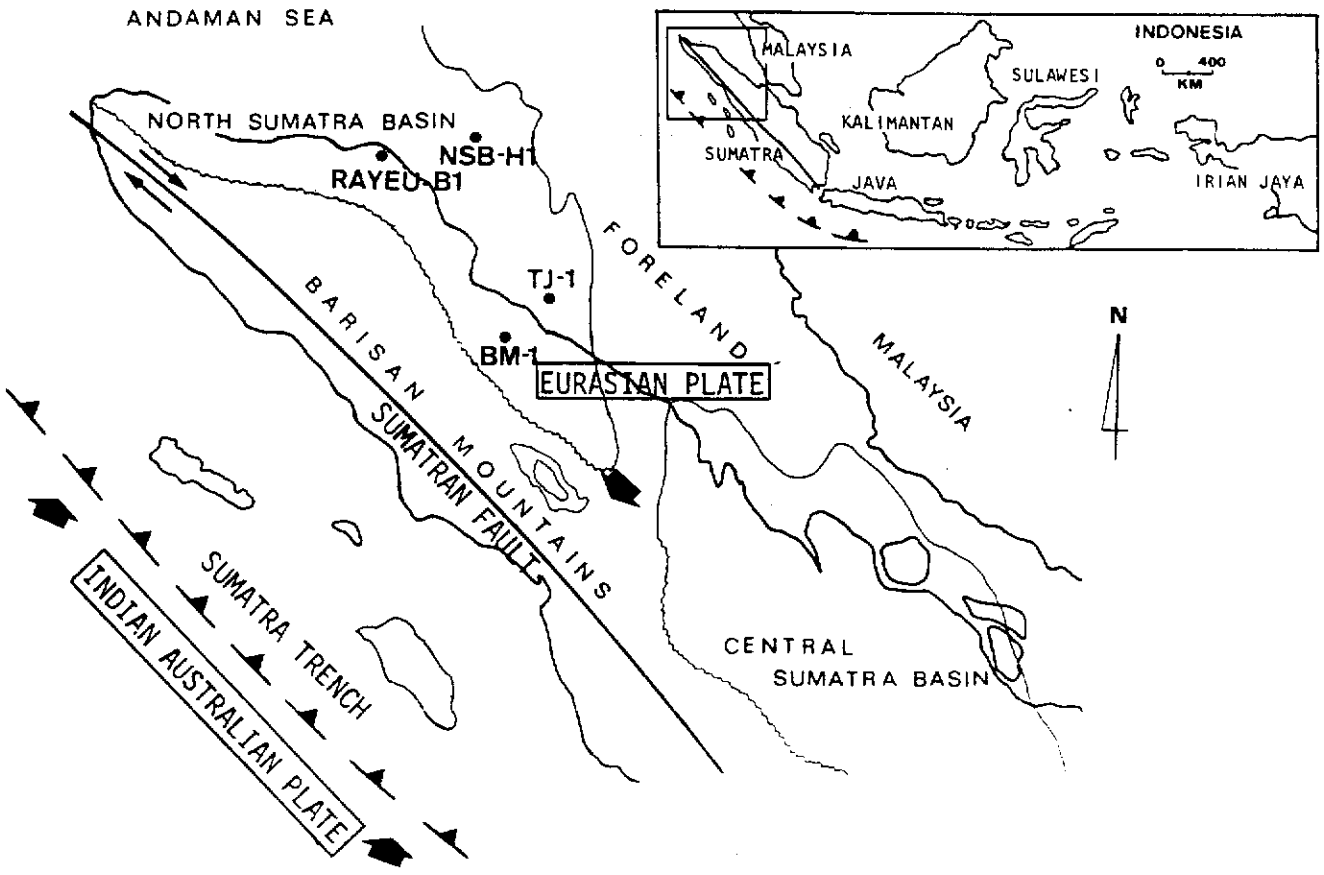
The North Sumatra Basin (Figure 4.1) is located within northern Sumatra and the surrounding continental shelf. The basin is bounded on the east by the Malaka Shelf, on the southwest by the Barisan Mountains and on the northern side by the Andaman Sea. The basin covers an area of approximately 60,000 square kilometres.

4.1.2 General Geology

Regional geology including tectonics of the basin has been reported in detail by many authors and the review in this section is based mainly upon reports by Kingston (1978), Situmeang and Davies (1986) and Sosromihardjo (1988). However, the lithostratigraphic nomenclature used in this study is based on the results from the joint survey of the North Sumatra Project by the Geological Survey of Indonesia and the Institute of Geological Sciences, United Kingdom, which have been summarised by Cameron et al. (1980).

The North Sumatra Basin is one of the foreland (back-arc or back-deep) basins of the Indonesian Island Arc system with Tertiary sediments deposited across a

Figure 4.1. Geographical location of the North Sumatra Basin. Arrows show plate motion.



pre-Tertiary meta-sedimentary complex. In general, Tertiary sedimentation appears to have begun with the development of isolated sub-basins of deposition formed in topographic lows and in down-faulted troughs. This occurred when the Indian-Australian Plate contacted the Eurasian Plate during the Upper Eocene. Initial sediments were fluviatile sands and conglomerates of the Bruksah (formerly Parapat) Formation. These coarse sediments were gradually succeeded by the dark grey to black shales of the Bampo Formation deposited in restricted marine conditions. The rapid change in depositional environment from fluviatile to marine probably resulted from block-faulting causing deeper water environments.

In Lower Miocene the subsidence became less active as reflected by the growth of reefal carbonates over the highs such as those observed within the Arun and Belumai Members. Within the lows, shallow marine calcareous shales of the Peutu Formation were deposited. During Middle Miocene the subsidence was reactivated probably due to generation of the Andaman Sea rifts. As a result the Lower Miocene reefs and shallow marine sediments were buried by the thick deep marine shale of the Baong Formation, marking the maximum transgressive cycle and the maximum subsidence of the basin during the Tertiary. However, the upper Baong Formation is characterised by sediments deposited in shallower water environments than the lower Baong, indicating the occurrence of regression

in the Upper Miocene. The initiation of this regional regression was attributed to the onset of tectonic compression which eventually led to the uplift of the Barisan Mountains.

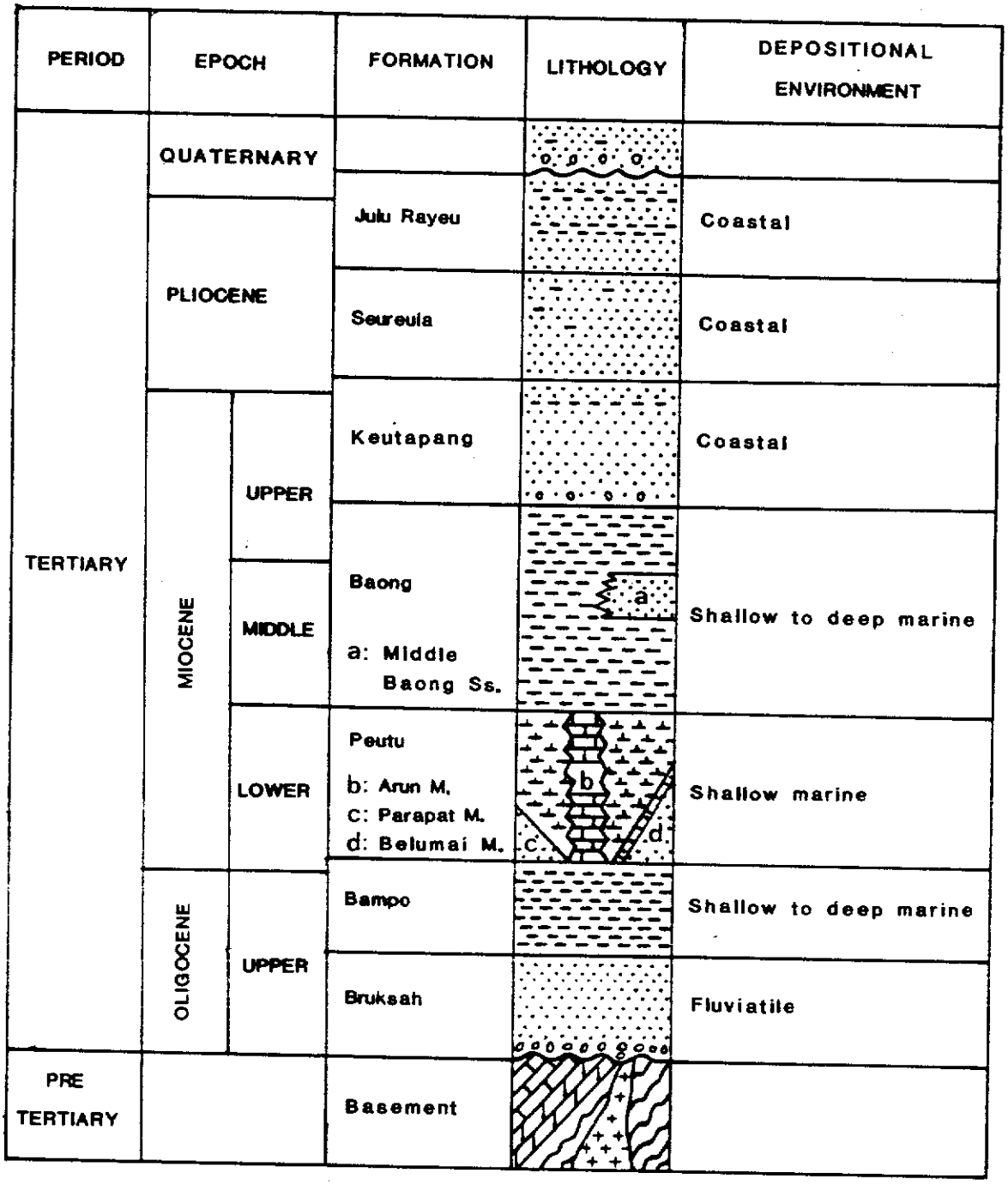
The compression became more intense during Plio-Pleistocene time resulting in regional uplift and shallower water environments as reflected by the Keutapang, Seureula and Julu Rayeu Formations. The generalised stratigraphy of the basin is shown diagrammatically in Figure 4.2, which is based on that proposed by Cameron et al. (1980).

4.1.3 Hydrocarbon Occurrences

The North Sumatra Basin is an important oil and gas province in Indonesia. Production in this basin started in 1893. Average daily production in 1985 was around 125,000 barrels of crude oil and 1.4 billion cubic feet of gas, which was about 10% of the crude oil and 40% of the gas produced by Indonesia (Soeparjadi et al., 1986).

Hydrocarbon production is mainly from two habitats namely (1) the pre-Baong which includes Lower Miocene carbonate reefs of the Arun Member (gas), sandstone and limestone reservoirs of the Belumai Member (oil) and (2) the post-Baong, that is Mio-Pliocene sandstones of the

Figure 4.2. Generalised stratigraphy of the North Sumatra.



Lower Keutapang Formation (oil) (Kingston, 1978; Mulhadiono and Sutomo, 1984). The Middle Baong Sandstone is also considered to be a good reservoir, but so far only minor accumulations of oil and gas have been observed in this unit (Mulhadiono and Sutomo, 1984; Kjellgren and Sugiharto, 1989).

4.2 SAMPLE CHARACTERISATION

4.2.1 Samples Studied

Twelve sedimentary rocks recovered as ditch cuttings from the Rayeu-B1 well and three crude oils were used in this study. The crude oils examined were obtained from the BM-1 well (on-shore) and the NSB-H1 and TJ-1 wells (off-shore) (Figure 4.1).

Table 4.1 shows general geological information for the sediments and crude oils. All of the information regarding the lithology of samples has been interpreted from the lithological log provided by Pertamina/Mobil Oil Indonesia. The sediments represent the Keutapang, Baong and Peutu Formations (Figure 4.2). Based on their lithology, the sediments were classified into three groups namely shales (samples D1-D4), carbonaceous shales (D5-D10), and calcareous shales (D11-D12). All the crude oils were trapped in the Belumai Member of the Peutu Formation.

4.2.2 Characteristics of Source Rocks

Calcium carbonate content and total organic carbon (TOC) content of the sediments are presented in Table 4.1. The calcium carbonate content of sample D11 and

Table 4.1. Geological information, Rock-Eval pyrolysis and bulk geochemical data of the sediments and crude oils.

NO	WELL NAME	DEPTH (m)	FORMATION	LITHOLOGY	$CaCO_3$ (Wt%)	TOC[a] (Wt%)	T_{max}[b] (^oC)	S_1[c] (Kg/t)	S_2[d] (Kg/t)	S_3[e] (Kg/t)	HI[f]	OI[g]	SOM[h] (ppm)	SAT (%)	ARO (%)	NSO (%)
SEDIMENTS[i]																
D1	Rayeu-B1	2530	Keutapang	Shale	9	0.51	402	0.21	0.90	0.85	176	167	390	14	7	79
D2	Rayeu-B1	2652		Shale	10	0.57	426	0.28	1.1	0.73	198	128	330	15	14	71
D3	Rayeu-B1	3070	Upper	Shale	15	1.1	429	0.32	1.3	2.0	120	159	1080	38	10	52
D4	Rayeu-B1	3183	Baong	Shale	14	1.6	430	0.39	1.4	2.1	88	128	840	27	9	64
D5	Rayeu-B1	3513		Siltstone + 10% coal	10	4.9	430	0.48	4.6	6.4	95	132	2110	56	18	26
D6	Rayeu-B1	3549		Siltstone + 10% coal	13	17	431	2.3	28	18	161	108	4830	19	15	66
D7	Rayeu-B1	3567	Lower	Siltstone + 20% coal	16	30	434	1.3	23	30	77	99	3880	21	20	59
D8	Rayeu-B1	3586	Baong	Shale + 10% coal	17	10	433	2.2	14	11	136	114	3560	25	21	54
D9	Rayeu-B1	3598		Shale + minor coal	17	4.5	436	0.47	1.9	2.7	41	60	1110	51	18	31
D10	Rayeu-B1	3647		Siltstone+ minor coal	12	8.9	435	0.72	4.6	8.0	52	90	1510	43	16	41
D11	Rayeu-B1	3872	Peutu	Shale, calcareous	44	3.0	436	0.28	1.8	1.7	60	58	1230	45	15	40
D12	Rayeu-B1	3900		Claystone, calcareous	39	3.2	438	0.40	1.7	1.7	53	55	1160	38	9	53
CRUDE OILS																
P1	BM-1	ND	Peutu[j]	Limestone[j]	-	-	-	-	-	-	-	-	-	63	13	24
P2	NSB-H1	1562	Peutu[j]	Sandstore[j]	-	-	-	-	-	-	-	-	-	80	5	15
P3	TJ-1	2550	Peutu[j]	Limestone[j]	-	-	-	-	-	-	-	-	-	77	7	16

a : Total organic carbon; b: Temperature maximum of S_2 peak; c: Quantity of free bitumens; d: Quantity of bound hydrocarbon; e : Quantity of CO_2; f: Hydrogen Index; g: Oxygen Index; h: Soluble organic matter; i: The sediments have been classified into three groups: D1-D4, shales; D5-D10, carbonaceous shales and D11-D12, calcareous shales; j: Refers to reservoir rock (Belumai Member); ND: No data

sample D12 is the highest among the sediments confirming their calcareous nature. The lower Baong sediments (D5-D10) contain the highest values of total organic carbon (TOC) because they consist of carbonaceous shales/siltstones.

Table 4.1 also shows results obtained from Rock-Eval pyrolysis. One of the pyrolysis parameters that is commonly used to indicate maturity is T_{max}. T_{max} or temperature corresponding to the maximum generation of pyrolytic hydrocarbons normally increases systematically with increasing depth and temperature of the sample. T_{max} values of the Rayeu-B1 sediments vary between 402^{o} and 438^{o}C. Tissot and Welte (1984) suggested that T_{max} at 435^{o}C was indicative of the onset of the zone of oil generation. Accordingly, at the Rayeu-B1 location, crude oil generation has probably occurred only in the deeper section of the well (sample D9 and deeper). However, the immature samples (e.g. samples D1-D4) were used in this correlation study as a model representing shale-type sediments.

Data regarding the amount of soluble organic matter (SOM) extracted from the sediments is also presented in Table 4.1. The SOM or crude oil was separated by liquid chromatography technique into saturate hydrocarbons, aromatic hydrocarbons and NSO. The saturate hydrocarbons and the aromatic hydrocarbons were then analysed using

gas chromatography and gas chromatography - mass spectrometry.

4.2.3 Gas Chromatographic (GC) Analyses

A C_{12+} Saturate Fractions

The soluble organic matter was further characterised by capillary gas-chromatographic analyses of the C_{12+} alkanes. Figure 4.3 shows the GC traces of saturate fractions for the sediments and crude oils. Broadly speaking, the shales and calcareous shales have similar geochemical properties and overall GC patterns which are characterised by having maxima in the distribution of n-alkanes at C_{17}-C_{18} and relatively low CPI values (1.0-1.2; Table 4.2). In contrast, the carbonaceous shales have GC patterns different to those of the shales and calcareous shales. The carbonaceous shales are characterised by a maximum at C_{24}-C_{27} in the n-alkanes (except sample D6 which has a bimodal distribution with maxima at C_{15} and C_{27}) and high CPI values (1.3-1.6; Table 4.2). An n-alkane distribution maximising below C_{19} with no marked odd/even predominance probably indicates marine algal input, while a distribution having a maximum at above C_{25} with a significant odd/even preference usually suggest a predominance of higher plants (Philp, 1985a).

Figure 4.3. Capillary gas chromatograms of the saturated hydrocarbon fractions from sediments and crude oils.

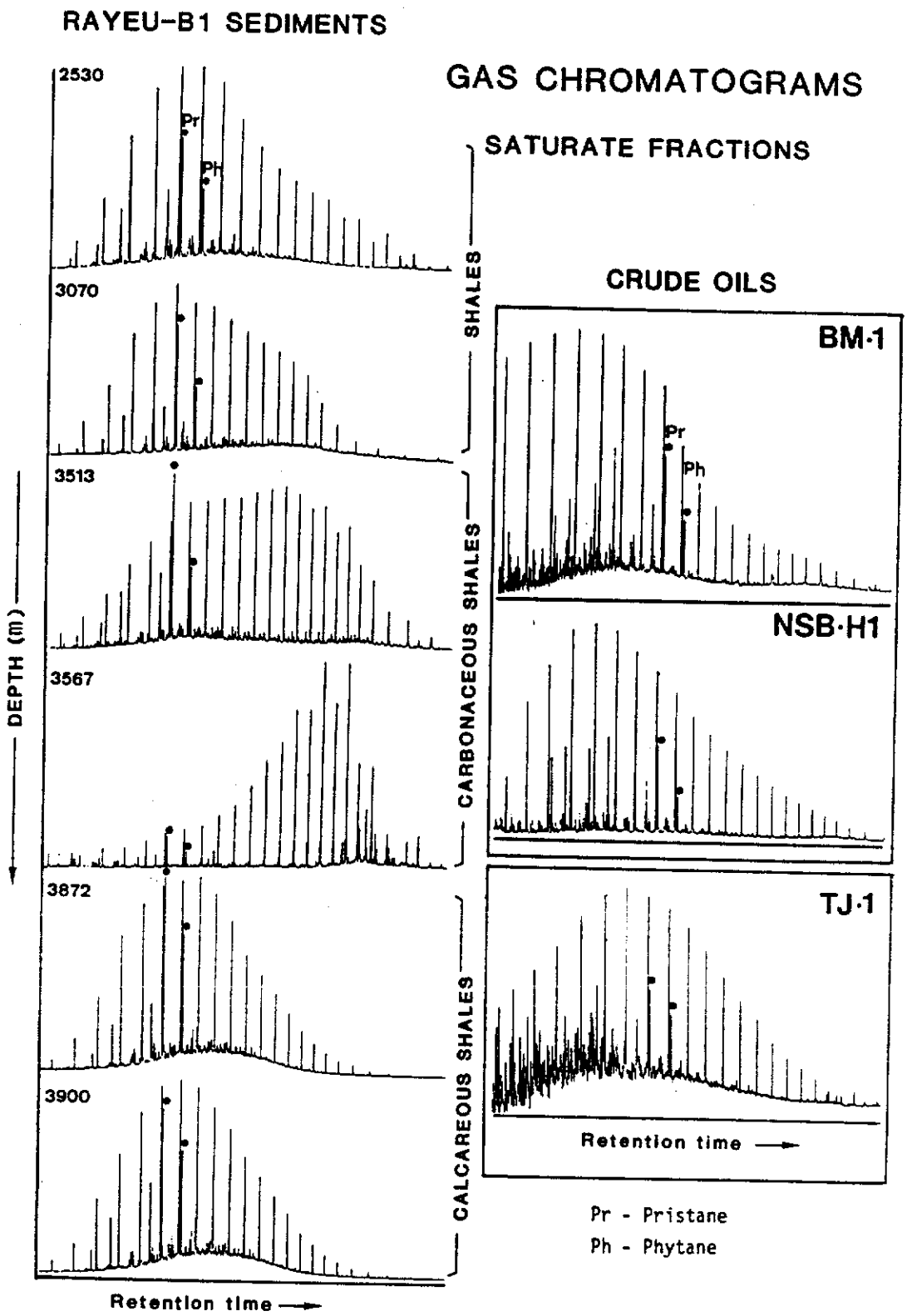


Table 4.2. Biomarker characteristics of sediments and crude oils resulting from variation in source material.

SAMPLE NO	N-ALKANES[a] MAXIMA	CPI	STERANES[a] $C_{27}\alpha\alpha R$ / $C_{29}\alpha\alpha R$	TERPANES[a] DOM TRIC	IP DOM TRIC	OLEANANE INDEX
D1	C_{18}	1.2	1.2	C_{23}	0.1	30
D2	C_{17}	1.1	1.2	C_{23}	<0.1	50
D3	C_{17}	1.0	1.1	C_{23}	0.1	50
D4	C_{18}	1.2	1.3	C_{23}	<0.1	38
D5	C_{24}	1.3	0.4	C_{20}	2.0	<5
D6	$C_{15}+C_{27}$	1.6	0.1	C_{20}	1.6	<5
D7	C_{27}	1.4	0.1	C_{20}	1.8	<5
D8	C_{25}	1.4	0.6	C_{23}	0.9	<5
D9	C_{24}	1.3	0.7	C_{23}	1.4	<5
D10	C_{25}	1.3	0.6	C_{23}	1.6	<5
D11	C_{19}	1.0	2.3	C_{23}	<0.1	10
D12	C_{18}	1.0	1.1	C_{23}	<0.1	10
P1	C_{13}	1.1	1.1	C_{23}	0.2	25
P2	C_{14}	1.0	1.3	C_{23}	0.4	120
P3	C_{16}	1.0	1.3	C_{23}	<0.1	5

a : Refer to Table 2.4.2 for methods of calculation and definition of abbreviations

The pristane/phytane values of all the sediments are within the range 1.4 to 2.2 (Table 4.3). Values of this ratio reflect the relationship between their precursors and the chemistry of the palaeoenvironment, for example low salinity (ten Haven et al., 1985, 1987) and oxic condition of sedimentation (Didyk et al., 1978) are both claimed to affect this parameter. Moreover, this ratio is also influenced by thermal maturation. Thus, the variation of this ratio probably reflects variation in depositional environment and in maturity.

The n-alkane distributions of the crude oils are similar to one another, with maxima between C_{14}-C_{16} and CPI values near unity (Table 4.2). Pristane/phytane values are also low with values near unity (Table 4.3). Comparing such distributions with those of the sediments, it is apparent that the n-alkane distributions of the crude oils have patterns which are similar to those of the shales and the calcareous shales.

B Aromatic Fraction

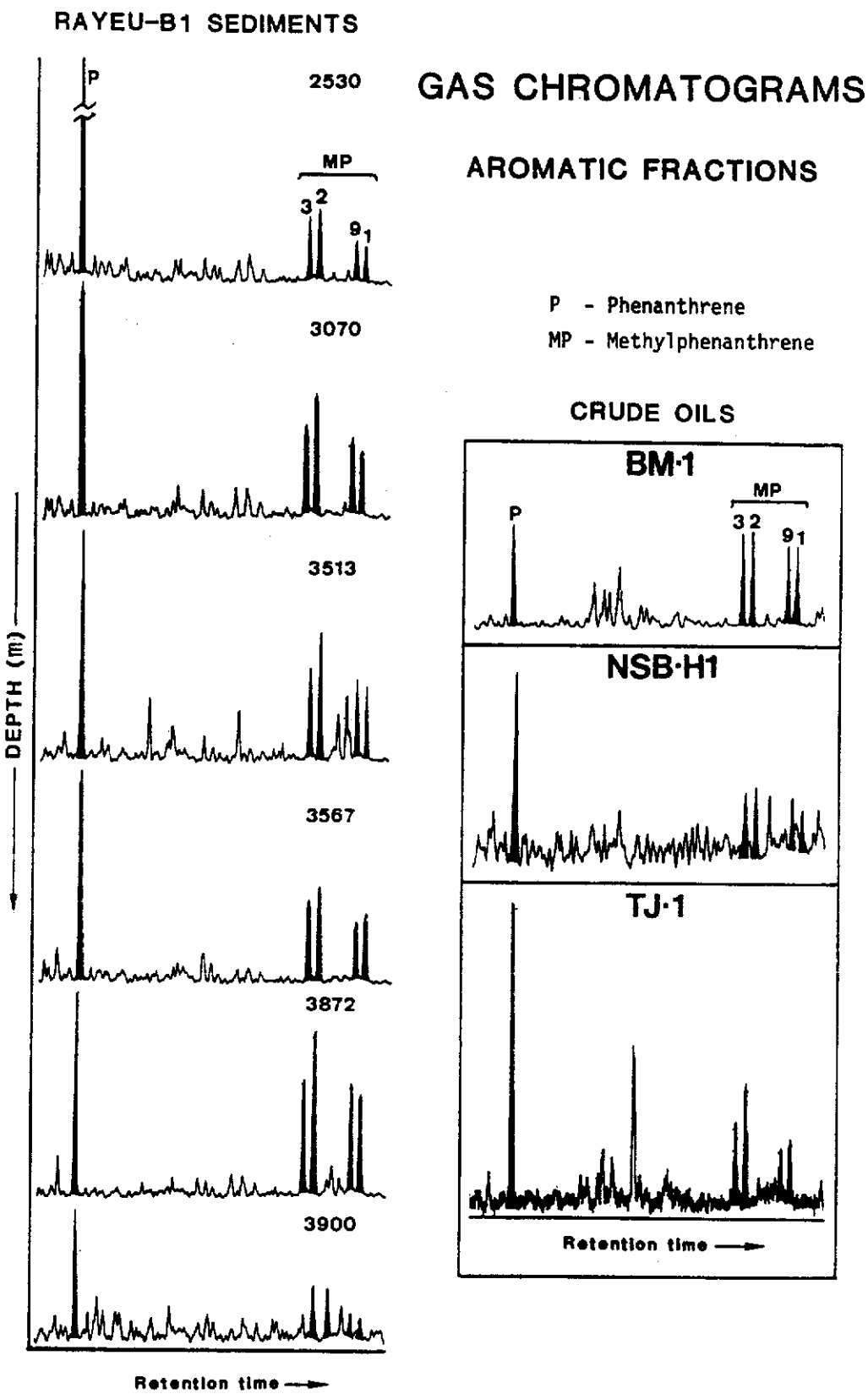
High resolution gas chromatography was carried out to examine the naphthalene and phenanthrene components. Figure 4.4 shows the distribution of phenanthrene and methylphenanthrenes in the sediments. These phenanthrenes can be used to estimate maturity in terms of vitrinite

Table 4.3. Biomarker characteristics of sediments and crude oils resulting from differences in depositional environment.

SAMPLE NO	Pr/Ph	STERANES[a] $\frac{C_{21}+C_{22}}{C_{29}}$	STERANES[a] DIASTERANE / STERANE	HOPANES[a] 30-NORHOPANE INDEX
D1	1.8	0.4	0.6	<5
D2	2.0	0.6	0.4	<5
D3	1.4	0.5	0.4	<5
D4	1.8	0.6	0.3	<5
D5	1.7	0.4	0.2	<5
D6	2.0	0.1	<0.1	<5
D7	2.0	0.1	<0.1	<5
D8	2.0	0.6	0.4	<5
D9	2.2	0.6	0.4	<5
D10	2.1	0.5	0.8	<5
D11	1.6	1.5	0.5	20
D12	1.7	1.7	0.6	25
P1	1.1	0.5	1.1	<5
P2	1.1	1.4	0.8	<5
P3	1.3	0.8	0.4	17

a : Refer to Section 2.4.2 for methods of calculation and definition of abbreviations

Figure 4.4. Partial gas chromatograms of aromatic fractions showing the distribution of phenanthrene and methylphenanthrenes.



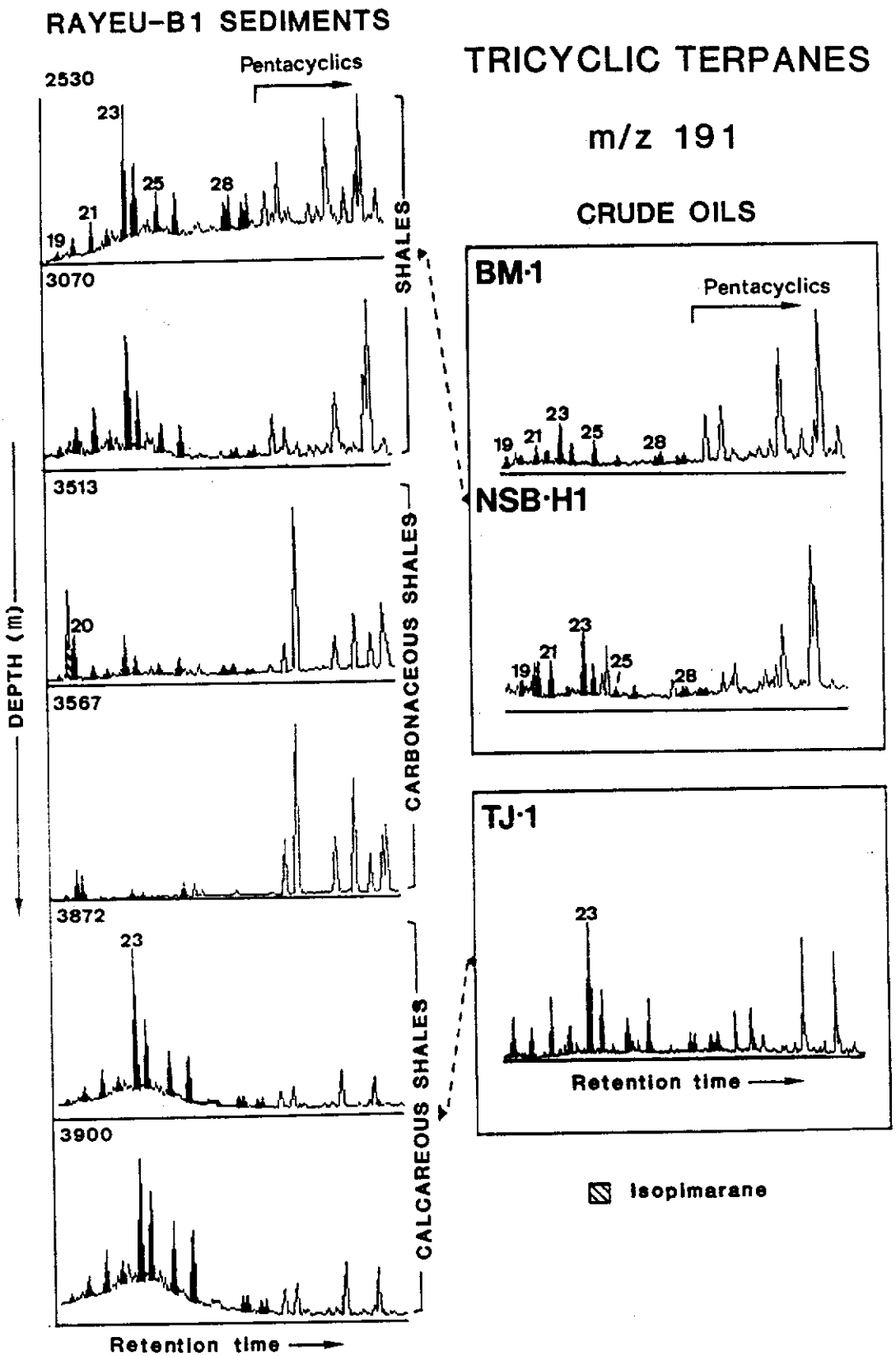
reflectance (Radke and Welte, 1983). More recently, dimethylphenanthrenes have also been used in maturity assessments (e.g. Radke, 1988). Table 4.4 shows the maturity data obtained from aromatic hydrocarbon, Rock-Eval and biomarkers. The aromatic data is variable with depth of the sediments. The apparent high maturity of the shallowest sample from 2530m may be due to the presence of older and more mature reworked organic matter making a significant contribution to the aromatic hydrocarbons. In the case of the Rayeu-B1 sediments, unfortunately, the concentrations of dimethyl-phenanthrenes were very low so that no reliable data regarding these compounds was obtained from either GC or GC-MS analyses.

4.2.4 GC-MS Analyses

A Tricyclic Terpanes

The tricyclic terpane distribution was determined by examining the m/z 191 mass chromatograms. Figure 4.5 illustrates the tricyclic terpane distributions of the sediments and crude oils. In evaluating such distributions, the tricyclics apparently fall into two groups. One group is characterised by a pattern in which the peak representing the C_{23} tricyclic terpane (see also DOM TRIC, Table 4.2) is the largest peak and the

Figure 4.5. Partial m/z 191 mass chromatograms showing the distribution of tricyclic terpanes in the sediments and crude oils. GC conditions were Program 1 (Section 2.3.4).

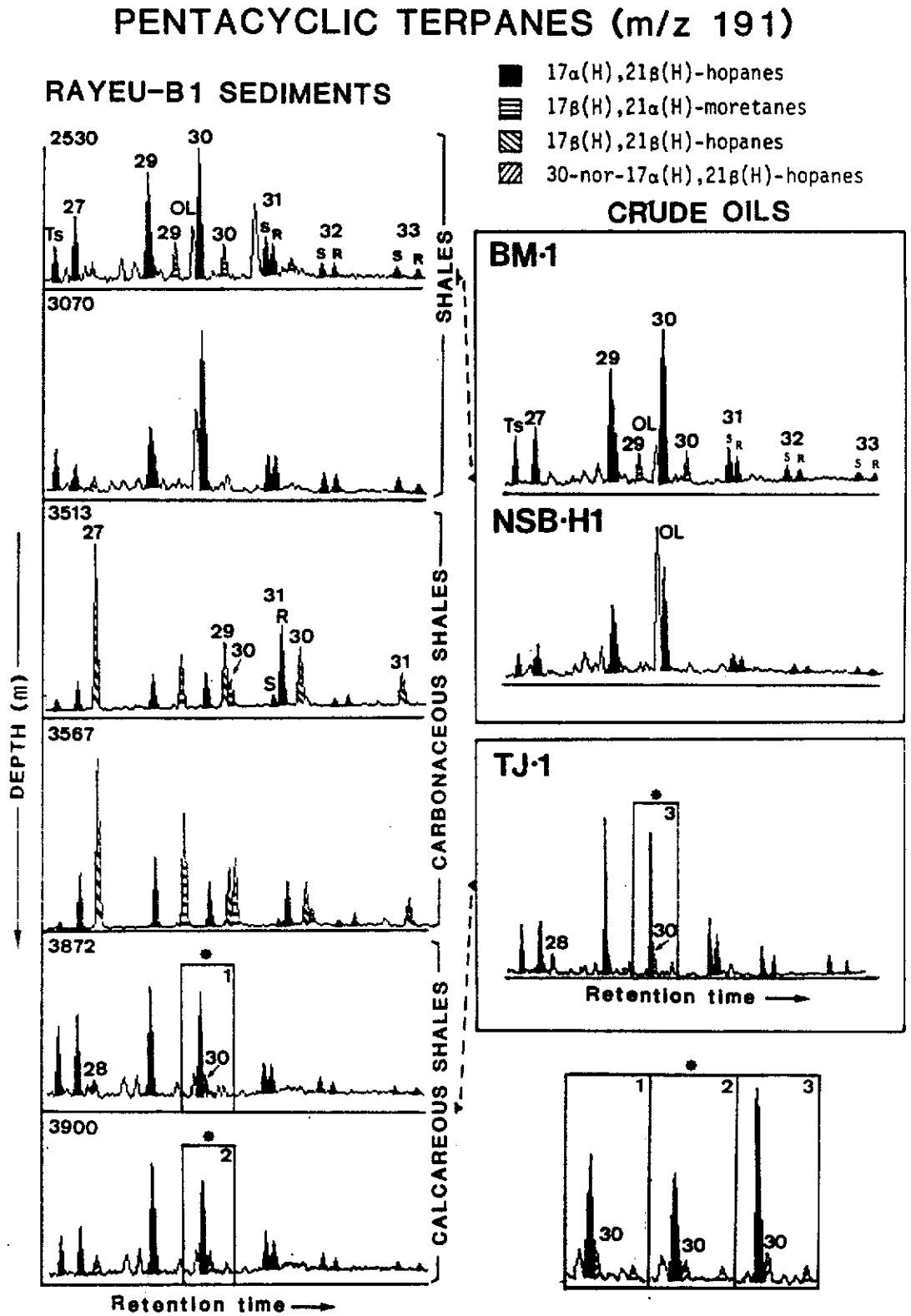


other in which the peak representing the C_{20} tricyclic terpane is the largest. The group which has the more abundant C_{23} is typical of most of the sediments except the three carbonaceous shales (D5-D7). All the crude oils belong to the group which has the abundant C_{23} tricyclic terpane. The predominance of the C_{20} member of the tricyclic terpanes, as well as the abundance of isopimarane (see also IP/DOM TRIC, Table 4.2) suggest that the organic matter in the carbonaceous shales was derived in large part from terrestrial plants, particularly gymnosperms (Simoneit, 1977; Noble, 1986 and references therein). The presence of some isopimarane in the NSB-H1 sample also suggests a significant land plant contributions to the source of this crude oil.

B Pentacyclic Terpanes

The pentacyclic terpane distributions in the sediments and oils were also examined from m/z 191 mass chromatograms. Representative m/z 191 mass chromatograms for selected sediments and crude oils are presented in Figure 4.6. 18α(H)-Oleanane is present significantly in the shales (see also Table 4.2). The oleanane abundance in shales is probably related to the distance of the sample location from the basin edge and the source of angiosperm-derived debris. In the carbonaceous shales and the calcareous shales, oleanane is present in only

Figure 4.6. Partial m/z 191 mass chromatograms showing the distribution of pentacyclic terpanes in the sediments and crude oils. GC conditions were Program 1 (Section 2.3.4).



trace amount, as shown by the values of the Oleanane Index of 10 or less, indicating no significant input (Table 4.2). Crude oils BM-1 and NSB-H1 contain 18α(H)-oleanane. The high concentration of 18α(H)-oleanane in the NSB-H1 oil is also consistent with the presence of isopimarane in this sample.

The hopane-type triterpanes in the shales and calcareous shales belong mostly to the 17α(H),21β(H)-hopane series; however, there are substantial differences. In the shales the C_{30} 17α(H)-hopane is slightly more abundant than the C_{29} member, whereas in the calcareous shales the C_{29} 17α(H)-hopane is slightly more abundant than the C_{30} homologue. Furthermore, the calcareous shales are also characterised by the presence of the 30-nor-17α(H)-hopanes (Figure 4.6; see also 30-Norhopane Index in Table 4.3). Such compounds have been demonstrated in Chapter 3 to occur widely in carbonate-rich sediments or crude oils from carbonate sources.

In contrast, the pentacyclic terpane distributions in the carbonaceous shales are dominated by 17β(H), 21β(H)-hopanes and 17β(H),21α(H)-moretanes. The ββ hopanes represent the predominantly biologically synthesised configuration and are the most unstable. In comparing the αβ and the βα hopanes, the βα hopanes (moretanes) are less stable. Thus, the

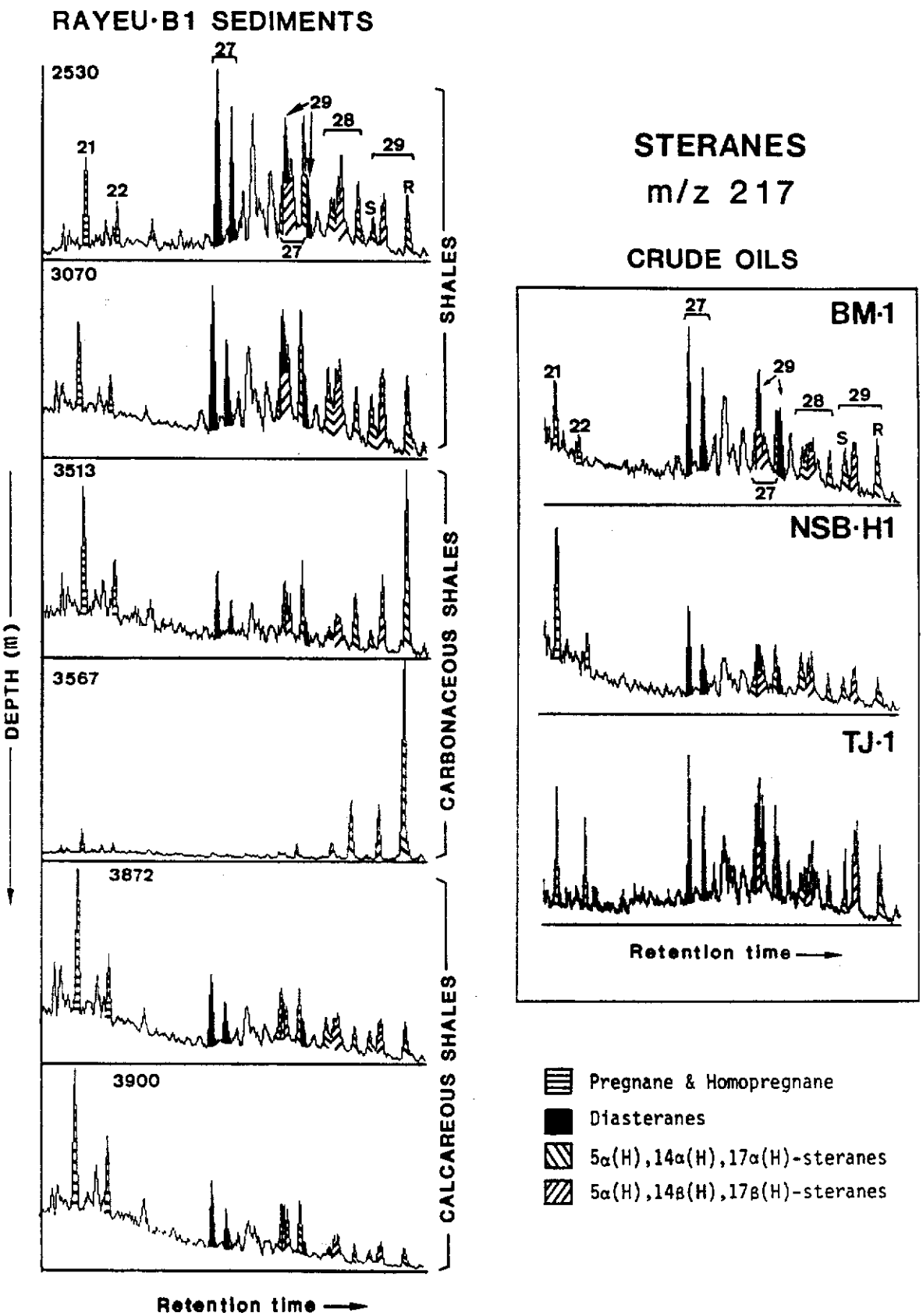
relative abundance of $\beta\beta$ hopanes and $\beta\alpha$ moretanes in the carbonaceous shales, and the fact that the 22R stereoisomers are more abundant than the 22S stereoisomers for the extended hopanes, constitute strong biomarker signatures for immaturity.

On the basis of the distribution of the hopane-type triterpanes, the crude oils can be classified into two groups. Two crude oils (BM-1 and NSB-H1) are characterised by predominance of the C_{30} member in their $\alpha\beta$ hopane distribution and the absence of the 30-nor-17α(H)-hopane compounds. One crude oil (TJ-1) is characterised by predominance of the C_{29} homologue in its $\alpha\beta$ hopanes and the presence of the 30-nor-17α(H)-hopanes. The pentacyclic terpane distribution of the TJ-1 oil appears to be relatively similar to those of the calcareous shales, whereas the distributions in the BM-1 and NSB-H1 oils resemble those of the shales.

C Steranes

Figure 4.7 shows m/z 217 mass chromatograms representative of sterane distributions in the sediments. In general, the sterane distributions can be classified into three groups which correlate well with the grouping obtained using sample lithologies. The shales are

Figure 4.7. Partial m/z 217 mass chromatograms showing the distribution of steranes in the sediments and crude oils. GC conditions were Program 1 (Section 2.3.4).



characterised by relatively low amounts of C_{21} and C_{22} steranes and higher proportions of C_{27} $\alpha\alpha$ steranes relative to C_{29} $\alpha\alpha$ steranes (see also Table 4.2 and Table 4.3). The carbonaceous shales are characterised by a low to very low abundance of C_{21} and C_{22} steranes and lower proportions of C_{27} steranes relative to C_{29} $\alpha\alpha$ steranes. In contrast, the calcareous shales are characterised by relatively high abundances of C_{21} and C_{22} steranes and higher proportions of C_{27} $\alpha\alpha$ steranes relative to C_{29} $\alpha\alpha$ steranes (Table 4.2 and Table 4.3). Relatively high abundances of C_{21} and C_{22} steranes have been observed in sediments and crude oils associated with hypersaline and carbonate environments (ten Haven et al., 1985; Fu et al., 1986; Price et al., 1987). The precursors of such compounds are not yet established (ten Haven et al., 1985), but they might be derived by the removal of the side chain from the normal sterane structure by certain bacteria (Moldowan et al., 1985). The C_{21} and C_{22} sterane distributions of the calcareous shales are consistent with those reported for carbonates (Price et al., 1987).

The C_{27}/C_{29} sterane ratios shown in Table 4.2 shows a clear difference between the carbonaceous shales and the other groups. Although care must be excercised when inferring organic input from sterane carbon number distributions (Volkman, 1986), the high relative

abundance of C_{29} steranes is consistent with an input of higher plant material to the sediments (Huang and Meinschein, 1976, 1979). The greater abundance of C_{27} compared with the C_{29} steranes is often associated with an algal input (Huang and Meinschein, 1976,1979).

Information about depositional environment can be obtained from the relative abundance of the C_{29} diasteranes and C_{29} steranes. Diasteranes occur in most sediments and crude oils, but their abundances are relatively low in samples having anoxic or alkaline depositional environments (McKirdy et al., 1984; Fu et al., 1986; Price et al., 1987). Such features have been suggested to result from the absence of acidic clays to catalyse steroid rearrangement process (Rubinstein et al., 1975). Most of the North Sumatra Basin sediments contain relatively high abundances of C_{29} diasteranes suggesting low alkalinity or high oxicity of their depositional environments. Three members of the carbonaceous shales group (D5-D7), however, show very low abundances of diasteranes which may indicate an alkaline and/or anoxic depositional environment (Table 4.3).

The sterane distribution patterns of the crude oils are relatively uniform except for differences in the abundances of C_{21} and C_{22} steranes (Table 4.3). The BM-1 oil contains relatively low abundances of C_{21} and C_{22} steranes, while the NSB-H1 and TJ-1 oils contain

higher abundances of these compounds than the BM-1 oil (Figure 4.7). Other sterane distribution features of the crude oils are similar to those of the shales and calcareous shales groups.

4.2.5 Thermal Maturity of the Source Rocks and Crude Oils

Table 4.4 shows maturity data for sediments and crude oils. T_{max} values of the Rayeu-B1 sediments vary between 402 and 438°C. If T_{max} at 435°C is considered indicative of the onset of oil generation (Tissot and Welte, 1984), the values of T_{max} suggest that crude oil generation would have occurred only in the deeper section of the well (from sample D9 and deeper).

A maturity parameter which is widely used is the proportion of the two diastereomeric forms (20S and 20R) of C_{29} $\alpha\alpha$ steranes. The sterane maturity data for the sediments and crude oils is presented in Table 4.4. In the Rayeu-B1 sequence the 20S/20R values tend to cluster into two groups: one associated with the shales and calcareous shales, and the other associated with the carbonaceous shales. This phenomenon is probably due to the combined effects of the mineral matrices and maturity on the 20S/20R values, a conclusion which is in good agreement with that of Strachan et al. (1989). It appears that the processes by which the 20S/20R ratio changes are

Table 4.4. Maturity data for the sediments and crude oils.

NO	Tmax (°C)	STERANES[a] $C_{29}\alpha\alpha$ 20S/20R	STERANES[a] $\frac{C_{29}\beta\beta}{\beta\beta+\alpha\alpha}$	HOPANES[a] Tm/Ts	HOPANES[a] C_{30} M/H	AROMATICS[a] MPI-1	AROMATICS[a] $\%R_c$
D1	402	0.4	0.4	2.0	0.3	0.7	0.8
D2	426	0.4	0.3	1.7	0.2	0.7	0.8
D3	429	0.6	0.4	1.2	0.1	0.7	0.8
D4	430	0.5	0.4	1.4	0.2	0.8	0.9
D5	430	0.2	0.3	3.6	0.7	0.8	0.9
D6	431	0.1	0.2	31	1.6	0.8	0.9
D7	434	0.1	0.2	32	2.1	0.9	0.9
D8	433	0.2	0.4	2.3	0.5	0.9	0.9
D9	436	0.2	0.4	1.8	0.5	0.8	0.9
D10	435	0.3	0.5	1.8	0.6	0.8	0.9
D11	436	0.6	0.5	1.2	0.1	0.9	0.9
D12	438	0.8	0.5	0.9	0.1	0.9	1.0
P1	-	0.9	0.5	1.2	0.2	1.2	1.1
P2	-	1.1	0.6	1.4	0.1	1.0	1.0
P3	-	0.9	0.6	1.0	0.1	0.8	0.9

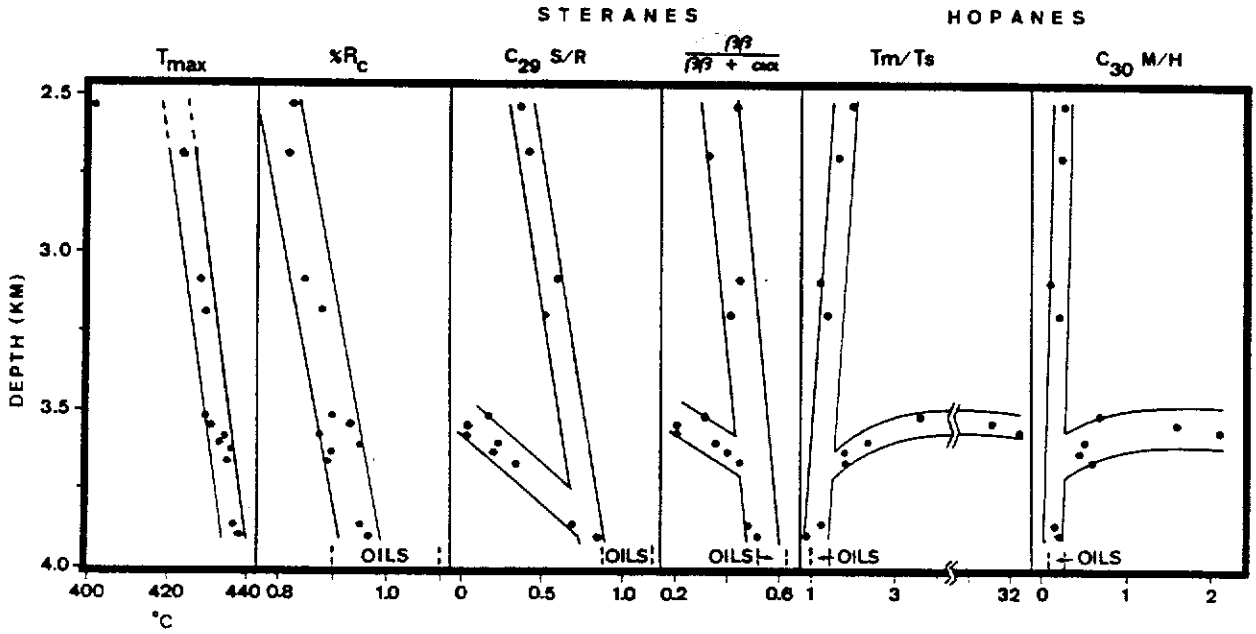
a : Refer to Section 2.4.2 for methods of calculation and definition of abbreviations

less favoured in a coaly (carbonaceous) matrix than in a shaly matrix.

Interestingly, other maturity parameters such as the ratio of C_{29} $\beta\beta/(\beta\beta+\alpha\alpha)$ steranes, Tm/Ts and the ratio of moretane to hopane behave similarly to the 20S/20R ratio (Table 4.4; Figure 4.8). Thus, in considering isomeric ratios of biomarkers as maturity indicators, the data obtained in this study suggests that the apparent isomerisation rates in steranes and hopanes are influenced by the rock matrix.

Maturity assessment on the basis of the sterane and hopane parameters reveals that sediment D12 and probably sediment D11 (both belong to the Peutu Formation) are marginally mature. This is supported by the fact that the values of their maturity parameters are close to those of the crude oils (Table 4.4; Figure 4.8). The biomarker ratios of the crude oils themselves indicate marginal (BM-1 and TJ-1) to moderate maturity (NSB-H1). However, other sediments such as the carbonaceous shales of the lower Baong Formation may also have experienced high temperature, but since they contain carbonaceous (coaly) material changes in their biomarker ratios are relatively retarded. These results show that maturity assessments using these biomarker parameters should be used with extreme caution when the mineral matrix is variable.

Figure 4.8. Plots of the maturity parameters against depth for the Rayeu-B1 sediments. For comparison, the approximate ratios of the crude oils are indicated within the dashed vertical bands.



Differences in the isomer ratios caused by mineral matrix effects appear to have less effect on the aromatic parameters as shown by relatively normal behaviour of the $\%R_c$ (Table 4.4; Figure 4.4 and Figure 4.8). However, Radke (1987) has pointed out that maturity values obtained from aromatic fractions tend to be different for different types of oils. For the crude oils originating from a mixture of types III and II kerogens, the onset of oil generation occurs at R_c = 0.9 (Radke, 1987). Accordingly, by this criterion most of the sediments would be judged as marginally mature.

An alternate explanation for the apparent high maturity of the shallow shale samples and the lower maturity of the underlying coals involves reworking of older, more mature, organic matter into the shales. In cases where a shale is formed from redeposition of eroded sediments containing mature organic matter, and where there was little incorporation of new organic matter produced in the water column; then organic extracts of such rocks will reflect the old redeposited organic matter. Clearly, if such a shale had been deposited over a coal measure, then the situation described here could arise.

Some evidence supporting the reworking hypothesis could be obtained by examining TOC and composition of the SOM. A shale whose organic composition is dominated by reworked mature coals should contain a very high proportion of aromatic hydrocarbons relative to saturated hydrocarbons.

4.4 CORRELATION BETWEEN SOURCE ROCKS AND CRUDE OILS

Comparison of the geochemical properties which include GC traces of saturate fractions, the distributions of tricyclic terpanes, pentacyclic terpanes and steranes are presented in Figure 4.3 and Figures 4.5-4.7. The correlation parameter that proved to be the most useful in indicating that the TJ-1 oil was most probably sourced from the Peutu calcareous shales is the pentacyclic terpane distribution (Figure 4.6). It is apparent that the Peutu sediments (3872m and 3900m depth) have pentacyclic terpane patterns comparable to that of the TJ-1 oil. Moreover, the Peutu sediments as well as the TJ-1 oil contain the 30-nor-17α(H)-hopanes which are a characteristic feature of carbonate samples. Other geochemical properties such as the distribution of n-alkanes (Figure 4.3) and the distribution of tricyclic terpanes (Figure 4.5) of the Peutu sediments are also well correlated to those of the TJ-1 oil.

The geochemical properties of the shales which belong to the Keutapang and upper Baong Formations are similar in most respects to those of the BM-1 and NSB-H1 oils, except for their thermal maturity properties such as ratios of 20S/20R and $\beta\beta/(\beta\beta+\alpha\alpha)$ C_{29} steranes and the ratio of moretane/hopane (Table 4.4). All the maturity indicators suggest that the shales from Rayeu-B1

location are immature, and thus they are not likely to be the source of the BM-1 and NSB-H1 oils. These results suggest that crude oil of the BM-1 and NSB-H1 types may have been generated from the Keutapang and upper Baong Formations at other locations in the basin where these shales are more mature. Alternatively, these crude oils may have been derived from source rocks with similar source and depositional characteristics to those of the Keutapang and upper Baong shales but which have reached higher maturities. Possible source candidates could be the Peutu shale or deeper formations such as the Bampo Formation which comprises mainly shales deposited in shallow to deep marine conditions. However, no samples from these formations were available for the present study.

A summary of characteristic features used to classify the crude oils and to correlate them with the source rocks is given in Table 4.5.

Table 4.5. Characteristic features used to classify the crude oils and to correlate them with the source rocks.

PARAMETERS	CRUDE OILS		SOURCE ROCK TYPES		
	P1-P2	P3	SHALES D1-D4	CARBONACEOUS SHALES D5-D10	CALC. SHALES D11-D12
30-NORHOPANES	-	++	-	-	++
ISOPIMARANE	+	-	+	+++	-
DOM. HOPANES	30$\alpha\beta$	29$\alpha\beta$	30$\alpha\beta$	27$\beta\beta$	29$\alpha\beta$
SUBDOM. HOPANES	29$\alpha\beta$	30$\alpha\beta$	29$\alpha\beta$	22R-31$\alpha\beta$ or 29$\beta\alpha$	30$\alpha\beta$
OLEANANE	+++	+	+++	-	+

$\alpha\beta$: 17α(H),21β(H)-hopane; number denotes carbon number
$\beta\beta$: 17β(H),21β(H)-hopane
$\beta\alpha$: 17β(H),21α(H)-hopane
\- : Not detected
\+ : Low
++ : Medium
+++ : Abundant

4.5 CONCLUSIONS

The use of specific biological markers, that is the 30-nor-17α(H)-hopanes, in conjunction with other biological markers (n-alkanes, steranes, tricyclic and pentacyclic terpanes) was effective in identifying the source facies of crude oils. The TJ-1 crude oil is most likely to have been derived from a carbonate-rich source rock with similar characteristics to the sediments of the Peutu Formation at Rayeu-B1. The maturity of the Peutu Formation also appears to be sufficient at this location to have generated the TJ-1 crude oil. The BM-1 and the NSB-H1 crude oils should have been expelled from formation(s) with similar source and depositional characteristics to the shales of the upper Baong and Keutapang Formations at Rayeu-B1 but with higher maturity than is observed at this location.

Isomeric ratios of biomarkers have been shown in this study to be severely affected by differences in source and mineral matrices, thus making their applications in maturity assessment unreliable. The use of the Rock-Eval T_{max} and the aromatic hydrocarbons as maturity parameters appears to be more reliable in cases where there is marked variation in the organic matter type and rock matrices such as the coaly (carbonaceous) and shaly rock types encountered in this study.

REFERENCES

Albaiges J. and Torradas J.M. (1974) Significance of the even carbon n-paraffin preference of a Spanish crude oil. Nature 250, 567-568.

Alexander R., Cumbers M. and Kagi R.I. (1984a) Geochemistry of some Canning Basin crude oils. In The Canning Basin, W.A.: Proc. Geol. Soc. Aust./Pet. Expl. Soc. Aust. Symposium, Perth (ed. P.G. Purcell), pp. 353-358.

Alexander R., Kagi R. and Sheppard P. (1984b) 1,8-Dimethylnaphthalene as an indicator of petroleum maturity. Nature 308, 442-443.

Alexander R., Kagi R.I., Noble R. and Volkman J.K. (1984c) Identification of some bicyclic alkanes in petroleum. Org. Geochem. 6, 63-70.

Alexander R., Kagi R.I., Rowland S.J., Sheppard P.N. and Chirila T.V. (1985) The effects of thermal maturity on distributions of dimethylnaphthalenes and trimethyl- naphthalenes in some ancient sediments and petroleums. Geochim. Cosmochim. Acta 49, 385-395.

Alexander R., Strachan M.G., Kagi R.I. and van Bronswijk W. (1986) Heating rate effects on aromatic maturity indicators. In Advances in Organic

Geochemistry, 1985 (eds. D. Leythaeuser and J. Rullkotter), pp. 997-1003. Pergamon Journals, Oxford.

Alexander R., Kagi R.I., Toh E. and van Bronswijk W. (1988) The use of aromatic hydrocarbons for assessment of thermal histories of sediments. In The North West Shelf, Australia: Proc. Pet. Expl. Soc., Aust. Symposium, Perth (eds. P.G. and R.R. Purcell), pp. 559- 562.

Allan J., Bjoroy M. and Douglas A.G. (1977) Variation in the content and distribution of high molecular weight hydrocarbons in a series of coal macerals of different ranks. In Advances in Organic Geochamistry, 1975 (eds. R. Campos and J. Goni), pp. 633-654. Enadimsa, Madrid.

Aquino Neto F.R., Trendel J.M., Restle A., Connan J. and Albrecht P.A. (1983) Occurrence and formation of tricyclic and tetracyclic terpanes in sediments and petroleums. In Advances in Organic Geochemistry, 1981 (eds. M. Bjoroy et al.), pp. 659-667. John Wiley & Sons, Chichester.

Bailey N.J.L., Krouse H.R., Evans C.R. and Rogers M.A. (1973) Alteration of crude oils by water and bacteria - Evidence from geochemical and isotope

studies. Bull. AAPG. 57, 1276-1290.

Brassell S.C., Comet P.A., Eglinton G., Isaacson P.J., McEvoy J., Maxwell J.R., Thomson I.D., Tibbets P.J.C. and Volkman J.K. (1980) The origin and fate of lipids in the Japan Trench. In Advances in Organic Geochemistry, 1979 (eds. A.G. Douglas and J.R. Maxwell), pp. 375-392. Pergamon Press, Oxford.

Bray E.E. and Evans E.D. (1961) Distribution of n-paraffins as a clue to recognition of source beds. Geochim. Cosmochim. Acta 22, 2-15.

Brooks J.D., Gould K. and Smith J.W. (1969) Isoprenoid hydrocarbons in coal and petroleum. Nature 222, 257-259.

Cameron N.R., Clarke M.C.G., Aldiss D.T., Aspden J.A. and Djunuddin A. (1980) The geological evolution of Northern Sumatra. Proc. Indonesian Petr. Assoc. 9th Ann. Convention, pp. 149-187.

Connan J. (1984) Biodegradation of crude oils in reservoirs. In Advances in Petroleum Geochemistry I (eds. J. Brooks and D. Welte), pp. 299-335. Academic Press, London.

Connan J. and Dessort D. (1987) Novel family of

hexacyclic hopanoid alkanes (C_{32}-C_{35}) occurring in sediments and oils from anoxic palaeoenvironments. Org. Geochem. 11, 103-113.

Connan J., Bouroullec J., Dessort D. and Albrecht P. (1986) The microbial input in carbonate-anhydrite facies of a sabkha palaeoenvironment from Guatemala: A molecular approach. In Advances in Organic Geochemistry, 1985 (eds. D. Leythaeuser and J. Rullkotter), pp. 29-50. Pergamon Journals, Oxford.

Dastillung M., Albrecht P. and Ourisson G. (1980) Aliphatic and polycyclic alcohols in sediments: Hydroxylated derivatives of hopane and of 3-methylhopane. J. Chem. Research, 168-169.

Dembicki H., Meinschein W.G. and Hattin D.E. (1976) Possible ecological and environmental significance of the predominance of even carbon number C_{20}-C_{30} n-alkanes. Geochim. Cosmochim. Acta 40, 203-208.

Didyk B.M., Simoneit B.R.T., Brassell S.C. and Eglinton G. (1978) Organic geochemical indicators of palaeoenvironmental conditions of sedimentation. Nature 272, 216-222.

van Dorsselaer A., Ensminger A., Spyckerelle C., Dastillung M., Seiskind O., Arpino P., Albrecht P., Ourisson P., Brooks P.W., Gaskell S.J., Kimble B.J., Philp R.P., Maxwell J.R. and Eglinton G. (1974) Degraded and extended hopane derivatives (C_{27} to C_{35}) as ubiquitous geochemical markers. Tetrahedron Lett. 14, 1349-1352.

Eglinton T.I. and Douglas A.G. (1988) Quantitative study of biomarker hydrocarbons released from kerogens during hydrous pyrolysis. Energy and Fuels 2, 81-88.

Ekweozor C.M. and Strausz O.P. (1983) Tricyclic terpanes in the Athabasca oil sands: Their geochemistry. In Advances in Organic Geochemistry, 1981 (eds. M. Bjoroy et al.), pp. 746-766. John Wiley & Sons, Chichester.

Ekweozor C.M. and Udo O.T. (1988) The oleananes: Origin, maturation and limits of occurrence in Southern Nigeria sedimentary basins. In Advances in Organic Geochemistry, 1987 (eds. L. Mattavelli and L. Novelli), pp. 131-140. Pergamon Journals, Oxford.

Ekweozor C.M., Okogun J.I., Ekong D.E.U. and Maxwell J.R. (1979a) Preliminary organic geochemical studies of samples from the Niger Delta, Nigeria - II.

Ensminger A., Joly G. and Albrecht P. (1978) Rearranged steranes in sediments and crude oils. Tetrahedron Lett. 18, 1575-1578.

Espitalie J., Laporte J.L., Madec M., Marquis F., Leplat P., Paulet J. and Boutefeu A. (1977) Methode rapide de caracterisation des roches meres de leur potentiel petrolier et de leur degre d'evolution. Rev. Inst. Fr. Petr. 32, 23-42.

Fan P. and Zhang B. (1988) Biomarker characteristics of nonmarine oils in China. In Advances in Organic Geochemistry, 1987 (eds. L. Mattavelli and L. Novelli), pp. 627-632. Pergamon Journals, Oxford.

Fowler M.G. and Douglas A.G. (1987) Saturated hydrocarbon biomarkers in oils of Late Precambrian age from Eastern Siberia. Org. Geochem. 11, 201-203.

Fu J., Sheng G., Peng P., Brasell S.C., Eglinton G. and Jiang J. (1986) Peculiarities of salt lake sediments as potential source rocks in China. In Advances in Organic Geochemistry, 1985 (eds. D. Leythaeuser and J. Rullkotter), pp. 119-126. Pergamon Journals, Oxford.

Gallegos E.J. and Moldowan J.M. (1989) The effect of

injection hold time on GC resolution and the effect of collision gas on mass spectra in geochemical 'biomarker' research. Preprints 34, 159-169.

Gassemann G. (1981) Chromatographic separation of diastereomeric isoprenoids for the identification of fossil fuel contamination. Mar. Pollut. Bull. 12, 78-84.

Goodwin N.S., Park P.J.D. and Rawlinson T. (1983) Crude oil biodegradation. In Advances in Organic Geochemistry, 1981 (eds. M. Bjoroy et al.), pp. 650-658. John Wiley & Sons, Chichester.

Goosens H., de Leeuw J.W., Schenck P.A. and Brassell S.C. (1984) Tocopherols as likely precursors of pristane in ancient sediments and crude oils. Nature 312, 440-442.

Grantham P.J. (1986) Sterane isomerisation and moretane/ hopane ratios in crude oils derived from Tertiary source rocks. Org. Geochem. 9, 293-304.

Grantham P.J., Posthuma J. and Baak A. (1983) Triterpanes in a number of Far-Eastern crude oils. In Advances in Organic Geochemistry, 1981 (eds. M. Bjoroy et al), pp. 675-683. John Wiley & Sons, Chichester.

ten Haven H.L. and Rullkotter J. (1988) The diagenetic of taraxer-14-ene and oleanane isomers. Geochim. Cosmochim. Acta 52, 2543-2548.

ten Haven H.L., de Leeuw J.W. and Schenck P.A. (1985) Organic geochemical studies of a Messinian evaporitic basin, northern Apennines (Italy) I: Hydrocarbon biological markers for a hypersaline environment. Geochim. Cosmochim. Acta 49, 2181-2191.

ten Haven H.L., de Leeuw J.W., Peakman T.M. and Maxwell J.R. (1986) Anomalies in steroid and hopanoid maturity indices. Geochim. Cosmochim. Acta 50, 853-855.

ten Haven H.L., de Leeuw J.W., Rullkotter J. and Sinninghe Damste J.S. (1987) Restricted utility of the pristane/phytane ratio as a palaeoenvironment indicator. Nature 330, 641-643.

ten Haven H.L., de Leeuw J.W., Sinninghe Damste J.S., Schenck P.A., Palmer S.E. and Zumberge J.E. (1988) Application of biological markers in the recognition of palaeo- hypersaline environment. In Lacustrine Petroleum Source Rocks (Geol. Soc. Spec. Publ. 40).(eds. A.J. Fleet, K. Kelts and M.R. Talbot), pp. 123-140. Blackwell, Oxford.

ten Haven H.L., Rohmer M., Rullkotter J. and Bisseret P. (1989) Tetrahymanol, the most likely precursor of gammacerane, occurs ubiquitously in marine sediments. Geochim. Cosmochim. Acta 53, 3073-3079.

Hills I.R., Whitehead E.V., Anders D.E., Cummins J.J. and Robinson W.E. (1966) An optically active triterpane, gammacerane in Green River, Colorado, oil shale bitumen. J. Chem. Soc., Chem. Commun., 752-754.

Hoffman C.F., Mackenzie A.S., Lewis C.A., Maxwell J.R. Oudin J.L., Durand B. and Vandenbroucke M. (1984) A biological marker study of coals, shales and oils from the Mahakam Delta, Kalimantan, Indonesia. Chem. Geol. 42, 1-23.

Hoffman C.F., Foster C.B., Powell T.G. and Summons R.E. (1987) Hydrocarbon biomarkers from Ordovician sediments and the fossil alga Gloeocapsomorpha prisca Zalessky 1917. Geochim. Cosmochim. Acta 51, 2681-2697.

Huang W.Y. and Meinschein W.G. (1976) Sterols as source indicators of organic materials in sediments. Geochim. Cosmochim. Acta 40, 323-330.

Huang W.Y. and Meinschein W.G. (1979) Sterols as

ecological indicators. Geochim. Cosmochim. Acta 43, 739-745.

Hunt J.M. (1979) Petroleum Geochemistry and Geology. Freeman, San Francisco.

Jackson M.J., Sweet I.P. and Powell T.G. (1988) Syudies on petroleum geology and geochemistry, Middle Proterozoic, McArthur Basin, Northern Australia I: Petroleum potential. APEA Journal 28, 283-302.

Jiang Z., Philp R.P. and Lewis C.A. (1988) Fractionation of biological markers in crude oils during migration and the effects on correlation and maturation parameters. In Advances in Organic Geochemistry, 1987 (eds. L. Mattavelli and L. Novelli), pp. 561-571. Pergamon Journals, Oxford.

Kemp P., Lander D.J. and Orpin C.G. (1984) The lipids of the rumen fungus Piromonas communis. J. Gen. Microbiol. 130, 27-37.

Kingston J. (1978) Oil and gas generation, migration and accumulation in the North Sumatra Basin. SEAPEX Proc. IV, 158-182.

Kjellgren G.M. and Sugiharto H. (1989) Oil geochemistry: A clue to the hydrocarbon history and prospectivity

of the southeastern North Sumatra Basin, Indonesia. Proc. Indonesian Petr. Assoc. 18th Ann. Convention, pp. 363-384.

Lafargue E. and Barker C. (1988) Effect of water washing on crude oil composition. Bull. AAPG 72, 263-276.

Larcher A.V., Alexander R. and Kagi R.I. (1987) Changes in configuration of extended moretanes with increasing sediment maturity. Org. Geochem.11, 59-63.

Lewan M.D. and Williams J.A. (1987) Evaluation of petroleum generation from resinites by hydrous pyrolysis. Bull. AAPG 71, 207-214.

Lewan M.D., Bjoroy M. and Dolcater D.L. (1986) Effects of thermal maturation on steroid hydrocarbons as determined by hydrous pyrolysis of Phosphoria Retort Shale. Geochim. Cosmochim. Acta 50, 1977-1987.

Leythaeuser D. and Schwarzkopf Th. (1986) The pristane/ n-heptadecane ratio as an indicator for recognition of hydrocarbon migration effects. Org. Geochem. 10, 191-197.

Leythaeuser D., Mackenzie A., Schaefer R.G. and Bjoroy M.

(1984) A novel approach for recognition and quantification of hydrocarbon migration effects in shale-sandstone sequences. Bull. AAPG 68, 196-219.

Mackenzie A.S. (1984) Applications of biological markers in petroleum geochemistry. In Advances in Petroleum Geochemistry Vol. 1 (eds. J. Brooks and D. Welte), pp. 115-214. Academic Press, London.

Mackenzie A.S. and McKenzie D. (1983) Isomerization and aromatization of hydrocarbons in sedimentary basins formed by extension. Geol. Magazine 120, 417-470.

Mackenzie A.S., Patience R.L., Maxwell J.R., Vandenbroucke M. and Durand B. (1980) Molecular parameters of maturation in the Toarcian shales, Paris Basin, France - I. Changes in configuration of acyclic isoprenoid alkanes, steranes and triterpanes. Geochim. Cosmochim. Acta 44, pp. 1709-1721.

Mackenzie A.S., Lewis C.A. and Maxwell J.R. (1981) Molecular parameters of maturation in the Toarcian shales, Paris Basin - IV. Laboratory thermal alteration studies. Geochim. Cosmochim. Acta 45, 2369-2376.

Mackenzie A.S., Brassell S.C., Eglinton G. and Maxwell

J.R. (1982) Chemical fossils: The geological fate of steroids. Science 217, 491-504.

Mallory F.B., Gordon J.T. and Conner R.L. (1963) The isolation of a pentacyclic triterpenoid alcohol from a protozoan. J. Amer. Chem. Soc. 85, 1362-1363.

McEvoy J. and Giger W. (1986) Origin of hydrocarbons in Triassic Serpiano oil shales: Hopanoids. In Advances in Organic Geochemistry, 1985 (eds. D. Leythaeuser and J. Rullkotter), pp. 943-949. Pergamon Press, Oxford.

McKirdy D.M., Aldridge A.K. and Ypma P.J.M. (1983) A geochemical comparison of some crude oils from Pre-Ordovician carbonate rocks. In Advances in Organic Geochemistry, 1981 (eds. M. Bjoroy et al.), pp. 99-107. John Wiley & Sons, Chichester.

McKirdy D.M., Kantsler A.J., Emmet J.K. and Aldridge A.K. (1984) Hydrocarbon genesis and organic facies in Cambrian carbonates of the Eastern Officer Basin, South Australia. In Petroleum Geochemistry and Source Rock Potential of Carbonate Rocks (AAPG Studies in Geology, No. 18) (ed. J.G. Palacas), pp. 13-31. AAPG, Tulsa.

Mello M.R., Telnaes N., Gaglianone P.C., Chicarelli M.I., Brassell S.C. and Maxwell J.R. (1988) Organic geochemical characterisation of depositional palaeoenvironments of source rocks and oils in Brazilian marginal basins. In Advances in Organic Geochemistry, 1987 (eds. L. Mattavelli and L. Novelli), pp. 31-45. Pergamon Journals, Oxford.

Mitterer R.M., Dzou I.P., Miranda R.M. and Caughey M.E. (1988) Extractable and pyrolyzed hydrocarbons in shallow-water carbonate sediments, Florida Bay, Florida. In Advances in Organic Geochemistry, 1987 (eds. L. Mattavelli and L. Novelli), pp. 283-294. Pergamon Journals, Oxford.

Moldowan J.M., Seifert W.K. and Gallegos E.J. (1985) Relationship between petroleum composition and depositional environment of petroleum source rocks. Bull. AAPG 69, 1255-1268.

Moldowan J.M., Lee C.Y., Sundararaman P., Salvatori T., Alajbeg A., Gjukic B. and Demaison G.J. (1989) Source correlation and maturity assessment of select oils and rocks from the Central Adriatic Basin (Italy and Jugoslavia). Preprints 34, 112-121.

Mulhadiono and Sutomo J.A. (1984) The determination of

economic basement of rock formation in exploring the Langkat - Medan area, North Sumatra Basin. Proc. Indonesian Petr. Assoc. 13th Ann. Convention, pp. 75-107.

Noble R.A. (1986) A Geochemical study of bicyclic alkanes and diterpenoids hydrocarbons in crude oils, sediments and coals. PhD thesis. University of Western Australia, Perth.

Noble R., Alexander R. and Kagi R.I. (1985) The occurrence of bisnorhopane, trisnorhopane and 25-norhopanes as free hydrocarbons in some Australian shales. Org. Geochem. 8, 171-176.

Oehler J.H. (1984) Carbonate source rocks in the Jurassic Smackover Trend of Mississippi, Alabama, and Florida. In Petroleum Geochemistry and Source Rock Potential of Carbonate Rocks (AAPG Studies in Geology No. 18) (ed. J.G. Palacas), pp. 71-96. AAPG, Tulsa.

Orr W.L. (1974) Changes in sulfur content and isotopic ratios of sulfur during petroleum maturation - Study of Big Horn Basin Paleozoic oils. Bull. AAPG 58, 2295- 2318.

Ourisson G., Albrecht P. and Rohmer M. (1979) The

hopanoids: Palaeochemistry and biochemistry of a group of natural products. Pure Applied Chem. 51, 709-729.

Ourisson G., Albrecht P. and Rohmer M. (1984) The microbial origin of fossil fuels. Sci. Am. 251, 44-51.

Palacas J.G., Anders D.E. and King J.D. (1984) South Florida Basin - A prime example of carbonate source rocks of petroleum. In Petroleum Geochemistry and Source Rock Potential of Carbonate Rocks (AAPG Studies in Geology No. 18) (ed. J.G. Palacas), pp. 71-96. AAPG, Tulsa.

Palmer S.E. (1984) Effect of water washing on C_{15+} hydrocarbon fraction of crude oils from northwest Palawan, Philippines. Bull. AAPG 68, 137-149.

Peakman T.M., ten Haven H.L., Rechka J.R., de Leeuw J.W. and Maxwell J.R. (1989) Occurrence of (20R)- and (20S)-$\Delta^{8(14)}$ and Δ^{14} 5α(H)-sterenes and the origin of 5α(H),14β(H),17β(H)-steranes in an immature sediment. Geochim. Cosmochim. Acta 53, 2001-2009.

Philippi G.T. (1965) On the depth, time and mechanism of petroleum generation. Geochim. Cosmochim. Acta 29,

1021-1049.

Philp R.P. (1985a) Biological markers in fossil fuel production. Mass Spectrometry Reviews 4, 1-54.

Philp R.P. (1985b) Fossil fuel biomarkers - Application and Spectra. Elsevier, Amsterdam.

Philp R.P. and Gilbert T.D. (1986) Biomarker distributions in Australian oils predominantly derived from terrigenous source material. In Advances in Organic Geochemistry, 1985 (eds. D. Leythaeuser and J. Rullkotter), pp. 73-84. Pergamon Journals, Oxford.

Powell T.G. (1986) Petroleum geochemistry and depositional setting of lacustrine source rocks. Marine and Petr. Geol. 3, 200-219.

Price P.L., O'Sullivan T. and Alexander R. (1987) The nature and occurrence of oil in Seram, Indonesia. Proc. Indonesian Petr. Assoc. 16th Ann. Convention, pp. 141-173.

Radke M. (1987) Organic geochemistry of aromatic hydrocarbons. In Advances in Petroleum Geochemistry Vol. 2 (eds. J. Brooks and D. Welte), pp. 141-207. Academic Press, London.

Radke M. (1988) Application of aromatic compounds as maturity indicators in source rocks and crude oils. Marine and Petroleum Geology 5, 224-236.

Radke M. and Welte D.H. (1983) The Methylphenanthrene Index (MPI): A maturity parameter based on aromatic hydrocarbons. In Advances in Organic Geochemistry, 1981 (eds. M. Bjoroy et al.), pp. 504-512. John Wiley & Sons, Chichester.

Radke M, Welte D.H. and Willsch H. (1982a) Geochemical study on a well in the Western Canada Basin: Relation of the aromatic distribution pattern to maturity of organic matter. Geochim. Cosmochim. Acta 46, 1-10.

Radke M., Willsch H., Leythaeuser D. and Teichmuller M. (1982b) Aromatic components of coal: Relation of distribution pattern to rank. Geochim. Cosmochim. Acta 46, 1831-1848.

Ries-Kautt M. and Albrecht P. (1989) Hopane-derived triterpenoids in soils. Chem. Geol. 76, 143-151.

Rinaldi G.G.L., Leopold V.M. and Koons C.B. (1988) Presence of benzohopanes, monoaromatic secohopanes, and saturate hexacyclic hydrocarbons in petroleums from carbonate environments. In Geochemical

Biomarkers (eds. T.F. Yen and J.M. Moldowan), pp. 331-353. Harwood Academic Publishers, Chur.

Riva A., Salvatori T., Cavaliere R., Ricchinto T. and Novelli L. (1986) Origin of oils in Po Basin, northern Italy. In Advances in Organic Geochemistry, 1985 (eds. D. Leythaeuser and J. Rullkotter), pp. 391-400. Pergamon Journals, Oxford.

Riva A., Caccialanza P.G. and Quagliaroli F. (1988) Recognition of 18β(H)-oleanane in several crudes and Tertiary-Upper Cretaceous sediments. Definition of a new maturity parameter. In Advances in Organic Geochemistry, 1987 (eds. L. Mattavelli and L. Novelli), pp. 671-675. Pergamon Jornals, Oxford.

Rohmer M. and Ourisson G. (1976) Methylhopanes d'Acetobacter xylinum et d'Acetobacter rancens: Une nouvelle famille de composes triterpenique. Tetrahedron Lett., 3641- 3644.

Rubinstein I., Sieskind O. and Albrecht P. (1975) Rearranged sterenes in a shale: Occurrence and simulated formation. J. Chem. Soc., Perkin Trans I, 1833-1835.

Rullkotter J. and Philp P. (1981) Extended hopanes up to C_{40} in Thornton bitumen. Nature 292, 616-618.

Rullkotter J. and Wendisch D. (1982) Microbial alteration of 17α(H)-hopanes in Madagascar asphalts: Removal of C-10 methyl group and ring opening. Geochim. Cosmochim. Acta 46, 1545-1553.

Scalan R.S. and Smith J.E. (1970) An improved measure of the odd-even predominance in the normal alkanes of sediment extracts and petroleum. Geochim. Cosmochim. Acta 34, 611-620.

Seifert W.K. and Moldowan J.M. (1978) Applications of steranes, terpanes and monoaromatics to the maturation, migration and source of crude oils. Gochim. Cosmochim. Acta 42, 77-95.

Seifert W.K. and Moldowan J.M. (1979) The effect of biodegradation on steranes and terpanes in crude oils. Geochim. Cosmochim. Acta 43, 111-126.

Seifert W.K. and Moldowan J.M. (1980) The effect of thermal stress on source rock quality as measured by hopane stereochemistry. In Advances in Organic Geochemistry, 1979 (eds. A.G. Douglas and J.R. Maxwell), pp. 229-237. Pergamon Press, Oxford.

Seifert W.K. and Moldowan J.M. (1986) Use of biological markers in petroleum exploration. In Biological Markers in the Sedimentary Record (ed. R.B. Johns), pp. 261- 290. Elsevier, Amsterdam.

Seifert W.K., Moldowan J.M. and Demaison G.J. (1984) Source correlation of biodegraded oils. In Advances in Organic Geochemistry, 1983 (eds. P.A. Schenck, J.W. de Leeuw and G.W.M. Lijmbach), pp. 633-643. Pergamon Press, Oxford.

Sheng G., Fan S., Liu D., Su N. and Zhou H. (1980) The geochemistry of n-alkanes with an even-odd predominance in the Tertiary Shahejie Formation of northern China. In Advances in Organic Geochemistry,1979 (eds. A.G. Douglas and J.R. Maxwell), pp. 115-121. Pergamon Press, Oxford.

Simoneit B.R.T. (1977) Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance. Geochim. Cosmochim. Acta 41, 463-476.

Sinninghe Damste J.S., Rijpstra W.I., de Leeuw J.W. and Schenck P.A. (1989) The occurrence and identification of series of organic sulphur compounds in oils and sediment extracts: II. Their presence in samples from hypersaline and non-hypersaline palaeoenvironments and possible

application as source, palaeoenvironmental and maturity indicators. Geochim. Cosmochim. Acta 53, 1323- 1341.

Situmeang S. and Davies P.R. (1986) A geochemical study of Asamera's block 'A' production sharing contract area, North Sumatra Basin. Proc. Indonesian Petr. Assoc. 15th Ann. Convention, pp. 321-340.

Soeparjadi R.A., Valachi L.Z. and Sosromihardjo S. (1986) Oil and gas developments in Far East in 1985. Bull. AAPG 10, 1479-1565.

Sosromihardjo S.P.C. (1988) Structural analysis of the North Sumatra Basin with emphasis on synthetic aperture radar data. Proc. Indonesian Petr. Assoc. 17th Ann. Convention, pp. 187-209.

Spiro B. and Aizenshtat Z. (1977) Bacterial sulphate reduction and calcite precipitation in hypersaline deposition of bituminous shales. Nature 269, 235-237.

Strachan M.G., Alexander R. and Kagi R.I. (1988) Trimethylnaphthalenes in crude oils and sediments: Effects of source and maturity. Geochim. Cosmochim. Acta 52, 1255-1264.

Strachan M.G., Alexander R., van Bronswijk W. and Kagi R.I. (1989) Source and heating rate effects upon maturity parameters based on ratios of 24-ethylcholestane diastereomers. J. Geochem. Explor. 31, 285-294.

Summons R.E. and Powell T.G. (1987) Identification of aryl isoprenoids in source rocks and crude oils: Biological markers for the green sulphur bacteria. Geochim. Cosmochim. Acta 51, 557-566.

Summons R.E. and Jahnke L.L. (1990a) Identification of the methylhopanes in sediments and petroleum. Geochim. Cosmochim. Acta 54, 247-251.

Summons R.E. and Jahnke L.L. (1990b) Hopenes and hopanes methylated in ring-A: Correlation of the hopanoids from extant methylotrophic bacteria with their fossil analogues. In Biological Markers in Sediments and Petroleum (eds. J.M. Moldowan, P. Albrecht and R.P. Philp) (in press).

Summons R.E., Volkman J.K. and Boreham C.J. (1987) Dinosterane and other steroidal hydrocarbons of dinoflagellate origin in sediments and petroleum. Geochim. Cosmochim. Acta 51, 3075-3082.

Summons R.E., Powell T.G. and Boreham C.J. (1988)

Petroleum geology and geochemistry of the Middle Proterozoic McArthur Basin, Northern Australia. III. Composition of extractable hydrocarbons. Geochim. Cosmochim. Acta 52, 1747-1763

Talukdar S., Gallango O. and Chin-A-Lien M. (1986) Generation and migration of hydrocarbons in the Maracaibo Basin, Venezuela: An integrated basin study. In Advances in Organic Geochemistry, 1985 (eds. D. Leythaeuser and J. Rullkotter), pp. 261-279. Pergamon Journals, Oxford.

Thomas B.M. and Smith D.N. (1974) A summary of the petroleum geology of the Carnarvon Basin. APEA Journal 14, 66-76.

Tissot B.P. and Welte D.H. (1984) Petroleum formation and occurrence, 2nd ed., Springer-Verlag, Berlin.

Venkatesan M.I. (1989) Tetrahymanol: Its widespread occurrence and geochemical significance. Geochim. Cosmochim. Acta 53, 3095-3101.

Volkman J.K. (1986) A review of sterol markers for marine and terrigenous organic matter. Org. Geochem. 9, 83-99.

Volkman J.K., Alexander R., Kagi R.I., Noble R.A. and

Woodhouse G.W. (1983a) A geochemical reconstruction of oil generation in the Barrow Sub-basin of Western Australia. Geochim. Cosmochim. Acta 47, 2091-2105.

Volkman J.K., Alexander R., Kagi R.I. and Woodhouse G.W. (1983b) Demethylated hopanes in crude oils and their applications in petroleum geochemistry. Geochim. Cosmochim. Acta 47, 785-794.

Volkman J.K., Alexander R., Kagi R.I. and Rullkotter J. (1983c) GC-MS characterization of C_{27} and C_{28} triterpanes in sediments and petroleum. Geochim. Cosmochim. Acta, 47, 1033-1040.

Waples D. (1981) Organic geochemistry for exploration geologists. Burgess Publishing Co., Minneapolis.

Wardroper A.M.K., Brooks P.W., Humberston M.J. and Maxwell J.R. (1977) Analysis of steranes and triterpanes in geolipid extracts by automatic classification of mass spectra. Geochim. Cosmochim. Acta 41, 499-510.

Whitehead E.V. (1974) The structure of petroleum pentacyclanes. In Advances in Organic Geochemistry,1973 (eds. B. Tissot and F. Bienner), pp. 225-243. Editions Technip, Paris.

Yang W., Li Y. and Gao R. (1985) Formation and evolution of nonmarine petroleum in Songliao Basin, China. Bull. AAPG 69, 1112-1122.

Zander J.M., Caspi E., Pandey G.N. and Mitra C.R. (1969) The presence of tetrahymanol in Oleandra wallichii. Phytochem. 8, 2265-2267.

Zumberge J.E. (1987) Prediction of source rock characteristics based on terpane biomarkers in crude oils: A multivariate statistical approach. Geochim. Cosmochim. Acta 51, 1625-1637.

APPENDICES

Appendix 1. Geological Time Scale.

ERA	PERIOD		EPOCH	TIME (Ma)
Cenozoic	Quaternary		Holocene	0.01
			Pleistocene	1.8
	Tertiary	Neogene	Pliocene	5
			Miocene	26
		Palaeogene	Oligocene	37
			Eocene	53
			Palaeocene	65
Mesozoic	Cretaceous			136
	Jurassic			190
	Triassic			225
Palaeozoic	Permian			280
	Carboniferous			345
	Devonian			395
	Silurian			430
	Ordovician			500
	Cambrian			570
Pre Cambrian				

Appendix 2. List of Publications.

Strachan M.G., Alexander R., Subroto E.A. and Kagi R.I. (1989) Constraints upon the use of 24-ethylcholestane diastereomer ratios as indicators of the maturity of petroleum. Org. Geochem. 14, 423-432.

Subroto E.A., Alexander R. and Kagi R.I. (1990) 30-Norhopanes: Their occurrence in sediments and crude oils. Chem. Geol. (in the press).

Subroto E.A., Alexander R. and Kagi R.I. (1990) Identification of a homologous series of 2-methyl-30-nor-17α(H)-hopanes in crude oil. Org. Geochem. (in preparation)

Subroto E.A., Alexander R. and Kagi R.I. (1991) Biomarker characterisation of some crude oils and source rocks from the North Sumatra Basin (Indonesia) (in preparation for the Proceedings of the Indonesian Petroleum Association Convention 1991).