2 of 2. A.J. DUFFIN.

DOC. No: 87003210

DEPT. NAT. RES & ENV
PE904407

PETROLEUM POTENTIAL OF THE OTWAY BASIN - A REVIEW

3.1 INTRODUCTION

The origin and formation of petroleum can be described in general terms by the following successive stages:-

1. The formation of organic-rich, fine-grained sediments. The organic matter within the sediments has been subjected to three important processes:
   a) Photosynthesis.
   b) Deposition.
   c) Preservation.
2. Thermal degradation of the organic matter with the formation of petroleum molecules and a subsequent increasing temperature.
3. The expulsion of oil and gas from the fine-grained source rock, its migration through and final entrapment in a porous, permeable reservoir rock.
4. The thermal and/or biological alteration of petroleum in the reservoir rock, (Hood, Gutjahr and Heacock, 1975).

In this investigation it is the first two stages which are of primary concern.

3.2 OIL FORMATION

A general scheme of hydrocarbon generation is shown in

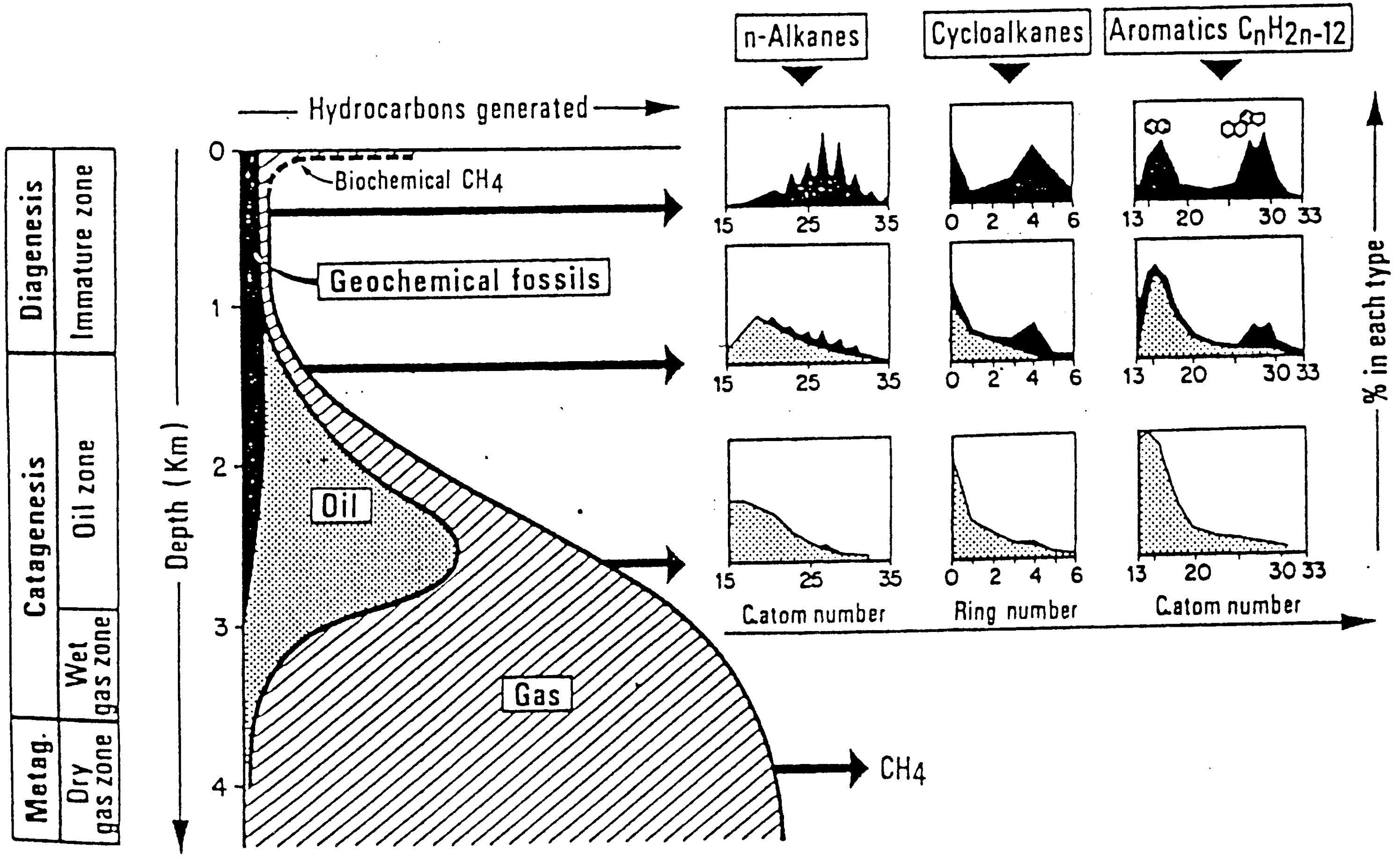


Fig. 40 General scheme of hydrocarbon formation as a function of burial of the source rock. The evolution of the hydrocarbon composition is shown in the insets for three struc-

fig. 40. The diagram shows the relative amount and the nature of hydrocarbons generated from sedimentary organic material as a function of burial depth, (Tissot etal., 1974). The evolution of organic matter in sediments can be summarized as follows:-

-Diagenesis:-

The system tends towards equilibrium; temperature and pressure increases are small. Microbial activity is the main agent of transformation and marsh gas (bacterially formed methane) is produced in relatively large quantities. The precursor to kerogen (insoluble organic matter) is formed at this stage.

- Catagenesis:-

There is a dramatic increase in the pressure and temperature leading to the thermal degradation (splitting of the bonds) of the kerogen and an alteration in the chemical and physical properties of the organic matter. Within this stage the fine-grained source rock becomes mature.

- Metagenesis:-

With increasing temperatures, organic matter decomposes into graphite and methane. Metagenesis eventually grades into metamorphism.

The fundamental principles of petroleum formation as stated above show that organic matter is very sensitive to temperature and, to a lesser extent, time. However, it should be realized that the total amount of hydrocarbons generated and the relative importance of the oil and gas depends on the composition of the original organic matter.

3.3 DIAGENESIS

The primary stage of petroleum formation occurs within the first few metres of sediment, where organic matter undergoes initial alterations to kerogen. The production and accumulation of this organic matter is therefore a most important stage in the formation of petroleum.

The primary mechanism of organic matter production is photosynthesis, whereby light energy is converted to chemical energy (producing organic matter) in the form of glucose. A basic pre-requisite for photosynthesis is the light absorbing green pigment - Chlorophyll.

Bacteria, phytoplankton, zooplankton and the higher plants are the main contributors of organic matter in the sediments. The chemical composition of the biomass is a complex mixture of many compounds, though four basic chemical constituents are found throughout. These are the biopolymers, (Dow, 1977; Hunt, 1979):-

a) Lipids.

b) Proteins.

c) Carbohydrates.

d) Lignin - Humic compounds.

The incorporation of organic matter into sediments ultimately depends on processes which not only conserve and concentrate, but also destroy and dilute, (Dow, 1978). It is estimated that the average preservation rate of the primary organic matter as organic carbon is less than 0.1%, (Tissot and Welte, 1984). Much organic debris is lost to dissolution, hydrolysis, oxidation and microbial activity.

The organic matter finally incorporated into the sediments undergoes microbial attack (biochemical degradation) transforming the proteins, carbohydrates and lipids to fulvic and humic acids. Further burial results in polycondensation as the organic material becomes progressively insoluble, producing humin - the precursor of kerogen. A final process of insolublization leads to the formation of kerogen, considered to be the main source of petroleum compound, (Tissot and Welte, 1984).

Diagenesis therefore is the process whereby biopolymers, through fractionation, partial destruction and rearrangement of the macromolecules, leads to geopolymers, (fig.41).

3.4 CATAGENESIS

Catagenesis results from an increase in temperature during burial in sedimentary basins and represents the principal stage of oil and wet gas formation. The decomposition of kerogen during catagenesis forms most of

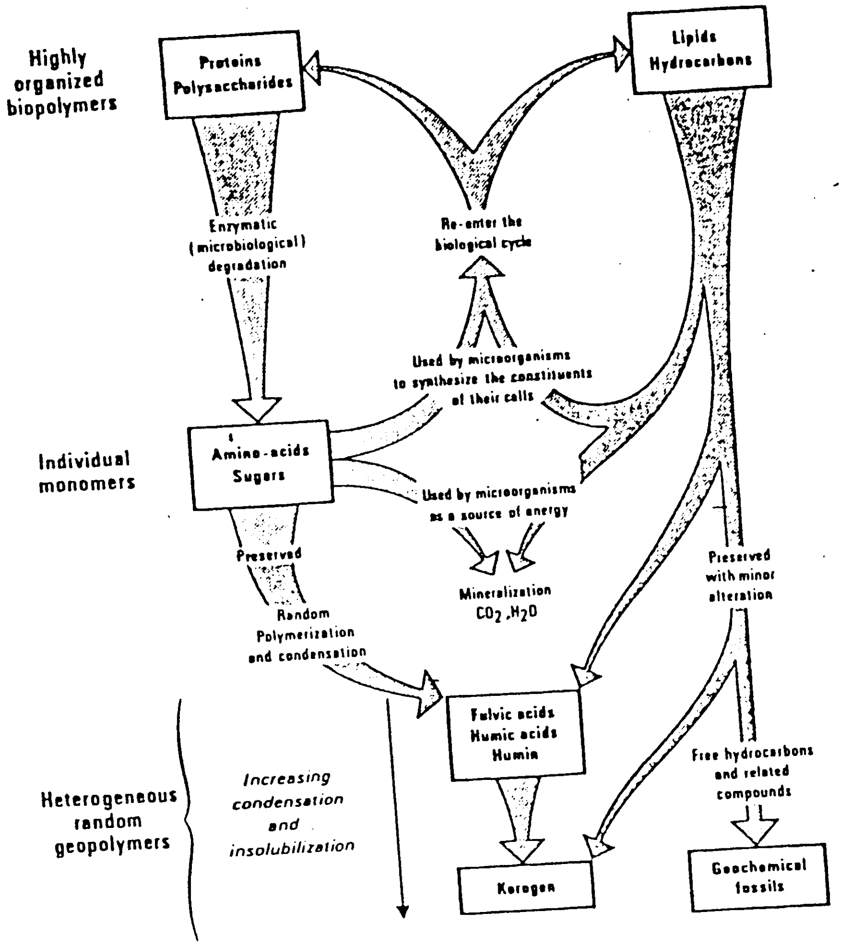


Fig. 41 The fate of organic material during sedimentation and diagenesis, resulting in two main organic fractions : Kerogen and geochemical fossils. (After Tissot and Welte, 1984).

the hydrocarbons. As burial temperatures rise to a threshold of intense generation, formation of large quantities of hydrocarbons results. This threshold can vary depending on:-

a) The ease of organic matter decomposition.

b) The rate of sedimentation.

There are two principle mechanisms of cracking such that the insoluble organic matter (kerogen) is altered by the breaking of the C - C bonds, (Hunt, 1979) (fig.42):-

-Thermal cracking : Whereby the reaction rates are increased by temperature;

-Catalytic cracking : Whereby the reaction rates are increased by catalysts, normally found in the clays. However, excessive amounts of water may lead to a reduced activity of many catalysts.

The progressive rearrangement of kerogen during catagenesis leads to the elimination of hydrocarbon chains and cycles, (Tissot and Welte, 1984). Medium to low molecular weight hydrocarbons become predominant, particularly normal and iso-alkanes, thus first crude oils and then gas are formed.

The end of catagenesis is reached with the disappearance of aliphatic carbon chains in kerogen and the development of ordering in the basic kerogen units.

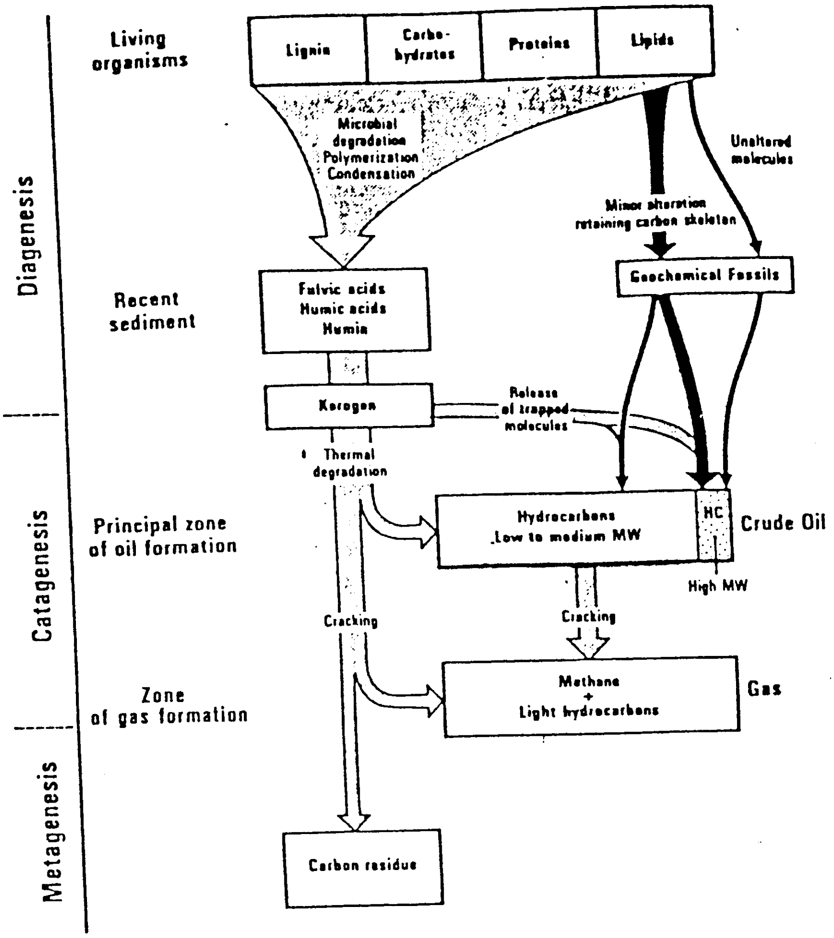


Fig. 42 Sources of hydrocarbons in geological situations, with regard to the evolution of organic matter. Geochemical fossils represent a first source of hydrocarbons in the subsurface (black solid arrows) Degradation of kerogen represents a second source of hydrocarbons (grey dotted arrows). (After Tissot and Welte, 1984).

3.5 METAGENESIS

Metagenesis is reached only at great depth precursing the true conditions of metamorphism (corresponding to the beginning of the greenschist facies).

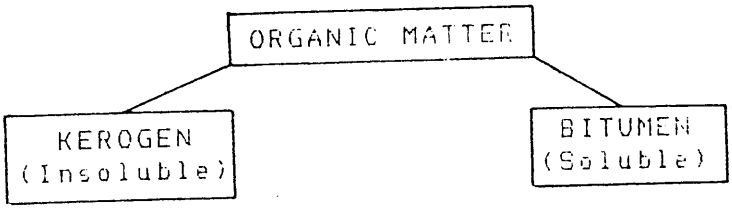
Only dry gas (methane) is generated at this stage accompanied by a structural rearrangement of the residual kerogen. The stacks of aromatic layers, previously distributed at random in the kerogen now gather to form larger clusters, (fig.43), (Tissot and Welte, 1984). The constituents of the residual kerogen are finally converted into graphitic carbon.

By the end of metagenesis it is no longer possible to generate or form petroleum.

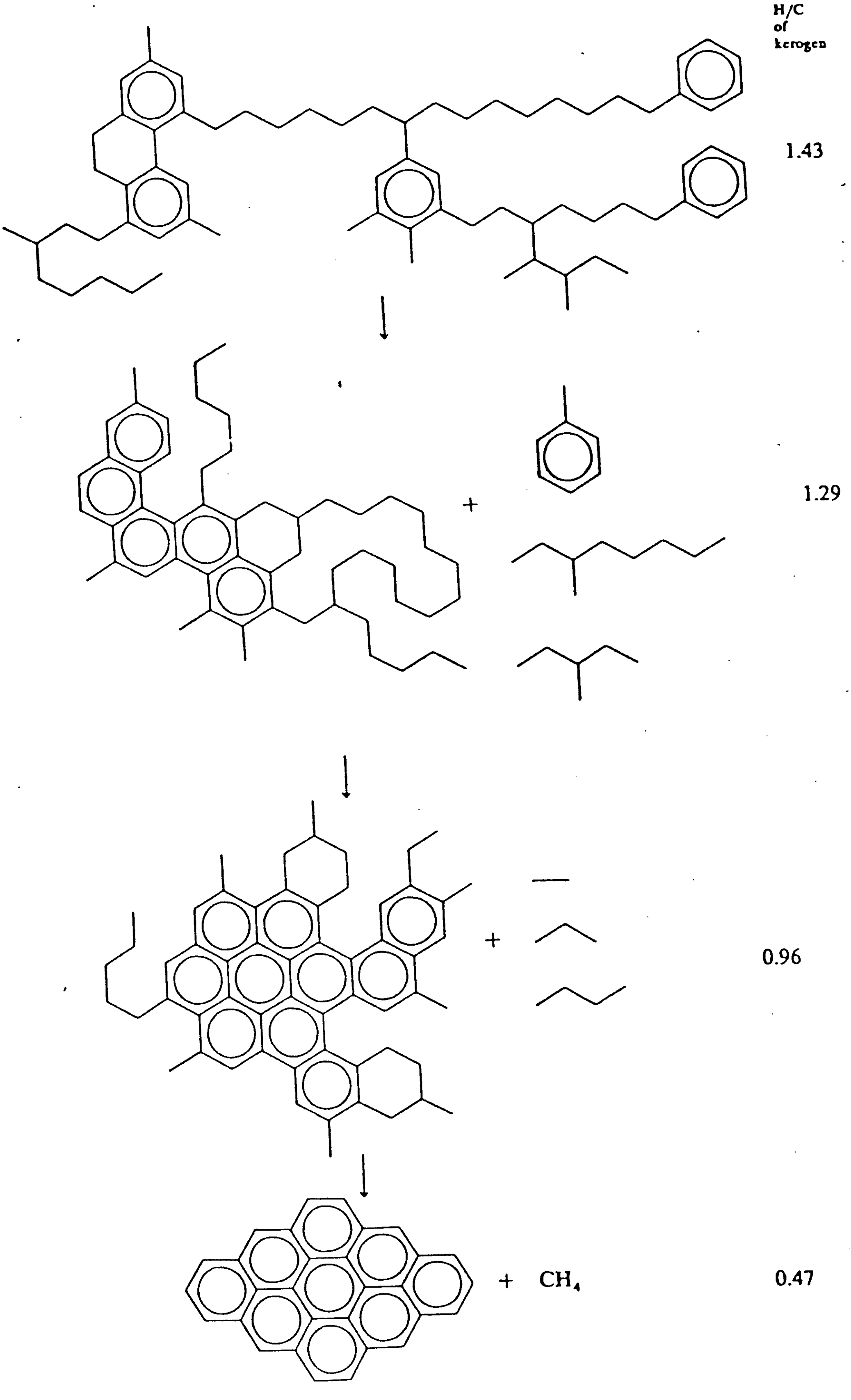
3.6 KEROGEN

Many studies have shown that most commercial hydrocarbons are generated by the thermal transformation of kerogen during the burial of source rocks.

Kerogen is defined as the portion of organic matter in sedimentary rocks that is insoluble in organic rocks, (Dow, 1977).



The quantity and quality of petroleum formed is ig. 43 The thermal alteration of kerogen involves hydrogen disproportionation reactions in which the kerogen loses hydrogen to form gasoline,wet gas and dry gas in succession.The hydrogen-depleted kerogen condenses and aromatizes to eventually from graphite. (After Hunt, 1976).



controlled by several factors typical to the kerogen, notably:-

a) Concentration.

b). Type.

c) Thermal maturity.

The major constituents of kerogen, determined by elemental analysis are Carbon, Hydrogen (critical in terms of convertibility to petroleum), Oxygen and minor quantities of Nitrogen and Sulphur, (Dow, 1977). Structurally kerogen is a macromolecule made of condensed cyclic nuclei, linked by heteroatomic bonds or aliphatic chains.

Different types of kerogen can be recognised by optical examination and physiochemical analysis. The composition of kerogens and their characteristic evolution paths can be compared to the composition of the coal macerals - Exinite, Vitrinite and Inertinite (Tissot etal., 1974). (fig.44).

It appears that three types of kerogen account for most existing kerogen, (fig.45),(Tissot and Welte, 1984).

Type I kerogen

1. Contains many aliphatic structures and few aromatic nuclei.

2. The H/C ratio is originally high and the O/C ratio relatively low.

3. The kerogen has a high genetic potential for

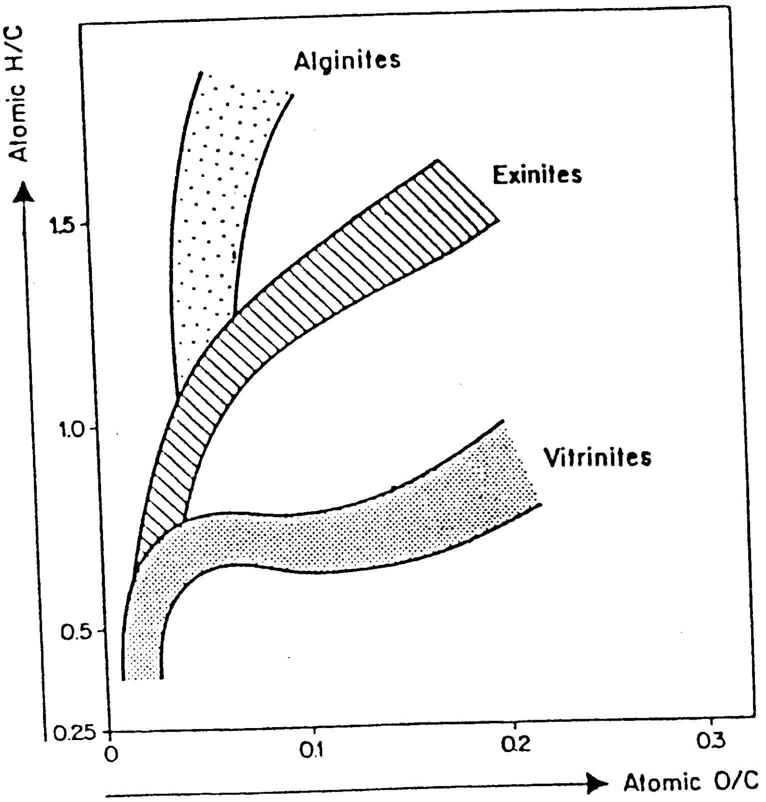


Fig. 44 Evolution paths of maceral groups in coals. (Tissot and Welte, 1984, after van Krevelen, 1961).

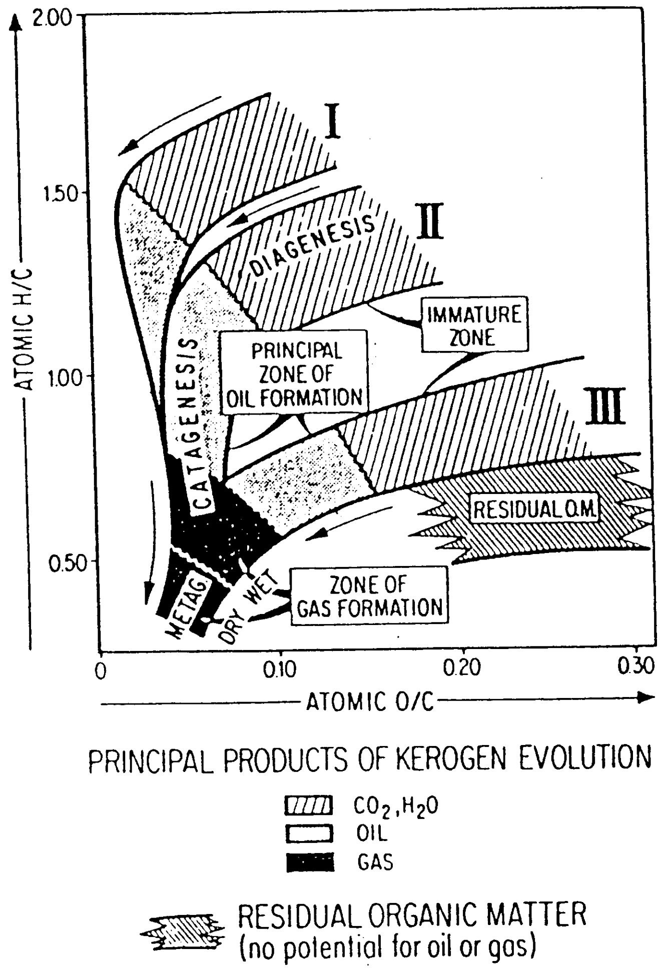


Fig. 45 Van Krevelen diagram showing types of kerogen, and principal products generated during thermal evolution of types I, II, and III kerogen. Residual organic matter has no potential for petroleum and no real evolution path. (After Tissot, 1984).

petroleum and is mainly derived from algal lipids, particularly those from lacustrine Botryococcus, (Tissot etal., 1974).

4. This type of kerogen is mostly deposited in lacustrine environments, (Tissot, 1984).

Type II Kerogen

1. Contains more aromatic and naphthenic rings.

2. The H/C ratio is generally lower than for type I, as is the petroleum potential. The O/C ratio however, is slightly higher.

3. This kerogen is usually related to marine organic matter and deposited in a reducing environment (Tissot, 1984).

Type III Kerogen

1. Contains mostly condensed polyaromatics and oxygenated functional groups.

2. The H/C ratio is low, although the O/C ratio is high.

3. The oil potential is low, however gas generation is still possible at depth.

4. This kerogen is mostly derived from terrestrial higher plants transported to a marine environment.

Type IV (Residual) Kerogen.

1. May consist of reworked, oxidized organic material,

or material deeply altered by subaerial weathering.

2. The H/C ratio is very low whilst the O/C is abnormally high.

3. This kerogen is a form of "dead carbon" with no potential for oil or gas, (Tissot and Welte, 1984).

The nature of the kerogen therefore is a factor that determines whether liquid oil and/or gas will be formed during the maturation process. A chemical and physical study of the insoluble organic matter can lead to characterising the various types of organic matter and thus evaluate the oil and gas potential of the formations.

Kerogen is unstable with respect to temperature, and increasing the burial depth of a sediment will lead to thermal evolution of the kerogen, (Welte, 1972, Dow, 1977). The thermal maturation of kerogen and the formation of petroleum hydrocarbons under the influence of geothermal heat are therefore interrelated.

As organic matter is very sensitive to temperature, a measurement of kerogen maturity can determine the degree of diagenesis within a sedimentary basin and thus the petroleum potential. Indeed many methods used to characterize source rocks and their potential to generate petroleum are based on kerogen studies.

3.7 SOURCE ROCK EVALUATION.

The following discussion reviews the methods and techniques used in assessing the capacity of a rock to generate petroleum hydrocarbons and establish a source rock evaluation.

3.8 TYPE OF ORGANIC MATTER

A distinction between the various organic types is essential for source rock appraisal as the different types of organic matter have different hydrocarbon potential.

Exinite Type : The remains of algae and plankton, generally derived from an aquatic environment. A high proportion of exinite leads to oil prone source rocks.

Vitrinite Type : The woody or herbaceous remains of higher plants, derived from subaerial environments. A high proportion of vitrinite leads to gas prone source rocks.

Inertinite Type : Organic material oxidized by abiogenic oxidation or aerobic oxidation prior to incorporation into the sediment. This form of kerogen cannot generate any hydrocarbons and is considered to be "dead carbon", (Tissot and Welte, 1984).

The organic types can be identified by optical microscope methods. The use of reflected and transmitted light microscopy together with fluorescence studies display characteristic features of the organic matter and can lead to the differentiation of each type.

3.9 SOURCE ROCK TYPE AND DEPOSITIONAL ENVIRONMENT

The composition of organic matter in a source rock is dependant upon its environment of deposition. As stated above, microscopy can identify the various organic types, however, a variety of chemical methods can determine the environment in which the source rock was deposited. This is an important factor as it has now been recognised that although terrestrial organic matter gives rise to gas and marine organic matter is the source of crude oil, terrestrial organic matter deposited in a reducing environment may give rise to crude oil. The enhanced preservation of hydrogen rich, lipid-rich organic matter in sediments deposited under anoxic water conditions is critical for the genesis of oil source beds, (Demaison and Moore, 1980). Such anaerobic residues are therefore potential precursors to oil-prone kerogen, whilst organic matter deposited under oxic water is hydrogen depleted and therefore gas-prone.

The relatively simple geochemical identification of organic matter is due to the obvious chemical differences seen in terrestrial plant matter, high in lignin and polysaccharides and marine organic matter which is high in protein and lipids, (Philippi, 1974).

The n-alkane distribution can be used as a method to determine the source type. Lipids, common to marine organic matter, show a predominance of C-16 and C-18 fatty acids. Vegetable waxes, found in terrestrial higher plants characteristically predominate around C-20 to C-34. The n-alkane distribution however, is also influenced by maturity, (see, 3.14(a)).

The parameter C-21 + C-22 / C-28 + C-29, (Philipp, 1974) can provide information about the source of organic matter. Generally a terrestrial source gives a value less than 1.2, whereas a marine source will result in a value greater than 1.5. Again this technique is influenced by the maturity of the source rock.

The proportion of saturates in the extracted organic matter can be related to the source type, (Woodhouse etal., 1982).

% SATS.	TYPE.
>15%	Terrestrial
15-30%	Mixed
<30%	Marine

To determine the deposition environment, the pristane / phytane (Pr : Ph) and pristane / nC-17 ratios have been used, (Lijmbach, 1975). The pristane / phytane ratio is determined from the area of the peaks that represent these compounds on the gas chromatography results. Information about the depositional environment is determined according to the following scale: (Powell and McKirdy, 1975).

Pr / Ph	DEP. ENVIRONMENT
<3.0	Reducing.

3.0 - 4.5	Reducing / Oxidising
>4.5	Oxidising

The pristane / nC-17 ratio is determined in the same manner as the Pr/Ph ratio. The following classification can be applied in the case of sediment extracts, Lijmbach (1975).

Pr / nC-17	DEP. ENVIRONMENT.
<1.0	Open marine.
1.0 - 1.5	Mixed.
>1.5	Peat swamp.

The use of geochemical fossils to determine the source rock type and as indicators of geological environments is now also widely employed. A full discussion of geochemical fossils, showing the significance and various uses of these fossil molecules as indicators of source type and palaeoenvironment is presented in the following chapter.

3.10 SOURCE ROCK CHEMISTRY

Determining the amount of organic matter within a sediment can lead to a general assumption of the source rock richness. Samples of the source rock are therefore analysed for total organic carbon (T.O.C.) and total extractable organic matter (E.O.M.). The E.O.M. is further separated into saturated hydrocarbons (SATS.), aromatic hydrocarbons (AROM.) and polar NSO containing organic compounds (POLAR), by medium pressure liquid chromatography, (Nicholas etal., 1981). Using empirically derived scales a source rock classification can be determined from the chemical analysis. Based on the % T.O.C. in clastic rocks, the following classification is generally accepted:

% T.O.C.	SOURCE ROCK
0 - 0.5	Poor
0.5 - 1.0	Fair
1.0 - 2.0	Good
2.0 - 4.0	Very Good
> 4.0	Excellent

The following scale is used to classify the source richness based on ppm E.O.M. (bitumen) data:

ppm E.O.M.	SOURCE ROCK.
0 - 500	Poor
500 - 1000	Fair
1000 - 2000	Good
2000 - 4000	Very Good
> 4000	Excellent

The total hydrocarbon (ppm SATS + AROM) and the ppm SATS. values can be used to classify source rock richness and oil source potential respectively.

ppm SATS + AROM	ppm SATS	CLASSIFICATION
0 - 300	0 - 200	Poor
300 - 600	200 - 400	Fair
600 - 1200	400 - 800	Good
1200 - 2400	800 - 1600	Very Good
> 2400	> 1600	Excellent

Finally a plot of the total hydrocarbon versus T.O.C. has been used, (Shibaoka etal., 1973),(Nicholas etal., 1981) to obtain a better rating of the source rock potential.

3.11 SOURCE ROCK MATURITY

Having established the potential a rock has to generate hydrocarbons, the source rock maturity must be resolved. It is generally accepted that hydrocarbon generation occurs between 60°C - 150°C. As stated earlier, the thermal evolution of a source rock, during diagenesis, catagenesis and metagenesis changes the physical and/or chemical properties of the organic matter and these properties may be considered as indicators for maturation. To be useful as a parameter of the degree of maturation, indicator properties should have certain characteristics, (Shibaoka etal., 1973):

- Sensitivity.
- Immobility.
- Ubiquitous distribution.

Parameters used to establish the level of maturity of a source rock include the optical examination of kerogen, physiochemical analysis of kerogen and the chemical analysis of extractable organic matter (bitumen).

3.12 OPTICAL INDICATORS OF MATURITY IN KEROGEN.

A visual study of kerogen in transmitted light is the basis for several scales of maturity, (Hood etal., 1975), including the colour scale of Gutjahr, based on the carbonization of spore and pollen and the thermal alteration index of Staplin (T.A.I.), based on the microscopic observations of both colour and structural alteration (fig.46). Both these scales are shown with the L.O.M. (Level of organic metamorphism) scale, proposed by Hood etal., (1975). L.O.M. is designed to have a linear variation as a function of depth and is continuous over the entire thermal range of interest in petroleum generation and destruction. The numerical scale used is from 0, at no burial to 20, at the anthracite / meta - anthracite boundary.

Examination of kerogen in reflected light and the resulting vitrinite reflectance data has become the most widely applied maturation scale, (Tissot and Welts, 1984). From the correlation of vitrinite reflectance with other maturation parameters and with the occurrence of oil and gas fields, the following stages can be distinguished, (Shibaoka etal., 1973, Hood etal., 1975, Tissot and Welte, 1984).

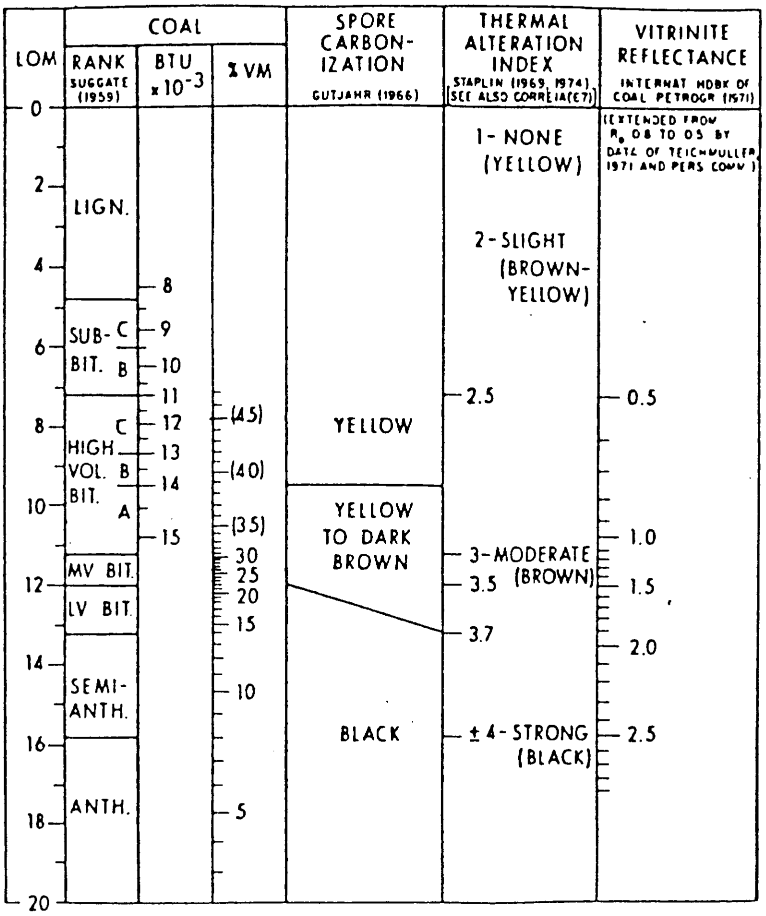


Fig. 46 Some scales of organic metamorphism. (After Hood etal., 1975).

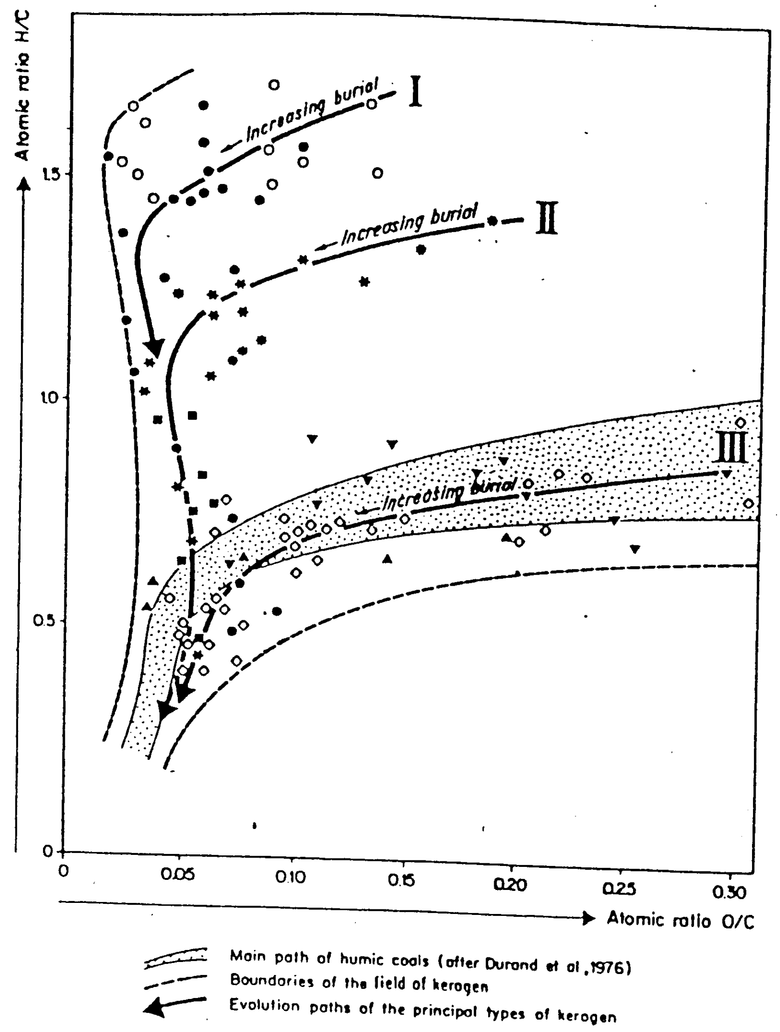
MEAN MAX. REFLECTANCE %	ZONE
<0.5	Pre - oil generation.
0.5 - 0.7	Diagenesis, source rock Immature.
0.7 - 1.3	Catagenesis, Main oil generation (the "oil-window")
1.3 - 2.0	Catagenesis, Main wet gas and condensate generation
> 2.0	Metagenesis, dry gas zone

3.13 PHYSIOCHEMICAL INDICATORS OF MATURITY IN KEROGEN.

Most kerogen properties evolve during the rearrangement of the kerogen structure with increasing burial. Of the various techniques used to determine thermal maturity many have to be considered more as research, rather than routine petroleum exploration tools.

The elemental analysis of kerogen, plotted on a Van Krevelen diagram gives a reasonably good idea of the maturation stage (fig.47), (Tissot etal., 1974). It is obvious that at least an analysis of C, H and O is required to plot the H/C, O/C ratios and establish the maturity of the kerogen.

A further chemical characteristic used to indicate the degree of maturation is the Carbon content of separated



Type	Age and/or formation	Basin, country	
I	Green River shales (Paleocene - Eocene)	Uinta, Utah, U.S.A.	●
	Algal kerogens (Botryococcus, etc...). Various oil shales		○
II	Lower Toarcian shales	Paris, France, W.Germany	✱
	Silurian shales	Sahara, Algeria and Libya	■
	Various oil shales		✱
III	Upper Cretaceous	Douala, Cameroon	◇
	Lower Mannville shales	Alberta, Canada	▲
	Lower Mannville shales (Mc Iver, 1967)	Alberta, Canada	▼

Fig. 47 The principal types and evolution paths of kerogen. Types I, II, and III are the most frequent, although kerogens of intermediate composition also occur. Evolution of kerogen composition with increasing burial is marked by an arrow along each evolution path, I, II, and III. (After Tissot and Welte, 1984)

kerogen and is similar to the use of the carbon content in coal. A correlation between the mean maximum reflectance (%) and carbon content of kerogen (%) has been established, (Shibaoka etal., 1973).

$\bar{R}o$%	C% (dry ash free)
0.5	76
0.7	82
1.0	86
1.3	89
2.0	91

Among the physical analysis of kerogen, electron spin resonance (E.S.R.) has been proposed as a routine method for measuring organic maturity. The E.S.R. signal in kerogen results from the occurrence of unpaired electrons, i.e. free radicals appearing as a result of splitting bonds. The spin density and the paramagnetic susceptibility (χp) are proportional and it has been shown that the χp increases with thermal evolution and organic maturity, (Tissot and Welte, 1984).

Further physical analysis of kerogen has been applied to characterize kerogen maturation, though these techniques tend to be regarded solely as research, rather than exploration tools e.g. infrared spectrophotometry and thermal analysis.

13.14 CHEMICAL INDICATORS OF MATURITY BASED ON BITUMEN.

Numerous methods have been developed using the amount, or the composition of the extractable organic matter (bitumen) to characterize the stage of thermal evolution.

The abundance of bitumen may be expressed as the bitumen ratio (E.O.M. : T.O.C.) or the hydrocarbon ratio (SATS : T.O.C.). From bitumen ratio data the following criteria can be used to assess the source rock maturity (Woodhouse etal., 1982) :

E.O.M./T.O.C.	MATURITY
0 - 50	Low
50 - 100	Moderate
>100	High

The composition of hydrocarbons is widely used in maturity studies. With increasing temperatures, new hydrocarbons are generated and indices reflecting compositional changes may be used to evaluate source rock maturation. To investigate the hydrocarbon composition, a C-12+ gas chromatography is carried out on the saturate fraction. The following information is commonly obtained from the gas chromatography analysis.

a) n - ALKANE DISTRIBUTION - can yield information about the level of maturity. Source rocks with a low degree of maturity have an n-alkane distribution high in the C-22+ range, with increasing maturation the n-alkane distribution shifts, becoming lower in the C-22+ range.

b) THE CARBON PREFERENCE INDEX (C.P.I.) - has probably received the greatest attention among methods using the chemical composition of bitumen. In recent sediments there is a predominance of molecules with odd numbers. Thermal degradation of kerogen generates alkanes without predominance, therefore the odd/even ratio will decrease. A good mature source rock must have generated enough hydrocarbons to reduce the odd/even ratio to a C.P.I. range of 0.9 - 1.3, (Hunt, 1979).

Several C.P.I. expressions have been proposed, however, the original definition is shown below as:

$$\text{C.P.I.} = \frac{1}{2} \quad \frac{C\text{-}25+C\text{-}27 \text{ ------- } +C\text{-}33}{C\text{-}24+C\text{-}26 \text{ ------- } +C\text{-}32} + \frac{C\text{-}25+C\text{-}27 \text{ ------- } +C\text{-}33}{C\text{-}26+C\text{-}28 \text{ ------- } +C\text{-}34}$$

Although the C.P.I. is used widely there are limitations in its use as the values can be influenced by the type of organic matter. Marine organisms for example synthesise odd/even chains only in the low molecular weight range and therefore C.P.I. values always approximate 1. Continental plants can have C.P.I. values up to 20 and therefore any samples with an appreciable terrestrial contribution can lead to C.P.I. values much greater than 1.

c) ISOPRENOID DISTRIBUTION - The abundance of isoprenoids varies with catagenesis and although the pristane and phytane isoprenoids are generally used to render information about the depositional environment, they can also provide an indication of maturation.

The pristane / nC-17 ratio is generally >1.0 for a very immature crude oil whilst the phytane / nC-18 ratio value decreases with increased maturation.

Further studies of possible thermal maturation indicators include:-

1. Percentage of aromatic protons (P.A.P.) in the aromatic fraction. The aromatic fraction of liquid petroleum is isolated and analysed by nuclear magnetic resonance spectroscopy. The percentage of aromatic protons is then determined. It has been shown that the P.A.P. value increases with increasing maturity for values ranging from 4 to 30, (Alexander etal., 1978, 1979).

Immature liquid petroleum - 8 - 12
Mature crudes - 20 - 26
Condensates - 26 - 30

2. Fission track analysis has recently been used to evaluate thermal histories, hydrocarbon potential and therefore the maturity of source rocks. The fission track dating method is dependent upon the accumulation of radiation damage from the spontaneous nuclear fission of 238 - U in Uranium bearing minerals over geological time.

The radiation damage is caused by two fragments from each fission event moving in opposite directions, so producing a single continuous linear defect or "track". Fission tracks in detrital apatites are known to be stable over geological time, only at relatively low temperatures. As the temperature is increased, so the tracks fade and are eventually lost. This process of track annealing occurs progressively over a certain temperature range, "the track annealing zone" and in the case of apatite, occurs between 70 °C and 125 °C (for times of the order of 10 million years). This temperature range is very close to the temperature interval of maximum generation of liquid hydrocarbon. The relationship between the apatite track annealing zone, the oil generation window, temperature and vitrinite reflectance is shown in fig. 48. Therefore, as the temperature increases with depth the apparent fission track age of apatite is observed to decrease (due to track annealing), eventually reaching zero at the bottom of the track annealing zone, (Gleadow etal., 1983).

3. The use of computerized gas chromatography mass spectrometry (G.C./M.S.) has enabled biological markers (geochemical fossils), particularly the sterane / triterpane fraction of petroleum to be used as maturity and source type indicators. The importance of geochemical fossils is discussed in the following chapter.

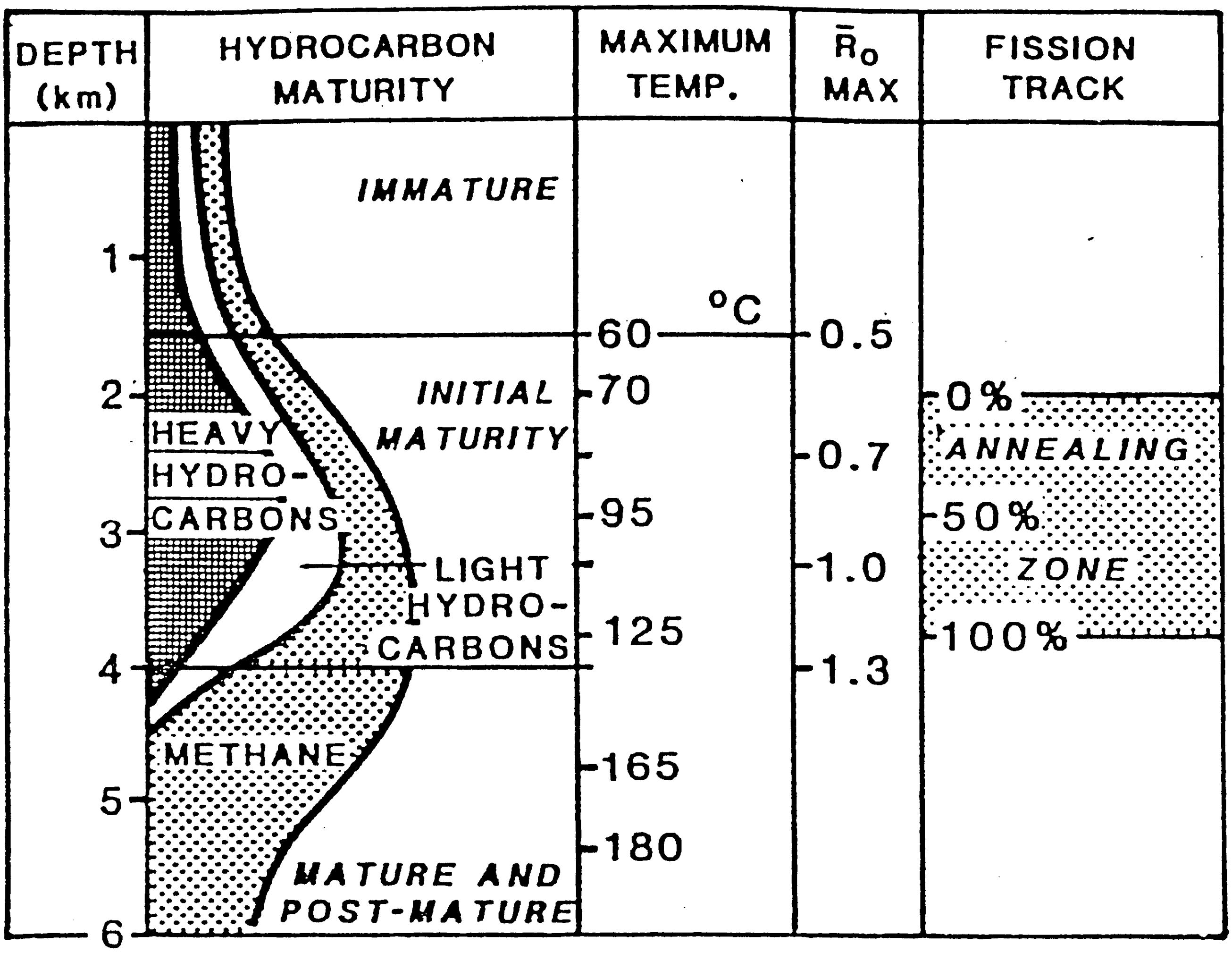


Fig. 48 The relationship between the fission track annealing zone in apatite,temperature,and hydrocarbon maturity (After Gleadow,Duddy,and Lovering, 1983).

3.15 PYROLYSIS

Rock - Eval Pyrolysis is probably the best routine tool for determining the source rock type and the maturation of organic matter. It is able to provide a rapid evaluation of the source rock potential, (Page and Kuhuel, 1980).

During the assay, the volatilized gases recorded and released are, progressively :-

S1.- Free hydrocarbon in the sample, broadly analogous to the extractable organic matter (bitumen) and is an indication of the level of oil and/or gas already generated by the sample according to the following scale:

S1 (mgHc/g rock)	CLASSIFICATION.
0.00 - 0.20	Poor
0.20 - 0.40	Fair
0.40 - 0.80	Good
0.80 - 1.60	Very Good
> 1.60	Excellent.

S2. - The residual hydrocarbons generated by the thermal cracking of the kerogen.

S3. - The amount of CO_2 of organic derivation generated during the cracking of kerogen.

Using these measurements a number of parameters for source rocks have been defined, (Nicholas etal., 1981).

S1 + S2 : The petroleum potential, this parameter is used as a measure of source rock richness, according to the following criterea:

S1 + S2 (mgHc/rock)	CLASSIFICATION
0.00 - 1.00	Poor
1.00 - 2.00	Marginal
2.00 - 6.00	Moderate
6.00 - 10.00	Good
10.00 - 20.00	Very Good
> 20.00	Excellent

S1/ (S1 + S2) : The production Index (P.I.), is a measure of the level of maturity and can reveal the presence of migrated hydrocarbons.

S1/ (S1 + S2)	CLASSIFICATION
< 0.1	Immature.
0.1 - 0.4	Oil window
> 0.4	Overmature.

Unusually high values can be interpreted as migrating hydrocarbons.

S2/T.O.C. : The Hydrogen Index (H.I.) relates the amount of residual hydrocarbon to the total organic carbon content.

S3/T.O.C. : The Oxygen Index (O.I.) relates the amount of residual carbon dioxide to the total organic carbon content.

The hydrogen index and the oxygen index reflect the elemental composition of the source rock kerogen. They can be plotted against one another to determine the kerogen type and therefore the source type, (Nicholas etal., 1981). High H.I. relative to O.I. typify oil-prone source or exinite kerogens. High O.I. however, typify gas prone source, or humic kerogens.

S2/S3 : The H/O ratio, in the absence of T.O.C. values, this parameter can be used as a gross indicator of kerogen quality. Arbitrary limits have been set to define oil and gas source.

5 or greater = oil source
5 - 2.5 = mixed oil and gas
2.5 or less = gas source

T max : The temperature corresponding to the S2 peak maximum. This value is used to indicate the state of organic maturity. The temperature increases with increasing maturity and indeed shows a very good correlation with other maturation parameters, such as vitrinite reflectance, (Tissot, 1984). The following scale can be used to relate T max values and maturity levels, (Page and Kuhuel, 1980).

T max (°C)	MATURITY
< 435	Immature
435 - 450	Oil generating
450 - 470	Gas generating
> 470	Over mature (cooked out)

3.16 GEOCHEMICAL ANALYSIS OF THE BELFAST MUDSTONE

- REVIEW OF RECENT RESULTS

There are three crucial factors for the characterization of a petroleum source rock:-

1. The state of maturity.

2. The amount of organic matter or organic richness.

3. The type or quality of organic matter.

From data provided by various petroleum companies, recently or actively involved in the Otway Basin, I have reviewed and discussed the source rock characteristics and potential of the Belfast Mudstone.

MATURITY

The vitrinite reflectance data, (fig.50) indicates that the basin is mature below 2675m, with the main oil window occuring to a depth of 4225m. This implies that in the offshore wells, Breaksea Reef #1A and Bridgewater Bay #1, the Belfast Mudstone is fully mature in Triton #1 (sidetrack), however, the upper Belfast Formation is immature, whilst onshore in Curdie #1, the Belfast Mudstone is fully immature.

A visual geochemical report of Breaksea Reef #1A also indicates that the maturity for oil was attained at approximately 2800m continuing to 4173m, where spore colours suggest post-maturity for oil. This is a similar oil window to that obtained from the vitrinite reflectance curve.

A measure of the production index (S1/(S1+S2)) further indicates that the Belfast Mudstone is mature in the Breaksea Reef #1A and Bridgewater Bay #1 wells, (see table,3).

Finally, the geothermal gradients of the Otway Basin, (see table,5), are seen to decrease from the east to west across the basin. If it is generally accepted that the onset of hydrocarbon generation occurs at a temperature of 60 °C, the temperature gradients indicate that a mature source rock section could be expected from a depth of about 1150m at Triton in the east, increasing to 2100m at Caroline in the west. There is therefore an apparent lagging of organic maturation behind temperature increase. This phenomena has also been noted in the Gippsland Basin, (Shibaoka & Bennett, 1977) and in the Bass Basin, (Nicholas etal., 1981).

SOURCE RICHNESS

From the total organic carbon values, (see table, 6), the Belfast Mudstone can be regarded as a fair to very good source rock with occasional results >2.0%. From the pyrolis results obtained from Breaksea Reef #1A and

Bridgewater Bay #1, (see table,3), the petroleum potential (S1 + S2), a measure of source rock richness, indicates that the Belfast Mudstone can be considered moderate. Using the extracted organic matter (E.O.M.) data from Triton #1, (see table,4) and plotting the hydrocarbon content (SATS and AROM) against T.O.C. (fig.51), the source rock richness is shown to be only fair.

SOURCE QUALITY AND KEROGEN TYPE.

Microscopic examination of the Belfast Mudstone samples reveals that the organic matter is predominantly inertinite, with only minor quantities of vitrinite and exinite, so indicating a poor gas potential.

This fact is further strengthened by the pyrolysis results (Breaksea Reef #1A and Bridgewater Bay #1) and the kerogen elemental results (Triton #1). The plot of the hydrogen index and the oxygen index for Breaksea Reef #1A and Bridgewater Bay #1, (fig.52) reflects the elemental composition of the source rock kerogen, much in the same way as a Van Krevelen plot for Triton #1, (fig.53). The results clearly indicate the poor quality (low Hydrogen content) of the organic matter and are suggestive of type III kerogen, although there are a few indications of oil potential.

GEOCHEMICAL ANALYSIS OF THE BELFAST MUDSTONE

FIG. 50 DEPTH REFLECTANCE CURVE FOR THE OTWAY BASIN

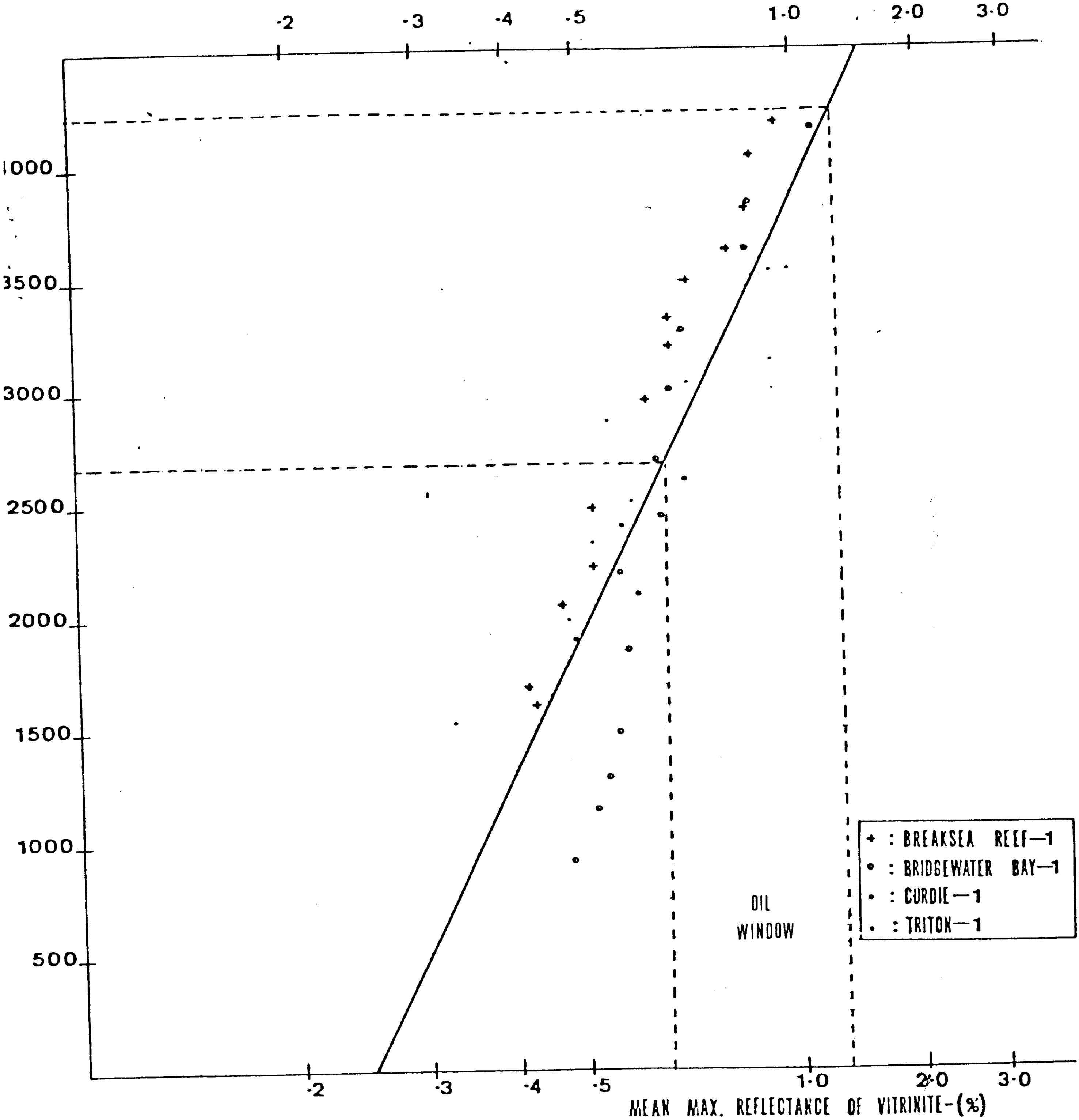


FIG. 51 SOURCE ROCK RICHNESS, FOR TRITON - 1 SIDETRACK

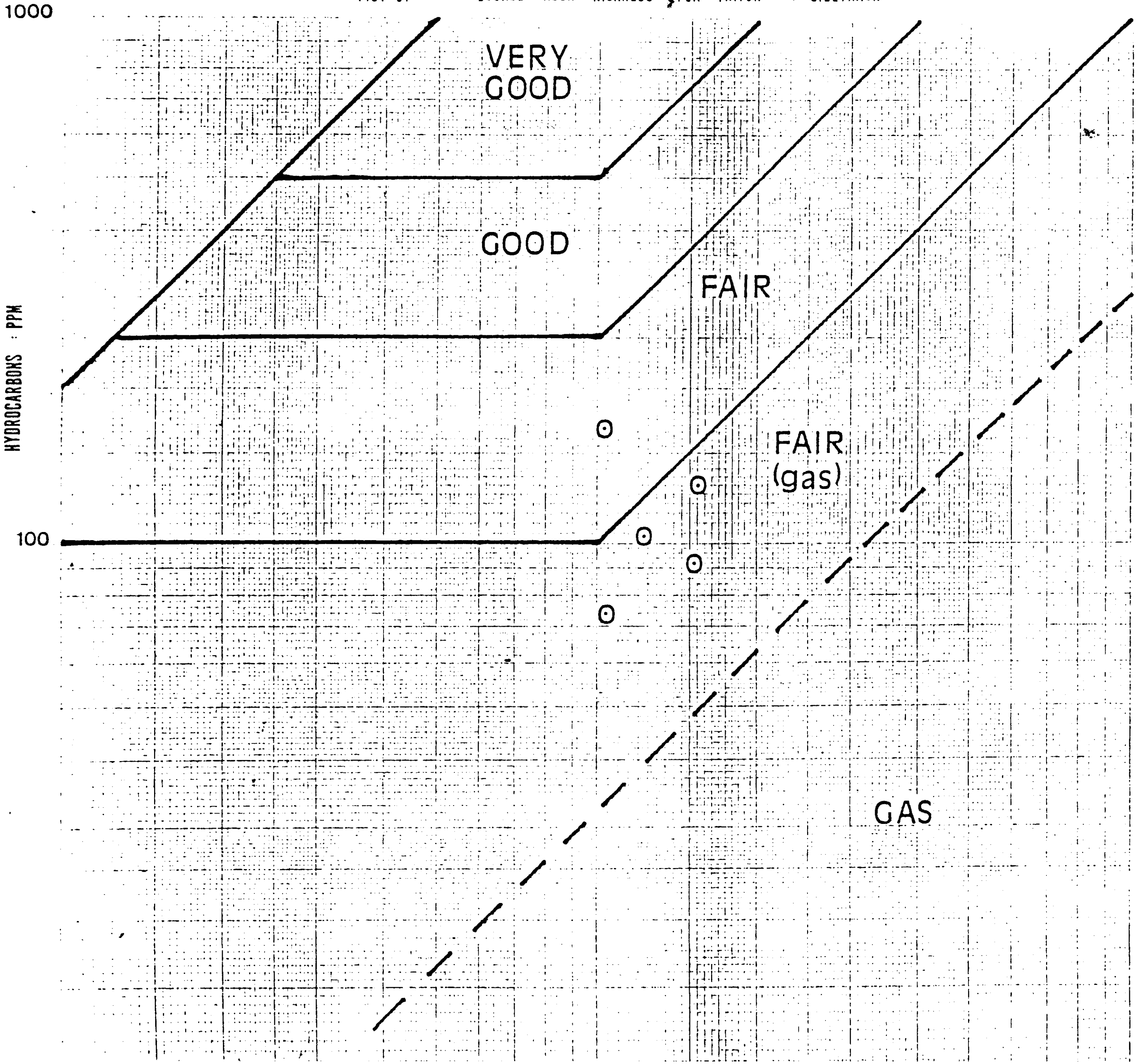


FIG. 52 HYDROGEN & OXYGEN INDICES PLOTTED FOR -

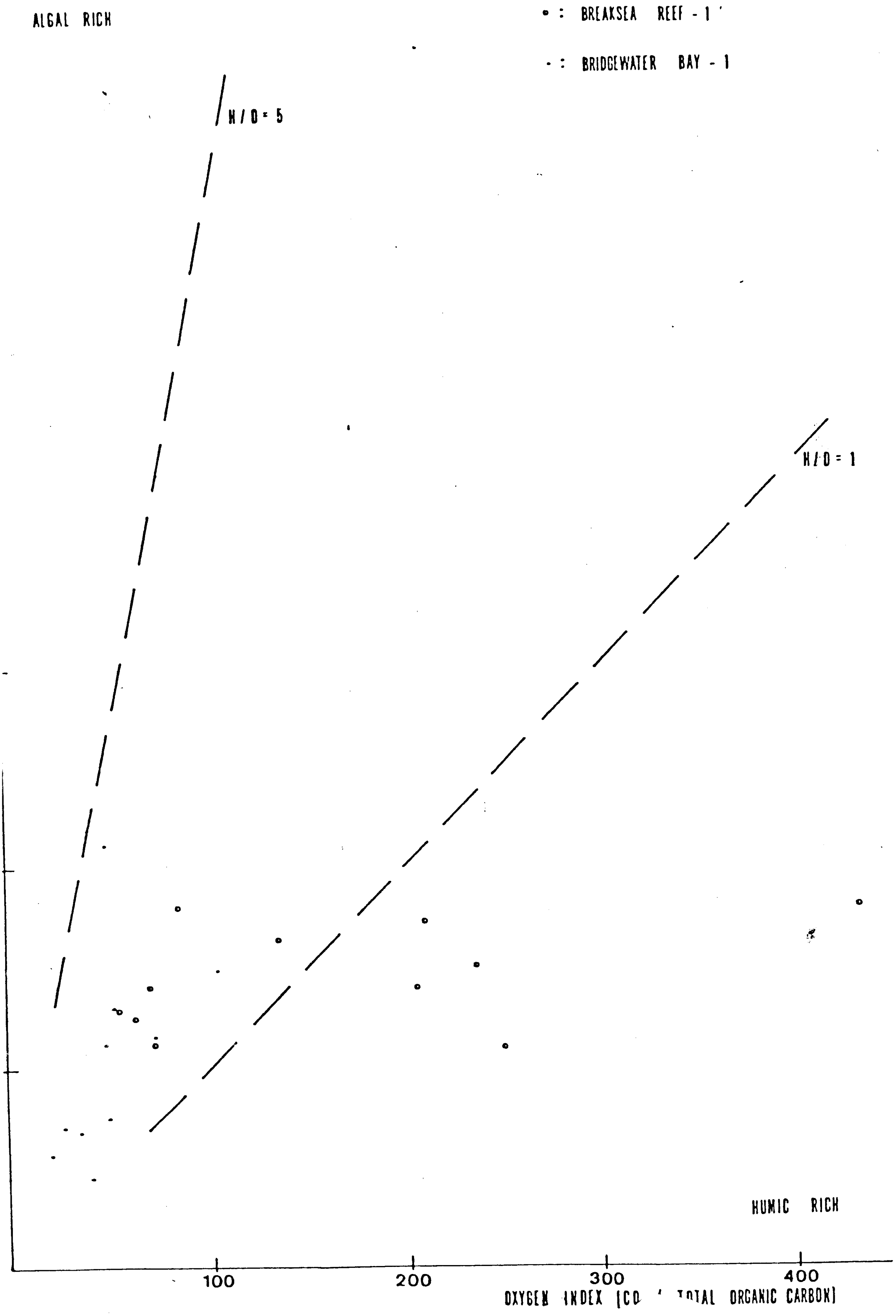


FIG. 53 BELFAST FRM: ELEMENTAL ANALYSIS OF KEROGEN FOR - TRITON - 1 SIDETRACK

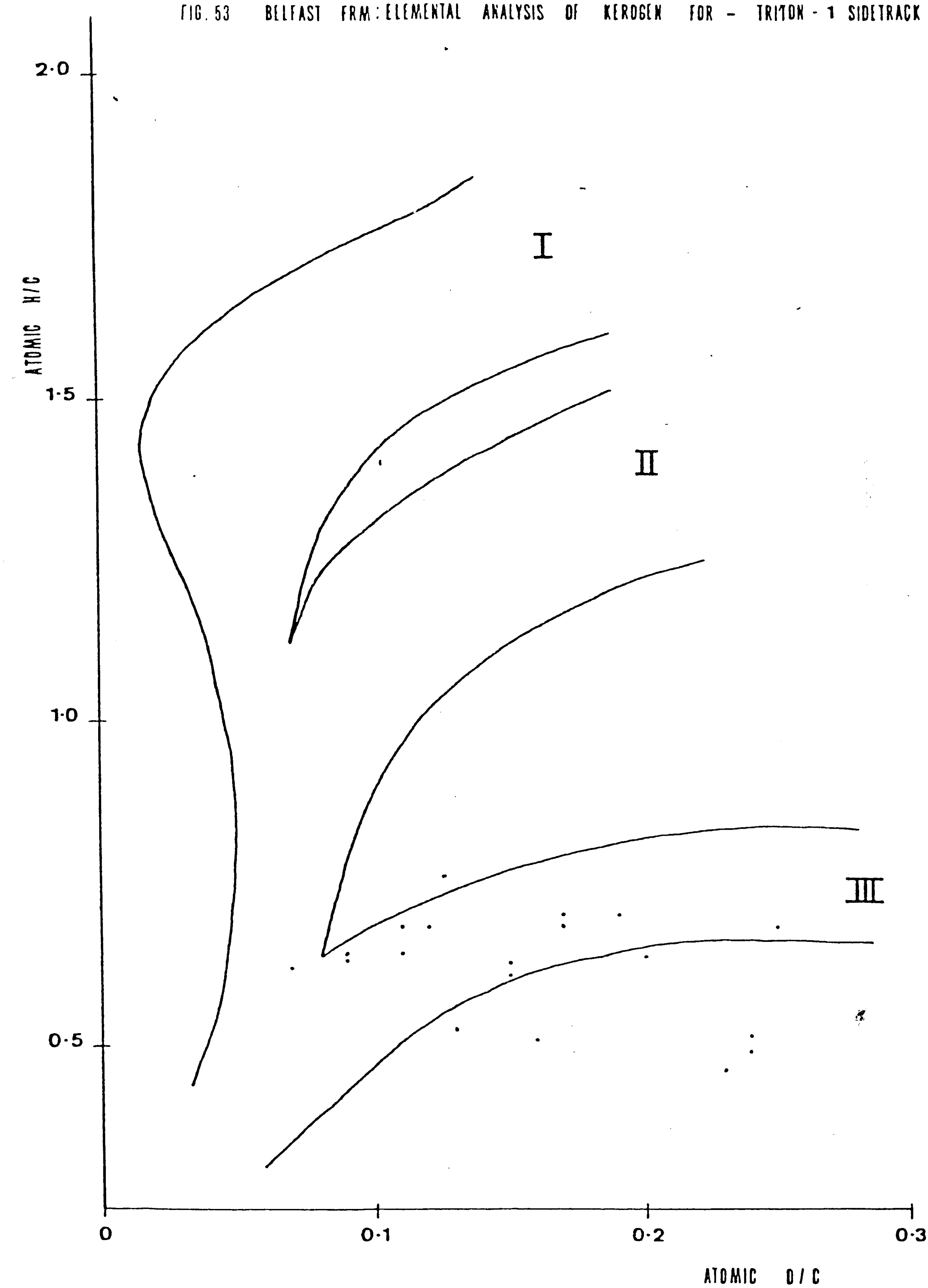


TABLE 2

VITRINITE REFLECTANCE (Ro) VALUES

TRITON # 1 (SIDETRACK)

DEPTH	Ro	FLUOR.	MACERAL TYPE
1530	0.33	Yel	I>V>E
1995	0.48	Or,Grn-Yel	I>E>V
2325	0.52	Yel-Or	I>E=V
2505	0.59	Yel-Or	I>E>>V
2865	0.55	Or	I>V>E
3028	0.71	Or	I>V (some oxidized V)
3125	0.93	None	Oxidized V>I>V
3520	0.93	None	Oxidized V>I>V
3527	0.99	None	Oxidized V>I>V

CURDIE # 1

DEPTH	Ro	FLUOR.	MACERAL TYPE
1900	0.49	Yel-Or	I>E=V
2100	0.60	Yel-Or	I>E>V
2400	0.57	Yel-Or	I>E>V
2600	0.70	Yel-Or	I>E=V (some oxidized V)

I = Inertinite
E = Exinite
V = Vitrinite

Grn = Green
Or = Orange
Yel = Yellow

TABLE 2 CONT.

VITRINITE REFLECTANCE (Ro) VALUES

BREAKSEA REEF # 1A

DEPTH	Ro	FLUOR.	MACERAL TYPE
1608.1	0.43	Yel-Or	I>>V>E
1694.1	0.42	Yel-Or	I>>V>E
2053.2	0.47	Yel-Or	I>>V>E
2222.0	0.52	Yel-Or	I>V>>E
2478.2	0.52	Or	I>>E>V
2944.0	0.62	-	-
3190.1	0.67	-	-
3310.0	0.67	Yel-Or	I>>E>V
3477.0	0.71	Yel-Or	I>>E>V
3613.1	0.81	Yel-Or	I>>E=V
3799.0	0.86	Yel-Or	I>>E>V
4027.1	0.88	Yel-Or	I>>E=V
4173.0	0.95	Or-Brn	I>>E=V

BRIDGEWATER BAY # 1

DEPTH	Ro	DEPTH	Ro
920	0.48	2690	0.64
1150	0.52	2990	0.67
1295	0.54	3265	0.70
1490	0.56	3620	0.86
1860	0.58	3830	0.87
2195	0.56	4150	1.29
2440	0.65		

I = Inertinite
E = Exinite
V = Vitrinite

Yel = Yellow
Or = Orange
Brn = Brown

TABLE 3

BELFAST MUDSTONE - ROCK EVAL PYROLYSIS

BREAKSEA REEF # 1A

DEPTH	TOC	S1	S2	S3	S1+S2	S1/(S1+S2) P.I.	S2/S3 H/O	S2/TOC H.I.	S3/TOC O.I.	T max
3194.0	0.71	0.36	0.79	1.82	1.15	0.32	0.43	111	250	438
3216.1	1.65	0.51	1.36	1.55	1.87	0.27	0.87	82	94	434
3245.0	1.49	0.33	1.35	1.35	1.68	0.20	1.00	91	91	434
3276.0	1.41	0.44	1.21	2.07	1.65	0.27	0.58	86	147	434
3310.0	1.76	0.51	2.17	1.37	2.68	0.19	1.58	123	78	440
3328.0	1.78	0.42	2.61	2.69	3.03	0.14	0.97	147	151	461
3351.0	2.92	1.18	3.73	1.83	4.91	0.24	2.03	126	63	433
3381.9	2.94	0.97	4.17	2.09	5.14	0.19	1.99	142	71	476
3460.0	0.63	0.11	0.40	12.90	0.51	0.22	0.03	63	2048	395
3477.0	2.34	0.54	3.19	1.79	3.73	0.15	1.78	136	76	451
3494.0	1.60	0.34	2.89	1.34	3.23	0.11	2.15	181	84	482
3516.0	1.66	0.37	2.21	2.07	2.58	0.14	1.06	133	125	439
3543.1	1.48	0.45	2.01	2.51	2.46	0.18	0.80	136	170	439
3570.0	1.13	0.58	1.94	2.38	2.52	0.23	0.81	172	211	453
3589.0	1.87	0.56	2.53	1.91	3.09	0.18	1.32	135	102	483
3613.1	1.16	0.35	1.28	1.35	1.63	0.22	0.94	110	116	441
3630.0	1.15	0.21	1.35	1.18	1.56	0.13	1.14	117	103	444
3638.0	0.48	1.72	0.77	3.15	2.49	0.69	0.24	160	656	414
3640.1	0.58	1.85	0.89	3.21	2.74	0.68	0.27	153	553	409
3648.1	0.56	1.03	0.42	11.19	1.45	0.72	0.03	75	1198	412
3655.0	0.87	4.01	1.56	3.77	5.57	0.72	0.41	179	433	415
3677.0	1.28	3.98	1.94	3.07	5.92	0.67	0.63	152	240	421
3693.0	1.38	0.46	2.27	1.95	2.73	0.17	1.16	164	141	479
3736.0	2.90	1.46	4.97	3.00	6.43	0.23	1.65	171	103	435
3751.0	1.96	0.34	2.79	1.38	3.09	0.11	1.99	140	70	470
3775.0	1.48	0.71	2.39	2.29	3.10	0.23	1.04	164	157	439
3799.0	2.18	0.50	3.05	1.70	3.55	0.14	1.79	140	78	468
3829.0	1.51	0.37	2.12	1.64	2.49	0.15	1.29	140	109	475
3868.0	2.68	0.62	3.42	1.51	4.04	0.15	2.26	128	56	445
3880.0	1.74	0.26	1.65	1.84	1.91	0.14	0.89	95	106	455
3987.0	1.49	0.38	1.67	1.09	2.05	0.19	1.53	112	73	450
4027.0	1.04	0.27	1.39	1.28	1.66	0.16	1.08	134	123	454
4053.0	0.93	0.25	1.16	1.00	1.41	0.18	1.16	125	108	478
4075.0	1.07	0.67	1.51	2.19	2.18	0.31	0.68	141	205	438
4173.0	1.06	0.48	1.14	1.20	1.62	0.30	0.95	108	113	458

TABLE 3 CONT.

LFAST MUDSTONE - ROCK EVAL PYROLYSIS

IDGEWATER BAY # 1

DEPTH	TOC	S1	S2	S3	S1+S2	S1/(S1+S2) P.I.	S2/S3 H/O	S2/TOC H.I.	S3/TOC O.I.	T max
2700	1.18	0.66	1.73	1.23	2.42	0.27	1.43	149	104	421
2750	1.12	0.13	0.63	0.24	0.76	0.17	2.63	56	21	483
2800	0.94	0.13	0.67	0.27	0.80	0.16	2.48	71	28	530
2850	1.06	0.13	0.30	0.20	0.43	0.30	1.50	28	18	428
2900	1.31	0.17	1.46	0.64	1.63	0.10	2.28	111	48	501
2945	1.26	0.22	2.66	0.63	2.88	0.08	4.22	211	50	536
3000	1.36	0.21	1.03	0.62	1.24	0.17	1.66	75	45	502
3050	1.31	0.25	1.71	0.70	1.96	0.13	2.44	130	53	505
3100	1.26	0.21	0.86	0.46	1.07	0.20	1.87	68	36	474
3150	1.46	0.19	0.66	0.61	0.85	0.22	1.08	45	41	433
3200	1.19	0.26	1.39	0.86	1.65	0.16	1.62	116	72	508
3250	1.29	0.12	0.68	0.58	0.86	0.21	1.17	52	44	435
3300	2.93	0.30	1.06	0.57	1.36	0.22	1.86	36	19	436
3350	1.86	0.24	1.02	0.53	1.26	0.19	1.92	54	28	454
3400	1.19	0.25	0.68	0.44	0.93	0.27	1.55	57	36	435
3450	1.23	0.33	0.73	0.61	1.06	0.31	1.20	59	49	436
3500	0.88	0.30	0.38	0.35	0.68	0.44	1.09	43	39	428
3550	1.55	2.72	1.40	0.75	4.12	0.66	1.87	90	48	434

3600 - TD : Invalid results due to sample contamination

TABLE 4

EOM DATA FOR TRITON - # 1 (SIDETRACK)

DEPTH	EOM (ppm)	HC (ppm)	NON HC (ppm)	EXTRACT COMPOSITITION %				
				SATS.	AROM.	N.S.O.	ASPH.	SULPHUR
1785	547	74	473	5.3	8.2	14.5	72.0	-
2085	1030	129	901	3.9	8.6	15.0	72.5	-
2415	682	92	590	3.8	9.7	11.4	75.1	-
2715	517	103	414	5.6	14.3	12.6	66.5	1.0
3075	734	167	567	8.6	14.3	13.3	63.9	-
3375	553	114	439	5.6	15.0	14.5	64.0	0.9

TABLE 5

GEOTHERMAL GRADIENTS IN THE OTWAY BASIN

WELL	GRADIENT ^{0}C/100m
CURDIE # 1	3.43
TRITON # 1 SIDETRACK	4.04
BRIDGEWATER BAY # 1	2.87
BREAKSEA REEF # 1A	2.50
CAROLINE # 1	2.09

TABLE 6

BELFAST MUDSTONE - TOC VALUES

TRITON # 1 (SIDETRACK)

DEPTH	TOC%	DEPTH	TOC%
1785	1.06	2505	1.41
1815	1.41	2520	1.52
1845	1.44	2535	1.41
1875	1.39	2565	1.37
1905	1.30	2580	1.41
1935	1.40	2595	1.29
1965	1.44	2625	1.29
1995	1.53	2655	1.27
2025	1.72	2685	1.39
2055	1.59	2715	1.23
2085	1.55	2730	1.15
2115	1.40	2745	1.26
2145	1.32	2775	1.18
2175	1.43	2805	1.29
2205	1.35	2835	1.02
2220	1.63	2850	1.04
2235	1.53	2855	1.01
2265	1.33	2895	0.99
2295	1.39	2910	1.16
2325	1.38	2925	1.14
2340	1.45	2955	1.04
2355	1.40	2985	1.13
2385	1.40	3015	1.03
2400	1.71	3028	1.09
2415	1.52	3045	0.89
2445	1.45	3075	1.03
2460	1.49	3105	0.91
2475	1.35	3125	0.75

AVERAGE : 1.30
MAXIMUM : 1.72 at 2025 m
MINIMUM : 0.75 at 3125 m

TABLE 6 CONT.

BELFAST MUDSTONE - TOC VALUES

BREAKSEA REEF # 1A

DEPTH	TOC%	DEPTH	TOC%
3194.0	0.71	3638.0	0.48
3216.1	1.65	3640.1	0.58
3245.0	1.49	3648.1	0.56
3279.0	1.41	3655.0	0.87
3310.0	1.76	3677.0	1.28
3328.0	1.78	3693.0	1.38
3351.0	2.92	3736.0	2.90
3381.9	2.94	3751.0	1.96
3460.0	0.63	3775.0	1.48
3477.0	2.34	3799.0	2.18
3494.0	1.60	3829.0	1.51
3516.0	1.66	3868.0	2.68
3543.1	1.48	3880.0	1.74
3570.0	1.13	3987.0	1.49
3589.0	1.87	4027.0	1.04
3613.1	1.16	4053.0	0.93
3630.0	1.15	4075.0	1.07
		4173.0	1.06

AVERAGE : 1.51
MAXIMUM : 2.94 at 3381.9 m
MINIMUM : 0.48 at 3638.0 m

TABLE 6 CONT.

BELFAST MUDSTONE - TOC VALUES

BRIDGEWATER BAY # 1

DEPTH	TOC%	DEPTH	TOC%
2700	1.18	3150	1.46
2750	1.12	3200	1.19
2800	0.94	3250	1.29
2850	1.06	3300	2.93
2900	1.31	3350	1.86
2945	1.26	3400	1.19
3000	1.36	3450	1.23
3050	1.31	3500	0.88
3100	1.26	3550	1.55

AVERAGE : 1.35
MAXIMUM : 2.93 at 3300 m
MINIMUM : 0.88 at 3500 m

CURDIE # 1

DEPTH	TOC%	DEPTH	TOC%
1895-1915	1.65	2090-2110	1.90
1990-2010	1.78	2190-2210	1.91
		2290-2310	1.84

AVERAGE : 1.81
MAXIMUM : 1.91 at 2190-2210 m
MINIMUM : 1.65 at 1895-1915 m

TABLE 7

BELFAST FORMATION : ELEMENTAL ANALYSIS OF KEROGEN FOR - TRITON - 1 SIDETRACK

DEPTH	N%	C%	H%	O%	ASH%	H/C	O/C	N/C
1845	2.70	75.69	4.41	17.20	5.65	0.70	0.17	0.03
1895	2.83	69.90	3.95	23.32	5.55	0.68	0.25	0.03
1945	2.81	74.19	4.30	18.70	3.92	0.70	0.19	0.03
1995	2.61	75.84	4.32	17.23	4.92	0.68	0.17	0.03
2095	2.39	73.77	3.86	19.98	4.87	0.63	0.20	0.03
2295	2.56	80.30	4.54	12.60	3.35	0.68	0.12	0.03
2395	2.36	71.82	3.13	22.69	2.56	0.52	0.24	0.03
2495	2.48	81.49	4.50	11.54	3.26	0.66	0.11	0.03
2695	2.01	83.50	4.55	9.94	2.48	0.65	0.09	0.02
2795	2.01	78.54	4.20	15.25	6.43	0.64	0.15	0.02
2895	2.18	72.15	2.97	22.70	2.11	0.49	0.24	0.02
2910	1.87	79.31	5.09	13.73	2.57	0.77	0.13	0.02
2995	1.87	83.70	4.46	9.97	2.22	0.64	0.09	0.02
3095	1.79	78.47	3.98	15.75	17.42	0.61	0.15	0.02
3260	1.76	72.80	2.80	22.63	3.11	0.46	0.23	0.02
3280	2.01	81.78	4.63	11.58	2.42	0.68	0.11	0.02
3305	1.89	80.50	3.55	14.05	3.21	0.53	0.13	0.02
3325	1.97	77.74	3.29	17.01	2.34	0.51	0.16	0.02
3375	2.18	85.95	4.42	7.45	15.30	0.62	0.07	0.02

3.17 SUMMARY

The Belfast Mudstone is mature in much of the thick offshore sequences (although immature onshore, nearer the basin margin). The depth - reflectance curve of the Otway Basin, (fig.50), results in a typical maturation pattern distinctive of a Gippsland - type basin, (fig.49). Such a pattern is characterized by a relatively low reflectance gradient and low intercept value, (Shibaoka and Bennett, 1977). Despite the maturity attained in the Belfast Mudstone and the good total organic carbon values, the nature of the organic matter in these sediments, inertinite, is typical of kerogen type III. This leads to a gas prone, rather than an oil prone source rock.

The depositional environment of the Belfast Mudstone, determined by various methods, was near shore to marginal marine, leading to a large influx of terrestrial, non-marine organic matter. It has also been suggested (P.A.O.C, 1983), that the depositional environment was oxidising, again lowering the kerogen oil potential. So although mature and organically rich, the quality of the organic matter is poor.

There are indications however, of kerogen with some oil potential and should anaerobic conditions have prevailed within the depositional environment, the source rock potential of the Belfast Mudstone would be greatly enhanced.

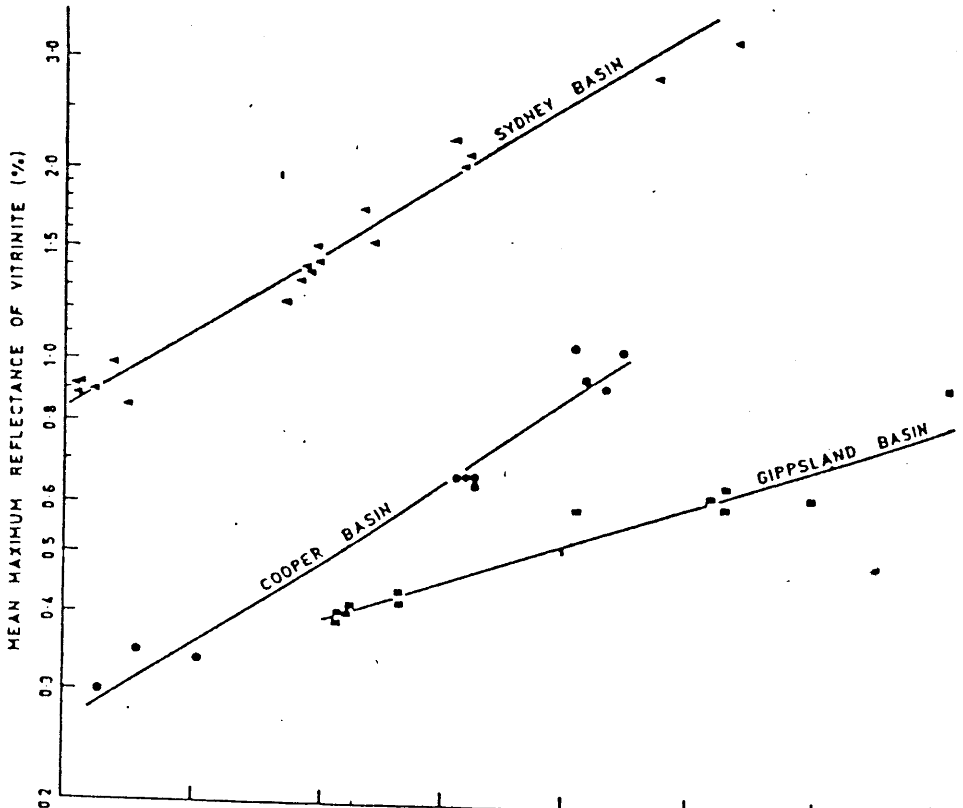


Fig. 49 Typical depth reflectance curves for three types of sedimentary basin:
- Sydney type basin.
- Cooper type basin.
- Gippsland type basin.

(After Shibaoka and Bennett, 1977).

CHAPTER 4

GEOCHEMICAL FOSSILS AND THEIR APPLICATION TO THE BELFAST MUSTONE

GEOCHEMICAL FOSSILS AND THEIR APPLICATION TO THE BELFAST MUDSTONE.

4.1 INTRODUCTION.

The value of organic geochemistry to petroleum exploration lies in the identification and distribution of various organic compounds found in crude oils and the source rocks that generate these oils. These compounds are known variously as "geochemical fossils" or "biological markers". The information fossil molecules can yield includes a knowledge of the source type, depositional environments, possible biodegradation and the possible resolution of oil/oil or oil/source rock correlation problems.

The application of various geochemical concepts and the use of geochemical fossils in petroleum exploration are reviewed in the following discussion.

4.2 GEOCHEMICAL FOSSILS

Geochemical fossils are defined as organic molecules which are synthesized by plants or animals and have survived unchanged, or suffered only minor alteration from their original structure during and after deposition of the organic matter in the sedimentary environment, (Eglington and Calvin, 1967).

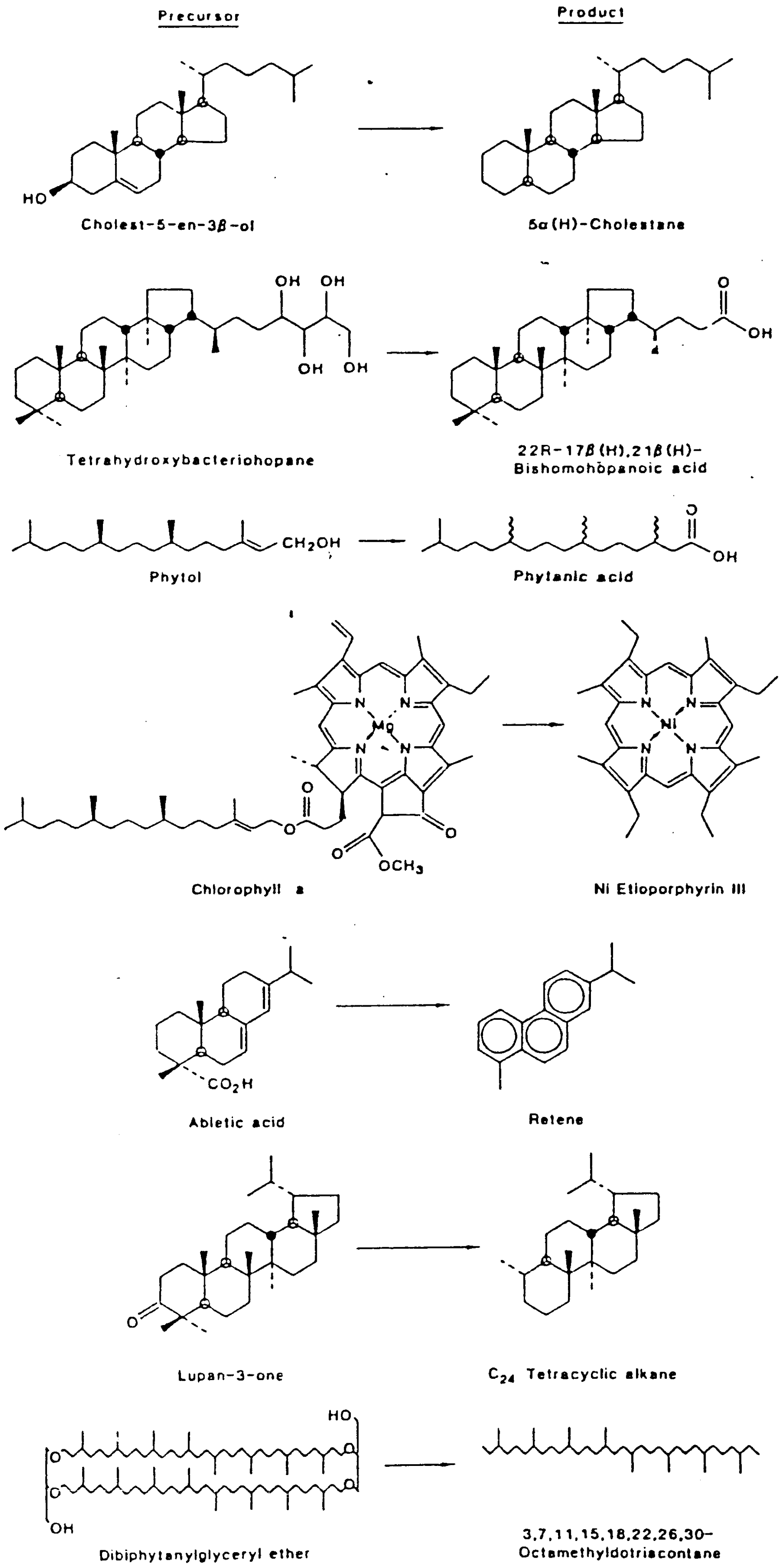
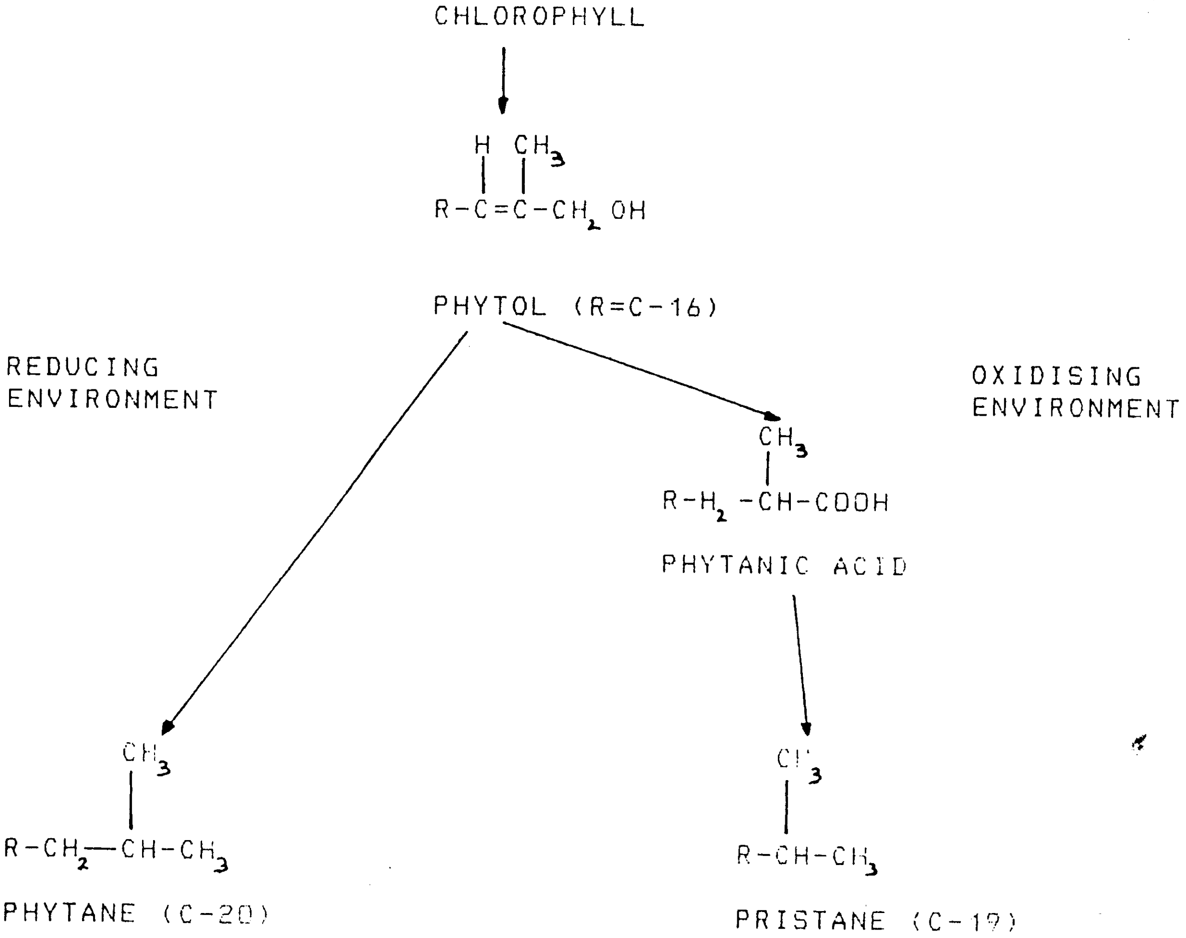


Fig. 54 Examples of precursor-product relationships. (After Mackenzie etal., 1982).

There are several classes of geochemical fossils, (fig.54) of which the more common classes are:-

n-ALKANES; these have been discussed in the previous chapter and are used to determine source type and maturity.

TERPANES; which include acyclic isoprenoids such as phytane and pristane and cyclic diterpenoids. Phytane and pristane are believed to be derived from chlorophyll and are used to indicate whether a sample was deposited in a reducing or oxidising environment, (fig.55).



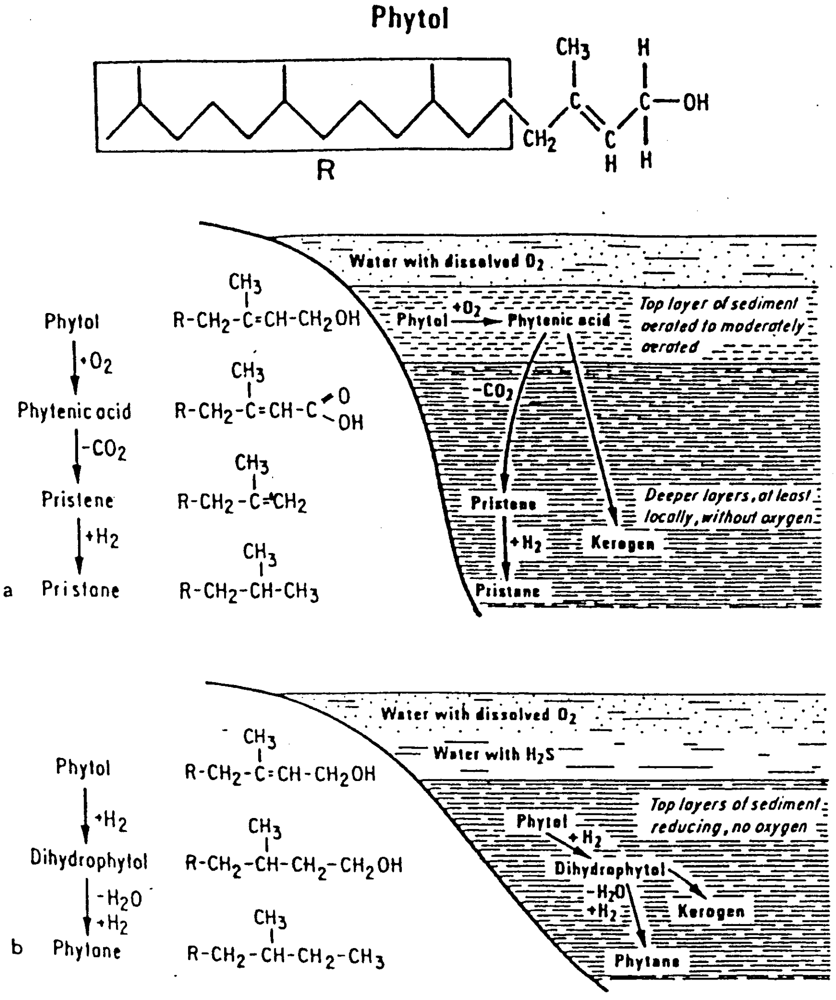


Fig. 55 Reductive and oxidative pathways from phytol to C-19 and C-20 isoprenoids.Pytol diagenesis in the presence of oxygen (a), and in the absence of oxygen (b). (After Tissot and Welte, 1984).

The cyclic diterpenoids indicate higher plants or resins and therefore a terrestrial source type.

STERANES AND TRITERPANES ; are derived from various algae, phytoplankton and bacteria. It is the steranes and a specific group of triterpanes, the hopanes, that have the greatest potential in petroleum exploration studies, (Philp and Gilbert, 1982).

Collectively these various classes reflect the conditions of production, preservation and accumulation of the sedimentary organic matter at the time of deposition. Since these conditions are variable in time and space, individual source rocks can be expected to carry a unique set of geochemical fossil markers, (Philp and Gilbert, 1980).

4.3 n - ALKANES

The relatively inert n-alkane molecules suffer little chemical alteration and so bear a strong imprint of their biochemical synthesis. They can however, become progressively diluted and obliterated with increasing depth of burial and age.

The use of n-alkanes to determine source type and maturity has been discussed earlier although further examples include the possible ecological and environmental significance inferred by a predominance of even carbon numbered, C-20 to C-30 n-alkanes. An environmental comparison of ancient and modern environments containing even carbon numbered n-alkanes and exhibiting similar distributions suggests that even carbon numbered n-alkanes are preferentially produced in highly saline, carbonate environments where aerobic and anaerobic bacteria have subsisted on the remains of blue-green algae, (Dembicki, Meinschein and Hattin, 1975).

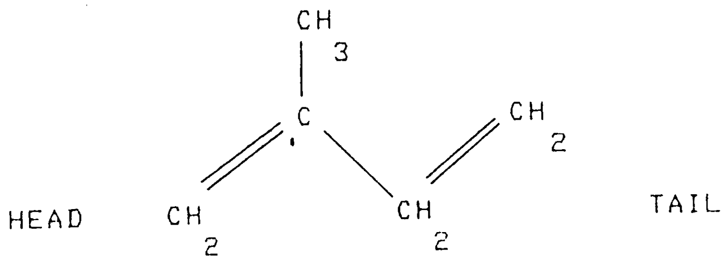
The generation of low molecular weight n-alkanes from organic matter in source beds has been used to ascertain depositional facies. The "organic facies" is determined by:

i) The nature of the biological material
ii) The depositional environment
iii) The early diagenetic conditions (oxidising or reducing).

When the organic facies is compared to the amount of hydrocarbons generated, a striking difference is revealed, depending upon the depositional facies. Organic matter derived from higher plants generate about 1000 times less C-2 to C-7 n-alkanes than organic matter derived from marine organisms, (Leythaenser, Schaefer and Weiner, 1979).

4.4 TERPANES

The terpanes are constructed from a biological precursor with the carbon skeleton of isoprene:



ISOPRENE UNIT

Common geochemical fossils of the terpane family include:

i) Regular isoprenoids; acyclic, branched, saturated molecules with a methyl group on every forth carbon atom. This implies a "head-to-tail" linkage of the isoprene units.

ii) Irregular isoprenoids; used to describe molecules with "head-to-head" or "tail-to-tail" linkage.

iii) Cyclic diterpenoids; commonly found in terrestrial plant resins.

The best known and most common acyclic isoprenoids are:

PRISTANE : 2,6,10,14,tetramethylpentadecane, (C-19)

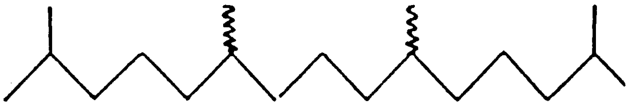
PHYTANE : 2,6,10,14,tetramethylhexadecane. (C-20)

The pristane/phytane (Pr/Ph) ratio has been widely used to obtain information on palaeoenvironments.

Environments consisting of an anoxic water column above anoxic sediments, (fig.56c) have low Pr/Ph values < 1. Alternating oxic/anoxic conditions, (fig.56b) result in Pr/Ph values 1. Totally oxic conditions, (fig.56a) produce Pr/Ph values > 1. Anoxic conditions evidently preserve the C-20 isoprenoid skeleton resulting in low Pr/Ph values, whilst the oxic conditions cause a greater degradation so that the C-20 skeleton is less likely to survive intact in the sediment leading to a high Pr/Ph ratio, (Didyk etal., 1978).

The stereochemistry of pristane has been used to provide information on the increasing maturity of a sediment.

PRISTANE



Isomer compatible
with an origin
from phytol, retains
the configuration at
the two chiral centres.

6(R),10(S).

Isomers from phytol
via reactions
leading to
epimerisation of
methyl branched
positions

6(R),10(R)

6(S),10(S)

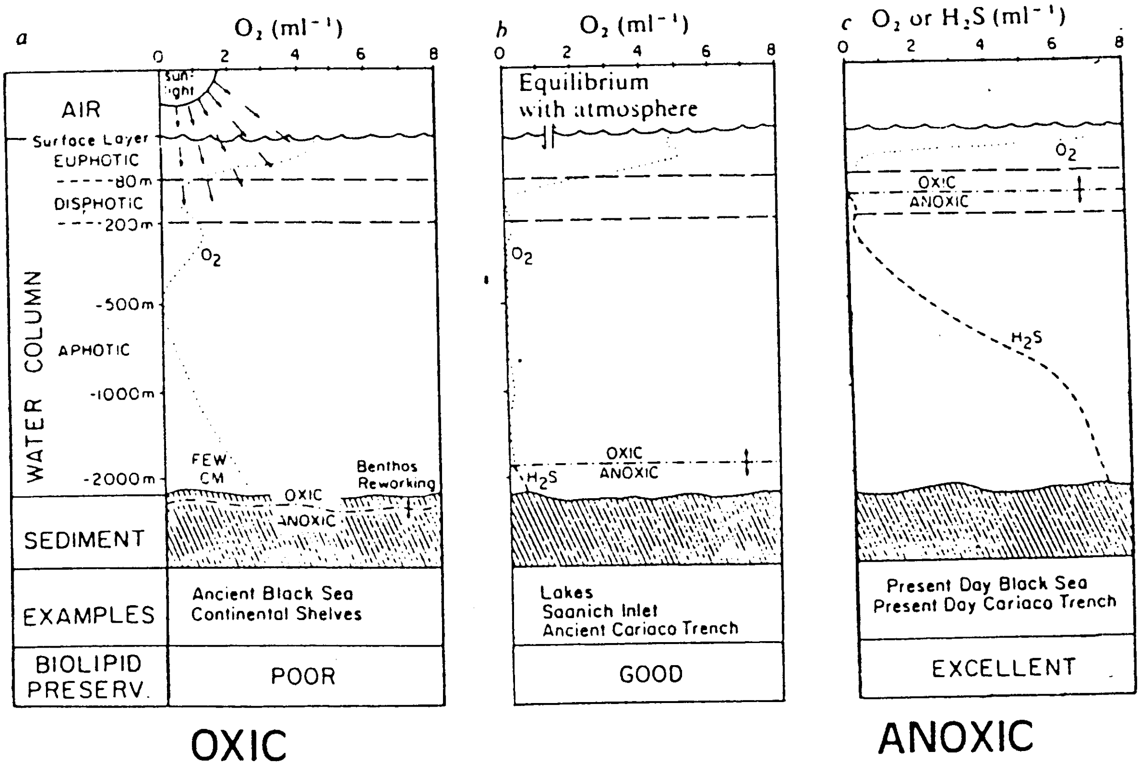


Fig. 56 A schematic representation of typical sedimentary environments. The water is divided into three zones:

- Euphotic : Photosynthesis occurs.
- Disphotic : Dim light and no effective plant production.
- Aphotic : Absence of light and no plant production.

Three levels of the oxicity/anoxicity interface are shown (_._._._._._). (After Didyk etal., 1978).

SAMPLE	LOCATION	AGE (m.y)	ISOMER ABUNDANCE		
			RS	RR	SS
Zooplankton	N.Sea	-	100	0	0
Messel Shale	W.Germany	50	100	0	0
Green River Shale	U.S.A.	50	80	20	
Irati Shale	Brazil	300	50	50	
Green River Crude	U.S.A.	50	50	50	
Halibut Crude	Australia	55	50	50	
Djatiburang Crude	Java	35	50	25	25

Table 8. (After Patience, Rowland and Maxwell 1978).

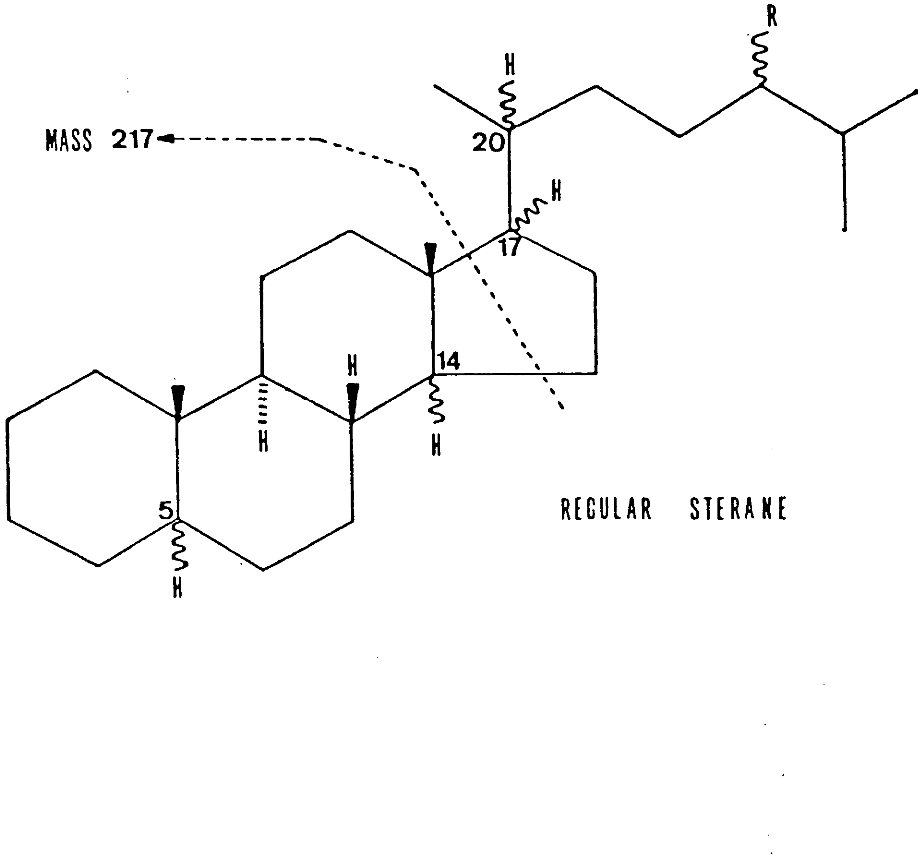
With increasing geological maturity there is a loss of stereospecificity in phytol-derived pristane. The immature zooplankton and Messel shale contain only the RS isomer. The mature samples however,exhibit varying amounts of RR/SS isomer configurations, (Patience, Rowland and Maxwell, 1978).

Whilst pristane and phytane are by far the most widely studied acyclic isoprenoids, the geochemical attributes of other isoprenoids have been studied. The occurrence of a regular C-25 isoprenoid hydrocarbon in highly saline sediments may represent a biological marker, possibly typical in representing a lagoonal, saline environment, (Waples, Haug and Welte, 1974).

Finally, unusual head-to-head linked isoprenoid hydrocarbons, found in the cell wall membranes of thermoacidophilic bacteria, have also been detected in petroleum. These two facts have been used as evidence for a ubiquitous and substantial contribution of bacterial cell wall lipids to crude oils, (Moldowan and Seifert, 1979).

Tricyclic diterpenoids are generally used as source type indicators and correlation parameters. Diterpenoids are widely distributed within the resins of higher plants, and the stability of diterpenoid hydrocarbons makes them extremely valuable as indicators of higher plants and resin contribution to sediments, coals and crude oils, (Philp, Simoneit and Gilbert 1981).

4.5 THE STERANES



REGULAR STERANE

Steroids form a group of compounds that are widely distributed in living organisms and can be used to illustrate the advances that have been made in understanding the biological origin and geological fate of the organic compounds in sediments.

The precursor sterols are successively transformed into stenones, stanones, stanols, sterenes and finally steranes, (fig.57), initially by microbial activity and later by physiochemical constraints, (Philp, 1981). The steps in this transformation result in a complex web linking biogenesis, diagenesis and catagenesis. Reactions involved during the geochemical fate of steroids allows an assessment of:-

1. Early diagenetic effects.
2. The region of thermal maturation
3. The aspects of the environment of deposition.

During early diagenesis, steroidal biolipids are converted into geolipids whereby their functionalities are altered by reduction, dehydration and hydroxylation, the stereochemical features however remain largely unaffected. As maturity increases, in late stage diagenesis and early catagenesis, the stereochemical features are altered by isomerization. Finally increasing maturity during late stage catagenesis results in aromatization of the molecules from mono- to tri-aromatics, (fig.58).

Throughout diagenesis and catagenesis the biolipids are

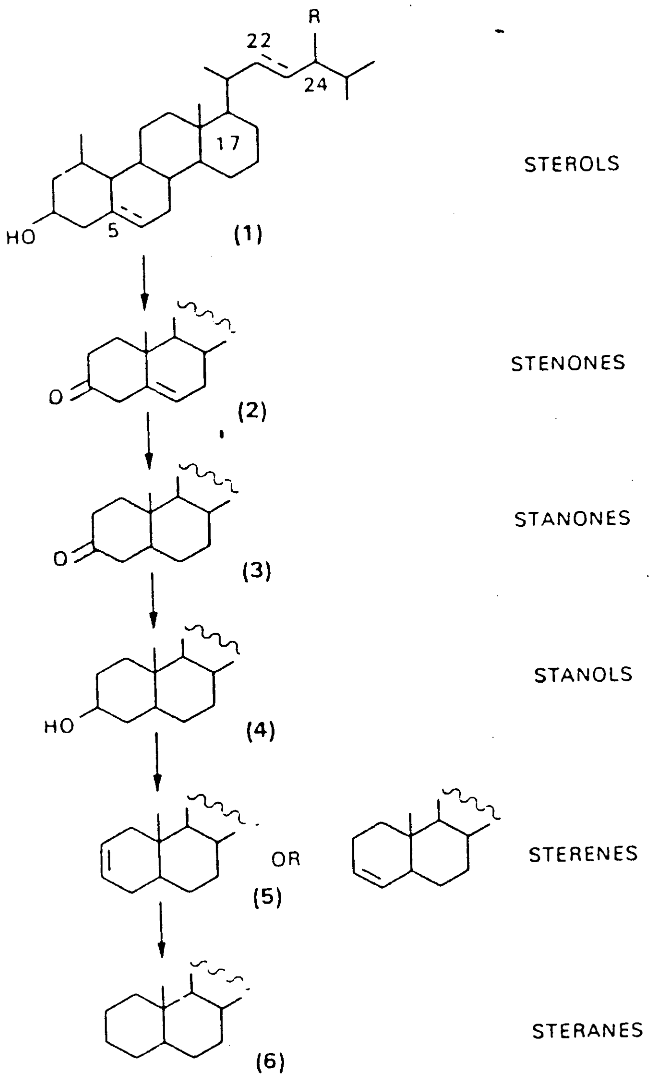


Fig. 57 Structures and inter-relation of various sterols found in contemporary envionments. (After Philp, 1981).

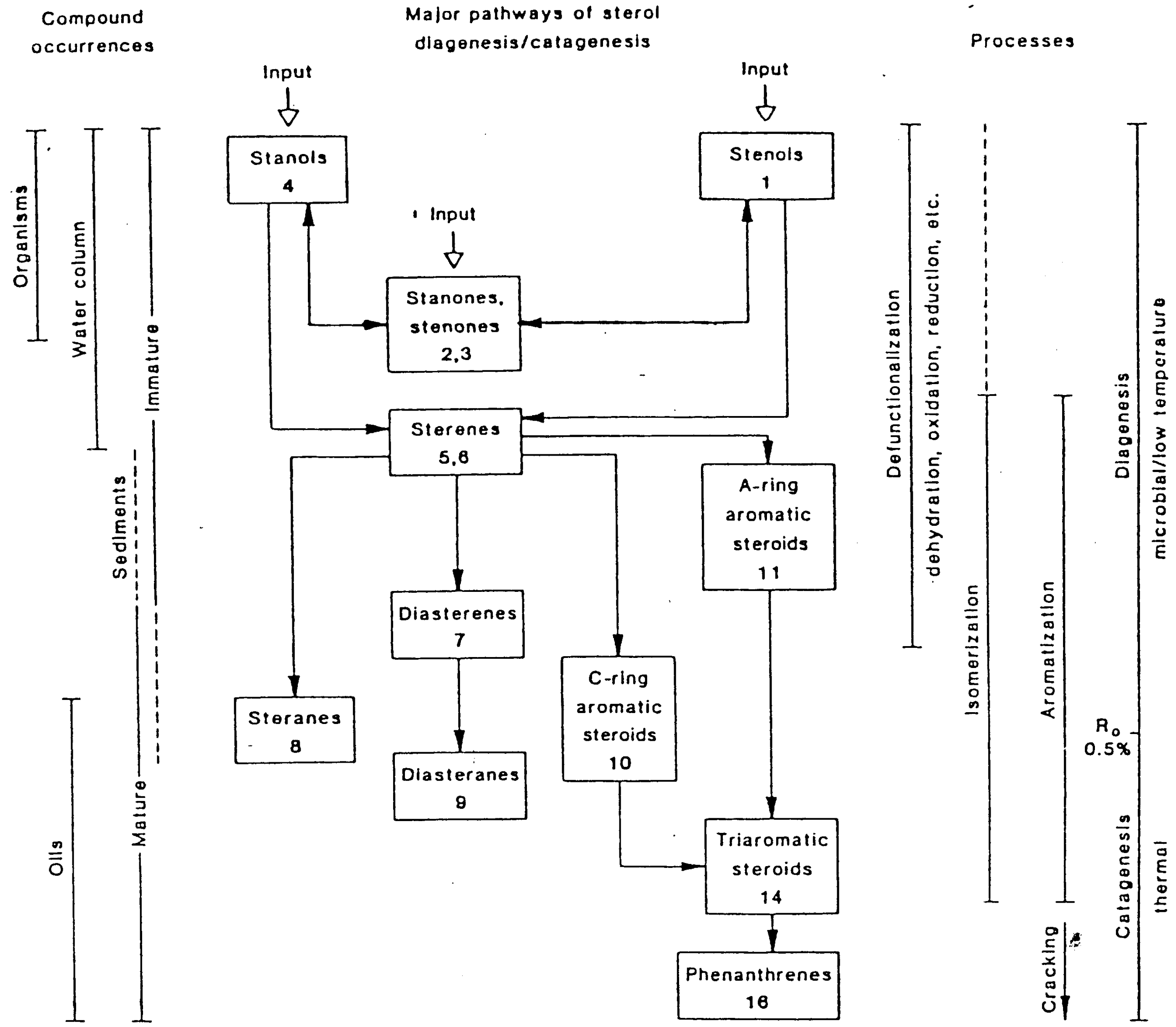


Fig. 58 A schematic summary of the presumed geological fate of the major natural product steroids.The biological and geological ranges of occurence of steroids and the main processes that effect the transformation of steroids are also shown. (After Mackenzie etal., 1982).

altered in a systematic, rather than random manner, with the relative abundance of the various steroidal lipids showing the progressive effects of diagenesis and catagenesis.

Sterol to sterane alteration can therefore be summarized as follows, (fig.59):

1. Microbial reduction of Δ^{5} - sterols to 5α(H) (and 5β(H)) stanols in the surface sediments.
2. Dehydration of the stanols to Δ^{2} - sterenes.
3. Δ^{2} - sterenes to $\Delta^{13(17)}$ - sterenes (which have been identified in older mature shales).
4. Saturated steranes.

Therefore the identification of Δ^{2} - sterenes in a sediment would suggest that only the earliest stage of diagenesis had occurred, (Dastillung and Albrect, 1977).

Correlating geochemical fossil data with depositional environments is apparent in that the geolipid markers can preserve a signature of the particular depositional environment. These markers can be used to assess the lipid input from algae, bacteria and terrestrial higher plants.

Because of the structural complexity of the steranes, their usefulness as geochemical fossils is greatly increased and has resulted in many studies that relate steranes to source type and maturity.

Sterol distribution has been suggested as an indication of various ecological systems, (Wen-Yen Huang and Meinschein, 1979). Plots of the C-27, C-28 and C-29 sterol contents of

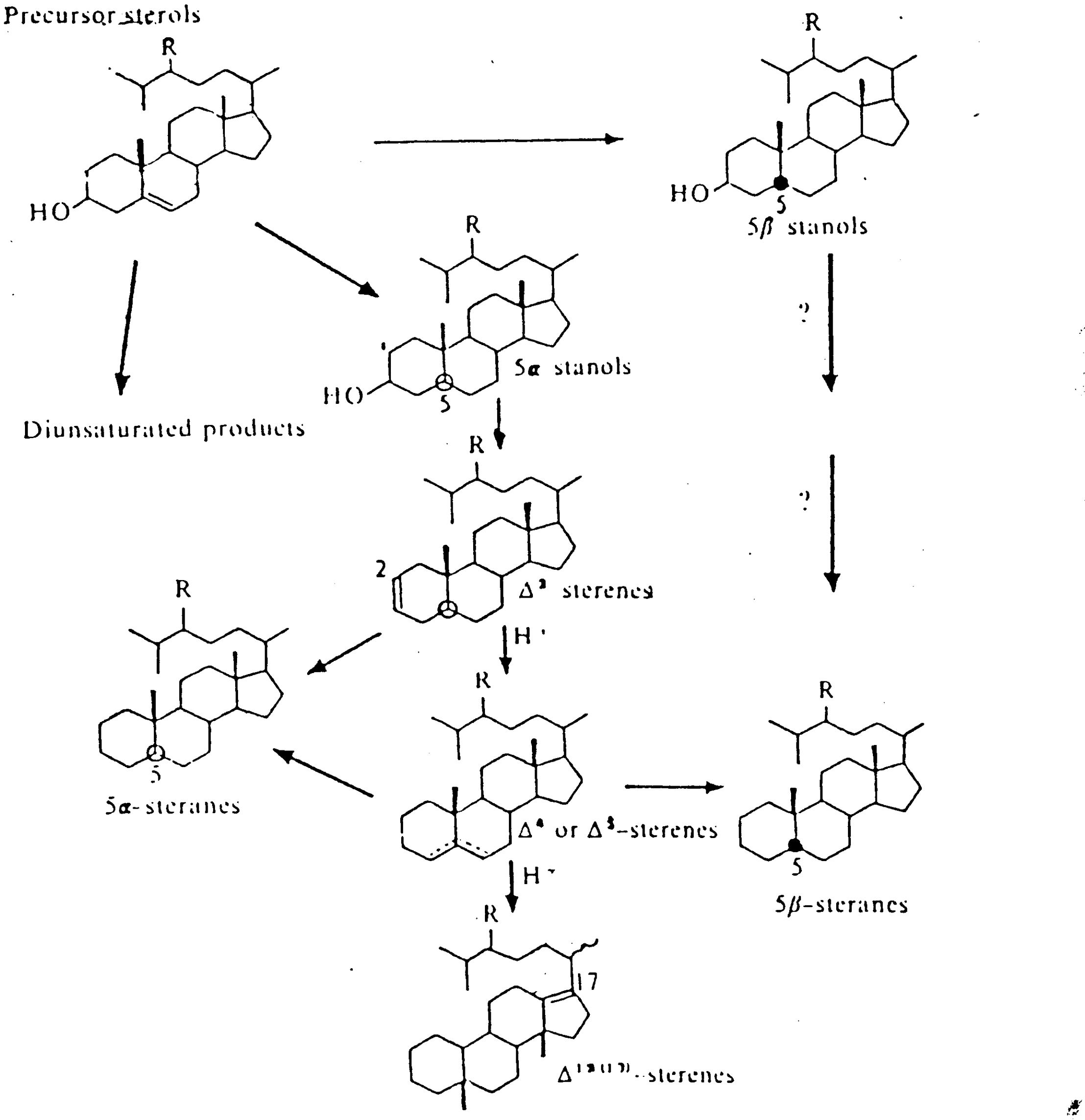


Fig. 59 Early transformation of sterols in the geological environment.
? = Process inferred.
R = H, CH_3, C_2H_5.
(After Dastillung and Albrecht, 1977).

marine plankton, higher plants, soils and lacustrine and marine sediments form discrete areas on a triangular diagram (fig.60). The dominant sources of C-27 sterols (zooplankton) and C-29 sterols (higher plants) exert the principal control, whilst C-28 sterols apparently play a less prominant role as both terrigenous and marine sources exist for these sterols. Although relationships between sterols and steranes are not fully known it is generally accepted that algal organic matter contain steranes in which the C-27 compounds are more abundant, whilst organic matter rich in land plants usually contain abundant C-29 compounds.

Although sterane structures are drawn in two dimensions, in reality these compounds have very complex three dimensional configurations. The configuration is actually determined by the spatial arrangement, or stereochemistry, at certain positions in the compound. The stereochemistry in turn will vary depending on the history experienced by the compounds after deposition.

For example, at the position numbered 5, 14 and 17 in the sterane structure there are two possible configurations referred to either as (H-atom is below the plane of the rest of the molecule) or (H-atom is above the plane of the rest of the molecule). Furthermore, the position numbered 20 is referred to as an asymmetric carbon atom and can give rise to two different arrangements referred to as either R or S, (fig.61).

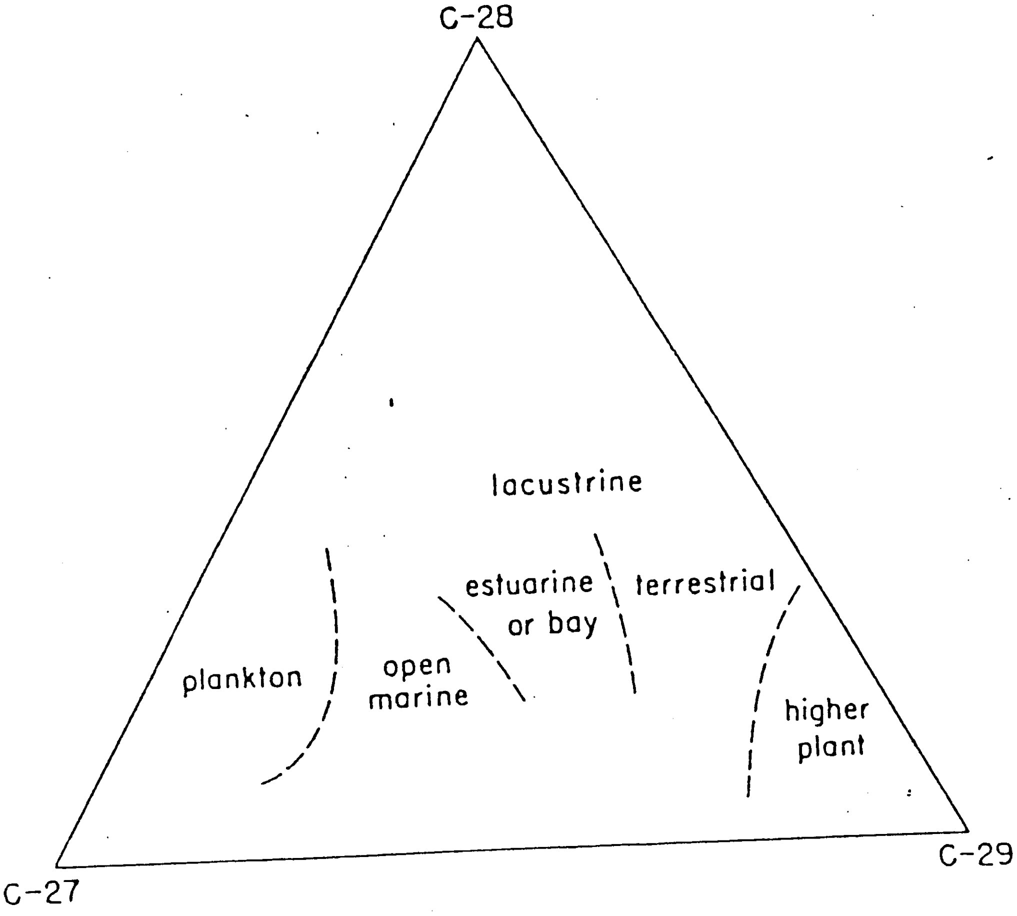


Fig. 60 Relationship between the sterol composition in biological sources and in the open marine, esturine or bay, lacustrine and terrigenous ecosystems. (After Wen-Yen Huang and Meinschein, 1979).

The biologically produced 5α(H),14α(H),17α(H) 20R stereoisomer in a C-29 sterane is converted in sediments to an approximately equal mixture of itself and the corresponding 5α(H),14α(H),17α(H) 20S configuration, (MacKenzie etal., 1982). The ratio of C-29, $\alpha\alpha\alpha$ 20S/($\alpha\alpha\alpha$ 20R+ $\alpha\alpha\alpha$20S), expressed as a percentage is about 25% at the onset of oil generation and increases almost linearly to a value of about 50% at the peak of oil generation. It has also been noted that the biologically produced 5α(H), 14α(H),17α(H), steranes are partially converted during catagenesis to the corresponding 5α(H),14β(H),17β(H), series. The percentage of the C-29 $\alpha\beta\beta$ component in the total C-29 steranes is another measure of maturation. The value of this parameter is about 25% at the onset of oil generation and increases exponentially to a value of about 70% at the peak of oil generation. The resultant stereochemistry depends on:

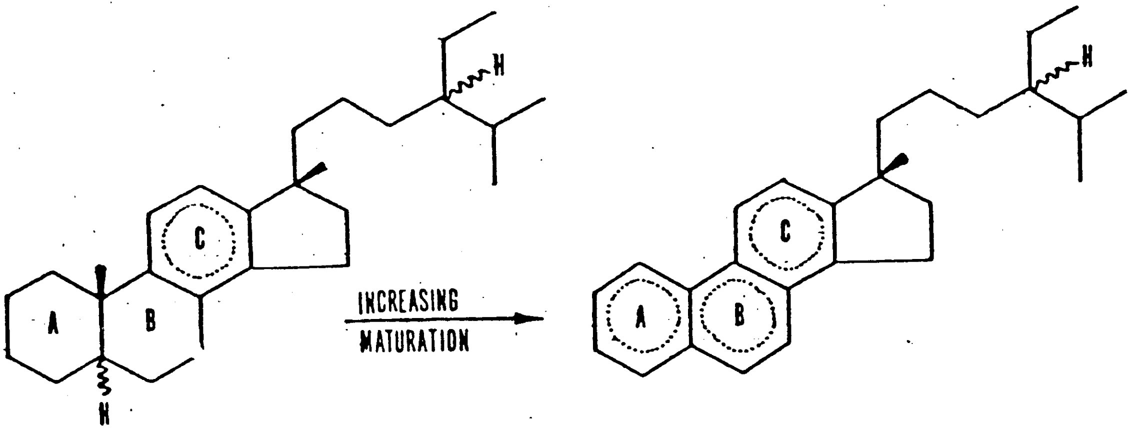
i) The source material

ii) Whether biodegradation of the precursors or products has occurred.

iii) The degree of maturation.

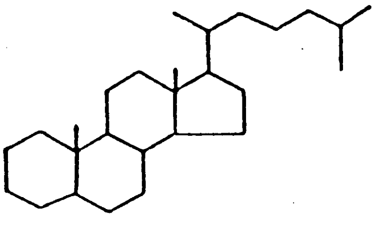
Thus, the stereochemistry of the sterane mixtures that are generated and found in crude oil and source rock extracts are unique for a particular set of conditions of the formation, (Philp and Gilbert, 1982).

Aromatic steroid hydrocarbons have been examined in a number of sedimentary sequences which contain a range of skeletal types, including two families, ABC-ring tri-aromatics and C-ring mono-aromatics, (Schaefle etal., 1978), (MacKenzie, Lamb and Maxwell, 1982). Changes in the relative abundances of these families with increasing maturation indicate that aromatization of C-ring mono-aromatics will occur in rings B and A with the loss of the nuclear methyl group on the A-B ring junction, (MacKenzie etal., 1982).

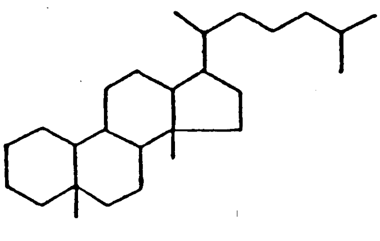


Aromatization of steranes.

Diasteranes, or rearranged steranes, are not produced biologically but are formed during early diagenesis from sterane precursors.



Regular Sterane

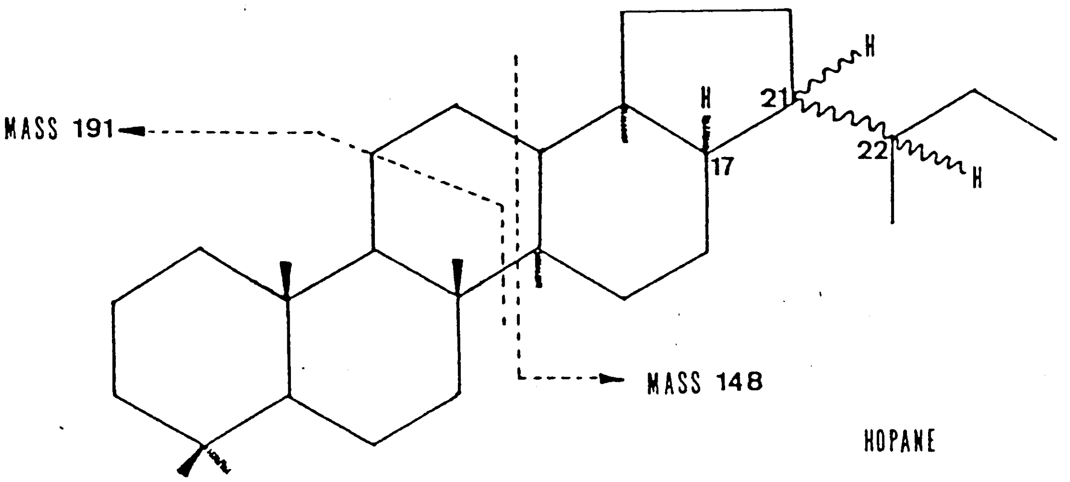


Diasterane (rearranged sterane)

This class of geochemical fossils reflects the complexity of the changes undergone by steroids in the geological environment. The diasteranes are useful as correlation markers among crude oils or between crude oils and their source rocks, (Ensminger, Joly and Albrecht, 1978).

The usefulness of steranes as geochemical fossils has been reviewed in the discussion above. Many workers have been able to use steranes in geochemical correlation studies, maturity studies and determining the thermal history of sediments. The extensive amount of literature and research on steranes bears witness to the growing importance of these geochemical fossils when investigating petroleum formation and its occurrence.

4.6 TRITERPANES - THE HOPANES



HOPANE

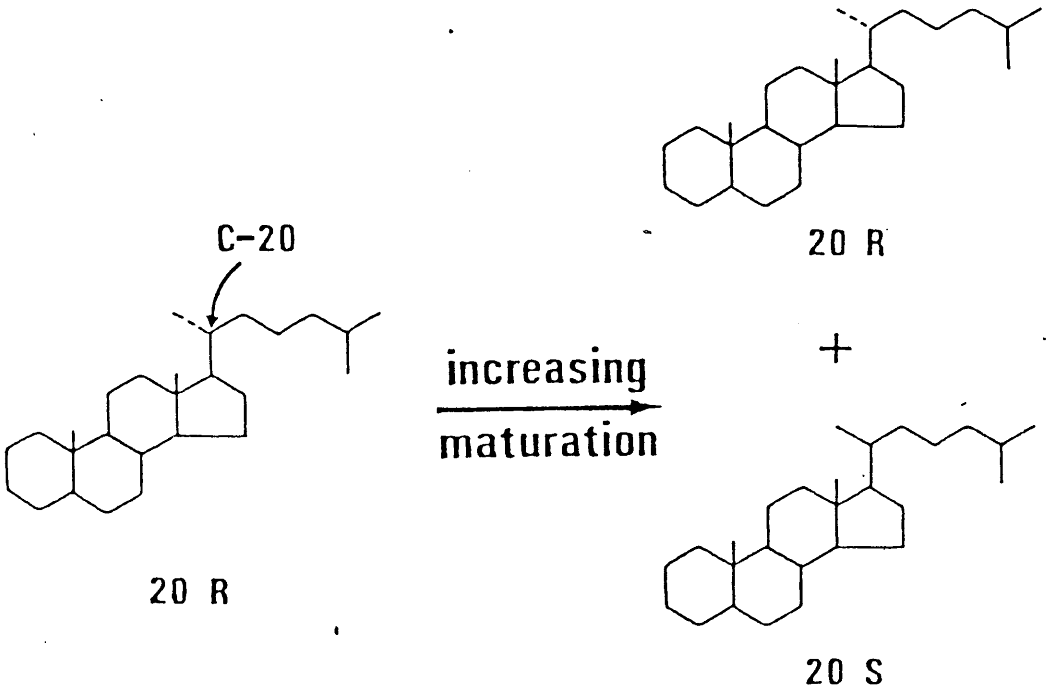


Fig. 61 Changes of configuration at C-20 in the steranes during burial.With increasing maturation the predominance of 20R is changed to equal amounts of 20R ans 20S. (After Tissot and Welte, 1984).

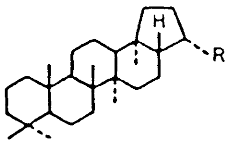
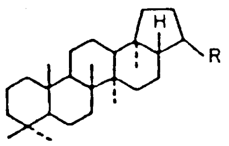
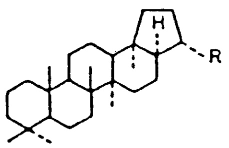
Structure	Series	Occurrence	Example of the Eocene shales in the Rhine Graben Locality maximum burial depth
	ββ-Hopane	Immature Sediments *(also in living organisms)*	Messel 200m
	βα-Hopane	Immature Sediments *(also in living organisms)*	
	αβ-Hopane	Sediments only	Stockstadt 1800m

Fig. 62 Stereochemistry of the hopane series. (After Tissot and Welte, 1984).

The pentacyclic triterpanes of the hopane family (C-27 to C-35) are widespread constituents of the membrane lipids in prokaryotes. It has been suggested that the hopanoids act in a structural role within the prokaryotic cells, in the same way as the sterols within the eucaryotic cells (Ourisson, Albrect and Rohmer, 1979).

It has been shown that the hopane-type triterpanes are ubiquitous biological markers and are found in almost every sample of sedimentary organic matter, (Ensimiger etal., 1973), (Van Dorsselaar etal., 1974). This includes the widest variety of samples, including young muds, lake or sea sediments, petroleums, lignites, shales and coals with ages ranging from a few years to 5×10^8 years.

Hopanes, like the steranes have a very complex polycyclic ring structure and are similarly sensitive to stereochemical changes during diagenesis and catagenesis. Hopanes can have two different stereochemical configurations at the carbon atom positions 17 and 21, resulting in three stereochemical series of hopane-type triterpanes:

(17α , 21β) H-hopane or $\alpha\beta$ hopane

(17β , 21α) H-hopane or $\beta\alpha$ hopane

(17β , 21β) H-hopane or $\beta\beta$ hopane

The α and β respectively refer to the position of the hydrogen atom at that carbon number being below or above the plane of the ring. Living organisms always synthesize

$\beta\beta$ hopane-type triterpanes (and sometimes the subordinate $\beta\alpha$ hopane-type). These configurations are thermally unstable and as the organic material is buried and subjected to maturation changes, the more thermally stable isomer $\alpha\beta$ hopane-type is generated, (fig.62). The ratio of (17β(H), 21β(H)) / (17α(H), 21β(H)) hopanes in source rock extracts thus decreases with increasing maturity, (Philp and Gilbert, 1982).

In more advanced stages, those hopanes which have a side chain of four or more carbon atoms, (C-31 to C-35 compounds) also have the ability to form R and S isomers at the C-22 position. Hopanes naturally occur with the 22R configuration, with increasing maturity however they convert to the 22S form and produce a mixture of 22R and 22S hopanes. The relative amounts of these R and S isomers reflects the thermal maturity of the oil or rock extract.

As with steranes, the stereochemistry of hopanes can provide vital clues to source rock maturity and in many cases this information is complementary to that obtained from the steranes, (Mackenzie etal., 1980). The use of hopanes in oil-oil, oil-source rock correlation has also been well documented. e.g. The geochemical correlation of Australian crude oil, (Philp, Gilbert and Friedrich, 1982) and the correlation of crude oils from the San Jorges Basin, Argentina, (Philp, 1983).

Finally, the relative abundances of steroids and triterpenoids in sediments can be used to determine the main source type.

Steroid-rich sediments are usually marine or lacustrine and in this respect, plankton may be the major source of steranes in geological conditions. Thus the ratio of steranes to hopanes in crude oils may indicate the origin of the main source material, i.e. planktonic when the sterane / hopane ratio is high, terrestrial when it is low, (Tissot and Welte, 1984).

To summarize, geochemical fossils are used for correlations (oil-oil and oil-source rock), for the reconstruction of depositional environments, as indicators of diagenesis and catagenesis and in determining the degree of biodegradation. Indeed the application of various biological markers has been able to assist the petroleum explorationist in palaeo-environment reconstruction, (Seifert and Moldowan, 1981).

4.7 ISOLATION AND ANALYSIS OF GEOCHEMICAL FOSSILS

The isolation, identifiction and separation of geochemical fossils present in crude oils and source rock extracts requires the use of fairly sophisticated instrumentation and techniques such as computerized gas-liquid chromatography (G.C.) and mass spectrometry (M.S.).

Prior to G.C.-M.S. studies the crude oil or source rock extract is fractionated using sequential elution adsorption liquid chromatography, so isolating three or four hydrocarbons from the sample, (Philp and Gilbert, 1980), (Gilbert, 1983).

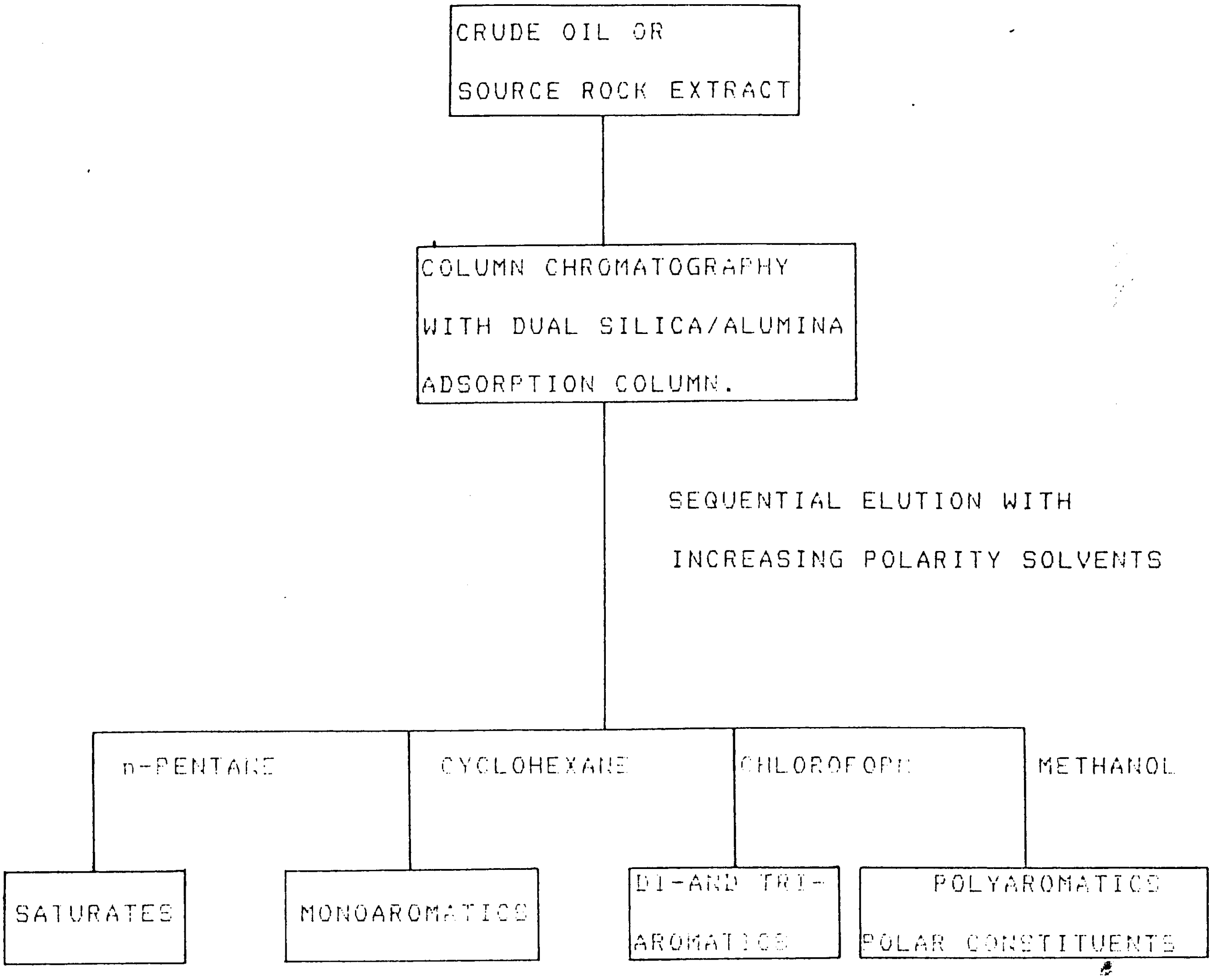


Table 9. (after Philp and Gilbert, 1980).

Initial analysis of the hydrocarbon fractions is made by gas chromatography before the more detailed analysis, using computerized gas chromatography mass spectrometry, (fig.63). The gas chromatograph contains a high resolution

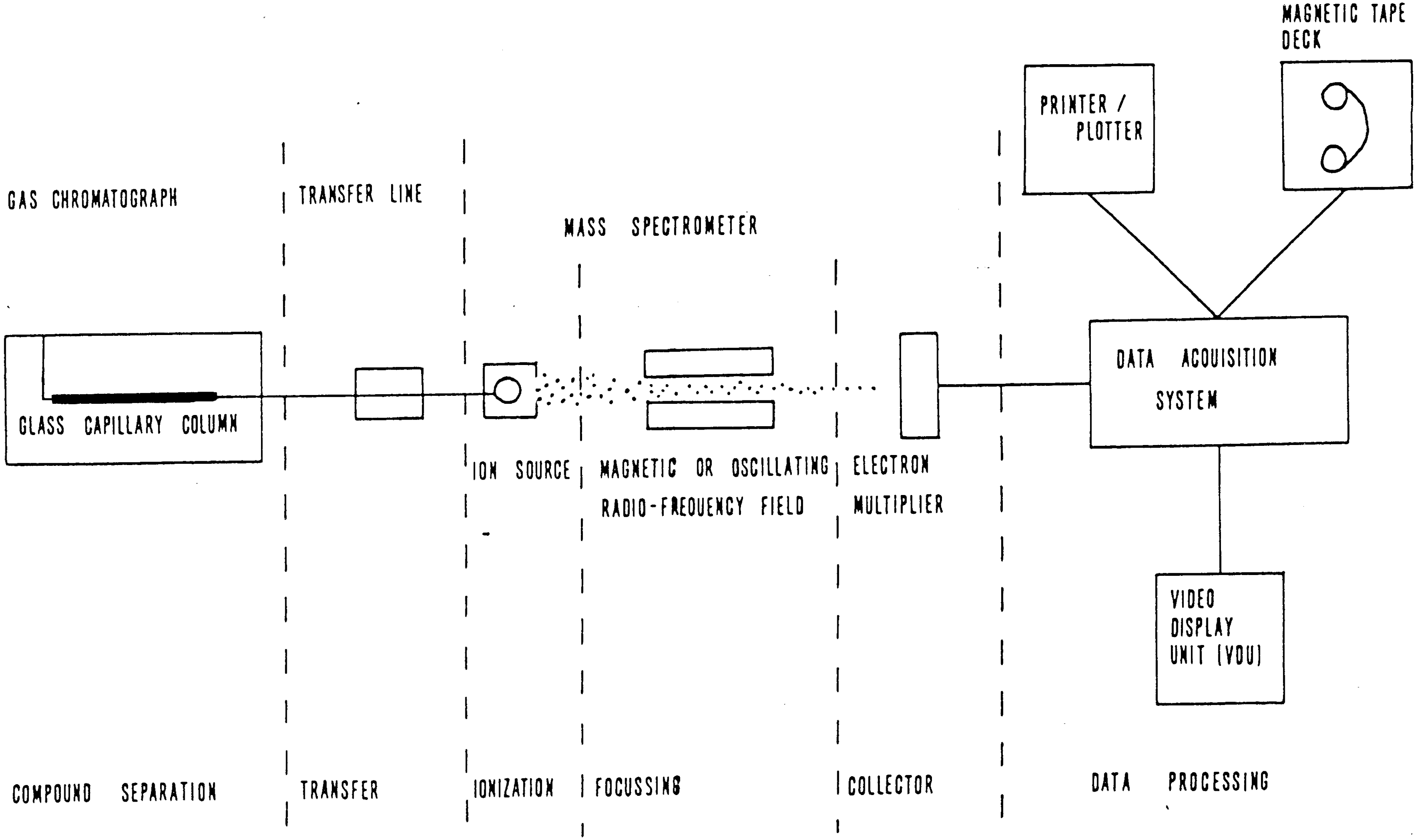


Fig. 63 Schematic diagram of a typical GC-MS system for use in the analysis of complex hydrocarbon mixtures. (Modified after Philp and Gilbert, 1981).

capillary column capable of separating compounds on the basis of their volatility, boiling point, stereochemistry, polarity or molecular weight, (Philp and Gilbert, 1982). As the separated compounds elute from the capillary column of the gas chromatograph they enter the ion source of the mass spectrometer where each compound is ionized by a stream of electrons and fragmented. The nature of the fragmentation depends on the structure of the original compound and results in a unique set of positively charged ions so allowing identification of the compound. The positively charged fragmented ions are directed to an electron multiplier through a magnetic or oscillating radio frequency field. The ions are separated (or focussed), on the basis of their mass to charge ratio and arrive at the electron multiplier where they are collected, detected and their intensities recorded.

A large amount of data is generated during the G.C.-M.S. analysis of a sample. The mass spectra of compounds are generally processed by computer and compound identification can be made rapidly as the spectral data is compared against a library of 20-40000 standard spectra stored in the computer. A listing of possible structures for the compound is then generated by the computer.

The first step in processing the data is to reconstruct a total ion current (T.I.C.) chromatogram. This chromatogram is very similar in appearance to that obtained by a gas chromatograph equipped with a flame ionization detector. However, by monitoring the intensity of a single characteristic ion only, (and not recording the total ion current) the sensitivity of the mass spectrometer is enhanced by several orders of magnitude. This can be seen in fig.64.

The ion most characteristic of steranes and used to detect its presence in crude oils or source rock extracts is at mass 217 or 149 (ref. sterane structural diagram), that for hopanes is at mass 191 or 148 (ref. hopane structural diagram), for normal alkanes at mass 71, 85 or 99 and for mono-aromatic steranes at mass 253. By monitoring, for example, the intensity of mass 217 and 191, the resulting chromatograms can be used to establish oil-oil and oil-source rock correlations and in maturity studies. It is this method of identification that forms the basis of many applications of organic geochemistry to petroleum exploration studies, (Philp and Gilbert, 1982).

Computerized gas chromatography-mass spectrometry is therefore essential for determining geochemical fossil distributions in oils and extracts and by combining the results with those from other geochemical techniques, it may be possible to establish a comprehensive picture of a sedimentary basin.

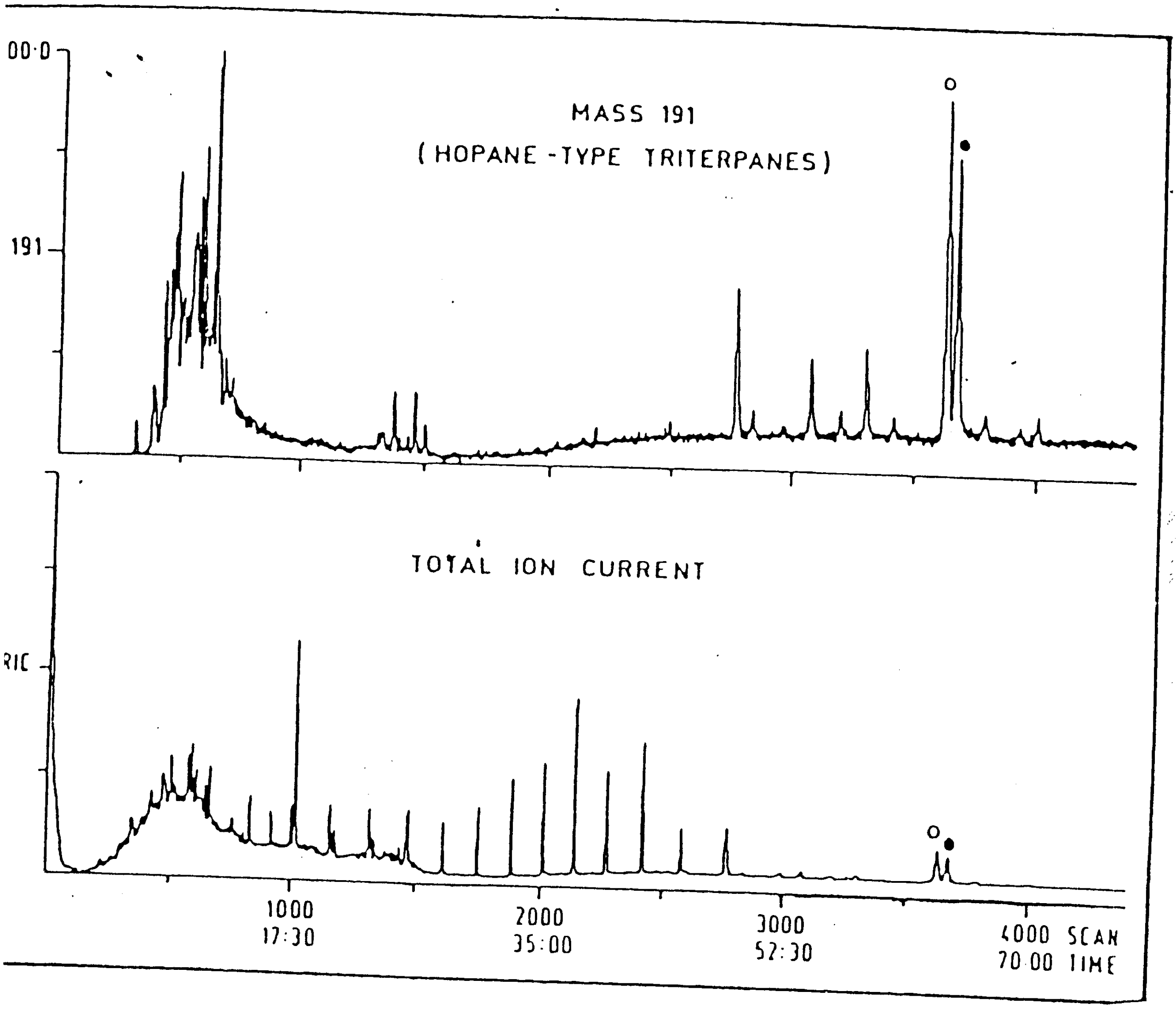


Fig. 64 A single ion plot of mass 191 compared with a T.I.C. chromatogram of a source rock extract. Open and closed circles are used to show relative positions of two triterpanes in a plot of mass 191 and T.I.C. trace. (After Philp and Gilbert, 1980).

4.8 A GEOCHEMICAL FOSSIL INVESTIGATION OF THE BELFAST MUDSTONE

INTRODUCTION

Although geochemical studies of the Belfast Mudstone have been limited, the conclusions suggest that whilst there may be some gas potential, the mudstone has no liquid hydrocarbon potential. It appears that most of the organics present in the Belfast Mudstone are of terrestrial origin, and if any marine organic material has been included, oxic conditions, prevalent during sedimentation, have oxidised the kerogen, thus destroying the liquid hydrocarbon potential of the organic matter.

Whilst geochemical data suggests that the Belfast Mudstone is a poor source rock, there appear to be some sections of the mudstone where organic material tends toward marine type II kerogen.

In this geochemical investigation samples indicating liquid hydrocarbon potential have been selected. It is hoped that the study might indicate certain horizons within the Belfast Mudstone have the potential to yield liquid hydrocarbons.

SAMPLE SELECTION.

The geochemical fossil investigation was limited to those samples displaying the best oil prone characteristics. Sample selection was made after carefully considering all geochemical data provided. Samples tested were from three recently drilled exploration wells :-

1. CURDIE # 1 (Belfast Mudstone 1893-2327m)

The entire Belfast mudstone appears to be immature and from microscopy studies seems to contain only organic material capable of generating gas.

Samples were selected due to the high T.O.C. values.

	Depth	T.O.C.
A	2100 - 2105	1.90
B	2190 - 2195	1.91
C	2300 - 2305	1.84

Table 10. Curdie # 1 Samples

2. BRIDGEWATER BAY # 1 (Belfast Mudstone 2682-4102m)

The Belfast Mudstone is thermally mature below 3295m. Below 3550m shale sloughing and the addition of Soltex to the mud system has led to sample contamination.

T.O.C. and pyrolysis results were used to select the samples. Particular attention was directed towards the S1 (Free hydrocarbon) values, the S1+S2 (Petroleum Potential) data and the H/O ratios. The samples selected have fair to good free hydrocarbon values, show marginal to moderate source rock richness displaying occasional mixed oil to gas potential.

	Depth	T.O.C.	S1	S1+S2	H/O
D	- 2700	1.18	0.66	2.42	1.43
E	- 2945	1.26	0.22	2.88	4.21
F	- 3050	1.31	0.25	1.96	2.44
G	- 3550	1.55	2.72	4.12	1.87

Table 11. Bridgewater Bay # 1 Samples

3. TRITON # 1 (SIDETRACK) (Belfast Mudstone 1730-3406m)

The Belfast Mudstone is thermally mature below 2900m, and below this depth it appears to have a good source potential, though for gas only.

From the elemental analysis of the kerogen and E.O.M. data, there appear to be some samples that tend toward type II kerogen with possible oil/gas potential.

Although there are high T.O.C. values in the sequence these decrease with increasing depth. With one exception, samples are selected for their elemental chararteristics and the E.O.M. (Hydrocarbon p.p.m.) extract.

	Depth	T.O.C.	H/C	O/C	H.C.(p.p.m)
H	- 2400	1.[illegible]	-	-	-
I	- 2915	1.16	0.77	0.13	-
J	- 3075	1.02	-	-	167
K	- 3275	-	0.62	0.07	114

Table 12. Triton # 1 (Sidetrack) Samples

THE GRADIENT ELUTION OF FOSSIL FUEL DERIVED HYDROCARBON

Procedure details - Theoretical

Before the source rock extracts can be studied on the G.C. - M.S. they must undergo fractionation. Fractionation of fossil fuel derived hydrocarbon mixtures is performed by sequential elution adsorbed liquid chromatography.

The principle of adsorption chromatography relies upon solvent molecules in the mobile phase competing with solute molecules for sites on the stationary (adsorbent) phase and involves the following set of equilibria:

$$\begin{tikzcd} & \text{Adsorbent.} \arrow[dl, shift left] \arrow[dr, shift left] & \\ \text{Solvent} \arrow[ur, shift left] \arrow[rr, shift right] & & \text{Solute} \arrow[ul, shift left] \arrow[ll, shift right] \end{tikzcd}$$

For a solute molecule to be adsorbed onto the stationary phase a solvent molecule must be first displaced from the surface. If it is assumed that the adsorbent possesses a polar surface (e.g. silica and alumina) then non polar groups (e.g. hydrocarbons) will have little affinity for the surface and will not displace the solvent molecules, therefore the solute molecules will not be retained and will be eluted. A polar functional group molecule will be retained until a solvent with a higher polarity displaces the solute from the surface of the stationary phase.

By utilizing the competing equilibria of various solvents, adsorbents and solutes, the required hydrocarbon fraction can be utilized.

By using a dual silica/alumina column, the properties of both adsorbents can be utilized during one analysis, thus giving a wide range of separation properties.

The selection of the solvents operates on the principle of functional group selectivity and can be physical or chemical depending on the nature of the interactions between the functional group and the separating medium. The solvent sequence that has been selected for the fractionation of fossil fuel derived hydrocarbons, n-pentane, cyclohexane, chloroform and methanol is shown in table 9.

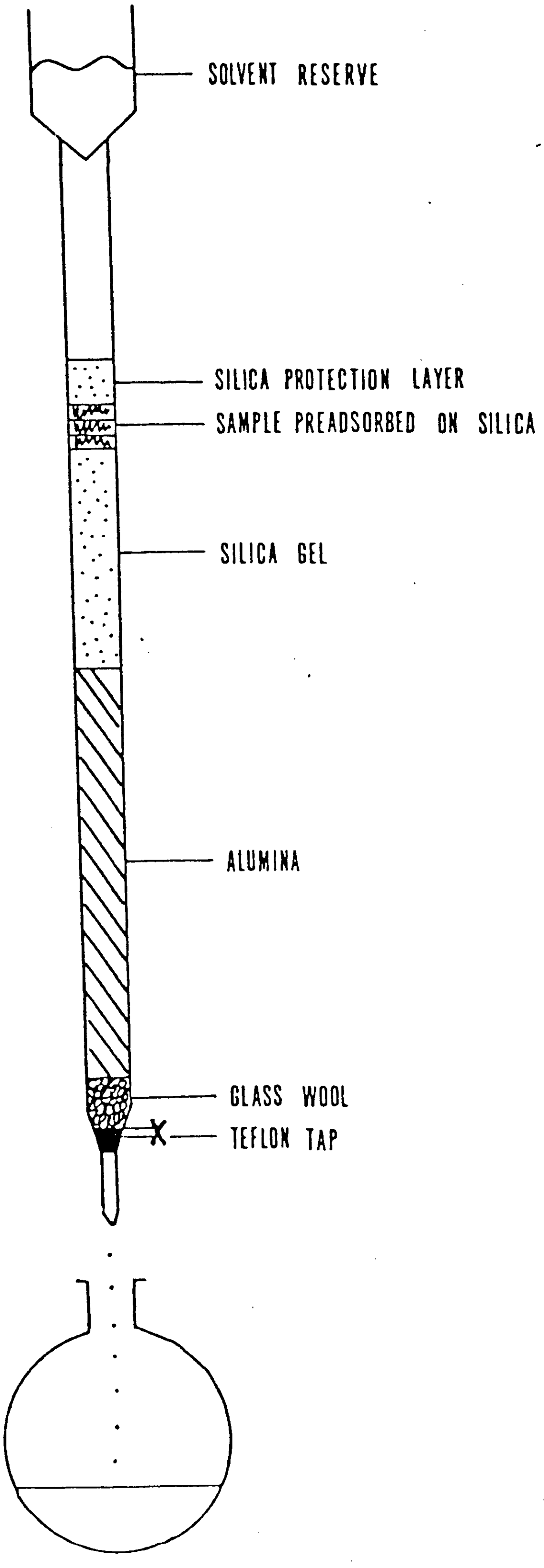
Procedure details - Experimental

A) Sample Preparation :- A Soxhlet system is conditioned prior to sample extraction by refluxing 100 ml. of dichloromethane (D.C.M.) for 12 hours. The source rock samples are crushed into a fine powder and a weighed amount of the powdered sample is placed in the Soxhlet thimble. The sample is refluxed for 48 hours, (setting 6 on the heat-bank) with 110 ml. of fresh D.C.M.

B) Column Preparation (fig. 65) :- The column, a 25 ml. burette with a teflon tap, is thoroughly cleaned with chromic acid, rinsed and left to drain. A glass wool plug, (washed with acid (HCl , 1 : 1) followed by a solvent, (D.C.M.)) is then placed in the column.

Column packing material, the adsorbents, consist

FIG. 65 ADSORPTION COLUMN



Silica Gel (100-200 mesh), Woelm, activated at 150 °C for 3 hours, and Aumina Oxide (Grade 1) Brockman, activated at 300 °C for 3 hours. Once activated the packing is added to the column, (100 ml. of sample requires 8g. of Alumina and 4g. of Silica).

It is necessary to slurry pack the Alumina by filling the column about half full with n-pentane and then gradually pouring in the alumina. The Silica Gel is added dry and tapped until it is tight within the column.

C) Sample Elution :- Once the Soxhlet refluxing is complete the sample is transferred to a small beaker and evaporated down to approximately 10 ml.

To overcome the problem of column plugging, channeling and the failure of the sample to adsorb during the introduction, the sample is preadsorbed in a small portion of D.C.M. and 1g. of activated silica gel. The preadsorbed sample is then air dried and introduced into the column. To avoid any sample disturbance during solvent addition, a small quantity of silica gel is then placed on top of the preadsorbed sample.

N.B. ; the column supports should never be allowed to dry out.

At least 150 ml. of A.R. grade n-pentane is poured through the column and the elutant containing the aliphatic fraction is collected in a 200 ml. round bottom flask. This process is repeated for the solvents; cyclohexane collecting the monoaromatics, chloroform collecting the di- and tri- aromatics and methanol collecting the polyaromatic fraction.

These fractions, collected in the round bottom flasks, are then evaporated down to approximately 5ml. and transferred to clean sample vials. These vials are retained for later G.C. - M.S. analysis.

G.C. - M.S. ANALYSIS

For the G.C. analysis a Packard gas chromatograph was utilized with a 12m B.P.I. column and using helium as the carrier gas. The temperature conditions were 50^{o}C to 280^{o}C at 10^{o}C / minute. A split injection (30:1) was made using 1 l of sample.

For the G.C. - M.S. analysis a Carlo Erba gas chromatograph was used with a 25m capillary (chrompack) SIL 5 column, helium again being the carrier gas. The temperature conditions were 50^{o}C to 280^{o}C at 10^{o}C / minute. A split injection (50:1) was made using 1 l of sample. The mass spectrometer, a Kratos MS 25RF operated with a filament current of 250 A and an electron energy of 70 ev.

EXPERIMENTAL RESULTS.

The G.C. results of the n-pentane fraction, (figs.67-75), shows that the normal alkanes have been identified against a standard hydrocarbon mixture of C-16 to C-22, (fig.66).

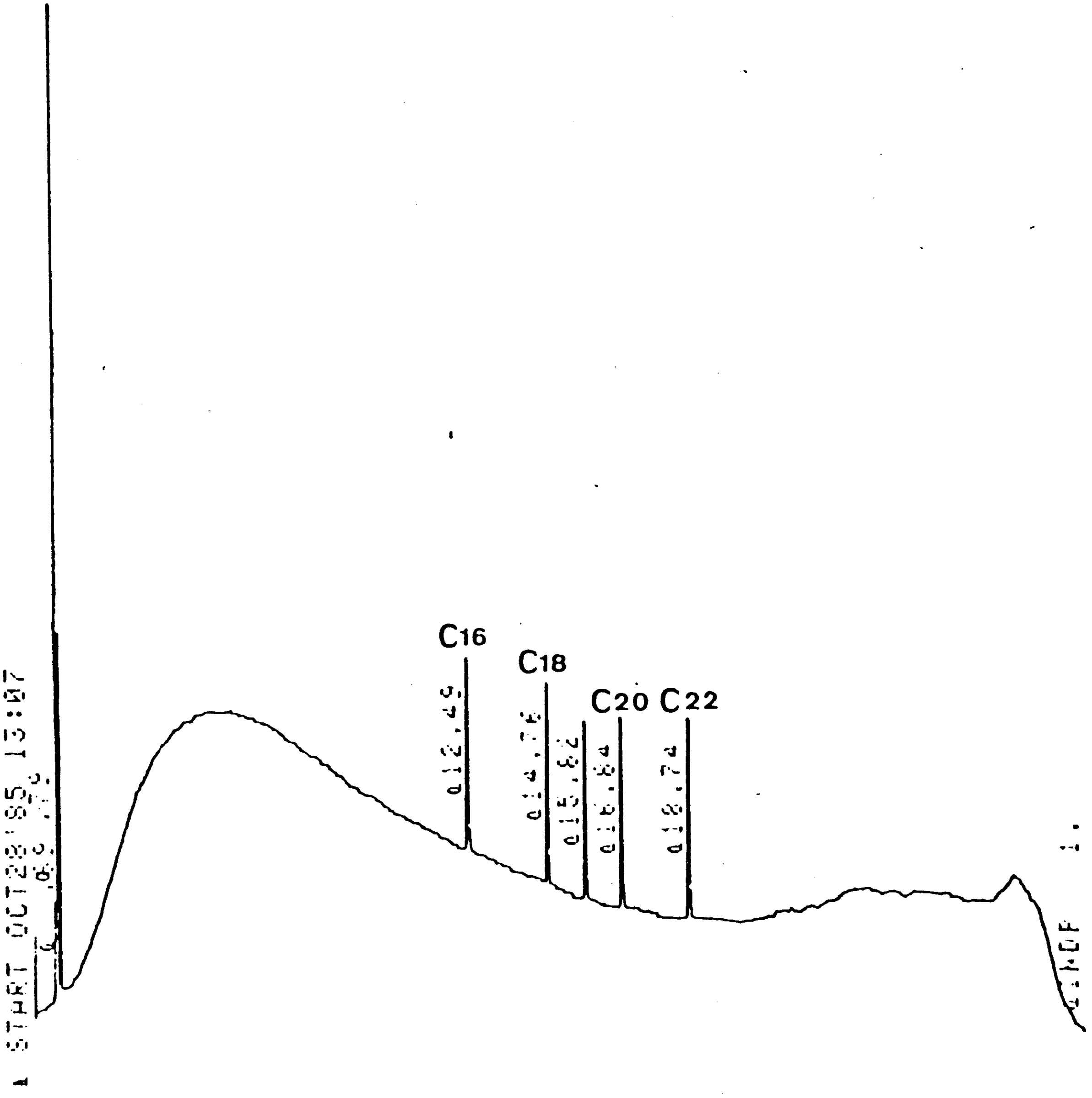


Fig. 66 Typical gas chromatograph of a hydrocarbon standard.

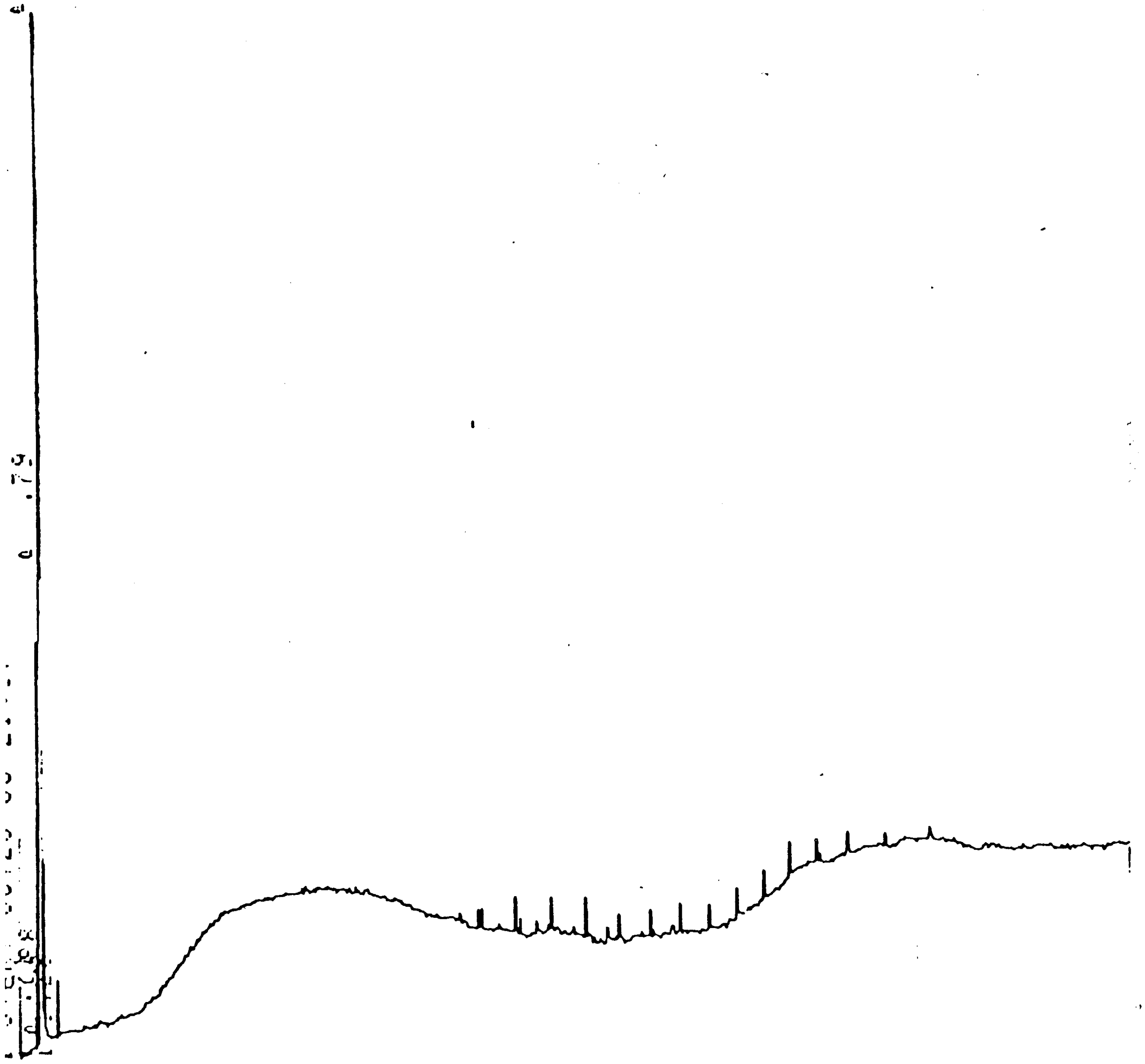


Fig. 67 Gas chromatograph of n-Pentane fraction , sample C.

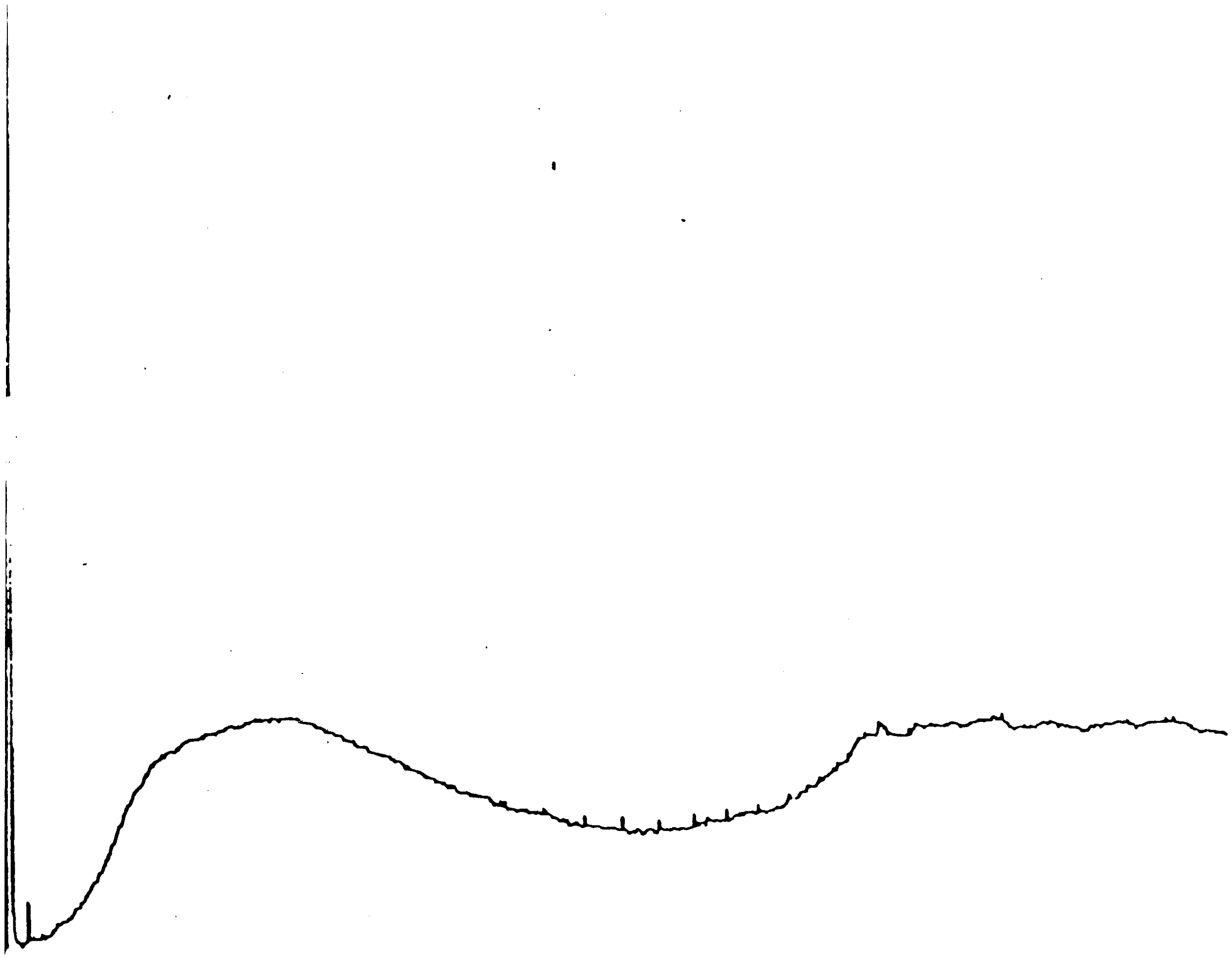


Fig. 68 Gas chromatograph of n-Pentane fraction , sample D.

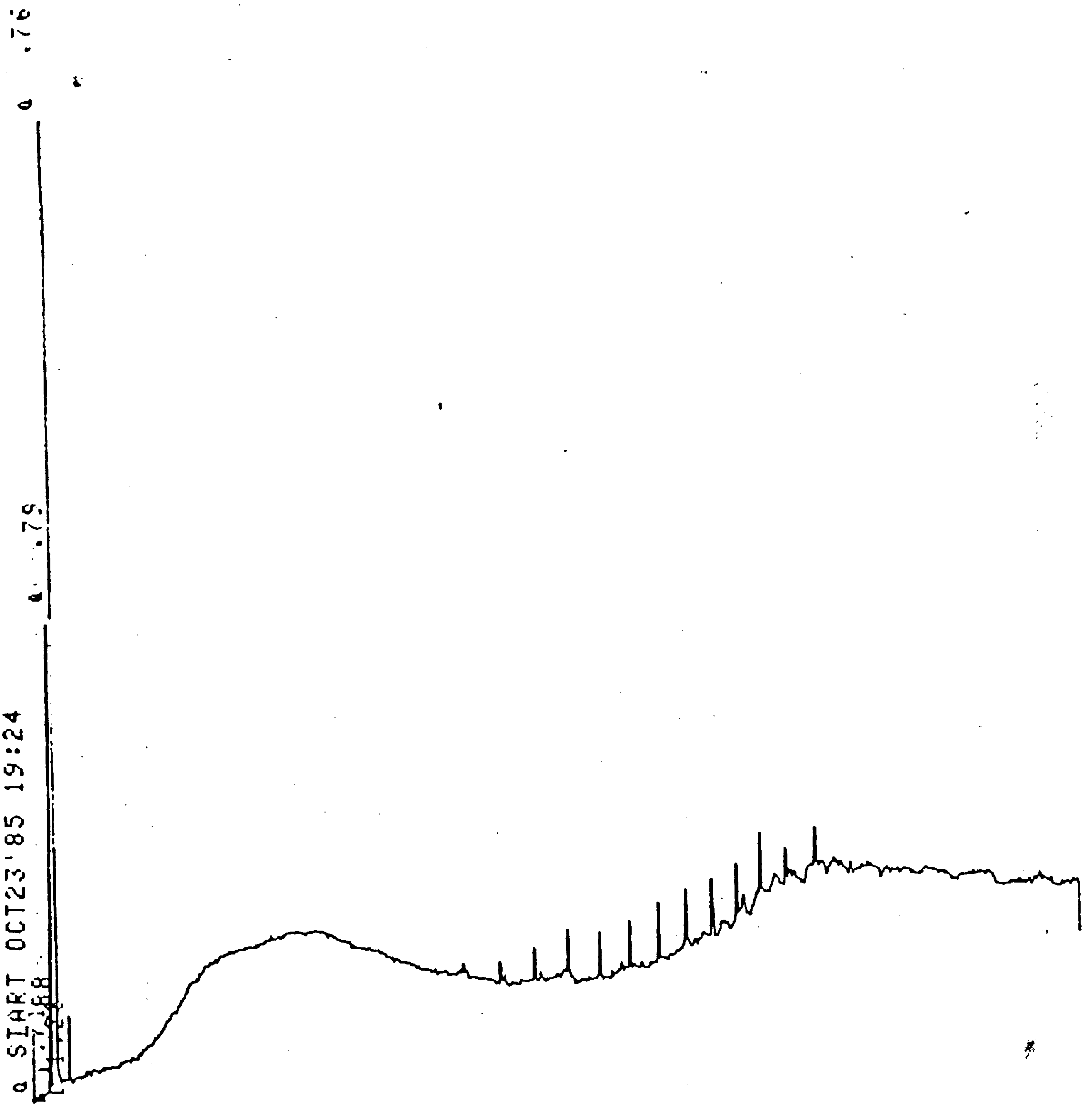


Fig. 69 Gas chromatograph of n-Pentane fraction , sample E.

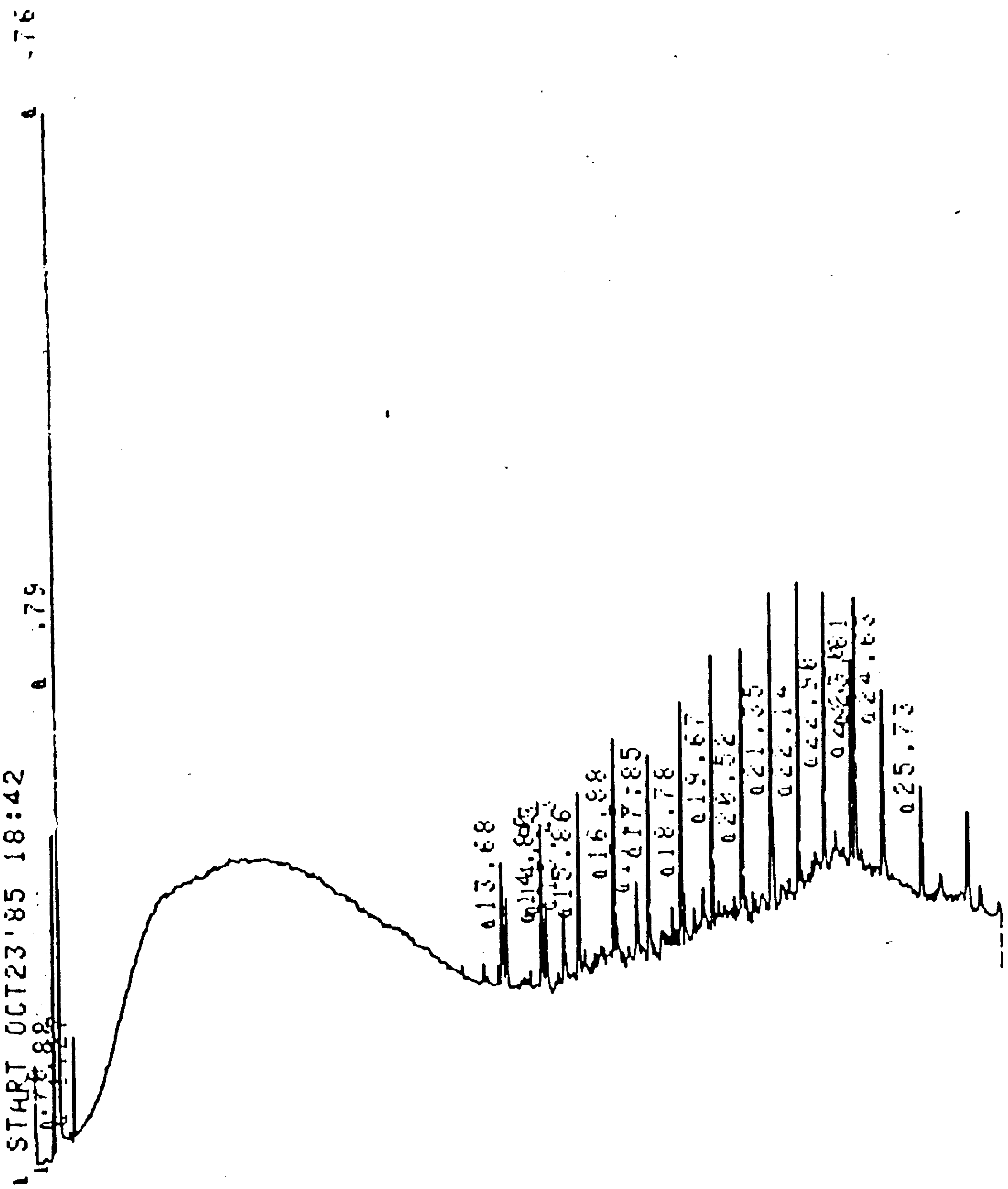


Fig. 70 Gas chromatograph of n-Pentane fraction , sample F.

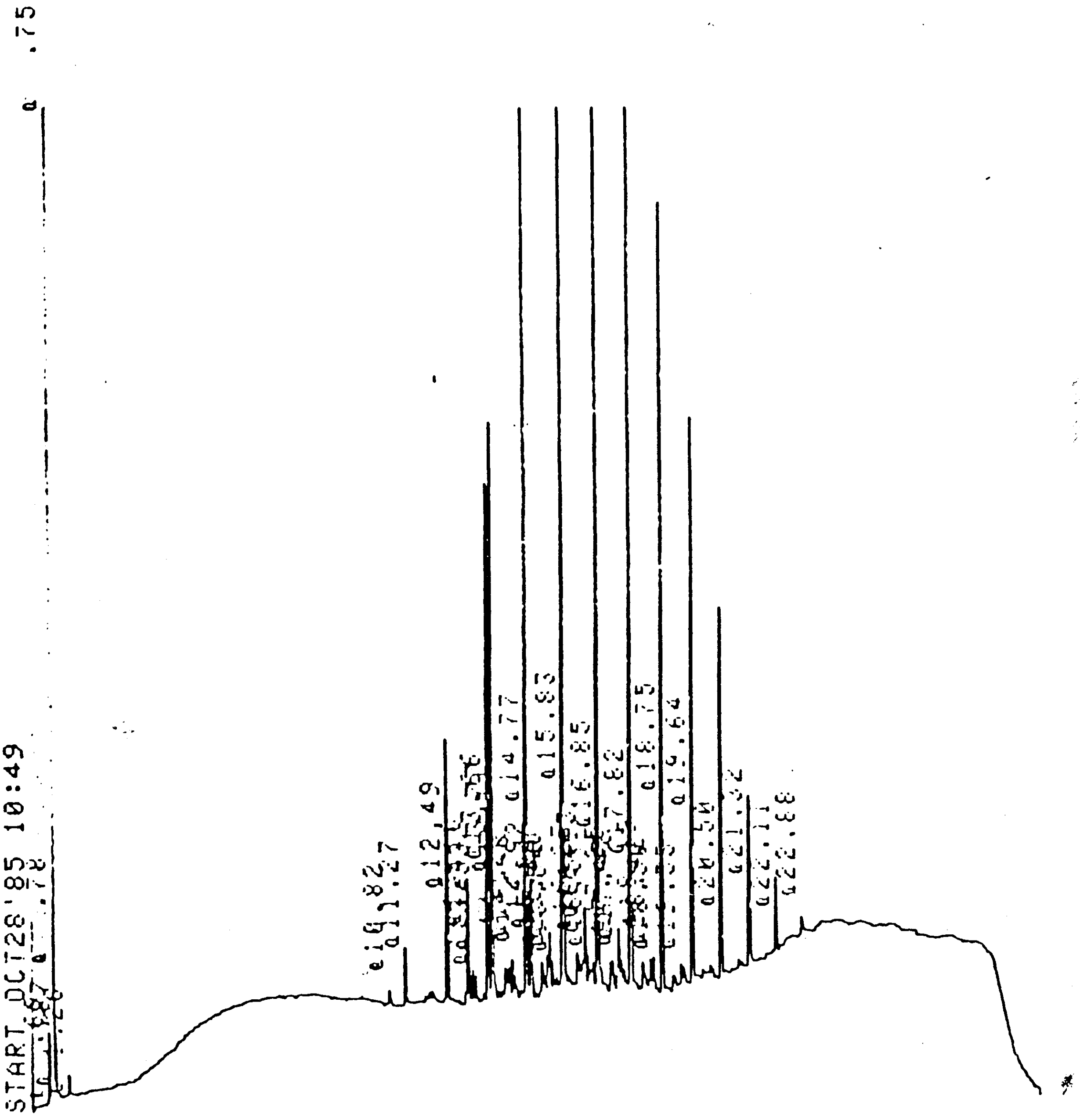


Fig. 71 Gas chromatograph of n-Pentane fraction , sample G.

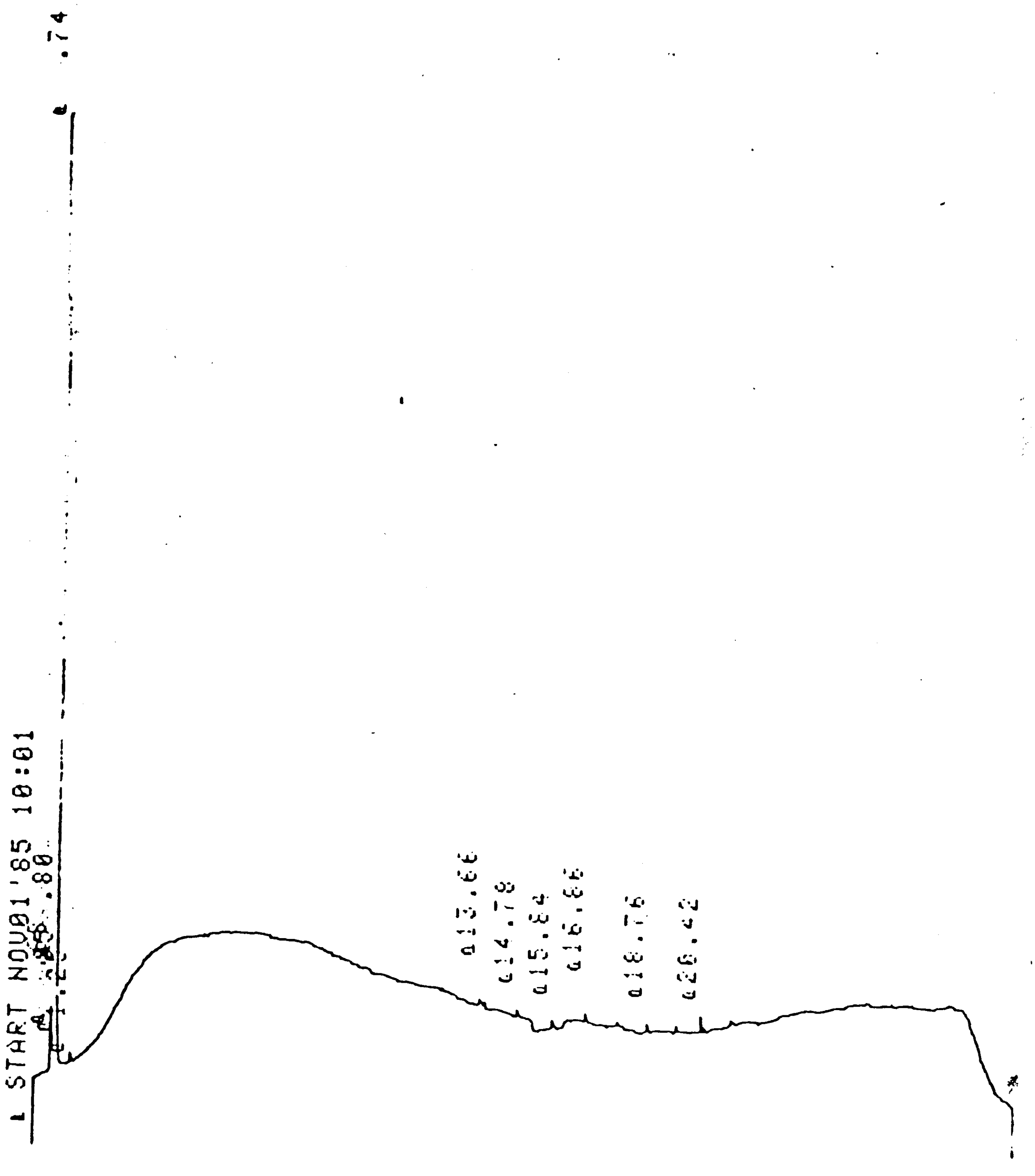


Fig. 72 Gas chromatograph of n-Pentane fraction , sample H.

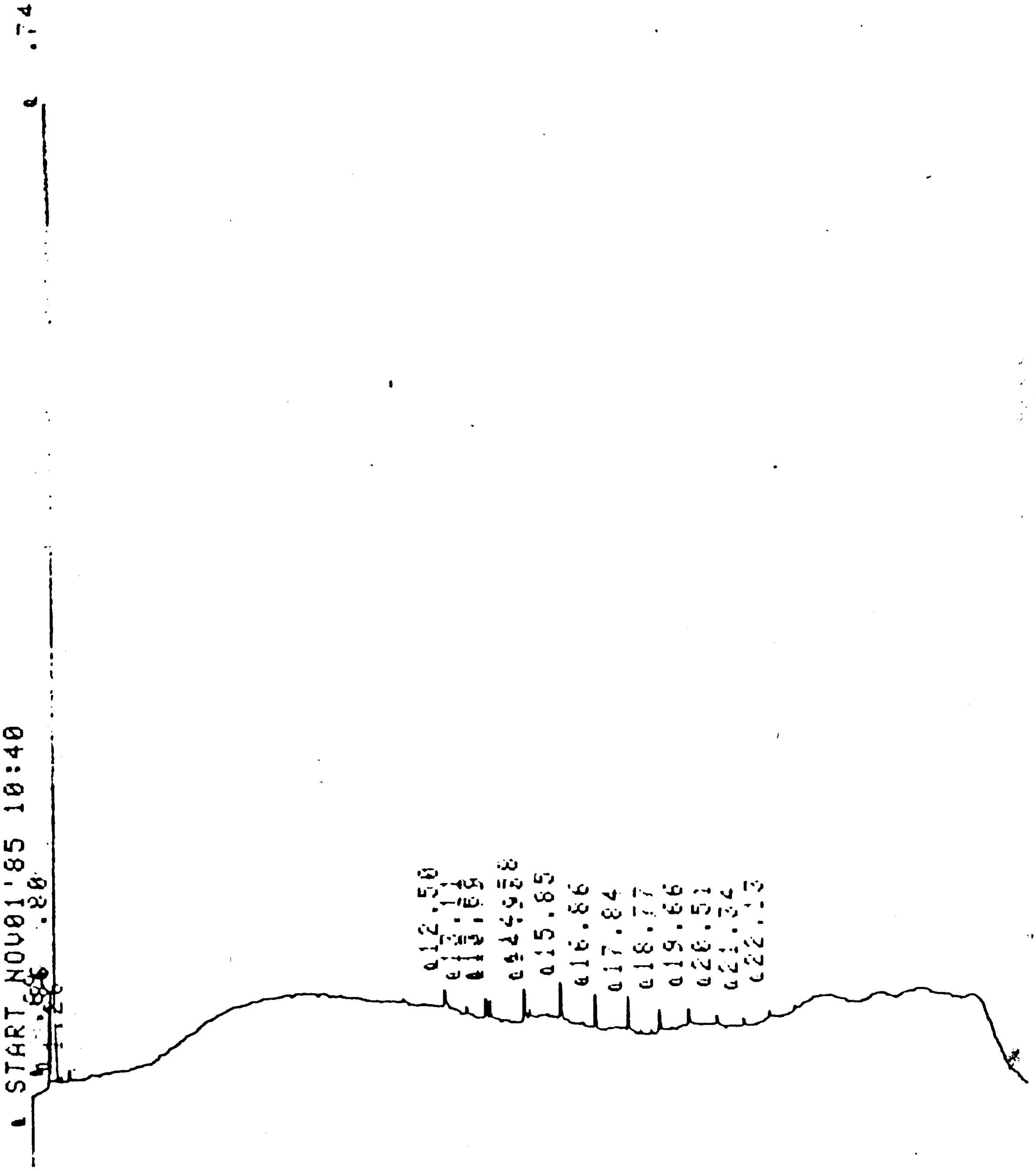


Fig. 73 Gas chromatograph of n-Pentane fraction , sample I.

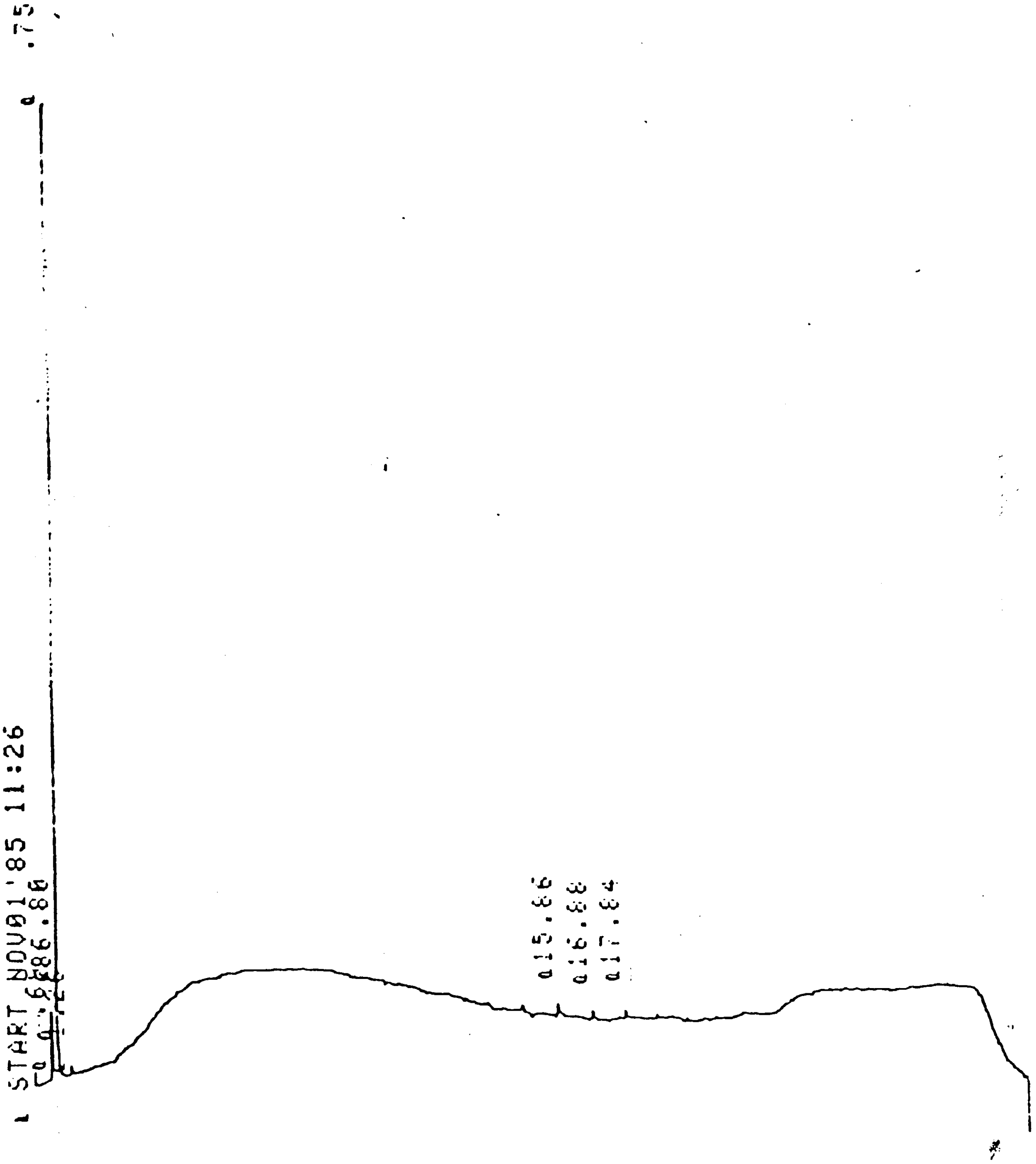


Fig. 74 Gas chromatograph of n-Pentane fraction , sample J.

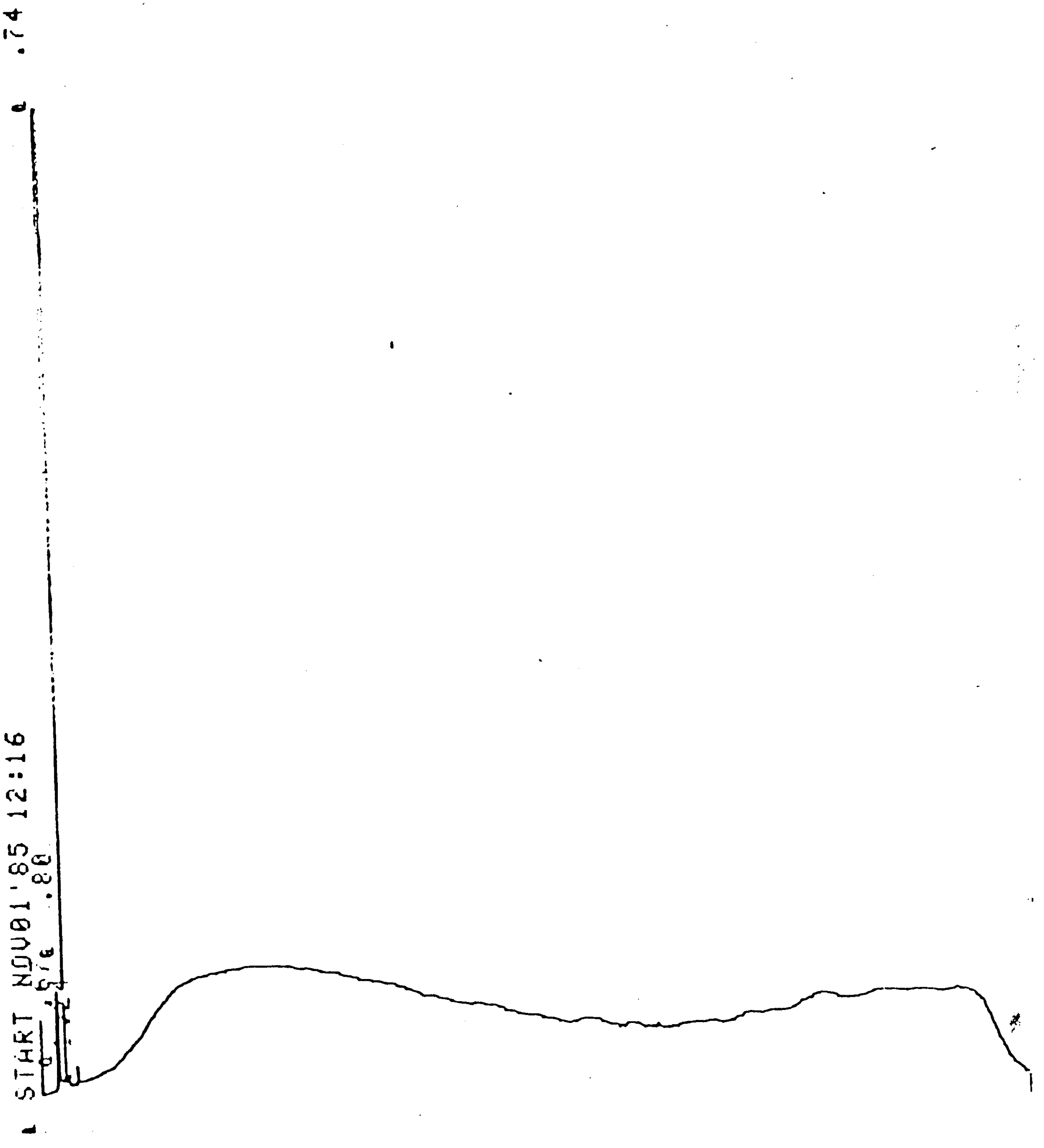


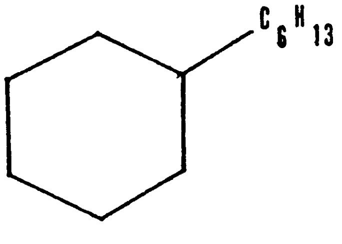
Fig. 75 Gas chromatograph of n-Pentane fraction , sample K.

By comparing the G.C. data with the standard hydrocarbon mixture, the following alkane distributions can be determined:

SAMPLE	ALKANE DISTRIBUTION	MATURITY
A	Not recorded	Immature
B	Not recorded	Immature
C	C-17 to C-31	Immature
D	Trace	Immature
E	C-18 to C-29	Immature
F	C-17 to C-32	Immature
G	C-15 to C-26	Mature
H	Trace	Immature
I	Trace	Mature
J	Trace	Mature
K	-	Mature

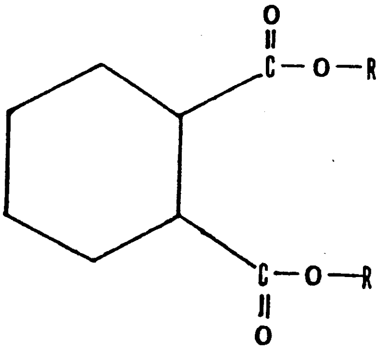
It has been stated earlier that the lipids common to marine organic matter result in a predominance of C-16 and C-18 fatty acids, whilst waxes from terrestrial higher plants are characterized by a predominance of C-20 to C-3[illegible]. From the distribution of the n-alkanes found in the samples it may be deduced that this is due to a mixed terrestrial / marine influence. It should be remembered that the sample selection was primarily made on the stronger tendency toward type II kerogen. Such distributions as recorded above may be evidence for certain horizons existing within the Belfast Mudstone that exhibit a stronger marine influence. The alkane distribution however is not dependent soley upon the organic source type, but also on the maturity of the rock. This is possibly the case seen in samples E, F and G. E and F are immature with a strong terrestrial influence, whilst G is mature and shows a mixed marine / terrestrial influence that could merely be the result of thermal maturation.

The G.C. results of the cyclohexane fraction was very disappointing and the chromatographs appear to be severely contaminated by the n-pentane elution. Mass spectral analysis confirmed the presence of hexylcyclohexane (a saturated alkane) and its homologs. M.S. analysis however, failed to detect the polycyclic or mono-aromatic structures of sterane or hopane. This is an unexpected result as it was assumed that hopanes particularly, were ubiquitons structures found in all environments of all ages, (Ourisson, Albrect and Rohmer, 1979).



hexylcyclohexane

Finally, the chloroform fraction was analysed, again disappointing G.C. results were obtained. Contamination was still a major problem, with the hexylcyclohexane structure again present. Phthalates were positively identified by M.S. analysis This is again a strange result as phthalate structures are related to plastics.



R = alkyl

Phthalate

DISCUSSION

The GC. and G.C. - M.S. analyses were largely unsatisfactory, but despite the apparent disappointment, the negative results have provoked a positive outcome, in reviewing the methodology and techniques used throughout the analysis.

Several points can be made that will hopefully improve the experimental procedure and facilitate subsequent geochemical fossil studies, these include :

1. The employment of solvents with a higher purity grade.

   Solvents used throughout the analysis were of of A.R. (Analytical Reagent) grade. This was thought not to be pure enough, possibly resulting in a residual water that inhibited the G.C results of the n-pentane fraction of samples A and B.

It would be advisable in future to re-distill A.R. grade solvents, thus increasing the purity and eliminating any possible contamination by residual water.

2. A modification of the adsorption column.

To reduce water absorption during the liquid chromatography process, the adsorption column should be placed in a fume cupboard. As a further measure to combat water absorption the solvent could be stored over a molecular sieve and the entire chromatographic process run within a closed system utilizing a two-way pump process drawing off a measured volume of solvent to be injected through the adsorption column and eluted into the sample collection reservoir.

Because saturated hydrocarbons were identified within the various fractions analysed, there was obviously a problem between the mobile and stationary phases of the column. This problem highlights the need to use purer solvents (see 1." above), during the liquid chromatography process.

3. Sample size and preparation.

The source rock samples tested weighed between 8.1g to 20.3g, (average 14.8g). It was thought that by increasing the sample size to approximately 30g mass spectral analysis and geochemical identification would have been made easier.

The samples were crushed by hand in a mortar and pestle before refluxing. Mechanical grinding to a uniform mesh size may have aided the refluxing process and liberated a greater amount of hydrocarbons.

The samples used in the study were ditch cuttings and may not have represented the true horizons I wished to examine. The samples tested may have been contaminated by "sloughing" shales, a notorious ocurrence within the Belfast Mudstone. Rather than ditch cutting core samples should be used if available, so enabling the samples to be both uncontaminated and from an exact depth.

Finally, there appeared to be contamination of the sample due to the mode of storage. The ditch cuttings used in the study had been stored in plastics bags for up to three years. The phthalates detected in the chloroform fraction may well be associated with the plastic bags used for sample storage. To overcome such contamination samples should be analysed soon after drilling or stored in air-tight tin cans.

4. Solute evaporation and storage.

After liquid chromatography the solute collected in the round bottom glass is evaporated down to approximately 5ml. This should have been done by rotary evaporation *not* by air drying as the solute can be contaminated by water reabsorption. Solute storage, prior to G.C. and G.C. - M.S. analysis should be minimal and in air-tight, sterile, glass vials, thus reducing any possibility of solute contamination.

5. Determination of the M.S. operating mode.

Though no steranes or hopanes were detected, it is almost certain that the structures occur in the samples. Their apparent non-presence is due to the operating mode of the mass spectrometer. In order to identify the steranes and hopanes a revised M.S. operating mode must be established.

6. Logistics.

The techniques employed involved more time than was available for the project. This resulted in curtailment of much of the research and many questions remain unanswered. The time factor became a great burden for experimental research that could not be rushed.

Further geochemical studies should realize the" time necessary to adequately persue the topic.

4.9 SUMMARY

Geochemical fossils including, n-alkanes, terpanes, steranes and hopanes can give a knowledge of :-

a) Source type

b) Depositional environment.

c) Maturity.

The use of G.C. and G.C. - M.S. has enabled the study of these various geochemical fossils to enhance and supplement source rock studies.

Samples showing a trend towards kerogen type II (mixed marine / terrestrial organic material) and a potential for liquid hydrocarbon were selected for further geochemical analysis. It was hoped that the additional data, combined with established findings would result in a comprehensive picture of the petroleum potential of the Belfast Mudstone.

The experimental techniques employed however were more complex and time consuming than expected. Data obtained from the G.C. and G.C. - M.C. was disappointing and resulted in an indecisive analysis of the source rock samples examined.

Despite inconclusive findings however, the study has provoked critical comments concerning methodology, enhancing constructive criticism for improved techniques and experimental detail in future geochemical studies.

CONCLUSIONS.

The study has not proved conclusively that the Belfast Mudstone is a good liquid hydrocarbon source rock. However, there are indications which suggest that as a source rock, a fair gas potential may exist.

The Belfast Mudstone has good T.O.C. values. This implies that organic material is present within the formation in an adequate quantity.

Thermal maturation indicators show that at deeper levels offshore the Belfast Mudstone is within the oil window and at Triton # 1 (sidetrack), Bridgewater Bay # and Breaksea Reef # 1A a mature Belfast Mudstone sequence has been penetrated.

The source rock type however, is not condusive for the generation of liquid hydrocarbons with vitrinite and inertinite present in large amounts. This indicates gas prone source rocks and kerogen type III.

There may be the possibility that horizons exist within the Belfast Mudstone, where a stronger marine influence is exhibited. If this were the case and marine organics were identified, the source rock potential for liquid hydrocarbons of the Belfast Mudstone offshore would be greatly enhanced.

Geochemccal identification of the organic types by G.C.-M.S. analysis was unfortunately inconclusive and although there was room to speculate that kerogen type II may well exist within the Belfast Mudstone, this was not supported by the findings.

Sparse offshore exploration within the Otway Basin and the great thickness of the Belfast sediment pile make further studies necessary. If drilling operations offshore increase and detailed geochemical analysis is conducted new light may be shed on the source rock potential of the Belfast Mudstone.

At present we are only able to conclude that the Belfast Mudstone is a gas prone source rock.

ACKNOWLEDGEMENTS

I wish to thank Beach Petroleum N.L., Ultramar Australia Inc., and Gas and Fuel for providing data and samples.

I am indebted to J. Fisher and K. Rastoll for their technical assistance and to T. Gilbert for supplying details of G.C. - M.S. analysis techniques.

I am also grateful to Dr. A. Link and Dr. H. Farthing for their helpful comments and thought provoking discussions on the topic.

Finally, my thanks to my wife, D. Shearer, for reading the manuscript and for her unflagging patience during its writing and to S. Doehnert for typing the manuscript.

REFERENCES

ALEXANDER, R., KAGI, R.I. and WOODHOUSE, G.W., 1978, Measurement of thermal maturation of petroleum by proton resonance spectroscopy; Nature, v.276, p. 598-599.

ALEXANDER, R., KAGI, R.I. and WOODHOUSE, G.W., 1979, A new method for measuring the maturity of petroleum in source rocks; A.P.E.A Journal, v.19, p. 90-93.

ALLIANCE OIL DEVELOPMENT (AUST.) N.L., 1967, Final well completion report, Caroline # 1, (unpubl.).

BEACH PETROLEUM N.L., 1982, Final well completion report, Curdie # 1, (unpubl.).

BOEUF, M.G., and DOUST, H., 1975, Structure and development of the southern margin of Australia; A.P.E.A Journal, v.15, p. 33-43.

CANDE, S.C., and MUTTER, J.C., 1982, A revised identification of the oldest sea-floor spreading anomalies between Australia and Antarctica; Earth and Planetary Sci. Letters, v.58, p.151-160

CATACOSINOS, P.A., 1973, Cambrian lithostratigraphy of the Michigan Basin; A.A.P.G. Bull., v.57, p. 2404-2418.

CHRIST, R.P.A., 1984, The tectonic development of Bass Strait; In: A.S.E.G. 2nd Australian Petroleum Geophysics Symposium (unpubl.). p. 296-337.

CHRISTIE, P.A.F., and SCLATER, J.G., 1980, An extensional origin for the Buchan and Witchground Graben in the North Sea; Nature, v.283, p. 729-732.

DASTILLUNG, M., and ALBRECT, P., 1977, 2-Sterenes as diagenetic intermediates in sediments; Nature, v.269, p. 678-679.

DEIGHTON, I., FALVEY, D.A., and TAYLOR, D.J., 1976, Depositional environments and geotectonic framework; Southern Australian continental margin; A.P.E.A., Journal, v.16, p. 25-36.

DEMAISON, G.J., and MOORE, G.T., 1980, Anoxic environments and oil source bed genesis; A.A.P.G. Bull., v.64, p. 1179-1209.

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. et Cosmochim. Acta., v.40, p. 203-208.

DENHAM, J.I., and BROWN, B.R., 1976, A new look at the Otway Basin; A.P.E.A Journal, v.16, p. 91-98.

DIDYK, B.M., etal., 1978, Organic geochemical indicators of palaeoenvironmental conditions of sedimentation; Nature, v.272, p. 216-222.

DOW, W.G., 1977, Kerogen studies and geological interpretations; Journal of Geochem. Exploration, v.7, p. 79-99.

DOW, W.G., 1978, Petroleum source beds on continental slopes and rises; A.A.P.G. Bull., v.62, p. 1584-1606.

EGLINTON, G., and CALVIN, C., 1967, Chemical fossils; Sci. Am., v.216, p. 32-43.

ENSMINGER, A., JOLY, G., and ALBRECHT, P., 1978, Rearranged steranes in sediments and crude oils; Tetrahedron Letters, No.18, p. 1575-1578.

ESSO EXPLORATION AND PRODUCTION AUSTRALIA INC., 1982. Final well completion report, Triton #1 (sidetrack), (unpubl.).

ETHERIDGE, M.A., BRANSON, J.C., and STUART-SMITH, P.G., 1985 Extensional basin forming structures in Bass Strait and their importance for hydrocarbon exploration; A.P.E.A., Jour v.25, p. 344-361.

FALVEY, D.A., 1974, The development of continental margins in plate tectonic theory; A.P.E.A. Journal, v.14, p. 95-106.

FALVEY, D.A., and DEIGHTON, I., 1982, Recent advances in burial and thermal geohistory analysis; A.P.E.A. Journal v.22, p. 65-81.

FALVEY, D.A., and MUTTER, J.C., 1981, Regional plate tectonics and the evolution of Australias passive continental margins; B.M.R. Journal of Aust. Geology and Geophys., v.6, p. 1-29.

GIBBS, A.D., 1984, Structural evolution of extension basin margins; J. Geol. Soc. London, v.141, p. 609-620.

GILBERT, T.D., The use of sequential elution adsorbtion liquid chromatography for the fractionation of fossil fuel derived hydrocarbon mixtures (unpublished).

GLEADOW, A.J.W., DUDDY, I.R., and LOVERING, J.F., 1983, Fission track analysis : A new tool for the evaluation of thermal histories and hydrocarbon potential; A.P.E.A. Jour., v.23, p. 93-102.

GRIFFITHS, J.R., 1971, Continental margin tectonics and the evolution of South East Australia; A.P.E.A. Journal, v.11 p. 75-79.

GUNN, P.G., 1975, Mesozoic - Cainozoic tectonic and igneous activity in South East Australia; J. of Geol. Soc. Aust., v.22, p. 218-222.

HAXBY, W.F., TURCOTTE, D.L., and BIRD, J.M., 1976, Thermal and mecanical evolution of the Michigan Basin; Tectonophysics, v.36, p. 57-75.

HOOD, A., GUTJAHR, C.C.M., and HEACOCK, R.L., 1975, Organic metamorphism and the generation of petroleum; A.A.P.G. Bull. v.59, p. 986-996.

HSU, W.J., 1965, Isostasy,crustal thinning, mantle changes and the disappearance of ancient land masses; Am. J. Sci., v.263, p. 97-109.

HUNT, J.M., 1979, Petroleum Geochemistry and Geology, San Francisco, W.H.Freeman and Co., pp.617

JARVIS, G.T., and McKENZIE, D.P., 1980, Sedimentary basin formation with finite extention rates; Earth and Planetary Sci. Letters, v.48, p. 42-52.

KLEMME, H.D., 1975, Geothermal gradients,heat flow and hydrocarbon recovery; In Petroleum and Global Tectonics (FISCHER, A.G., and JUDSON, S., Eds.) p. 252-304.

LE PICHON, X., and SIBUET, J.C., 1981, Passive margins : A model of formation; Jour. of Geophys. Res.,v.86,p.3708-3720.

LEYTHAEUSER, D., SCHAEFER, R.G., and WEINER, B., 1979, Generation of low molecular weight hydrocarbons from organic matter in source beds as a function of temperature and facies; Chem. Geol., v.25, p. 95-108.

LIJMBACH, G.W.M., 1975, The origin of petroleum; In Proc. 9th World Petroleum Congress, v.2, p. 357-369.

MacKENZIE, A.S., etal., 1980, Molecular parameters of maturation in the Toarcian Shales, Paris Basin, France - I. Changes in the configurations of acyclic isoprenoid alkanes, steranes, and triterpanes; Geochim. et Cosmochim. Acta, v.44 p. 1709-1721.

MacKENZIE, A.S., LAMB, N.A., and MAXWELL, J.R., 1982, Steroid hydrocarbons and the thermal history of sediments; Nature, v.295, p. 223-226.

MacKENZIE, A.S., etal., 1982, Chemical fossils : The geological fate of steroids; Science, v.217, p. 491-504.

McKENZIE, D., 1978, Some remarks on the development of sedimentary basins; Earth and Planetary Sci. Letters, v.40, p. 25-32.

McNICHOL, M.D., 1984, The structural development of the Otway Basin; In: A.S.E.G. 2nd Australian Petroleum Geophysics Symposium p. 509-525. (unpubl.).

MIDDLETON, M.F., and FALVEY, D.A., 1983, Maturation modelling in the Otway Basin, Australia; A.A.P.G. Bull., v.67, p. 271-279.

MOLDOWAN, J.M., and SEIFERT, W.K., 1979, Head-to-head linked isoprenoid hydrocarbons in petroleum; Science, v.204, p. 169-171.

NICHOLAS, E., etal., 1981, Petroleum potential of the Bass Basin; B.M.R. Journal of Aust. Geol. and Geophys., v.6, p. 199-212.

OURISSON, G., ALBRECT, P., and ROHMER, M., 1979, Hopanoids: Palaeochemistry and biochemistry of a group of natural products; Pure and Appl. Chem., v.51, p. 709-729.

PAGE, M.M., and KUHUEL, C., 1980, Rock-Eval Pyrolysis as a source rock screening technique; A.A.P.G. Bull., v.64 p. 762 (abstract only).

PARSONS, and SCLATER, J.G., 1977, An analysis of the variation of ocean floor bathemetry and heat flow with age; Jour. Geophys. Res., v.82, p. 802-825.

PATIENCE, R.L., ROWLAND, S.J., and MAXWELL, J.R., 1978, The effect of maturation on the configuration of pristane in sediments and petroleum; Geochim. et Cosmochim. Acta, v.42, p. 1871-1875.

PERRIER, R., and QUIBIER, J., 1974, Thickness changes in sedimentary layers during compaction history ; Methods for quantitative evaluation; A.A.P.G. Bull., v.58, p. 507-520.

PHILP, R.P., 1981, Diagenetic organic matter in Recent sediments and environments of deposition; B.M.R. Journal of Aust. Geol. and Geophys., v.6, p. 301-306.

PHILP, R.P., 1983, Correlation of crude oils from the San Jorges Basin, Argentina; Geochim. et Cosmochim. Acta, v.47, p. 267-275.

PHILP, R.P., and GILBERT, T.D., 1980, Application of computerized gas chromatography - mass spectrometry to oil exploration in Australia; A.P.E.A. Journal, v.20, p. 221-228.

PHILP, R.P., and GILBERT, T.D., 1982, Unusual distribution of biological markers in an Australian crude oil; Nature, v.299, p. 245-247.

PHILP, R.P., and GILBERT, T.D., 1982, Value of organic geochemistry to petroleum exploration - Boilogical markers aid oil explorers;

PHILP, R.P., GILBERT, T.D., and FRIEDRICH, J., 1982, Geochemical correlation of Australian crude oils; A.P.E.A. Journal, v.22, p. 188-199.

PHILP, R.P., SIMONEIT, B.R.T., and GILBERT, T.D., 1981, Diterpenoids in crude oils and coals of South Eastern Aust.; In Advances in Organic Geochemistry (BJOROY, M. etal., Eds.) p. 698-704.

PHILIPPI, G.T., 1974, The influence of marine and terrestrial source material on the composition of petroleum; Geochim. et Cosmochim. Acta, v.38, p. 947-966.

PHILLIPS AUSTRALIAN OIL COMPANY, 1983, Final well completion report, Bridgewater Bay # 1, (unpubl.).

POWELL, P.N.G., and McKIRDY, D.M., 1975, Geological factors controlling crude oil composition in Australia and Papua New Guinea; A.A.P.G. Bull., v.59, p. 1176-1197.

ROYDEN, L., SCLATER, J.G., and VON HERZEN, R.P., 1980, Continental margin subsidence and heat flow ; Important parameters in the formation of petroleum hydrocarbons; A.A.P.G. Bull., v.64, p. 173-187.

SAWYER, D.S., etal., 1983, Thermal evolution of the Baltimore Canyon Trough and Georges Bank Basin; In Studies in Continental Margin Geology (WATKINS, J.S., and DRAKE, C.L., Eds.,) A.A.P.G. Memoir 34, p.

SCHAEFLE, J. etal., 1978, Aromatic hydrocarbons from geological sources, VI new aromatic steroid derivatives in sediments and crude oils; Tetrahedron Letters, No.43, p.4163-4166.

SCLATER, J.G., and CHRISTIE, P.A.F., 1980, Continental streching; An explanation of the post-mid-Cretaceous subsidence of the Central North Sea Basin; Jour. of Geophys. Res., v.85, p. 3711-3739.

SEIFERT, W.K., and MOLDOWAN, J.M., 1981, Palaeoreconstruction by biological markers; Geochim. et Cosmochim. Acta, v.45, p. 783-794.

SHAFIK, S., 1983, Calcareous nannofossil biostratigraphy ; An assessment of Foraminifera and sedimentation events in the Eocene of the Otway Basin, Southeastern Australia; B.M.R Journal of Aust. Geol. and Geophys., v.8, p.1-17.

SHIBAOKA, M., and BENNETT, A.J.R., 1977, Patterns of diagenesis in some Australian sedimentary basins; A.P.E.A Journal, v.17, p. 58-63.

SHIBAOKA, M., BENNETT, A.J.R., and GOULD, K.W., 1973, Diagenesis of organic matter and occurrence of hydrocarbons in some Australian sedimentary basins; A.P.E.A. Journal, v.13, p. 73-80.

SLEEP, N.H., 1971, Thermal effects of the formation of Atlantic continental margins by continental break-up; Geophys. J.R. Astron. Soc., v.24, p. 325-350.

TAYLOR, D.J., 1964, The depositional environment of the marine Cretaceous sediments of the Otway Basin; A.P.E.A. Journal, v.4, p. 140-144.

TAYLOR, D.J., 1971, Foraminifera and the Cretaceous and Tertiary depositional history in the Otway Basin in Victoria; In the Otway Basin of Southeastern Australia. (WOPFNER, H. and DOUGLAS, J. G., Eds.), p. 217-233.

THOMAS, B.M., 1982, Land plant source rocks for oil and their significance in Australian basins; A.P.E.A. Journal, v.22, p. 164-178.

TISSOT, B., etal., 1974, Influence of nature and diagenesis of organic matter in formation of petroleum; A.A.P.G. Bull., v.58, p.499-506.

TISSOT, B., 1984, Recent advances in petroleum geochemistry applied to hydrocarbon exploration; A.A.P.G. Bull., v.68, p. 545-563.

ULTRAMAR AUSTRALIA INC., 1984, Final well completion report, Breaksea Reef # IA, (unpubl.).

VAIL, P.R., etal., 1977, Seismic stratigraphy and global changes of sea-level; In Seismic stratigraphy - Applications to hydrocarbon exploration (PAYTON, C.E., Ed.), A.A.P.G. Memoir 26, p. 49-212.

VAN DORSSELAAR, A., etal., 1974, Degraded and extended hopane derivatives (C-27 to C-35) as ubiquitous geochemical markers; Tetrahedron Letters, No.14, p. 1349-1352.

VAN HINTE, J.E., 1978, Geohistory analysis - Application of micropalaeontology in exploration; A.A.P.G. Bull., v.62, p. 201-222.

WAPLES, D.W., 1980, Time and temperature in petroleum formation : Application of Lopatins method to petroleum exploration; A.A.P.G. Bull., v.64, p. 916-926.

WAPLES, D.W., HAUG, P., and WELTE, D.H., 1974, Occurrence of a regular C-25 isoprenoid hydrocarbon in Tertiary sediments representing a lagoonal-type saline environment; Geochim. et Cosmochim. Acta., v.38, p. 381-387.

WEN-YEN HUANG and MEINSCHEIN, W.G., 1979, Sterols as ecological indicators; Geochim. et Cosmochim. Acta., v.43, p. 739-745.

WERNICKE, B., and BURCHFIEL, B.C., 1982, Modes of extention tectonics; Jour. of Structural Geol., v.4, p. 105-115.

WOODHOUSE, G.W., ALEXANDER, R., and KAGI, R.I., 1981, Geochemical evaluation of the Otway Basin; (unpublished rep.)

WOPFNER, H., and DOUGLAS, J.G., (Eds.), 1971, The Otway Basin of Southeastern Australian; Special Bulletin, Geological Surveys of South Australia and Victoria, pp. 464.

YARROW, G.R., BAYES, R.J. and WHIBLEY, M., 1981, A geological review of the Otway Basin (unpublished rep.)

YORATH, C.J., and HYNDMAN, R.D., 1983, Subsidence and thermal history of Queen Charlotte Basin; Can. J. Earth Sci., v.20, p. 135-159.