C-GC-MS and its application to crude oil analysis

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Abstract: The Gas Chromatograph linked to a Mass Spectrometer with computerised data acquisition capability (C-GC-MS) makes for a very versatile and powerful analytical tool. The important function of the GC-MS in petroleum exploration and production studies is its ability to detect BIOMARKERS.

What are biomarkers? They are organic compounds whose carbon skeleton give an unambiguous link with a known natural or biological product. Examples are isoprenoids, triterpanes, steranes, sterols etc. In other words they may be described as "chemical fossils." Their thermal stability in oils and sediments (source-rocks) make them very useful in oil to source rock correlation studies or determination of the number of oil pools present in an area. A study using GC-MS data on a number of "oil stained" rock samples from Southeast Asia and the Bahamas will be highlighted as an example to illustrate the usefulness of C-GC-MS in the recognition of petroleum and determination of its source and maturity.

INTRODUCTION

What is a C-GC-MS?

C-GC-MS (short for Computerised Gas Chromatography-Mass Spectrometry) basically consists of a gas chromatograph with a mass spectrometer as a detector (as opposed to the usual flame ionization detector [FID]). The equipment is controlled by computer; this also acquires the data and is used in its processing. This combination is very versatile as the gas chromatograph has the capability to separate very complex mixtures of organics whilst the mass spectrometer bombards each compound eluting off the GC column with electrons i.e. a very high electrical potential (commonly 50-70 eV) and smashes each molecule to ionic fragments. A magnetic separator detects and separates the ionised molecular fragments according to their mass and charge. Each compound thus produces a characteristic *mass spectrum* (see Spectra 1, 2, and 3) which may contain several hundred molecular fragments, depending on the structure of the particular molecule. A given GC run of an oil may reveal several compounds of related structure present within (for instance) an oil. By homing in on one diagnostic fragment ion (i.e. using *mass fragmentography*) (seeFigure 1) over part or the whole run, these compounds will be highlighted, and other compounds in which that ion is less prominent, will be suppressed. Thus the instrument can be used like a microscope, and by keying in particular ions, one can reveal several groups of compounds otherwise not easily distinguishable or detectable.
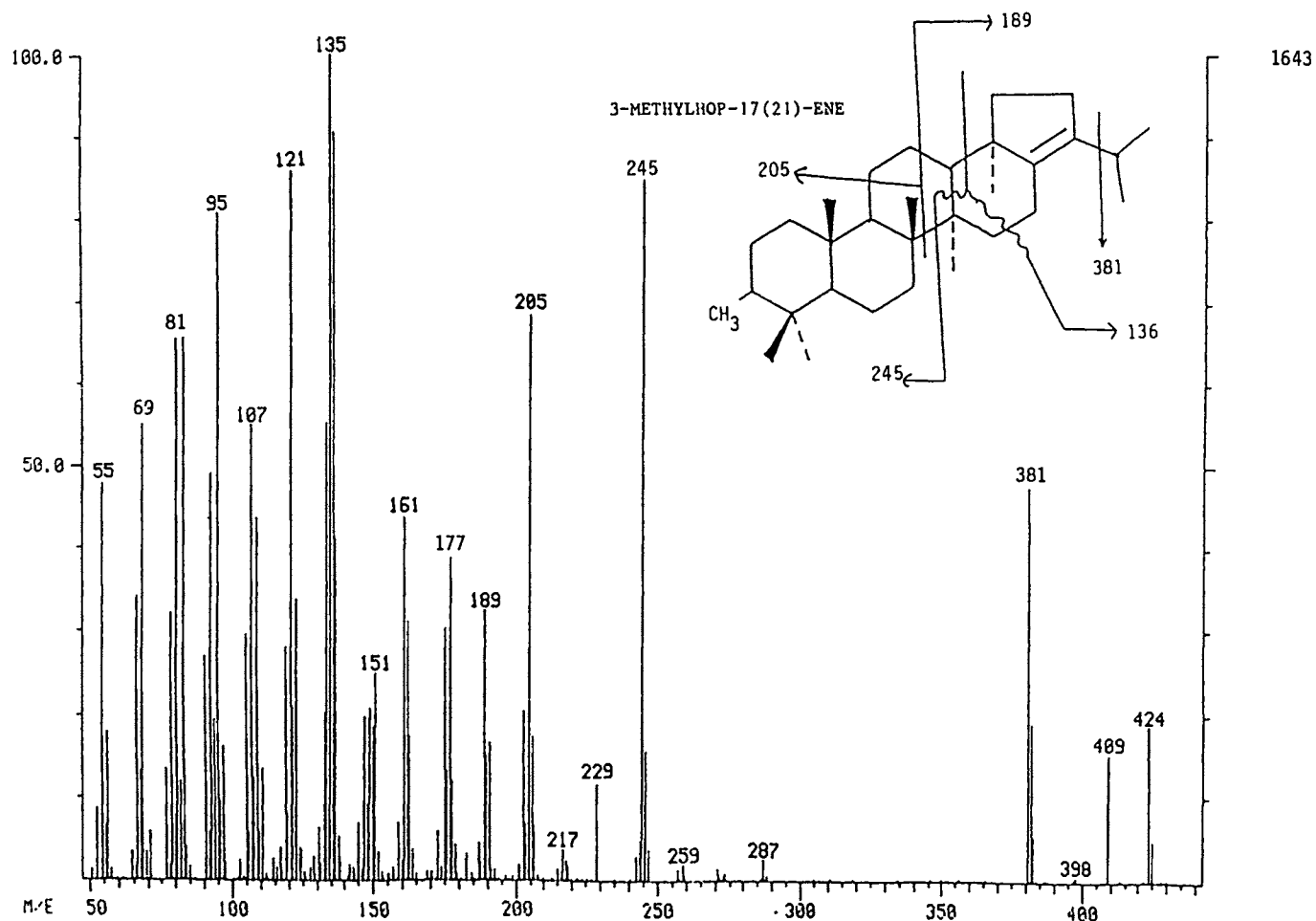
Spectra 1: Rationalisation of the mass spectra of various unknown triterpenes. Compounds are hypothesised to be 3-Alkylhop17(21)enes. Spectra 1, 2 and 3 are obtained on peaks marked A , B and C on Figure 1.
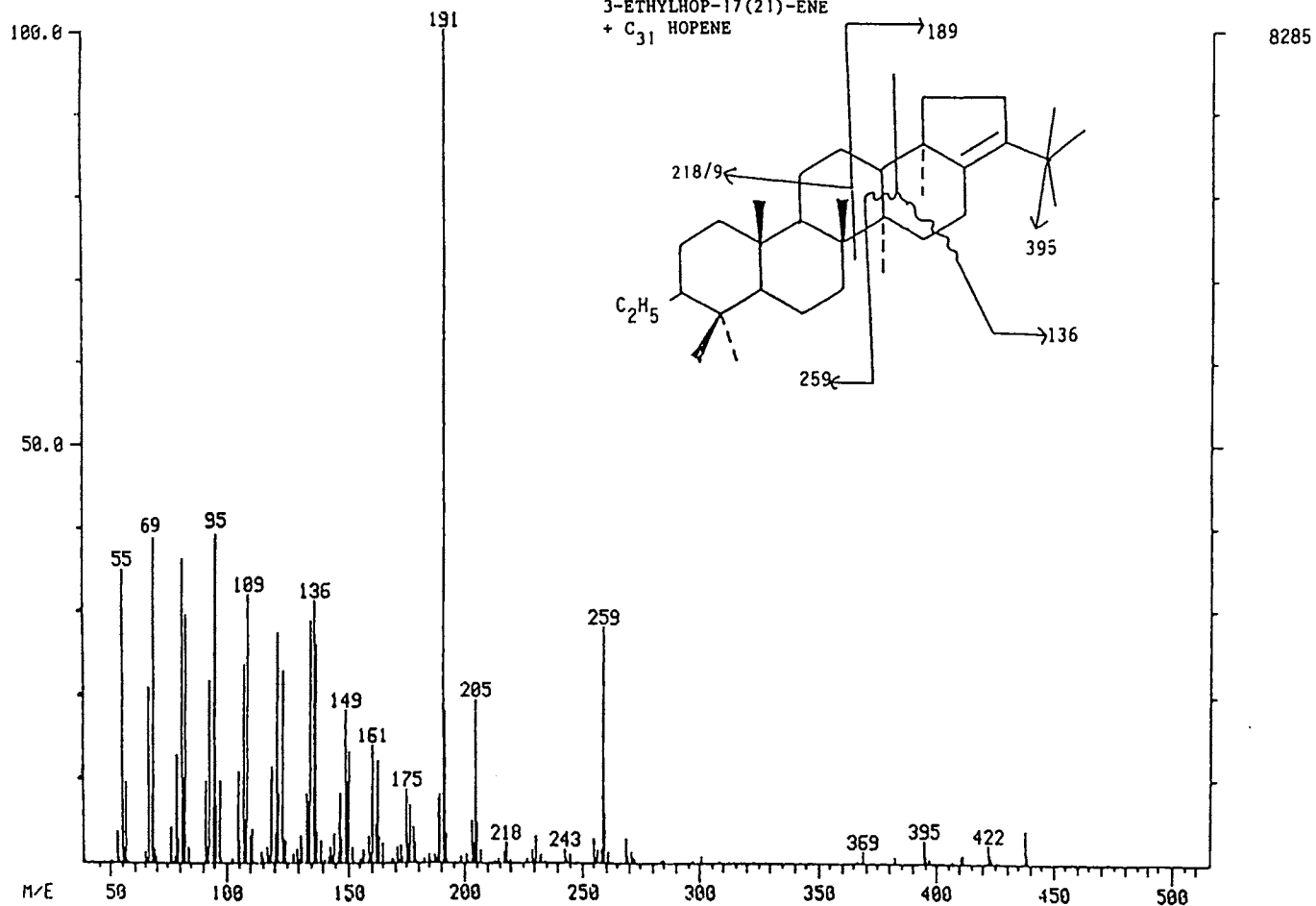
Spectra 2: Rationalisation of the mass spectra of various unknown triterpenes. Compounds are hypothesised to be 3-Alkylhop17(21)enes. Spectra 1, 2 and 3 are obtained on peaks marked A, B and C on Figure 1.
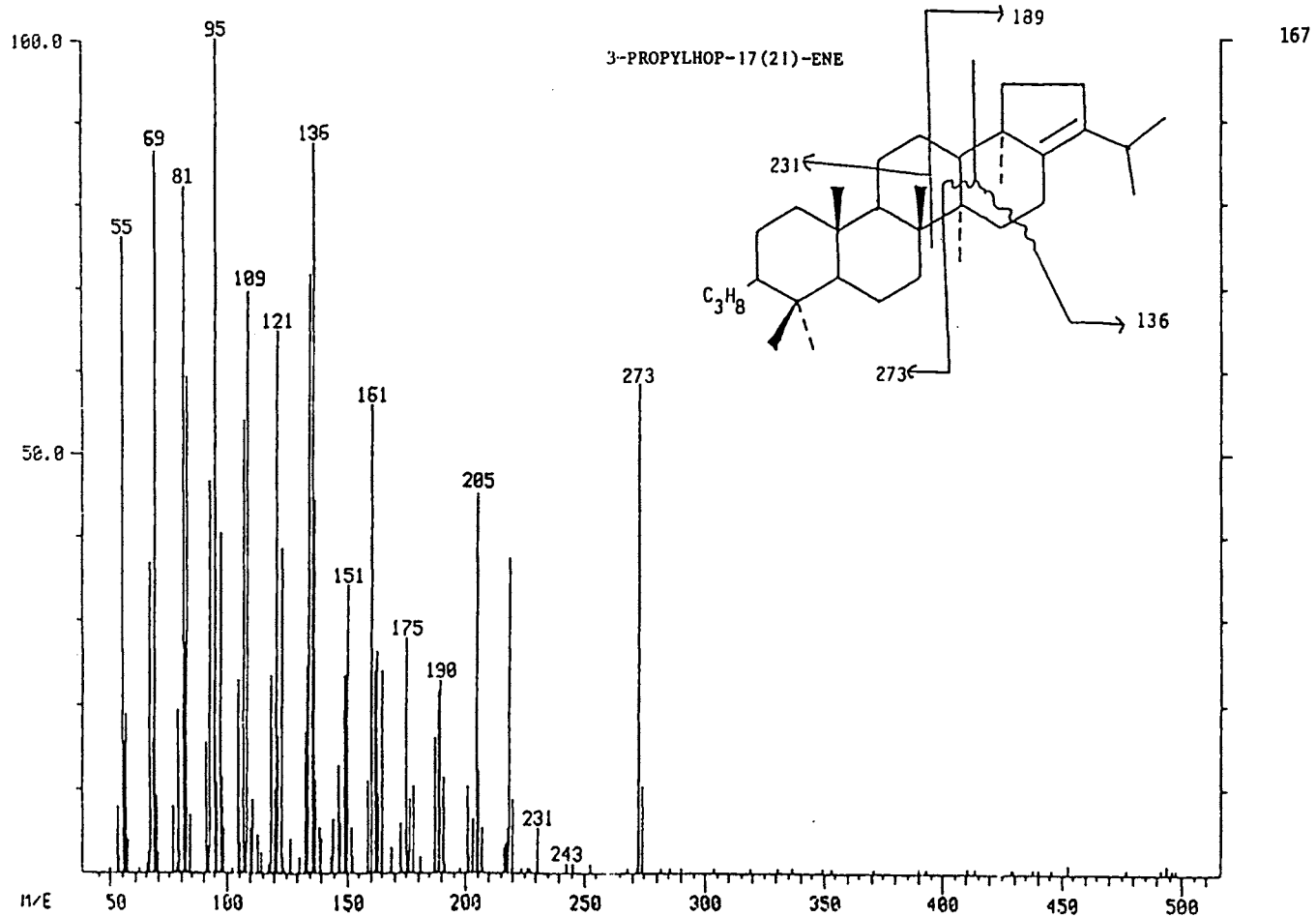
Spectra 3: Rationalisation of the mass spectra of various unknown triterpenes. Compounds are hypothesised to be 3-Alkylhop17(21)enes. Spectra 1, 2 and 3 are obtained on peaks marked A, B and C on Figure 1.
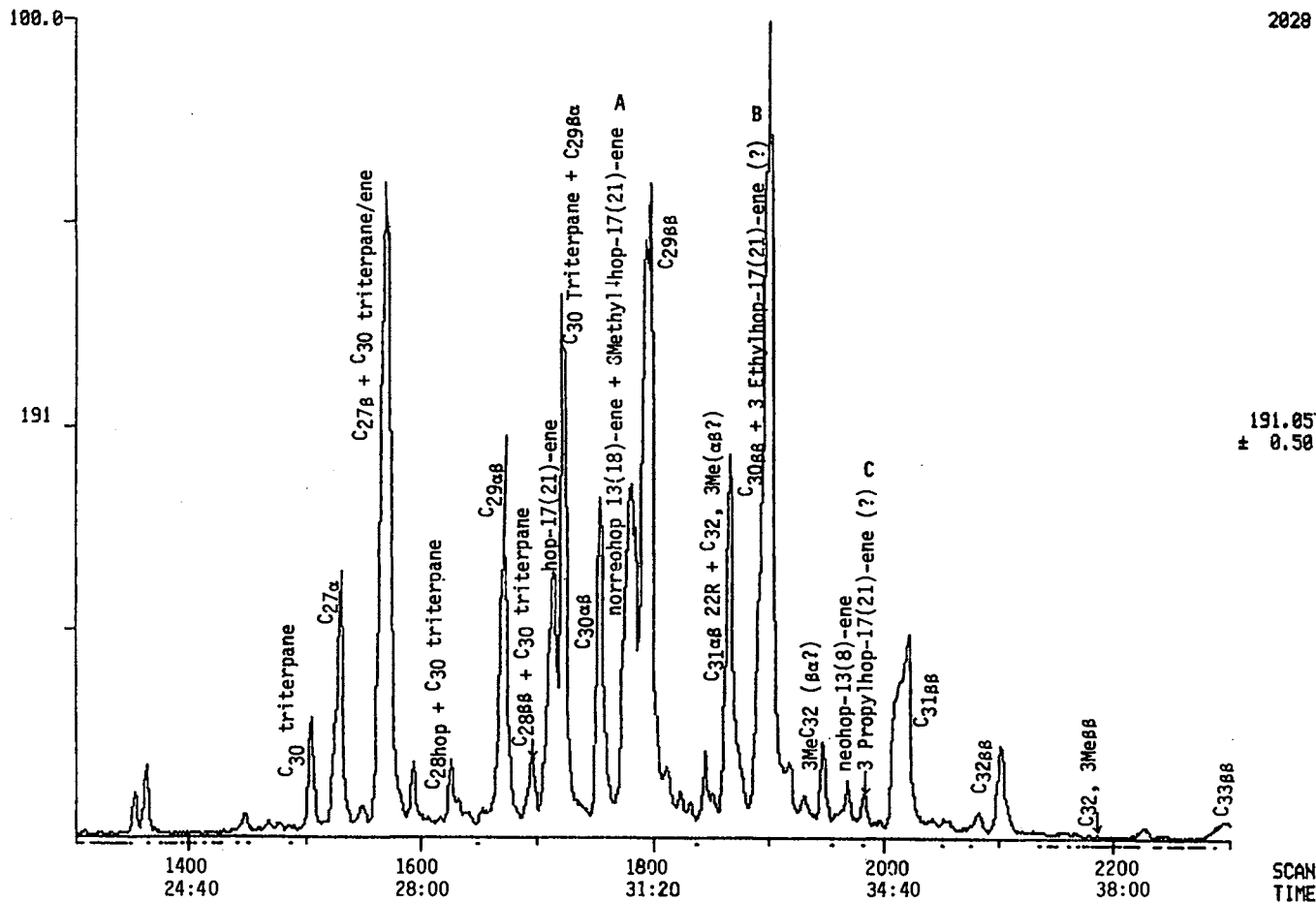
Figure 1: m/z 191 fragmentogram showing distribution of triterpenes and triterpanes from the saturated hydrocarbons of an immature S.E. Asian lacustrine source rock. N.B. numerous 3-alkyl hopanes and hopenes. For peaks marked A, B and C, see Spectra 1, 2 and 3.

C-GC-MS can be applied to the analysis of any organic mixture capable of being volatilised. Thus most organic gases, liquids and solids can be analysed on this equipment. Consequently natural gas, petroleum, tars, pitch, bitumen etc are commonly analysed using C-GC-MS, particularly when undertaking oil-source rock and oil-oil correlation studies. However, the versatility of the machine allows it to be used for many other organic products outside the field of geochemistry, thus pharmaceuticals, drug testing, cosmetics, food additives, flavourings, cooking oil, lubricants etc are commonly analysed using C-GC-MS.

Role of C-GC-MS in Petroleum Analysis

Historically petroleum analysis was for a long period restricted to simple fractionation steps and physical property tests. Thus API gravity determinations, viscosity measurements, boiling point curves, flash points, wax and sulphur contents etc. are some of the necessary preliminary steps in the determination of the commercial value of a crude and indispensable to every petroleum laboratory. However these analyses do not permit the isolation of the individual compounds which make up crude oil.

More sophisticated analyses attempt to isolate and characterise the individual constituents of petroleum. These techniques involve various forms of chromatography. Thus liquid column (LC) chromatography are used to quickly separate the saturated and aromatic hydrocarbons from the "polar" constituents of petroleum. Thin layer chromatography (TLC) is a more refined version of column chromatography and is also often used. Similarly, high performance liquid chromatography (HPLC) will readily separate the major constituents of petroleum. By a manipulation of the mixtures of chromatographic media used in the LC column (e.g. various grades of alumina or silica) or on the TLC plate, and by varying the solvent system, it is possible to further resolve some of the major compound "families" found in petroleum, particularly the aromatic hydrocarbons and pigment fractions. Thus the aromatics can be readily separated into mono, di, tri and polyaromatic fractions using simple chromatography (see Rowland et al, 1986). However the routine isolation and recognition of individual compounds from complex petroleum mixture can at present only be performed by using gas-chromatography (GC). Here an isolated hydrocarbon fraction (i.e. saturates or aromatic) is injected into a very thin bore fused quartz or glass column. The column is coated with a polymer, depending on the particular separation that is to be effected. For hydrocarbon mixtures the polymer phase chosen is generally OV-1 or OV-101 equivalents. The column has gas flowing through it, generally helium, nitrogen or hydrogen and is heated in a GC oven, compound detection is usually accomplished with the aid of an flame ionisation detector (FID).

Modern petroleum analysis is now routinely performed using gas chromatography and computerised gas-chromatography mass-spectrometry. By the

use of the simple preliminary fractionations discussed earlier (using liquid column or thin layer chromatography) petroleum can be quickly resolved into the saturated and aromatic hydrocarbons as well as "polars". Gas chromatography of the saturated fractions usually yields a series of n-paraffins (See Figure 2). The paraffins and short chain acyclic isoprenoids can quickly be identified by their retention index or just by recognising the characteristic patterns of a crude oil (See Figure 2). Co-injection with synthesized standards could be used to identify the n-alkanes though this technique would now only be applied to a far less well known series of compounds. However petroleum contains a very large number of minor napthenic components, (several thousand) and these cannot be readily identified by gas chromatography alone due to the complexity of the mixture. Clearly another more sophisticated tool is required for the detailed analysis of crude oils. The most powerful tool known at present for the routine analysis of complex mixtures is computerised gas chromatography-mass spectrometry.

By acquiring the GC-MS data into a computer it becomes possible to manipulate the data. Thus, as many of the compounds in crude oil form homologous or pseudohomologous series, it is very easy to use the computer to pick out diagnostic ions characteristic of whole suites of compounds. As an example, m/z 191 will pick out virtually all the triterpanes, as these nearly always give a characteristic $C_{14}H_{23}+$ fragment ion (i.e. mass 191) (see Figure 1), alternatively one can take a full mass spectrum for each compound (see Spectra 1, 2 and 3). The full mass spectrum reveals the major structural features of the molecule. As data can be easily retrieved and manipulated, the mass spectra of a number of compounds can be rapidly compared with the spectra from authentic standards, and this data, along with each compounds retention time, used in identification purposes.

Oils still contain large numbers of uncharacterized compounds, in particular many nitrogen and sulphur compounds remain unknown, even though an approximate idea of their structure can be obtained from mass spectrometry.

Very recent technological developments, has now made available C-GC-MS-IR. Here an infra red spectrum is provided with the mass spectrum. This will provide a very useful adjunct in distinguishing isomers of slightly different structure. In an average GC-MS analysis of Far East crudes there are commonly encountered numerous triterpenoids of unknown structure (see Figure 3). C-GC-MS-IR should help in clarifying the structure of some of these unknowns, however, some of these compounds are probably "bicadinane" isomers (Cox et al., 1986). The other mass spectrometric techniques such as MS/MS and FAB techniques are still mainly university research tools that are not yet widely applied in the industrial laboratory.
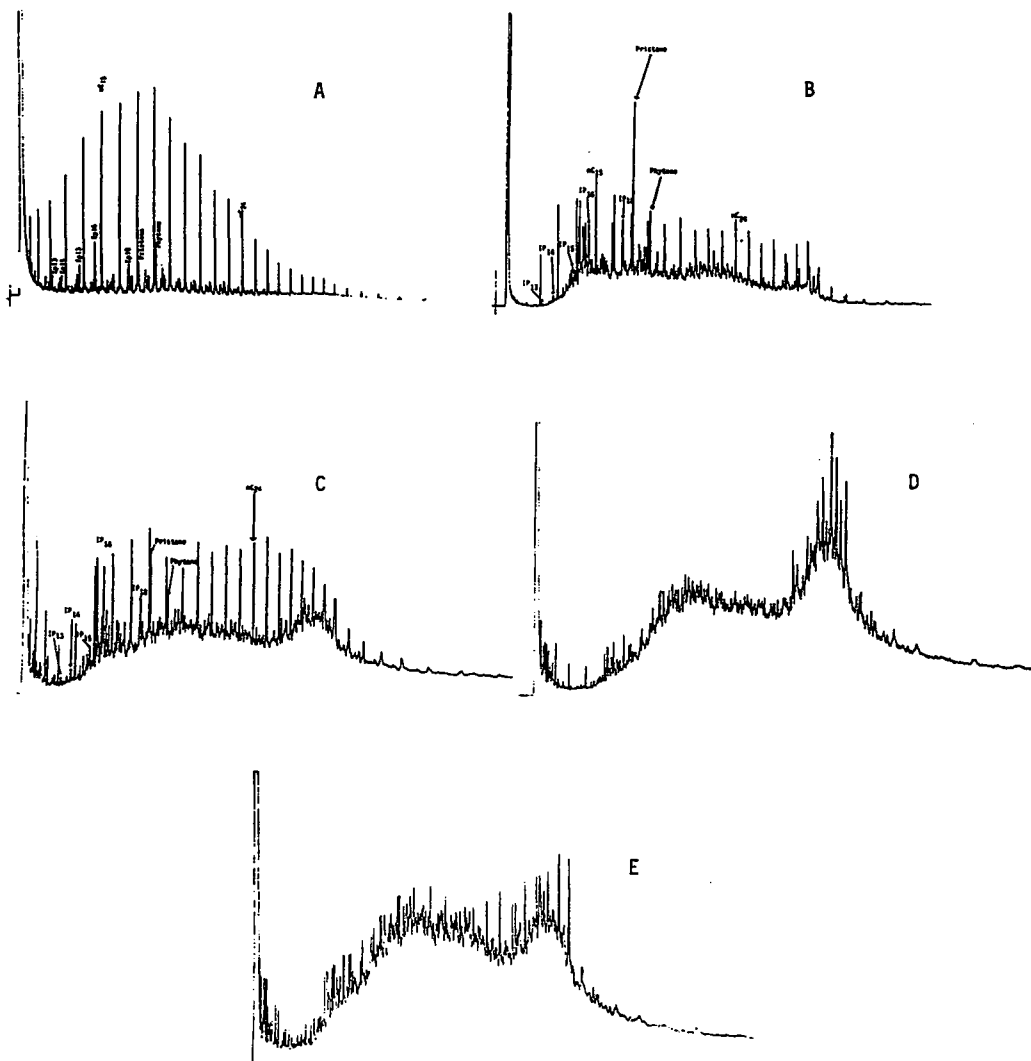
Figure 2: Gas chromatograms of the saturated hydrocarbons from five core samples. Note sample A shows no evidence of biodegradation and is a typical distribution from a light oil. Sample D shows extensive degradation as all the n-alkanes have been removed.
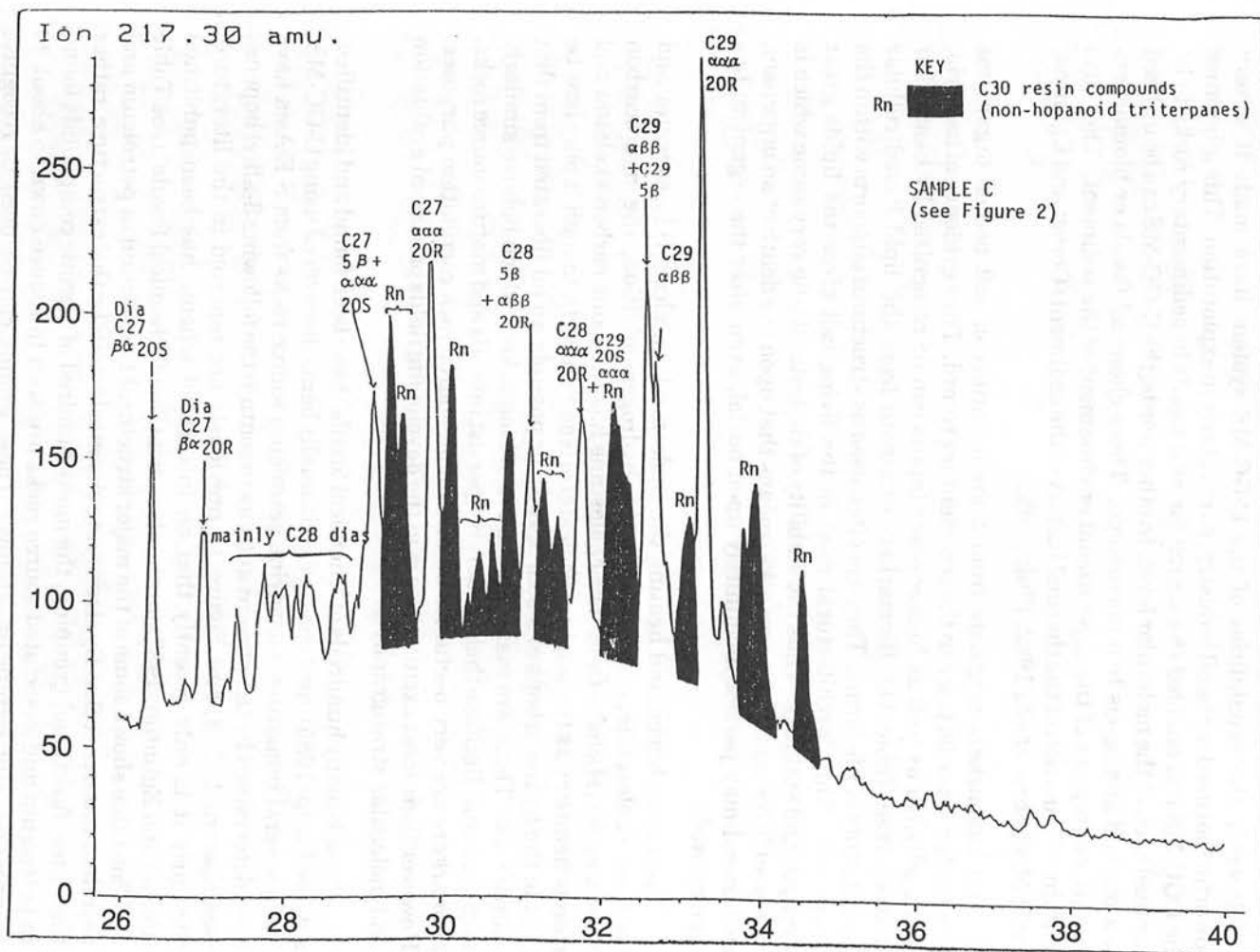
Figure 3: m/z 217 mass fragmentogram from the saturated hydrocarbons from Sample C (Figure 2). Samples A, D and E had identical distributions. Note large number of peaks marked Rn. These are presently uncharacterised resin (?) derived compounds presently found mainly in S.E. Asian crudes. Also note presence of "mature" steranes (αββ and ααα 20S)

The Search for Chemical Fossils

Recently the capabilities of the C-GC-MS system have made it a very powerful tool used in the oil industry, particularly in exploration. This is because the CGC-MS has enabled the search for new fossils in sedimentary rocks to be pursued even at the molecular level. In other words, the C-GC-MS can be utilized in a method analogous to a microscope. These chemical fossils or biomarkers contain an imprint of the depositional environment of the sediment. They also contain information of the thermal history of the sediment (Comet and Eglinton, 1987; Mackenzie *et al.*, 1982; Philp, 1985).

The biomarkers originate from a great variety of soft bodied organisms which often leave no trace in the sedimentary record. Thus evidence of bacteria, algae, jellyfish as well as higher plant inputs can be recognised by biomarker analysis (see Table 1). Biomarkers originate from the lipid based cellular constituents of life forms. They are often used as structural supports within the living cell. This "architectural role" in the living cell gives the lipids great strength and stability. Thus the stability of cholesterol (the very same which is responsible for many heart attacks) means that upon the death of an organism, cholesterol may persist indefinitely upon burial, even after the organism has decomposed.

Upon deep burial and heating the cholesterol (an alcohol) loses water and becomes cholestadiene and finally, by hydrogen addition, the hydrocarbon known as 5α (H)cholestane. The cholestane has the same carbon skeleton and stereochemistry as the original cholesterol (see Figure 4), though it may now be part of the hydrocarbons of a source rock, or possibly an oil liberated from that source rock. There are many thousands of biomarkers which behave similarly to cholesterol. Because their structures persist into oils and mature source rocks, biomarkers are very useful for oil-oil and oil-source rock correlation purposes. However their most exciting role is in the developing fields of basinal evaluation and molecular stratigraphy.

Though many hundreds of "chemical fossils" have been found and identified, e.g. see Philp (1985), new ones are continually being discovered using C-GC-MS. Thus several immature, lacustrine petroleum source rocks from S E Asia have been determined by the present authors to contain the following 3-alkyl hopenes (see Spectra 1, 2, 3, and Figure 1), previously not reported in the literature. Similarly it is only recently that an integrated scheme has been published (Comet and Eglinton, 1987) for the classification of "chemical fossils" (see Table 1). This table shows some of the major structural types found in petroleum and petroleum source rocks. By classifying chemical fossils by their structure, rather than their functional grouping, the many hundred of organic compounds found in petroleum and associated source rocks are seen to reduce down to about 20 environmentally significant groups. These groups can be used to recognise depositional environments within petroleum source rocks.

Table 1: Input Indicators (Grouped By Structure And Taxonomic Affinities)

Structure Number	Structural Grouping	High Plant Lipids (Terrestrial Markers)	Algal Lipids (Mainly Marine Markers)	Bacterial Markers and Lipids	Others
I	Straight chain (Short) $nC_{10}-nC_{20}$	Not very specific marker compounds, common in many algae and bacteria			
I	Straight chain (Long) $nC_{21}-nC_{30}$	Plant waxes[a] n-alkanes, n-acids n-alcohols n-ketones	b		
I	Straight chain (Very long) $nC_{37}-nC_{39}$		Nannop lankton lipids (coccoliths) polyunsaturated ketones and hydrocarbons		
II	Branched chain (Short) $C_{10}-C_{20}$			iso and antesio compounds, acids, alcohols esp. C_{15} (C_{17} compounds)	
II	Branched chain (Long) $C_{21}-C_{35}$	Alkanes and monomethyl alcohols		Unusual mid-chain branched $C_{19}-C_{30}$ alkanes found in some Pre-Cambrian oils	
III	Acyclic isoprenoid (Diterpenoid)	Phytal, C_{18} isoporenid ketone, phytene, pristane, phytane, etc are taxonomically non-specific productive indicators			
IV	Other acylic			Squalane, lycopane, C_{25} sesterpane, etc, are believed to be of archaebacterial origin	
V	Carotenoids	Very diverse origins found in great range of organisms depends on functionality		In sediments, taxonamic allocation	
VI	Cyclic diterpenoid fichtelite, simonellite	Dehydroabietic acid,[c] dehydroabietin, retene,		Extended diterpenaid[d]	

(Continue)

Table 1: Input Indicators (Grouped By Structure And Taxonomic Affinities) (Continue)

Structure Number	Structural Grouping	High Plant Lipids (Terrestrial Markers)	Algal Lipids (Mainly Marine Markers)	Bacterial Markers and Lipids	Others
VII	Hopanoid	3-Keto hydroxy derivatives and degraded tetracyclic alkanes/ alkenes aromatics		Diverse aerobic bacteria[a] cyanobacteria	
VIII	Nonhopanoid triterpenoid	Lupane, etc, (about 20[f] different structural types)		Fernenes found in[e] photosynthetic anaerobic bacteria	Gammacerane (Tetrahymarol found in protozoa)
IX	4-methyl steraids		Dinasteral (ex-dinaflagel lates) and possibly the other major 4-methyls in sediements	C_{28}-4-methyl steraids are found in methanotrophic bacteria	
X	Desmethyl steroids	Sitosterol	C_{26}-C_{27}-C_{28}-C_{30} sterals[h]		
XI	Polynuclear aromatics (PNA's)	Common in terresterial[j] sediments, coals, etc			
XII	Parphyrins and chlorins	Taxonomically non specific productivity indicators			

[a]Certain bacteria biasynthesise n-acids and n-alkanes in this carbon range, but with little or no carbon preference index.
[b]Same marine sediments contain a considerable range of diols and keto-ols in this carbon number range, they are probably of "algae" origin.
[c]Diagenetic derivatives of conifer resin.   [d]Possibly algae.
[e]The majority of hopanoids in sediments are probably bacterial .
[f]Those sediments containing a considerable range of non-hopanoid structures possibly contain an anglosperma input.
[g]Also in fems.   [h]Desemthyl steroids are not biosynthesized by bacteria.
[i]High plants commonly contain 24-ethyl groups in the R position, marine algae in the 24 S position.
[j]Ex-coal maceral/oil seep, etc (of indirect biological origin).
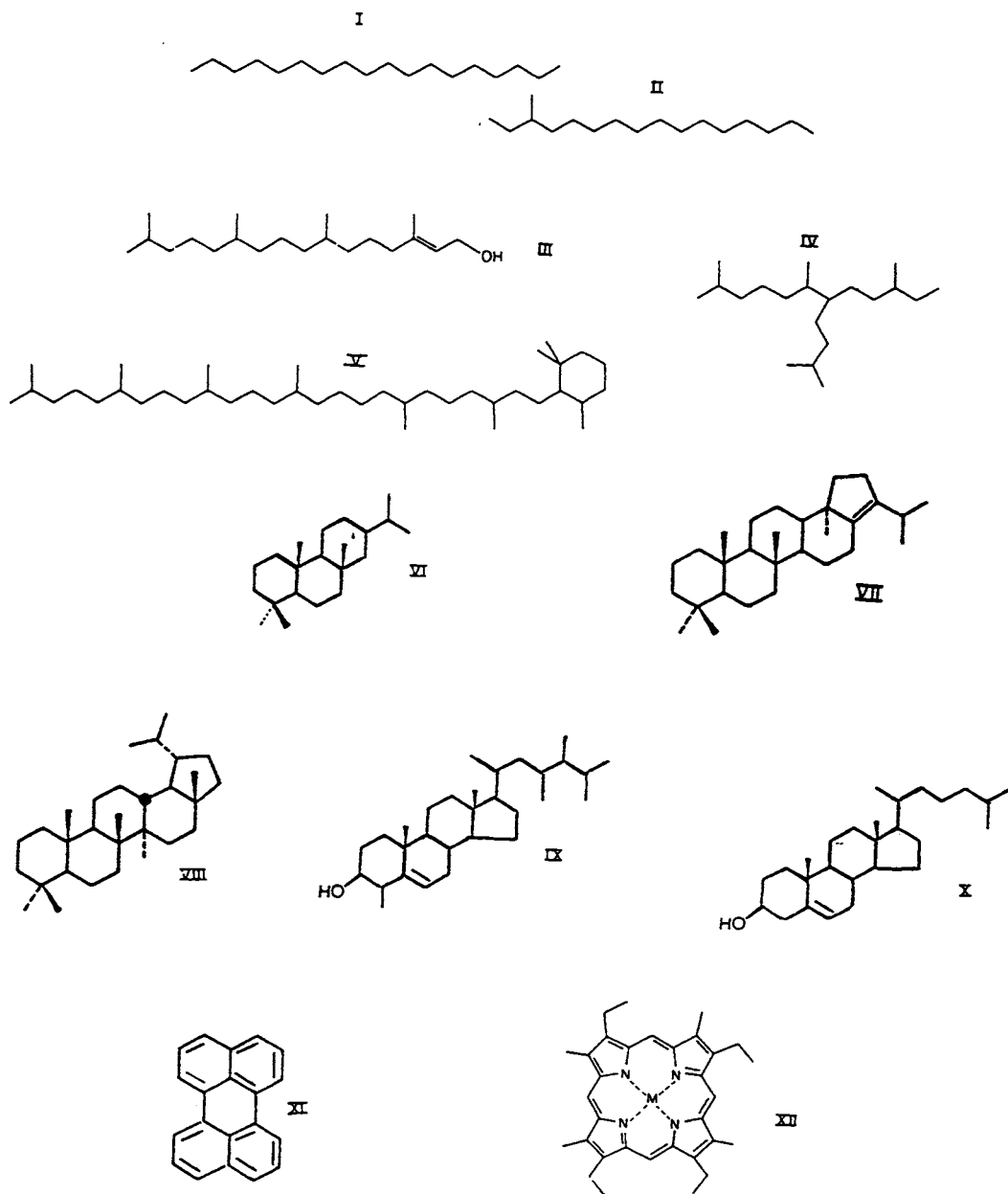
Structures
(see Table 1)

SIMPLIFIED SCHEME SHOWING THE TRANSFORMATION OF CHOLESTEROL
INTO PETROLEUM HYDROCARBONS

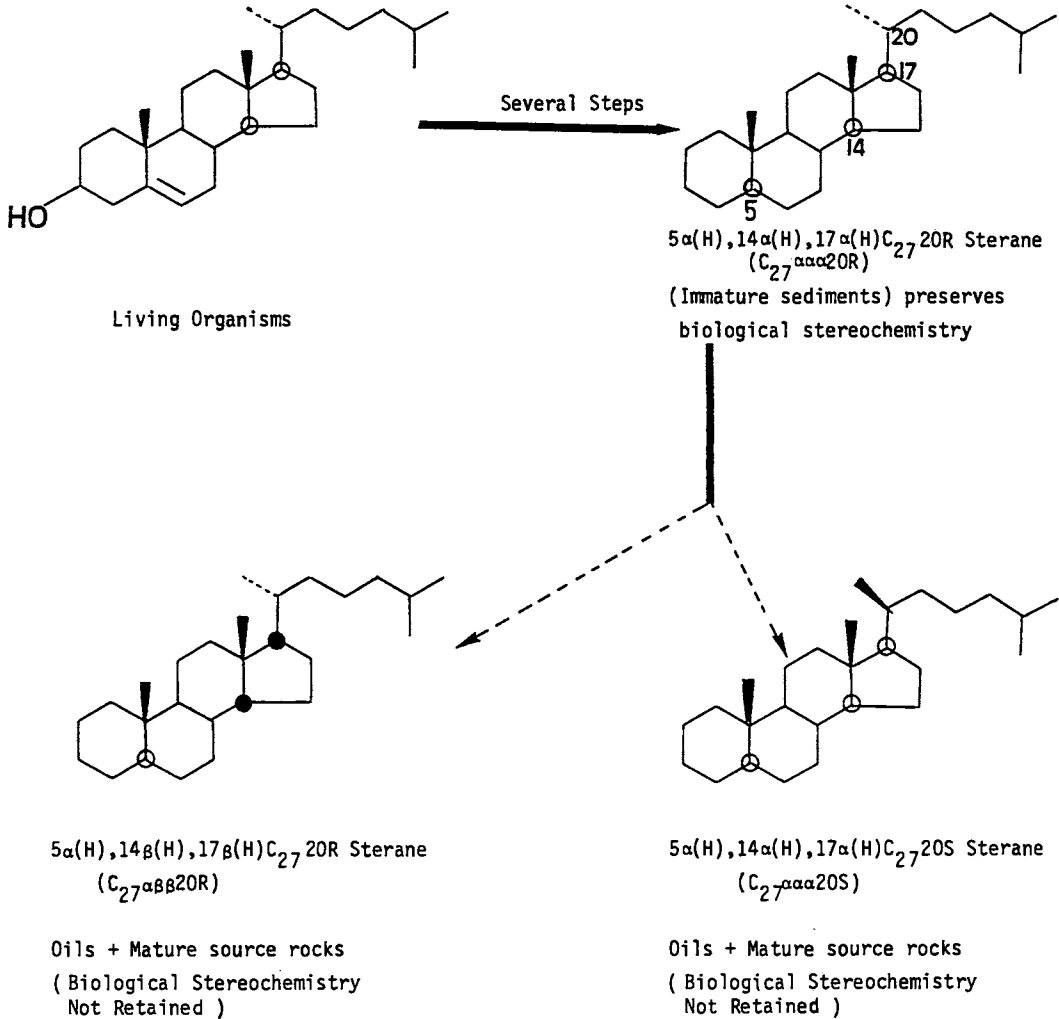CHOLESTEROL (found in living plants)   becomes   5α CHOLESTANE (found in oils and source rocks)

HO

Several Steps

Living Organisms

$5\alpha(H),14\alpha(H),17\alpha(H)C_{27}20R$ Sterane
$(C_{27}\alpha\alpha\alpha20R)$

(Immature sediments) preserves
biological stereochemistry

$5\alpha(H),14\beta(H),17\beta(H)C_{27}20R$ Sterane
$(C_{27}\alpha\beta\beta20R)$

Oils + Mature source rocks
(Biological Stereochemistry
Not Retained)

$5\alpha(H),14\alpha(H),17\alpha(H)C_{27}20S$ Sterane
$(C_{27}\alpha\alpha\alpha20S)$

Oils + Mature source rocks
(Biological Stereochemistry
Not Retained)

Figure 4:   Diagenetic/Maturation scheme showing the transformation of cholesterol into
petroleum hydrocarbons.

Another example of the application and advantages of mass spectrometry to petroleum analysis was the investigation of five (5) "dil-stained" cores from the S E Asia region. Solvent extraction and isolation of the aliphatic hydrocarbon fraction from these cores was followed by gas chromatography of the saturated hydrocarbons. The issues under question were: 1) Are the materials staining the cores petroleum or merely non-petroliferous bitumen? 2) If the staining material proved to be petroleum, how many kinds were present? 3) Was more than one source rock involved? 4) What kinds of input were significant in the source rocks? It proved to be possible to answer all of these questions using C-GC-MS data. However, gas-chromatography showed that many of the samples had lost their n-alkanes due to biodegradation, see Figure 2. Because of this it proved not to be possible to readily cross compare the extracts by the use of GC alone.

However C-GC-MS clearly showed the affinities of these samples. Four (4) of the samples gave mature sterane profiles (m/z 217). Thus the 5α (H)20R steranes and 5β(H) steranes commonly found in immature, recent sediments had given way to a petroleum assemblage dominated by abb steranes, diasteranes and 20S $\alpha\alpha\alpha$ steranes (see Figures 3). Thus it was possible to recognise these four (4) samples as being petroleum derived, mainly biodegraded "tars" (though one sample [Figure 2A] showed little evidence of biodegradation). Similarly, the hopane profile (m/z 191) (see Figure 5), was characteristic of petroleum. The complex pattern of hopenes and $\beta\beta$ hopanes found in recent sediments had been replaced by an immature petroleum assemblage of extended $\alpha\beta$ hopanes (note the 22S isomer in greater abundance than the 22R isomer).

These samples proved to be similar to others found in SE Asia in showing a considerable terrigenous input. Thus the triterpane distributions showed a number of biomarkers that probably originate from higher plants e.g. 18α(H)oleanane. However large numbers of higher plant compounds (triterpanes) were also present which presently cannot be identified (see Figure 5). These peaks are marked with Rn, they are presumed to originate from tropical tree resins, but their exact structure remains unknown at present. Some, but not all, of these compounds are probably "bicadinane" isomers. The sterane profile (m/z 217) also shows large numbers of these components (see Figure 3). The isolation and elucidation of the structure of these compounds remains to be undertaken by the academic community.

By contrast, one of the sediment samples (also bitumen stained) showed a very different sterane (m/z 217) and triterpane (m/z 191) profile. The steranes were dominated by 5α(20R) and 5β steranes. The $\alpha\beta\beta$ and 5α20S sterane isomers were present only in tiny amounts (see Figure 6). The distribution was interpreted as being indicative of an immature bitumen i.e. petroleum was not present in this sample. The triterpanes (m/z 191) similarly indicated the immaturity of the sample. In this case, the extended hopanes exhibited the 22R isomer in greater abundance than the 22S. This is characteristic of immature samples that have experienced some maturation, but insufficient to generate petroleum (see Figure 7 and Tables 2 & 3).

TABLE 2

STERANE IDENTIFICATIONS
(See Figure 3, 6 and 9)

Peak Component	Assignment
Dia C_{27} βα 20S	13β (H), 17α (H) - diacholestane (20S)
Dia C_{27} βα 20R	13β (H), 17α (H)- diacholestane(20R)
C_{27} ααα 20S	5α (H), 14α (H), 17α (H) - cholestane (20S)
C_{27} 5β	5β (H), 14α (H), 17α (H) - cholestane (20R)
C_{27} 5β	5β (H), 14α (H), 17α (H) - cholestane (20R)
C_{27} αββ 20R	5α (H), 14β (H), 17β (H) - cholestane (20R)
C_{27} αββ 20S	5α (H), 14β (H), 17β (H) - cholestane (20S)
C_{27} ααα 20R	5α (H), 14α (H), 17α (H) - cholestane (20R)
C_{28} ααα 20S	24-Methyl-5α (H), 14α (H), 17α (H)- cholestane (20S)
C_{28} 5β	24-Methyl-5β (H), 14α (H), 17α (H)- cholestane (20R)
C_{28} αββ 20R	24-Methyl-5α (H), 15β (H), 17β (H)- cholestane (20R)
C_{28} αββ 20S	24-Methyl-5α (H), 14β (H), 17β (H)- cholestane (20S)
C_{28} ααα 20R	24-Methyl-5α (H), 14α (H), 17α (H)- cholestane (20R)
C_{29} ααα 20S	24-Ethyl-5α (H), 14α (H), 17α (H) - cholestane (20S)
C_{29} 5β	24-Ethyl-5β (H), 14α (H), 17α (H) - cholestane (20R)
C_{29} αββ 20R	24-Ethyl-5α (H), 14β (H), 17β (H) - cholestane (20R)
C_{29} αββ 20S	24-Ethyl-5α (H), 14β (H), 17β (H) - cholestane (20S)
C_{29} ααα 20R	24-Ethyl-5α (H), 14α (H), 17α (H) - cholestane (20R)
Rn (C_{30})	Resin derived triterpanes (unknown)

N.B. Diasterane = Re-arranged Sterane

TABLE 3

TRITERPANE IDENTIFICATIONS
(See Figures 1, 5, 7 and 8)

Peak Component	Assignment
Ts	18α (H) 22, 29, 30-trisnorneohopane
Tm	17α (H) 22, 29, 30-trisnorhopane
C_{27}17 (21)	Trisnorhop-17 (21) -ene
C_{27}α	17α (H) -22, 29, 30-Trisnorhopane
C_{27}β	17β (H) -22, 29, 30-Trisnorhopane
C_{28} hop	C_{28}Hopane
C_{29}αβ	17α (H), 21β (H) -Norhopane
HOP-17 (21)-ene	As given
C_{29}βα	17β (H), 21α (H) -Norhopane
C_{30}αβ	17α (H), 21b (H) -Norhopane
Norneohop-13 (18) ene	As given
3 Methylhop-17 (21) ene	As given
C_{30}βα	17β (H), 21α (H) -Norhopane
C_{30}13 (18) ene	Neohop-13 (18) -ene
C_{29}ββ	17β (H), 21β (H) -30-Norhopane
C_{31}17 (21) ene	Homohop-17 (21) -ene
S-C_{31}αβ	17α (H), 21β (H) -Homohopane (22S)
R-C_{31}αβ	17α (H), 21β (H) -Homohopane (22R)
C_{32}3-Me (αβ?)	17α (H), 21β (H) -3-Methylhopane
C_{30}ββ	17β (H), 21β (H) -Hopane (22R)
3 Ethylhop-17 (21) ene?	As given
3 Me-C_{32} (βα?)	17β (H), 21α-3-Methylhopane
Neohop-13 (8) -ene	As given
3 propylhop-17 (21) ene (?)	As given
S-C_{32}αβ	17α (H), 21β (H) -bishomohopane (22S)
R-C_{32}αβ	17α (H), 21β (H) -Bishomohopane (22R)
S-C_{32}βα	17β (H), 21α (H) -Bishomohopane (22S)

(Continue)

TABLE 3 (continue)

TRITERPANE IDENTIFICATIONS
(See Figures 1, 5, 7 and 8)

| Peak Component	Assignment
R-$C_{32}\beta\alpha$	17β (H), 21α (H) -Bishomohopane (22R)
$C_{31}\beta\beta$	17β (H), 21β (H) -Homohopane (22R)
S-$C_{33}\alpha\beta$	17α (H), 21β (H) -Trishomohopane (22S)
R-$C_{33}\alpha\beta$	17α (H), 21$\alpha\beta$ (H) -Trishomohopane (22R)
$C_{33}\beta\alpha$	17β (H), 21α (H) -Trishomohopane
$C_{32}\beta\beta$	17β (H), 21β (H) -Bishomohopane (22R)
C_{32}-Me ($\beta\beta$)	17β (H), 21β (H) -Methyl homohopane
S-$C_{34}\alpha\beta$	17α (H), 21β (H) -Tetrakishomohopane (22S)
R-$C_{34}\alpha\beta$	17α (H), 21β (H) -Tetrakishomohopane (22R)
$C_{34}\beta\alpha$	17β (H), 21α (H) -Tetrakishomohopane
$C_{33}\beta\beta$	17β (H), 21β (H) -Trishomohopane (22R)
$C_{34}\beta\beta$	17β (H), 21β (H) -Tetrakishomohopane (22R)
S-$C_{35}\alpha\beta$	17α (H), 21β (H) -Pentakishomohopane (22S)
R-$C_{35}\alpha\beta$	17α (H), 21β (H) -Pentakishomohopane (22R)
OL (C_{30})	18α (H) -Oleanane
GM (C_{30})	Gammacerane
Tr	Unknown tricyclic terpane
R(C_{30})	Unknown triterpane (resin derived)
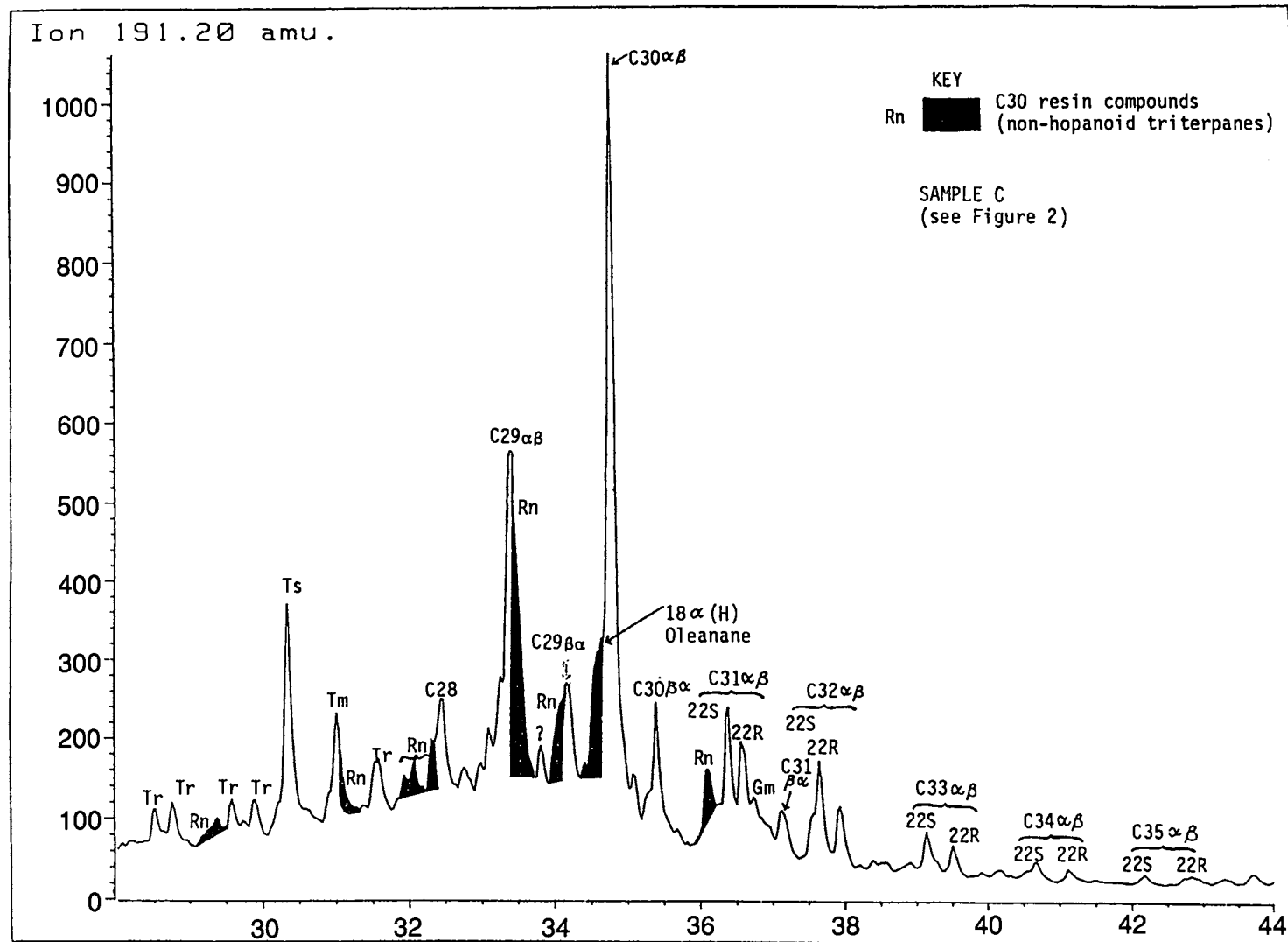
Figure 5: m/z 191 mass fragmentogram from the saturated hydrocarbons from Sample C (Figure 2). Samples A, D and E had identical distributions. Note large number of peaks marked Rn. These are presently uncharacterised resin (?) derived compounds presently found mainly in S.E. Asian crudes. Also note presence of "mature" hopanes i.e. extended αβ 22S isomers.
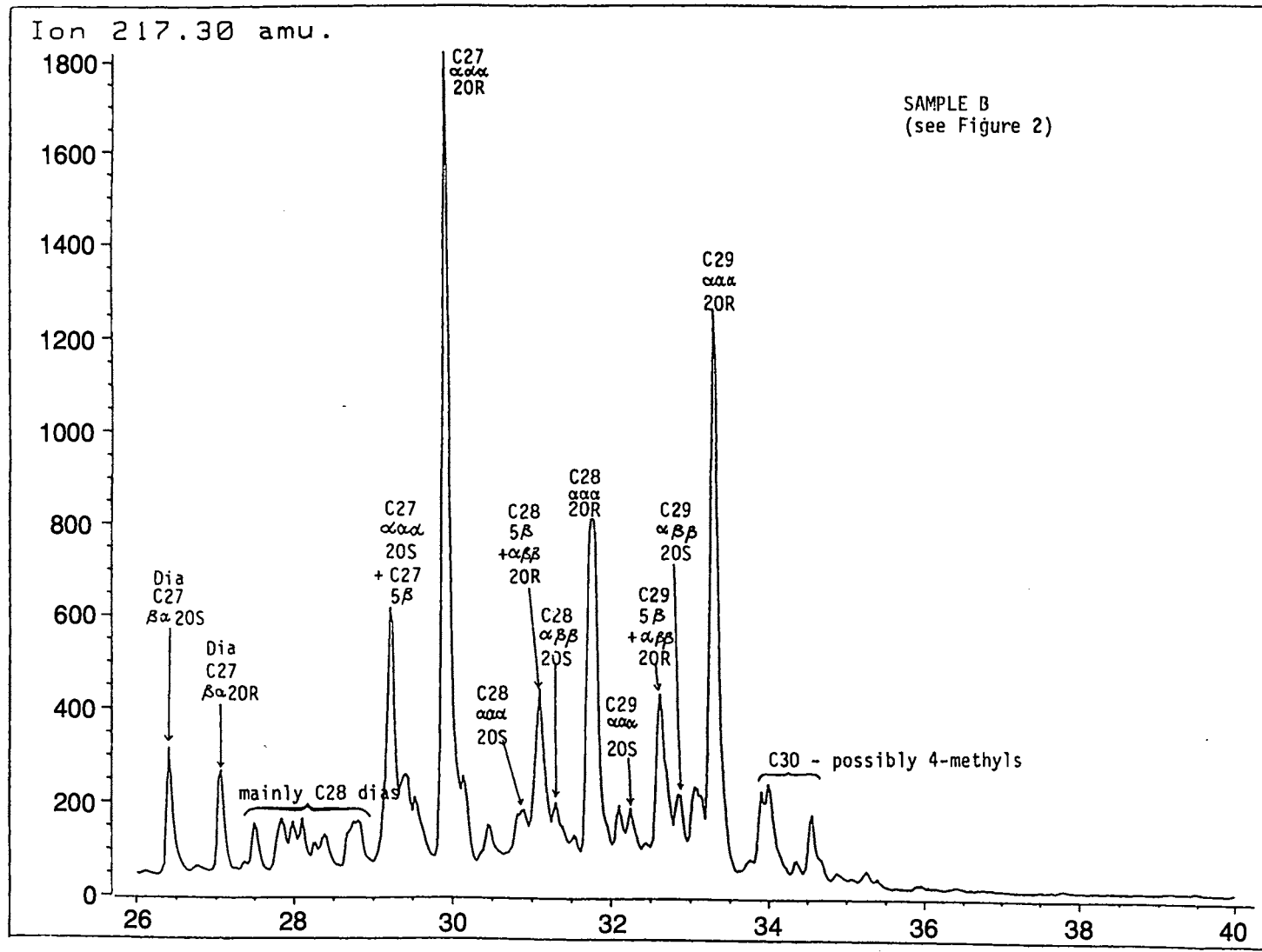
Figure 6: m/z 217 fragmentogram from the saturated hydrocarbons of Sample B (see Figure 2). Note simple sterane distribution and lack of unknown resin compounds. Also note lack of αββ and ααα 20S steranes. The sample is immature.
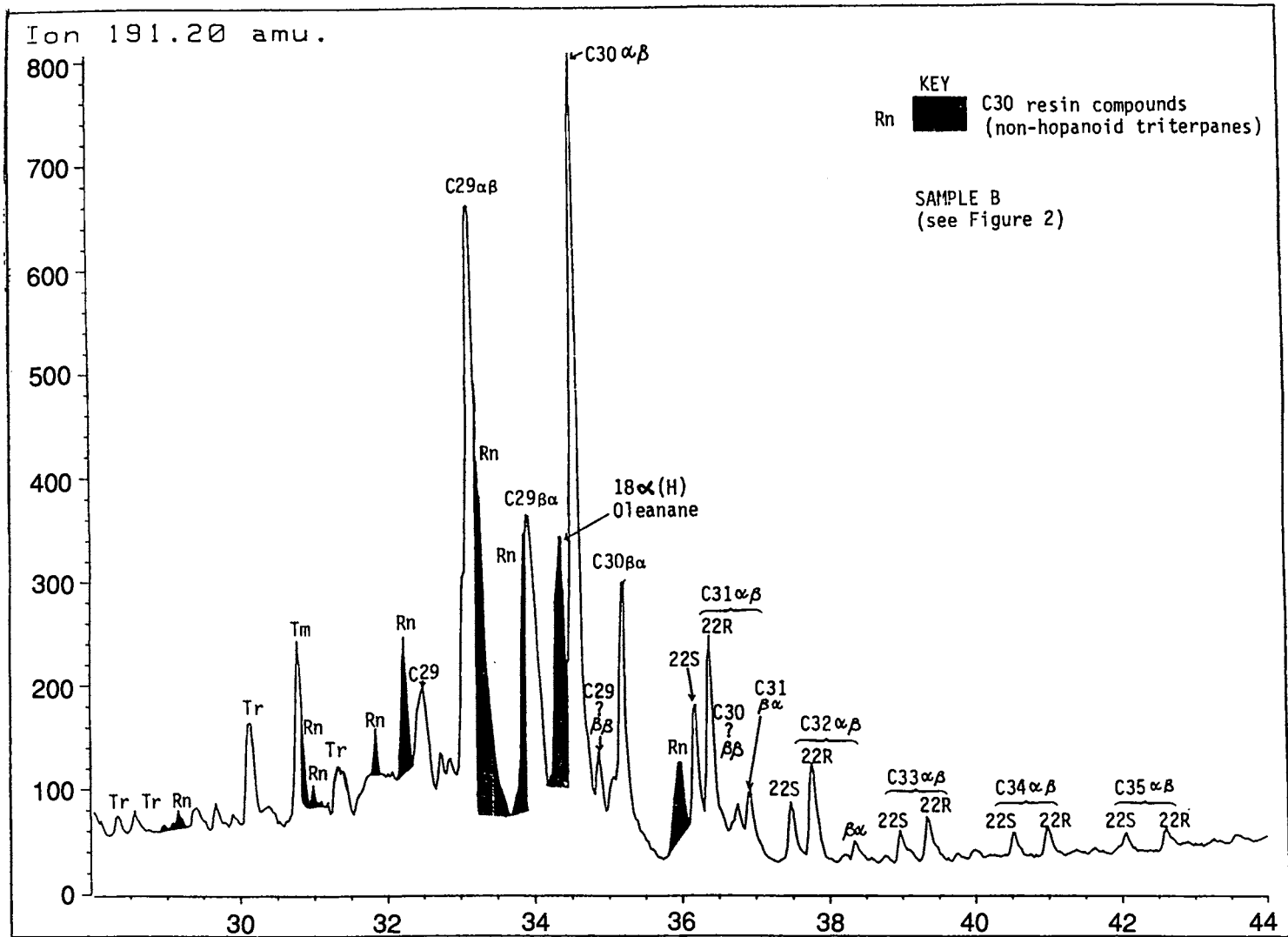
Figure 7: m/z 191 fragmentogram from the saturated hydrocarbons from Sample B (see Figure 2). Note the 22R αβ hopanes are present in greater abundance than the 22S αβ hopanes. This indicates sample immaturity. Also note resin (?) derived compounds.

Thus by the use of C-GC-MS on these five (5) samples, it proved possible to show:

1) That four (4) samples contained petroleum in various degrees of biodegration i.e. dead oil. The 5th sample contained mainly immature bitumen.

2) That the oil was sourced from a single terrigenous/lacustrine source rock, rich in higher plant detritus.

Another example of the recognition of petroleum biomarkers using C-GC-MS was undertaken on samples collected from the Ocean Drilling Project (ODP) Leg 101, Bahamas. The biomarker patterns from four (4) samples were described. These samples consisted of carbonaceous limestones, (from site 635B) and two gypsum samples and a dolomite (from site 627B); all these samples were mid-Cretaceous age.

Examination of the biomarkers distributions within the saturated hydrocarbon fraction from these four (4) samples showed that the two carbonaceous limestones contained sterane distributions similar to that shown in Figure 6. However the triterpanes assemblage still contains hopenes such as Neohop-13(18)-ene and Hop17(21)-ene i.e. similar to Figure 1. These are commonly found only in very immature sediments (Comet, McEvoy *et al.*, 1986). Similarly many of the hopanes have $\beta\beta$ "immature" stereochemistry. The sterane profile (m/z 217) is similar to the distribution in Figure 6, i.e. dominated by $5\alpha(H)20R$ and $5\beta(H)$ steranes. Hence the steroid and triterpenoid nuclei from the carbonaceous limestones retain their original biosynthetic stereochemistry, as would be expected from highly immature sediments.

By contrast, both the gypsum and dolomite samples contained migrated oil. This is shown in Figures 8 and 9. Figure 8 shows the m/z 191 fragmentogram i.e. the triterpane distribution found in both samples. Here the situation is more subtle as a mixture of immature bitumen and migrated oil is present. Thus an "incompatible" combination of triterpenes and $\beta\beta$ hopanes from immature bitumen are mixed with the extended $\alpha\beta22S$ hopanes present only in oils and mature source rocks. Similarly in the sterane series, the immature $\alpha\alpha\alpha20R$ steranes are predominant over a "background" of mature sterane biomarkers i.e. the $\beta\beta$ and $\alpha\alpha\alpha20S$ steranes (see Figure 9).
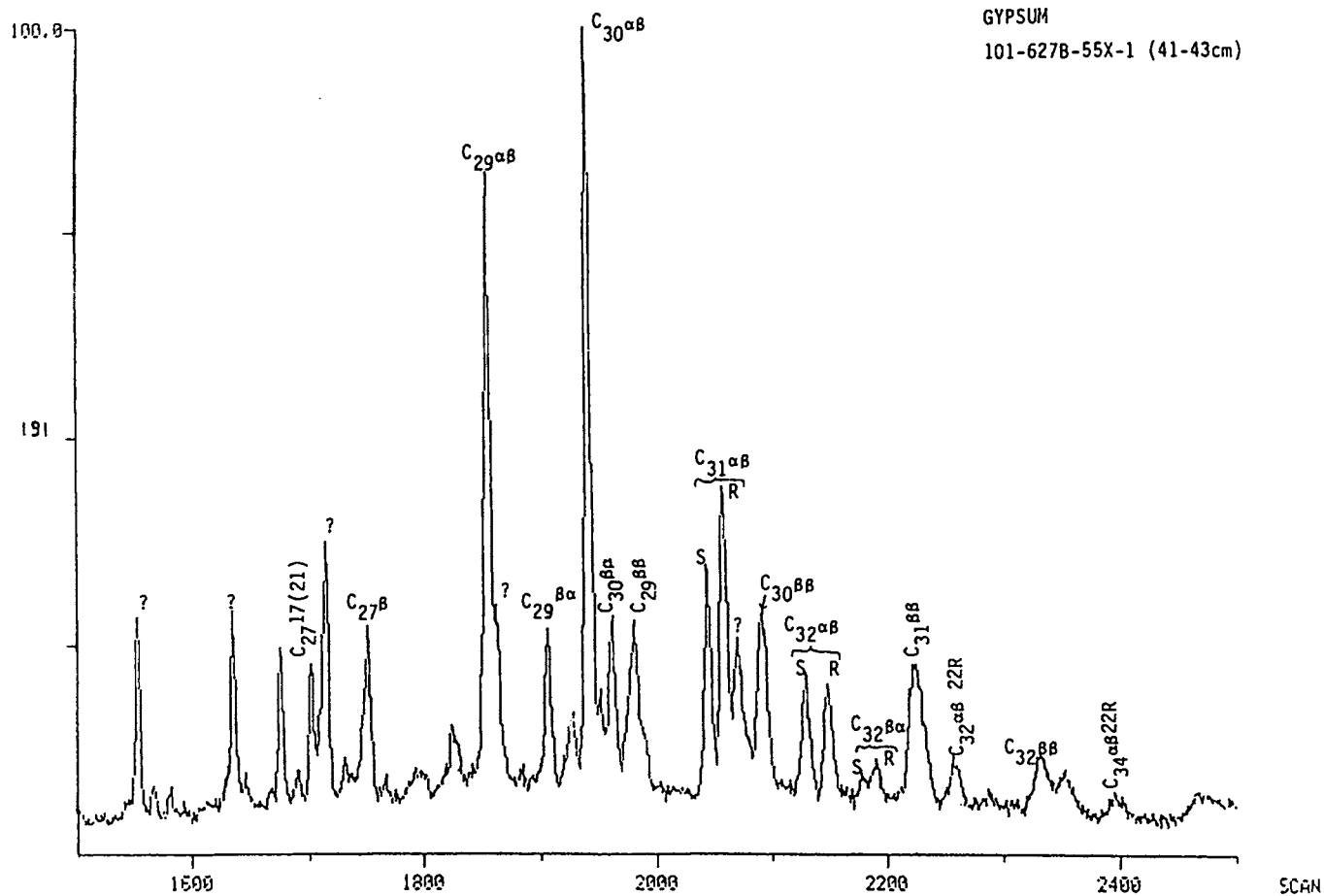
Figure 8: m/z 191 fragmentogram from the saturated hydrocarbons from a marine gypsum sample (evaporite) from the Bahamas. This sample [101-627B-55X-1(41-43)] was sampled on board ship (ODP Leg 101). Note mixture of "mature" biomarkers (extended $\alpha\beta$ hopanes) and immature bitumen ($\beta\beta$ hopanes and triterpenes).
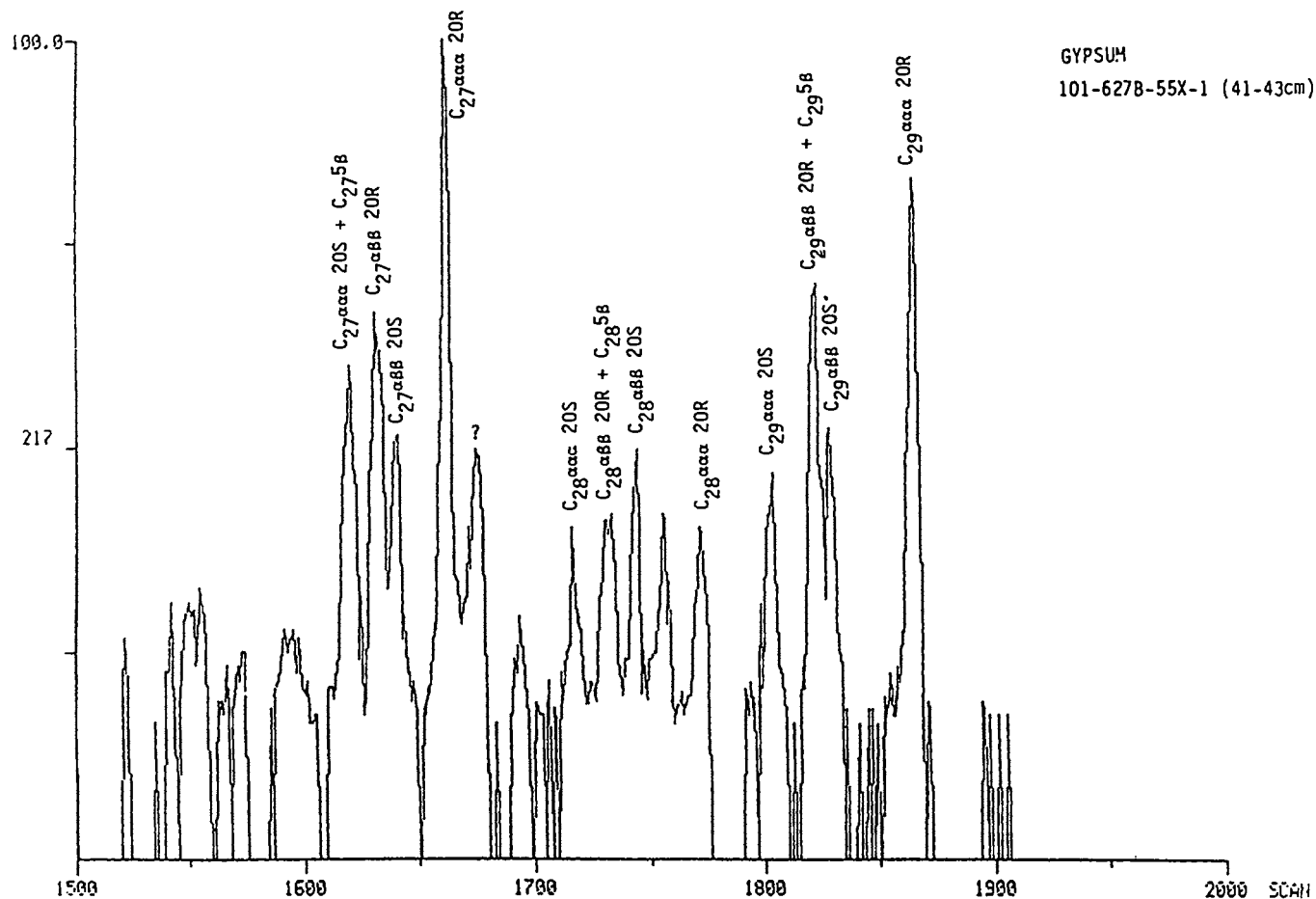
Figure 9: m/z 217 fragmentogram from the saturated hydrocarbons from a marine gypsum sample (evaporite) from the Bahamas. This sample [101-627B-55X-1(41-43)] was sampled on board ship (ODP Leg 101). Note "background" of mature biomarkers ($\alpha\beta\beta$ and $\alpha\alpha\alpha$ 20S steranes). However two most prominent peaks are "immature" isomers i.e. $\alpha\alpha\alpha$ 20R. Sample was interpreted as a mixture of oil and immature bitumen.

CONCLUSIONS

1) Less than one milligram of crude oil can be reliably identified and quantitated using C-GC-MS, even when the oil is highly degraded.

2) Many of the key components of a crude oil can be reliably and quickly identified.

3) Petroleum is shown to be composed of the "molecular remains" of once living organisms. These include soft bodied micro-organisms as well as higher plants.

4) Even when petroleum has been biodegraded to an intractable tarry residue, the biomarker assemblage it contains indicates its provenance and maturity. This makes biomarker study indispensable for forensic work, particularly where crude oil or high-boiling point distillates are involved.

5) The original environment of deposition as a crude oil may be glimpsed by an investigation of its biomarker composition.

6) The thermal history of an oil may be calculated by observing the ratio of various isomers of certain key biomarkers such as stigmastane (C_{29} sterane) and the extended hopanes.

7) New compounds are continually being discovered within petroleum. S E Asians crudes, in particular, are rich in compounds of presumed terrigenous origin, but of unknown structure.

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