

SOUTH AUSTRALIA
DEPARTMENT OF MINES AND ENERGY



OPEN FILE ENVELOPE NO. 5876

OTWAY BASIN

SOURCE ROCK STUDIES - DATA
(Reports for the period
October 1981 - July 1991)

Submitted by
various petroleum exploration companies plus
SADME project officers

1991

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ENVELOPE 5876

TENEMENT AND TENEMENT HOLDERS: not related.

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	McKirdy, D.M., 1987. Source-rock evaluation of the Casterton Beds in Robertson 1, Otway Basin, SA. Amdel report F 6638/87 (Part 1) (unpublished), for Ultramar Australia Inc., dated 13 March 1987.	5876 R 14 Pgs 746-749
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McKirdy, D.M., Cox, R.E., O'Leary, T. and Watson, B.L., 1986. Source rock and reservoir bitumen analysis, Crayfish A-1, Otway Basin, SA. Amdel report F 6429/86 (Part 3 - Final) (unpublished), for Chevron Overseas Petroleum Ltd, dated 19 September 1986.	5876 R 23 Pgs 897-951
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REPORT:	Padley, D., 1991. Preliminary evaluation of the source rock potential of the Eumeralla Formation in Chama 1a and Geltwood Beach 1, Otway Basin (University of Adelaide, Department of Geology and Geophysics, consultant's report for Sagasco Resources Ltd, July 1991).	MESA NO. 5876 R 25 Pgs 977-997
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SEPARATELY HELD DATA

THESIS (held in MESA Library)

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29 November 1985

F 1/1/291
F 6176 - Part 2 (Final)

The Director-General
South Australian Department of Mines
and Energy
PO Box 151
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Attention: Dr D. Gravestock

REPORT F 6176 - Part 2 (Final)

YOUR REFERENCE: SR 28/1/57/5 DG:AF, letter dated
27 February, 1985

TITLE: Otway Basin coastal bitumens : elemental
and stable isotopic compositions, and
biological marker geochemistry

MATERIAL: Bitumen

LOCALITIES: Nine stranding sites between CAPE OTWAY,
VICTORIA and NINETY MILE BEACH, SOUTH
AUSTRALIA

IDENTIFICATION: As in Table 1 of report

DATE RECEIVED: 28 February 1985

WORK REQUIRED: Bitumen analyses as agreed.
Interpretation

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1. INTRODUCTION

A suite of ten coastal bitumens from nine different stranding sites in the Otway Basin was selected for organic geochemical analysis (Table 1, Fig. 1). Nine of these bitumens formed part of an earlier study sponsored by Ultramar Australia Inc. and Australian Aquitaine Petroleum Pty Limited (McKirdy, 1985). An additional sample was collected by A. Hill (SADME) from a locality near Cape Otway, Victoria, in January 1985.

The aims of the present investigation are twofold:

1. To determine, on the basis of its elemental, isotopic and biomarker composition, whether the Lion Headland bitumen is a weathered, transported equivalent of one of the four bitumen families found in the western Otway Basin; and
2. Using elemental (C, H, N, S) and stable isotope (δD , $\delta^{34}S$) data, to test the hypothesis that the variety of bitumen types represented in the Otway Basin (paraffinic to aromatic-asphaltic; 0.3-3.3% S) may reflect a secular increase in the salinity of the lacustrine palaeoenvironment envisaged for their ?Late Jurassic - Early Cretaceous source rocks (McKirdy and Morton, 1985).

Preliminary data were forwarded to the client on 18 June, 1985 as an interim report. This final report presents an interpretation of the results of the full analytical program.

2. ANALYTICAL TECHNIQUES

Details of the analytical techniques are given in Appendix 1.

3. RESULTS

Analytical data are summarised and presented herein as follows:

	<u>Table</u>	<u>Figure</u>
<u>Lion Headland Bitumen</u>		
Physical properties	2,3	-
Bulk composition	3	2
$\delta^{13}C$ of saturates, aromatics	3,4	3
Saturated hydrocarbons	3,5	4,5
GC-MS of naphthenes	5,6	6-14
<u>Otway Basin Bitumens</u>		
Elemental composition	7	15-17
δD , $\delta^{34}S$ of bitumen	8	15-17

4. LION HEADLAND BITUMEN

4.1 Physical Properties and Bulk Composition

The low gravity (13.2°API), high pour point (57°C) and aromatic-intermediate bulk composition (Fig. 2) of the Lion Headland bitumen are typical of the weathered waxy crude oils which strand along the Otway Basin coastline (McKirdy, 1985). The high resins content of this bitumen (37.6% : Table 3) makes it one of the most weathered samples so far analysed. This is consistent with the substantial evaporative loss of light ends evident from the bitumen's skewed saturates distribution (Fig. 4) and *n*-alkane profile (Fig. 5).

Biodegradation, although not as pronounced as in some samples, has occurred as part of the weathering process, and is responsible for the moderately high pristane/*n*-heptadecane and phytane/*n*-octadecane ratios (Tables 3 and 5, Figs. 4 and 5).

It is clear from its sulphur content (S = 2.1% : Table 3) and carbon isotopic composition (Fig. 3) that the Lion Headland sample belongs to the Family 3 group of coastal bitumens (McKirdy, 1985).

4.2 Source Affinity

The carbon isotopic composition (Fig. 3), high botryococcane content (Table 6, Fig. 4), low pristane/phytane ratio (pr/ph <1), and C₂₇-C₂₉ sterane distribution (Fig. 13) of the bitumen concur in highlighting its *freshwater algal origin*.

The source rock of the parent oil was deposited in a deep, stratified lake with an anoxic hypolimnion (McKirdy, 1985). The high sulphur content of the bitumen implies, first, the presence of sufficient sulphate in the bottom waters of the lake to permit the generation of abundant H₂S via bacterial sulphate reduction; and, second, that Fe²⁺ and other cationic concentrations were low enough to avoid inorganic sequestration of all the available H₂S.

Inspection of the m/z 231 mass fragmentogram (Fig. 12) indicates that C₃₀ (and lower molecular weight) 4-methylsteranes are present in similar abundance (parameter 21, Table 6) to those observed in other Family 3 bitumens. These compounds are derived from 4-methylsterols synthesised by freshwater dinoflagellates (Robinson et al., 1984).

Comparison of peak intensities at appropriate retention times for C₃₀ 4-methylsteranes in the m/z 217 and m/z 231 fragmentograms suggests that other compounds (probably C₃₀ steranes) may be coeluting. C₃₀ steranes have recently been proposed as markers of marine-derived organic matter (Moldowan et al., 1985), although this is by no means proven (J.K. Volkman, pers. comm.).

4.3 Maturity and Migration

Maturation-dependent parameters 4-6 and 10-12 (Table 5) reveal that the Lion Headland bitumen has a maturity within the range displayed by other Otway Basin coastal bitumens (Fig. 14). However, it displays no geochromatographic evidence of long-distance migration in the subsurface.

5. ELEMENTAL AND ISOTOPIC COMPOSITION OF COASTAL BITUMENS, OTWAY BASIN

The elemental and new isotopic data presented in Tables 7 and 8 substantiate the previous recognition of multiple oil families in the Otway Basin (Figs. 15-17). Unfortunately, a sample of Family 2 bitumen (McKirdy, 1985) was not available for the present study.

Family 1 bitumens ($\delta D = -136$ to -139 ‰) are appreciably more depleted in deuterium than are those of Families 3 and 4 ($\delta D = -97$ to -107 ‰; Figs. 15 and 16) and provide yet another useful parameter on which to base oil-oil correlations. However, when considered in the light of recent literature on D/H and $^{13}C/^{12}C$ ratios in crude oils (Rigby et al., 1981; Schoell, 1984 a, b), these isotopic data are difficult to interpret in terms of source rock environment.

There is a reasonable correlation between $\delta^{34}S$ and S content in the Otway Basin coastal bitumens so far analysed (Fig. 17). This correlation is explicable in terms of increasing sulphate concentration, and hence increasing salinity of the lake (or lakes) in which the source rocks of the bitumens were deposited. The degree of isotopic fractionation between ^{34}S and ^{32}S that occurs during bacterial sulphate reduction is inversely proportional to the availability of sulphate (i.e. the greater the concentration of sulphate in the anoxic hypolimnion, the greater the isotopic difference between starting sulphate and product H_2S ; it is the latter which becomes incorporated in the source rock kerogen, and ultimately the oil).

Two Family 3 bitumens, including the Lion Headland sample, appear to be atypically enriched in ^{32}S and plot off trend in Figure 17. The reason for this anomaly is not clear.

Further interpretation of the sulphur isotope data is inhibited by the current lack of information on:

- (1) the occurrence and isotopic composition of lacustrine and/or marine sulphate in the Cretaceous sequence of the Otway Basin;
- (2) whether the source rocks of the bitumens were deposited in a single deep rift-associated lake which became progressively more saline; or, alternatively, in a number of separate lakes with different water chemistries.

6. CONCLUSIONS

1. Coastal bitumen collected recently from Lion Headland near Cape Otway is a weathered, transported example of the main type of bitumen (Family 3 : McKirdy, 1985) washed ashore at localities to the west of Portland.
2. Whole-bitumen δD and $\delta^{34}S$ values and elemental data (particularly H/C atomic ratios) are an effective means of establishing oil-oil correlations for coastal bitumens from the Otway Basin.
3. The previous recognition of four families of coastal bitumen in the Otway Basin (McKirdy, 1985) is substantiated by the results of the present investigation.
4. Our present understanding of the source rocks from which the Otway Basin coastal bitumens were derived (biota, palaeoenvironment, kerogen type) is summarised in Figure 18 (from McKirdy and Morton, 1985).

7. RECOMMENDATION

It is recommended that sediments of the Otway Group be searched for sulphur-bearing minerals, with a view to establishing the isotopic composition of Early Cretaceous non-marine and/or marine sulphate and co-existing sulphide in the Otway Basin.

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TABLE 1: COASTAL BITUMEN SAMPLES SELECTED FOR ORGANIC
GEOCHEMICAL ANALYSIS

State	Stranding Locality*	Sample No. (OCB-)
Victoria	Lion Headland, near Cape Otway	LH
	Shelley Beach, Bridgewater Bay	1
	Descartes Bay, S end	3,4
	Nelson Ocean Beach	8
South Australia	Cape Northumberland	10
	Nene Valley, 2 km NW of shacks	13
	Geltwood Beach, opp. N end of Lake Bonney	18
	The Nine Mile Sandhill, opp. S end of Lake St Clair	32
	Ninety Mile Beach, 5 km N of The Granites	38

*Lion Headland sample collected by A. Hill. Samples from other localities (Fig. 1, from McKirdy, 1985a) collected by D.R. Vinall.

TABLE 2: PHYSICAL PROPERTIES OF COASTAL BITUMEN FROM LION HEADLAND,
NEAR CAPE OTWAY, VICTORIA

Specific gravity (15°C)	=	0.9779
API gravity (60°F)	=	13.2 °API
Pour point	=	+57°C

AMDEL COASTAL BITUMEN ANALYSIS

BASIN: OTWAY

LOCALITY: LION HEADLAND

POUR POINT = 57 (DEG.C)

API GRAVITY = 13.2

TOTAL SULPHUR = 2.1 (WT %)

BULK COMPOSITION (WT %)

n+iso PARAFFINS	11.9
NAPHTHENES	23.9
AROMATICS	18.7
RESINS	37.6
ASPHALTENES	7.8

CARBON ISOTOPIC COMPOSITION (per mil rel to PDB)

SATURATES	-26.66
AROMATICS	-26.38

N-ALKANE DISTRIBUTION IN SATURATES

C-NO.	%	C-NO.	%	C-NO.	%	C-NO.	%	C-NO.	%
12	.0	18	1.8	24	2.4	30	8.2	36	3.2
13	.0	19	2.0	25	3.2	31	8.4	37	3.3
14	.1	20	1.6	26	4.5	32	8.3	38	2.4
15	.4	21	1.7	27	5.8	33	7.5	39	.8
16	.8	22	1.8	28	7.2	34	6.6	40	1.5
17	1.3	23	2.0	29	8.1	35	4.9	41	.0

CARBON PREFERENCE INDEX (C-23 TO C-33)

C.P.I. = 1.01

ISOPRENOID RATIOS

TMTD/pristane ratio	.28
norpristane/pristane ratio	.69
pristane/phytane ratio	.81
pristane/C-17 ratio	.90
phytane/C-18 ratio	.79

TABLE 4: CARBON ISOTOPIC DATA ON C₁₂₊ HYDROCARBONS
IN COASTAL BITUMEN FROM LION HEADLAND NEAR
CAPE OTWAY, VICTORIA

Sample	$\delta^{13}\text{C}_{\text{PDB}} \text{ ‰}$		CV*
	Saturates	Aromatics	
OCB-LH	-26.66	-26.38	-2.76

*Canonical variable (after Sofer, 1984):

$$\text{CV} = -2.53 \delta^{13}\text{C}_{\text{sat}} + 2.22 \delta^{13}\text{C}_{\text{arom}} - 11.65$$

TABLE 5: BIOMARKER PARAMETERS OF SOURCE, MATURITY, MIGRATION AND BIODEGRADATION IN COASTAL BITUMEN FROM LION HEADLAND NEAR CAPE OTWAY, VICTORIA

AMDEL Sample Nos.	Locality	STERANES							TERPANES					ACYCLIC ALKANES				
		Parameter*	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
MS-205 (OCB-LH)	Lion Headland	43:21:36	0.85	0.89	0.93	1.3	1.33	0.23	0.04	1.2	0.20	1.6	0.89	-	0.81	-	0.40	0.79

*See key (next page) for derivation and specificity of each parameter. Parameter 6 corrected for co-eluting 4-methylsterane.

H14

KEY TO BIOMARKER PARAMETERS OF SOURCE, MATURITY, MIGRATION AND BIODEGRADATION

Parameter	* Derivation	Specificity
1	$C_{27} : C_{28} : C_{29} \text{ } 5\alpha(H)14\alpha(H)17\alpha(H) \text{ } 20R \text{ steranes}$	Source
2	$C_{29} \text{ } 5\alpha(H)14\alpha(H)17\alpha(H) \text{ } 20R \text{ sterane} / C_{27} \text{ } 5\alpha(H)14\alpha(H)17\alpha(H) \text{ } 20R \text{ sterane}$	Source
3	$C_{29} \text{ } 13\beta(H)17\alpha(H) \text{ } 20R \text{ diasterane} / C_{27} \text{ } 13\beta(H)17\alpha(H) \text{ } 20R \text{ diasterane}$	Source
4	$C_{29} \text{ } 5\alpha(H)14\alpha(H)17\alpha(H) \text{ } 20S \text{ sterane} / C_{29} \text{ } 5\alpha(H)14\alpha(H)17\alpha(H) \text{ } 20R \text{ sterane}$	Maturity, Biodegradation
5	$C_{27} \text{ } 13\beta(H)17\alpha(H) \text{ } 20S \text{ diasterane} / C_{27} \text{ } 13\beta(H)17\alpha(H) \text{ } 20R \text{ diasterane}$	Maturity
6	$C_{29} \text{ } 5\alpha(H)14\beta(H)17\beta(H) \text{ } 20R \text{ sterane} / C_{29} \text{ } 5\alpha(H)14\alpha(H)17\alpha(H) \text{ } 20R \text{ sterane}$	Maturity, Migration
7	$C_{29} \text{ } 13\beta(H)17\alpha(H) \text{ } 20R+20S \text{ diasteranes} / C_{29} \text{ } 5\alpha(H) \text{ steranes}$	Migration, Source
8	$C_{31} \text{ tricyclic terpane} / C_{30} \text{ } 17\alpha(H)21\beta(H) \text{ hopane}$	Source
9	$C_{27} \text{ } 17\alpha(H)-22,29,30\text{-trisanorhopane} / C_{27} \text{ } 18\alpha(H)-22,29,30\text{-trisanorhopane} (T_m/T_s)$	Maturity, Source
10	$T_s / C_{30} \text{ } 17\alpha(H)21\beta(H) \text{ hopane}$	Maturity
11	$C_{32} \text{ } 17\alpha(H)21\beta(H) \text{ } 22S \text{ homohopane} / C_{32} \text{ } 17\alpha(H)21\beta(H) \text{ } 22R \text{ homohopane}$	Maturity
12	$C_{30} \text{ } 17\beta(H)21\alpha(H) \text{ moretane} / C_{30} \text{ } 17\alpha(H)21\beta(H) \text{ hopane}$	Maturity
13	$C_{29} \text{ } 17\alpha(H)-25\text{-norhopane} / C_{29} \text{ } 17\alpha(H)-30\text{-norhopane}$	Biodegradation
14	pristane / phytane	Source
15	2,6,10-trimethyltridecane / pristane	Maturity
16	pristane / <u>n</u> -heptadecane	Source, Biodegradation, Maturity
17	phytane / <u>n</u> -octadecane	Source, Biodegradation, Maturity

* Ratios calculated from peak areas as follows:

Parameters 1-6 $m/z = 217$ mass fragmentogram

Parameter 7 $m/z = 217, 259$ mass fragmentograms

Parameters 8-13 $m/z = 191$ mass fragmentogram

Parameters 14-17 capillary gas chromatogram of alkanes or whole oil/extract

TABLE 6: SUPPLEMENTARY SOURCE-DEPENDENT BIOMARKER PARAMETERS IN
COASTAL BITUMEN FROM LION HEADLAND NEAR CAPE OTWAY,
VICTORIA

Locality & Sample No.	<u>Botryococcane</u> <u>n-C₂₉</u>	Botryococcane Index	<u>Hopane</u> <u>Sterane</u>	<u>4-Me Sterane</u> <u>Sterane</u>
Lion Headland OCB-LH	0.27	129	2.8	0.20
Parameter*	18	19	20	21

*Ratios calculated from peak areas in mass fragmentograms of naphthenes and gas chromatograms of total alkanes as follows:

18. Botryococcane/n-nonacosane (GC)
19. Botryococcane x 100/C₃₇-C₄₀ head-to-head isoprenoid alkanes (m/z 183)
20. C₃₀ 17 α (H)21 β (H)hopane/C₂₉ 5 α (H) steranes (m/z 191, 217)
21. C₃₀ 5 α (H)14 α (H)17 α (H) 20S+20R 4-methylsteranes/C₂₇ + C₂₉ 5 α (H)14 α (H)17 α (H) 20S + 20R steranes (m/z 217,231)

TABLE 7: ELEMENTAL DATA ON TEN COASTAL BITUMENS FROM
THE OTWAY BASIN

Sample No.	C	H	N	S*	Ash	H/C atomic
Weight %						
OCB - 1	85.18	13.07	1.20	0.3	0.5	1.83
OCB - 3	81.36	11.71	0.81	2.1	0.5	1.71
OCB - 4	84.20	12.21	1.04	1.6	0.3	1.73
OCB - 8	84.60	12.26	1.33	2.4	0.8	1.73
OCB - 10	84.52	12.29	1.45	1.8	0.2	1.73
OCB - 13	84.16	12.14	0.65	1.4	0.2	1.72
OCB - 18	85.14	12.25	0.81	2.6	0.3	1.71
OCB - 32	85.05	9.78	0.97	3.3	0.2	1.37
OCB - 38	85.67	12.94	0.82	0.3	<0.2	1.80
OCB - LH	84.41	11.66	0.25	2.1	0.4	1.65

*By ICP (data from McKirdy, 1985a, except for OCB - LH).

TABLE 8: HYDROGEN AND SULPHUR ISOTOPIC DATA* ON TEN
COASTAL BITUMENS FROM THE OTWAY BASIN

Sample No.	δD ‰	$\delta^{34}S$ ‰
OCB- 1	-136	-2.2
OCB- 3	-97	-0.2
OCB- 4	-100	-4.9
OCB- 8	-98	-4.6
OCB-10	-98	-5.4
OCB-13	-99	-4.9
OCB-18	-100	-5.6
OCB-32	-107	-6.8
OCB-38	-139**	-1.4
OCB-LH	-97	-2.5

*D/H and $^{34}S/^{32}S$ ratios reported using the conventional δ notations relative to standard mean ocean water (SMOW) and meteoritic troilite, respectively.

**Mean of duplicate analyses (-138, -140).

FIGURE 1

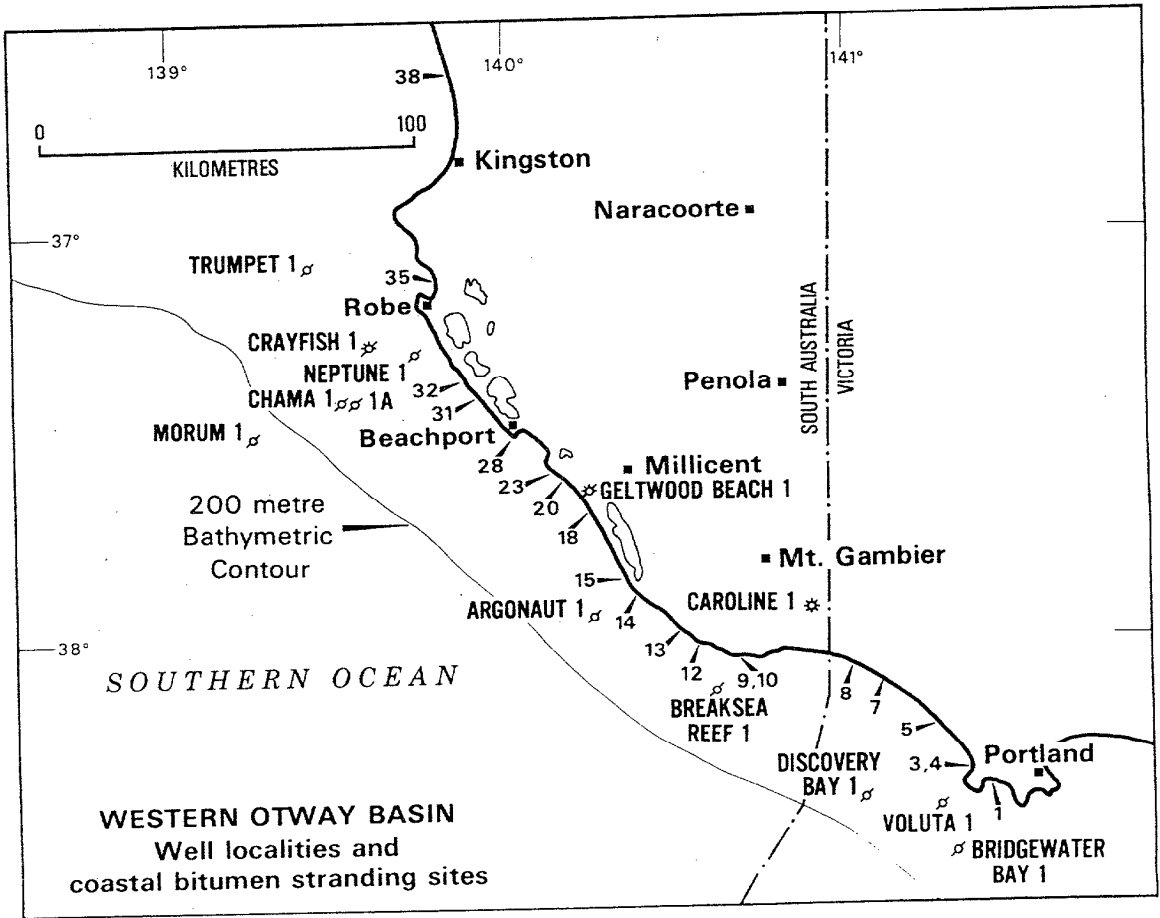


FIGURE 2

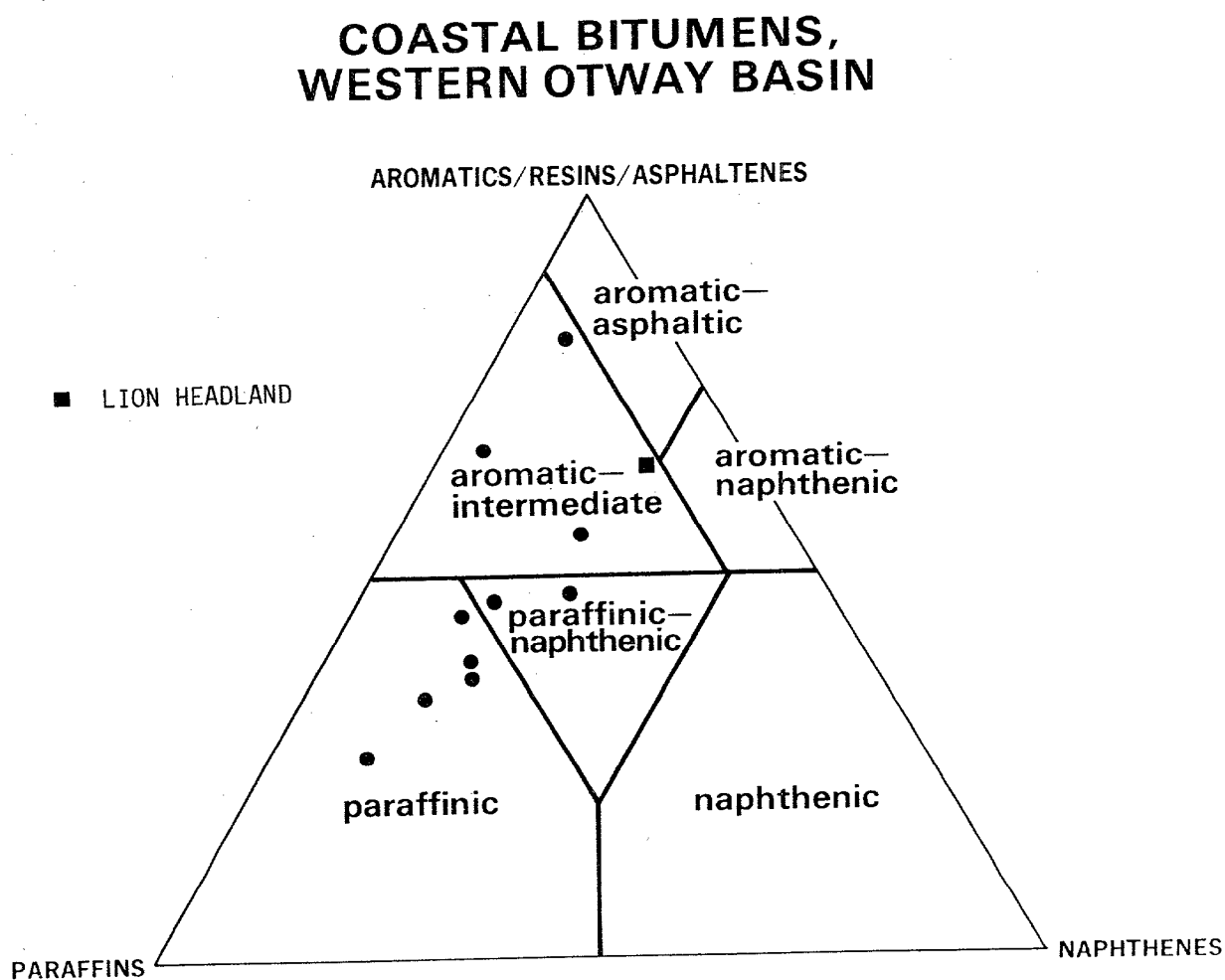


FIGURE 3

CARBON ISOTOPIC COMPOSITION AND SULPHUR CONTENT

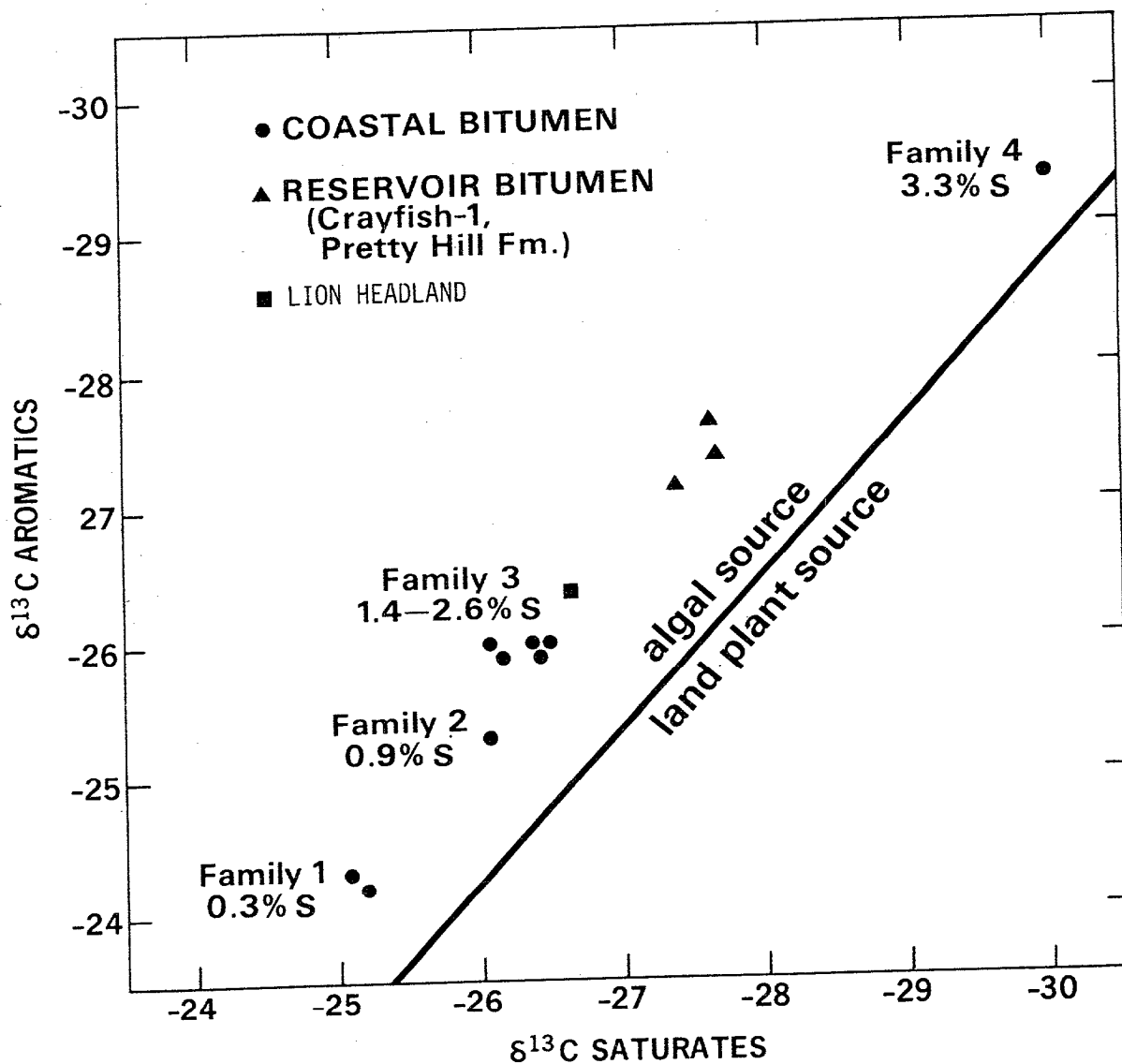


FIGURE 4

COASTAL BITUMEN
LION HEADLAND, NEAR CAPE OTWAY
SATURATES

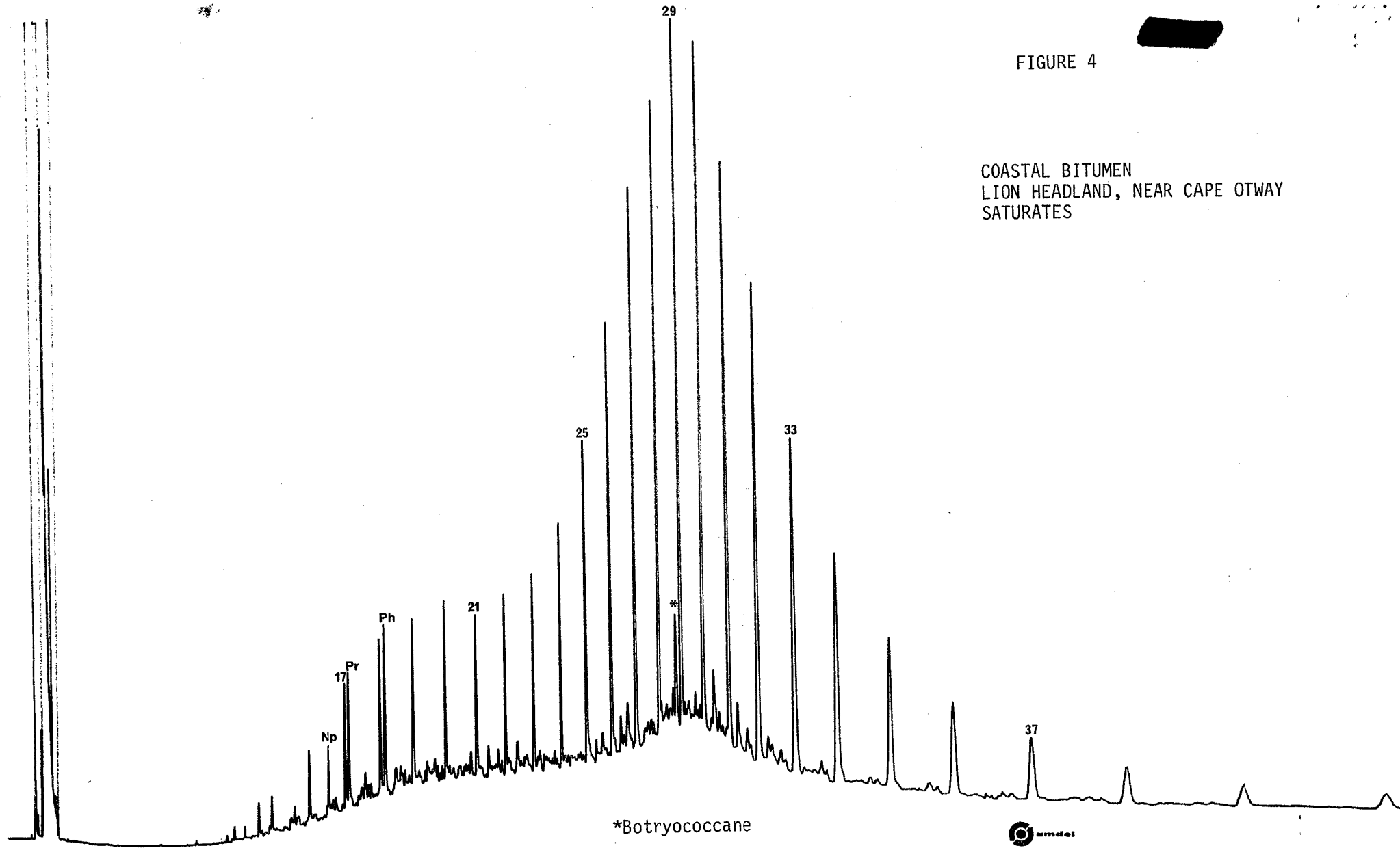
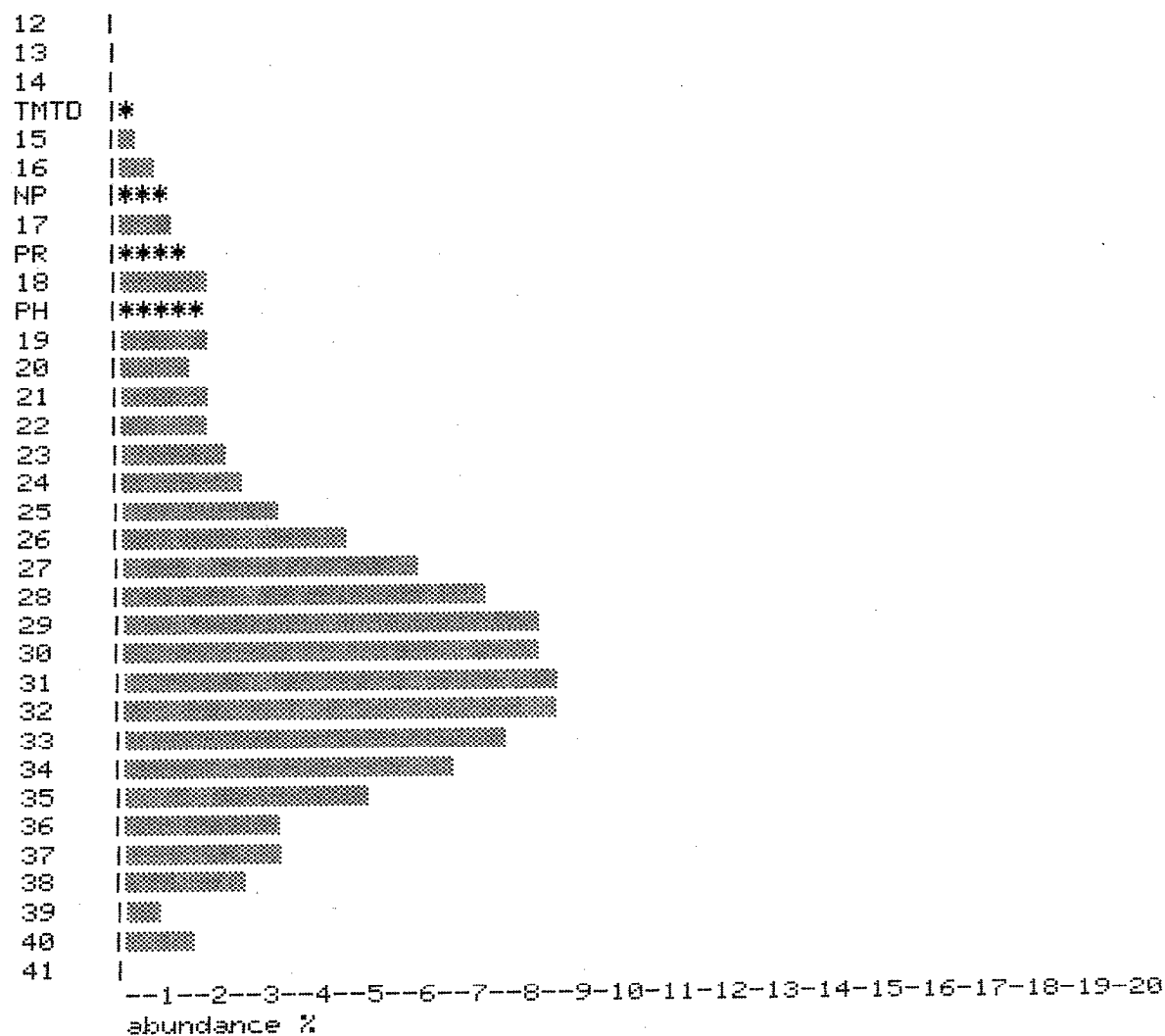


FIGURE 5

OTWAY BASIN COASTAL BITUMEN
LOCALITY LION HEADLAND

N-ALKANE AND ISOPRENOID DISTRIBUTION IN SATURATES



KEY TO MASS FRAGMENTOGRAMSm/z 191

1-6	C ₂₀ -C ₂₅	tricyclic terpanes
7	C ₂₄	tetracyclic terpane
8	C ₂₆	tricyclic terpane
9	C ₂₇	18 α (H)-22,29,30-trisnorhopane (Ts)
10	C ₂₇	17 α (H)-22,29,30-trisnorhopane (Tm)
11	C ₂₈	17 α (H)-28,30-bisnorhopane
12	C ₂₉	17 α (H)-25-norhopane
13	C ₂₉	17 α (H)21 β (H) norhopane
14	?C ₃₁	tricyclic terpane
15	C ₂₉	17 β (H)21 α (H) moretane
16	C ₃₀	17 α (H)21 β (H) hopane
17	C ₃₀	17 β (H)21 α (H) moretane
18-22	C ₃₁ -C ₃₅	17 α (H)21 β (H) 22S (left) and 22R (right) homohopanes

m/z 205

1	C ₂₈	3-methyltrisnorhopanes
2	C ₂₉	norhopane
3	C ₃₀	3-methylnorhopane
4	C ₃₀	hopane
5	C ₃₁	3-methylhopane
6	C ₃₁	22S homohopane
7	C ₃₂	22S 3-methylhomohopane + C ₃₁ 22R homohopane
8	C ₃₂	22R 3-methylhomohopane
9-12	C ₃₃ -C ₃₆	3-methylhomohopanes

m/z 217, 259

1	C ₂₁	sterane
2	C ₂₂	sterane
3 & 4	C ₂₇	20S and 20R diasteranes
5 & 8	C ₂₇	5 α (H)14 α (H)17 α (H) 20S and 20R steranes
6	C ₂₇	5 α (H)14 β (H)17 β (H) 20R sterane
7	C ₂₇	5 α (H)14 β (H)17 β (H) 20S sterane + C ₂₉ 20S diasterane
9	C ₂₉	20R diasterane
10 & 13	C ₂₈	5 α (H)14 α (H)17 α (H) 20S and 20R steranes
11 & 12	C ₂₈	5 α (H)14 β (H)17 β (H) 20R and 20S steranes
14 & 17	C ₂₉	5 α (H)14 α (H)17 α (H) 20S and 20R steranes
15 & 16	C ₂₉	5 α (H)14 β (H)17 β (H) 20R and 20S steranes

FIGURE 6

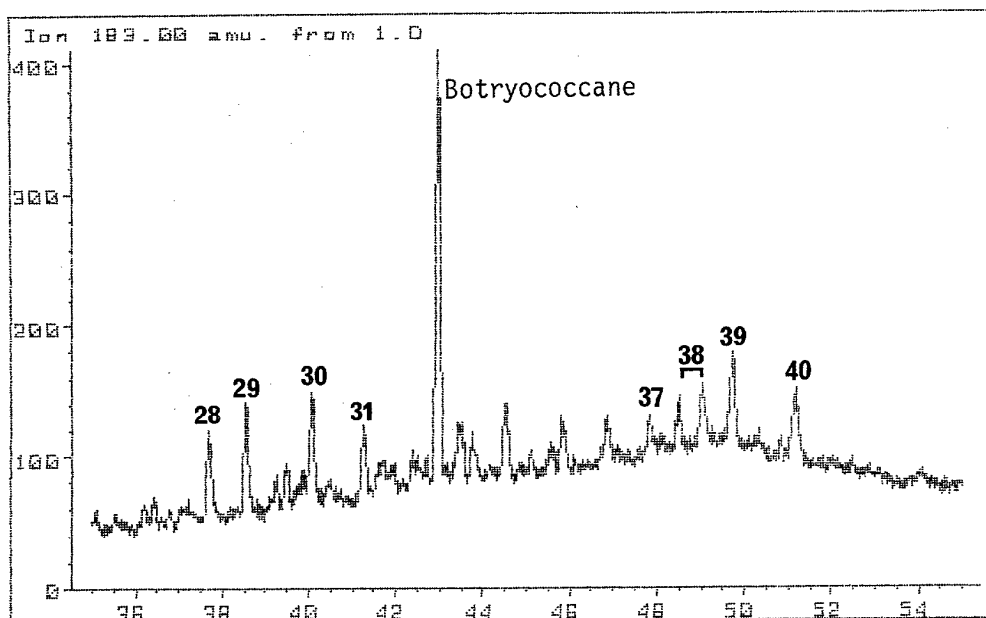
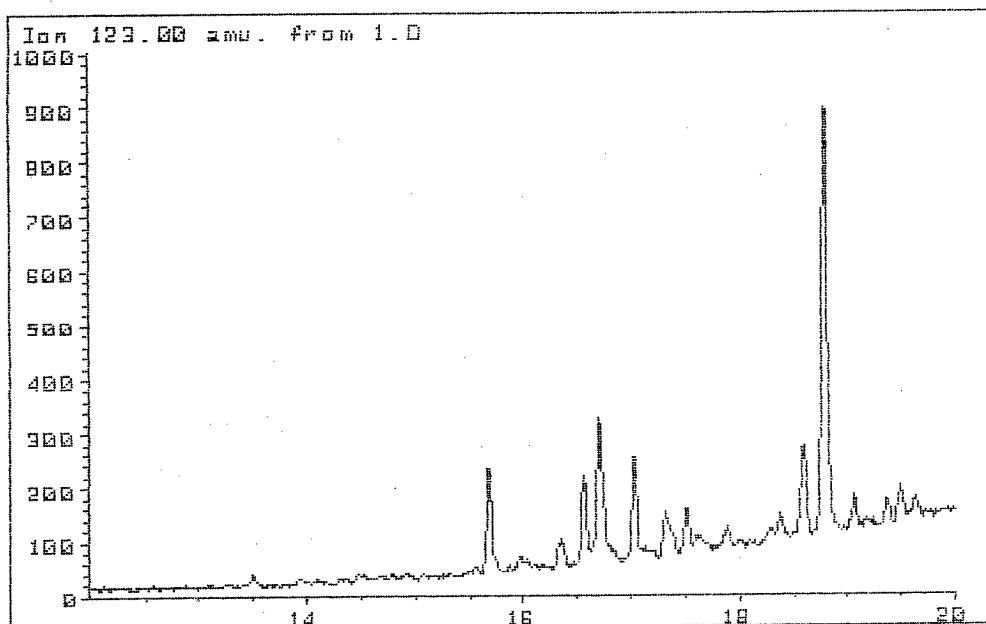


FIGURE 7

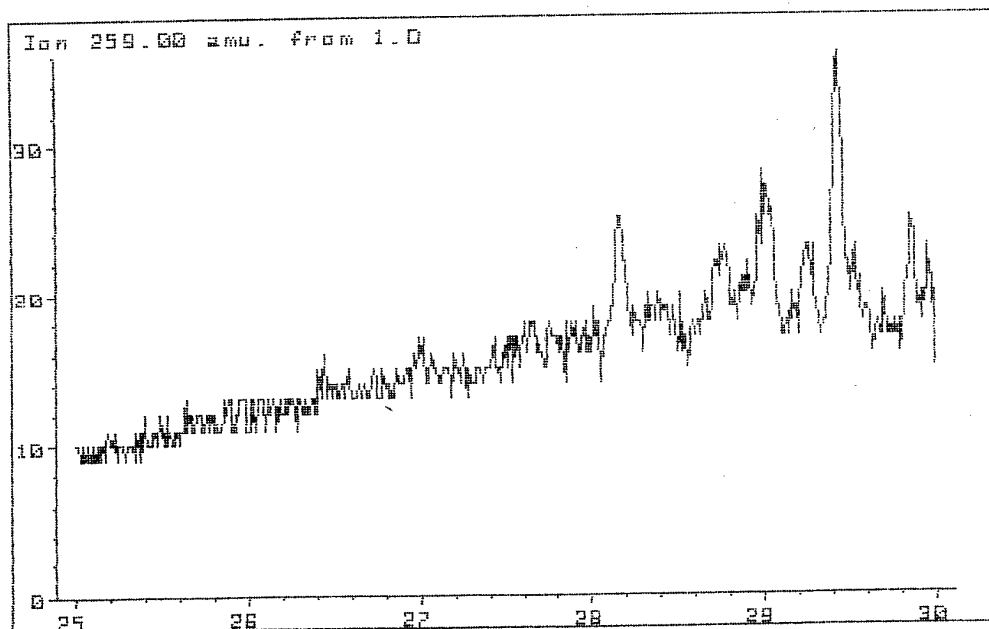
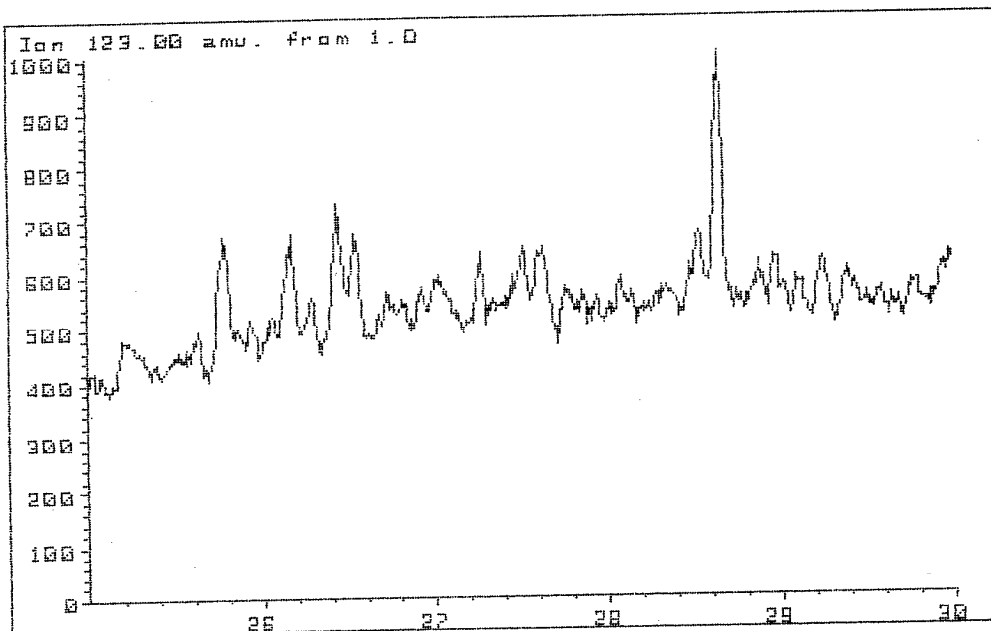


FIGURE 8

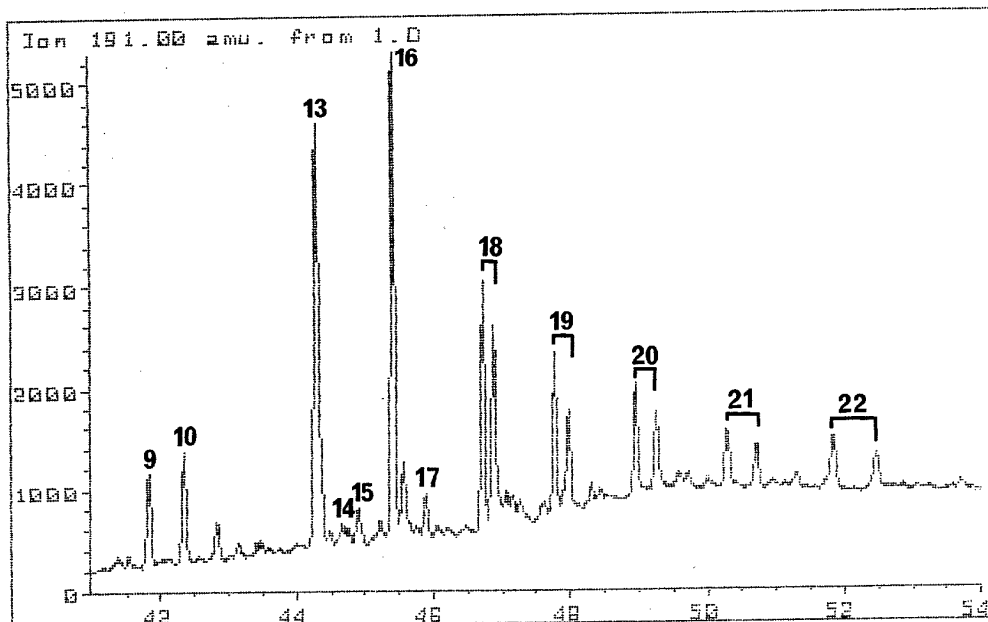
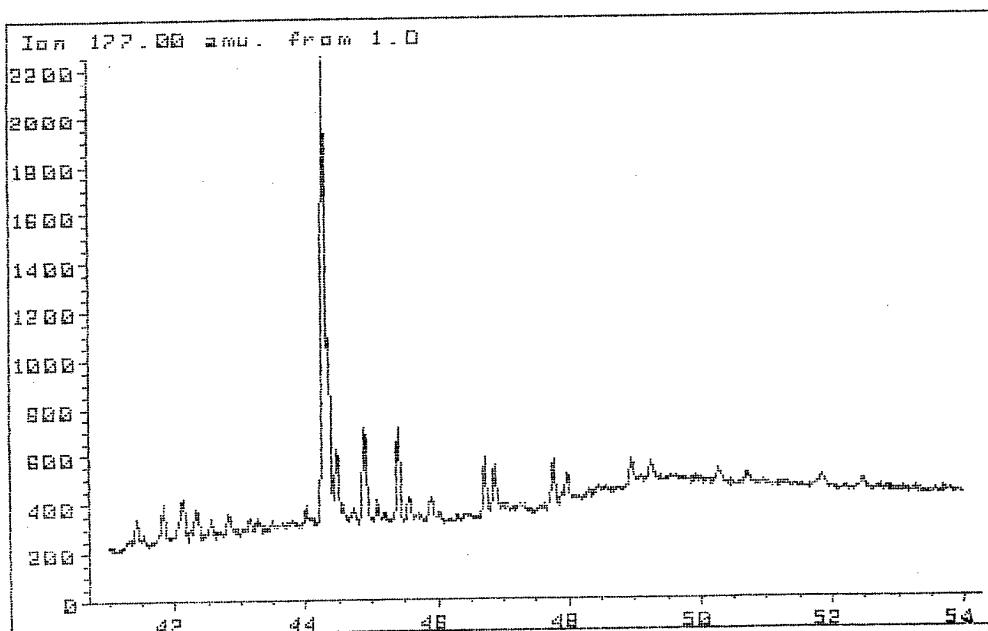


FIGURE 9

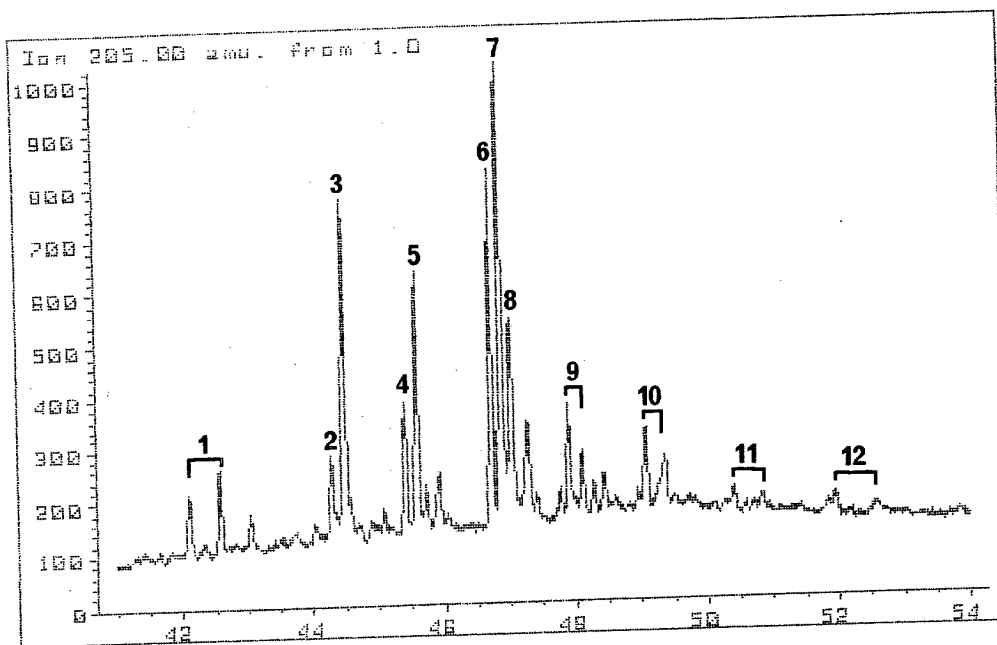
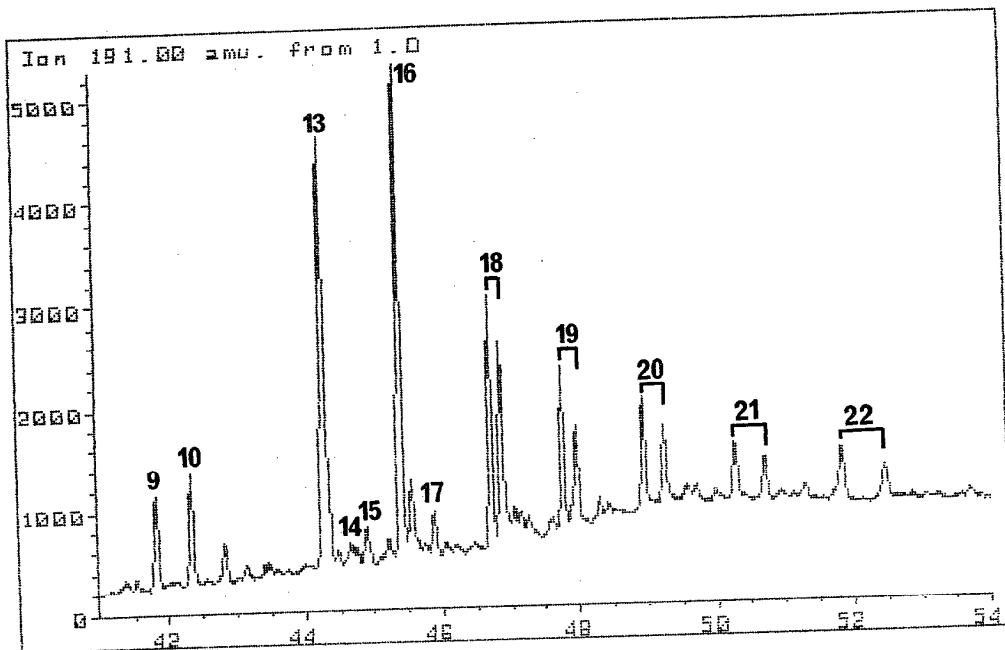


FIGURE 10

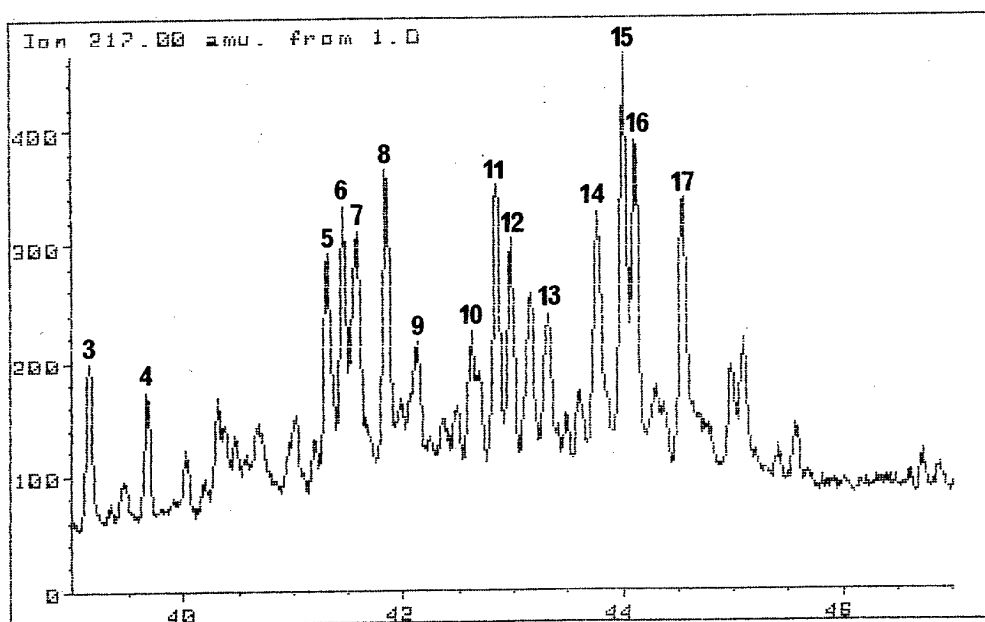
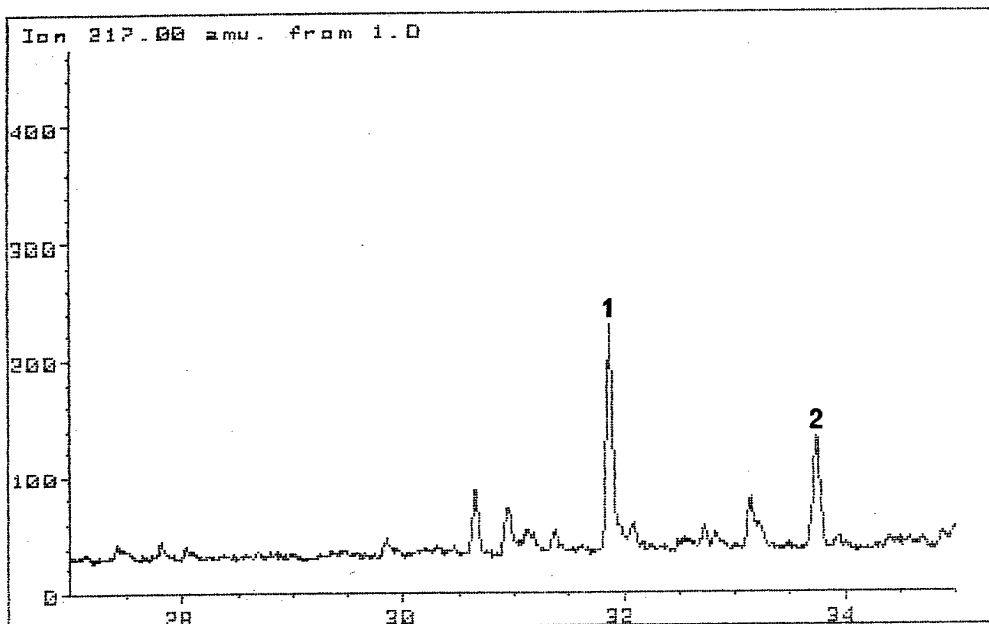


FIGURE 11

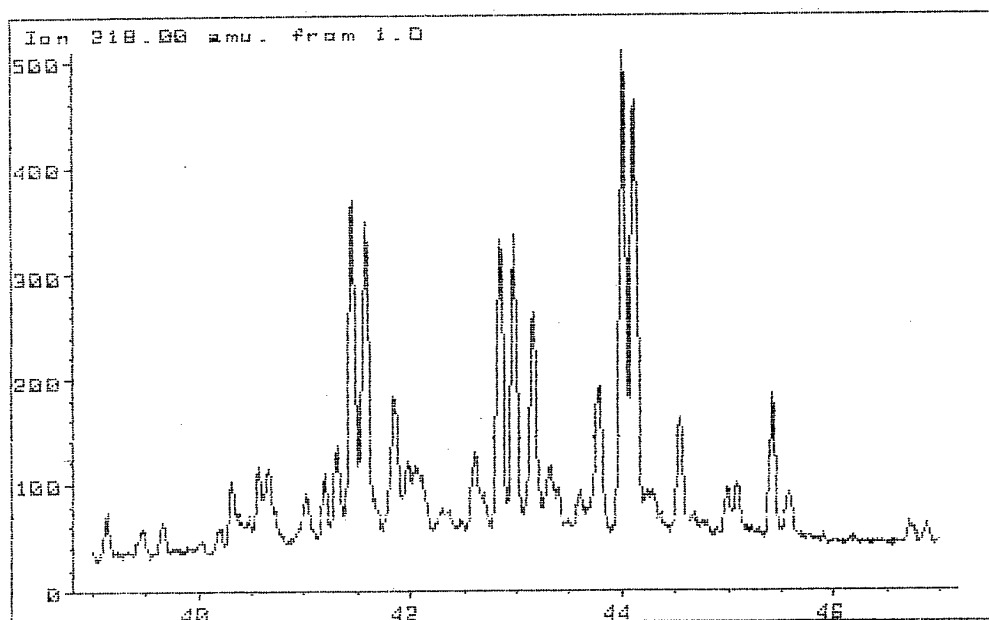
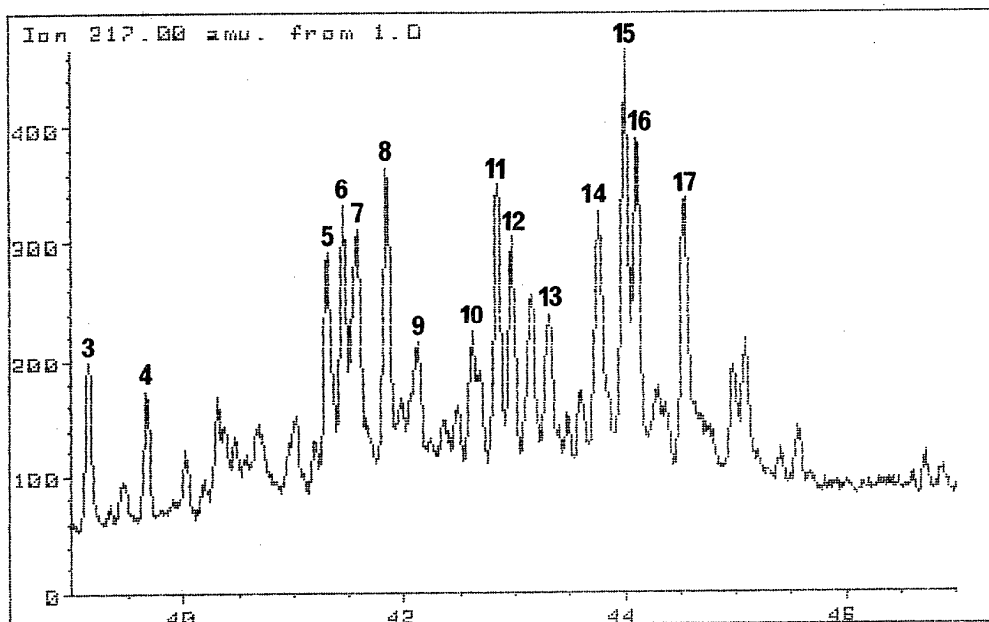


FIGURE 12

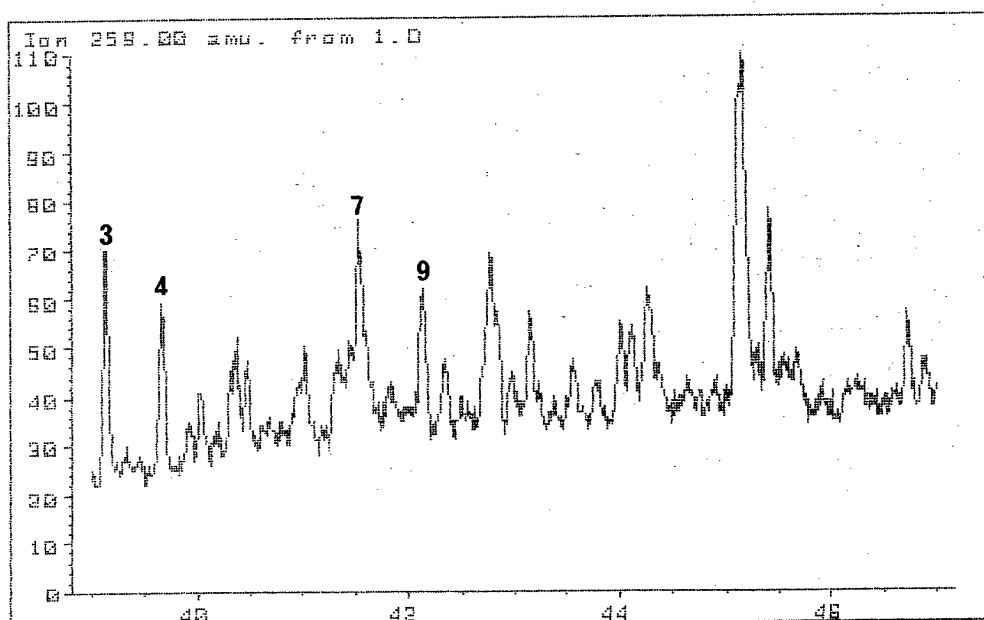
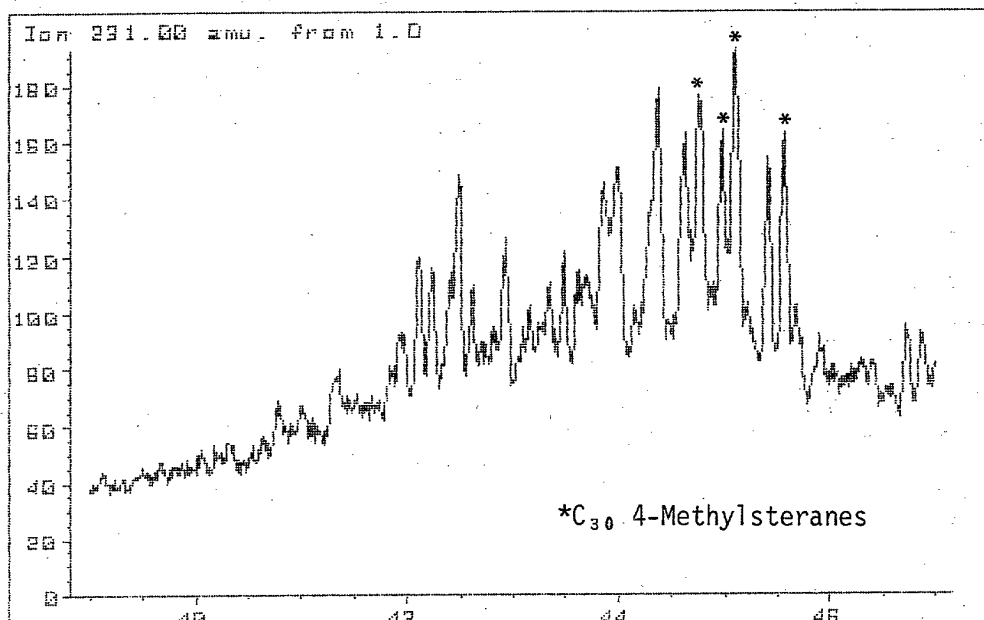


FIGURE 13

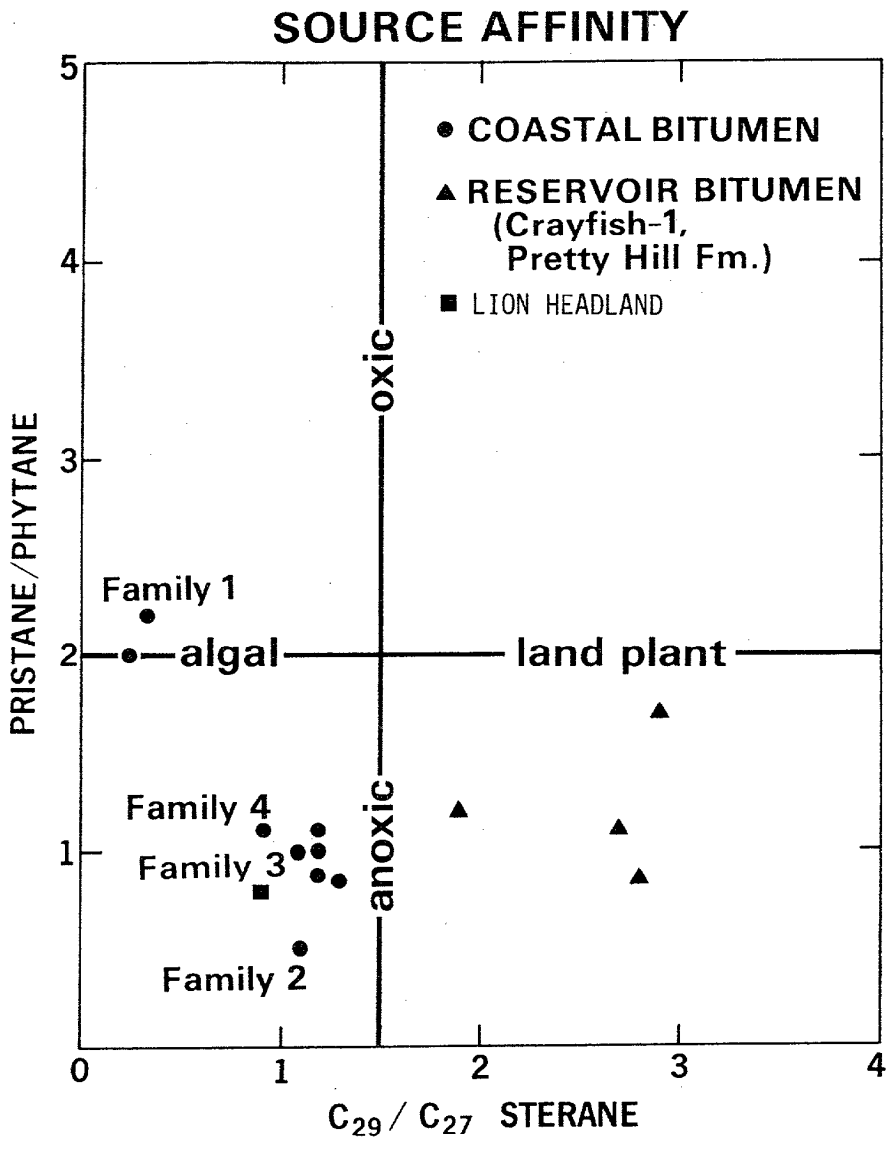


FIGURE 14

MATURITY and MIGRATION

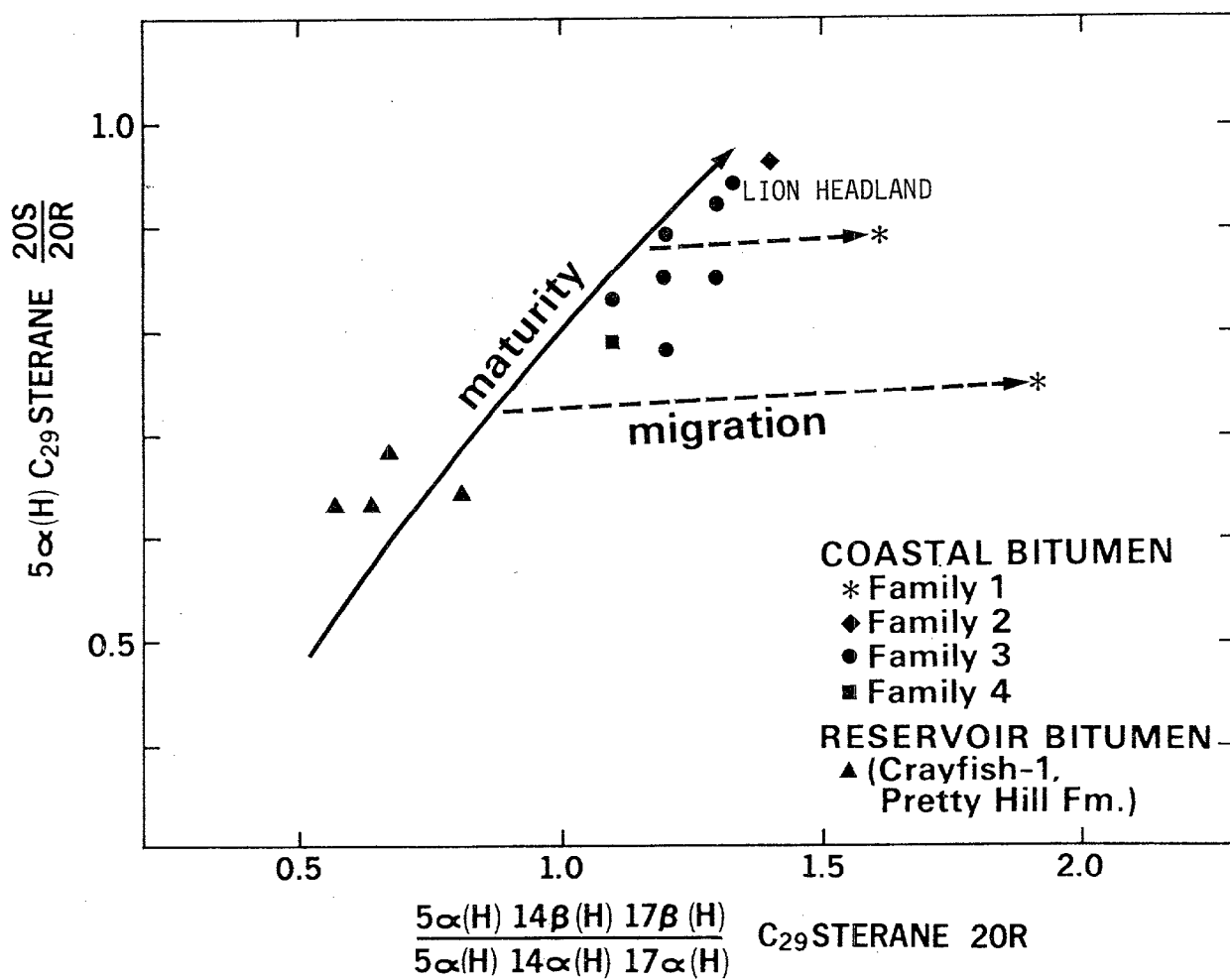


FIGURE 15
ELEMENTAL AND HYDROGEN ISOTOPIC COMPOSITION OF
OTWAY BASIN COASTAL BITUMENS

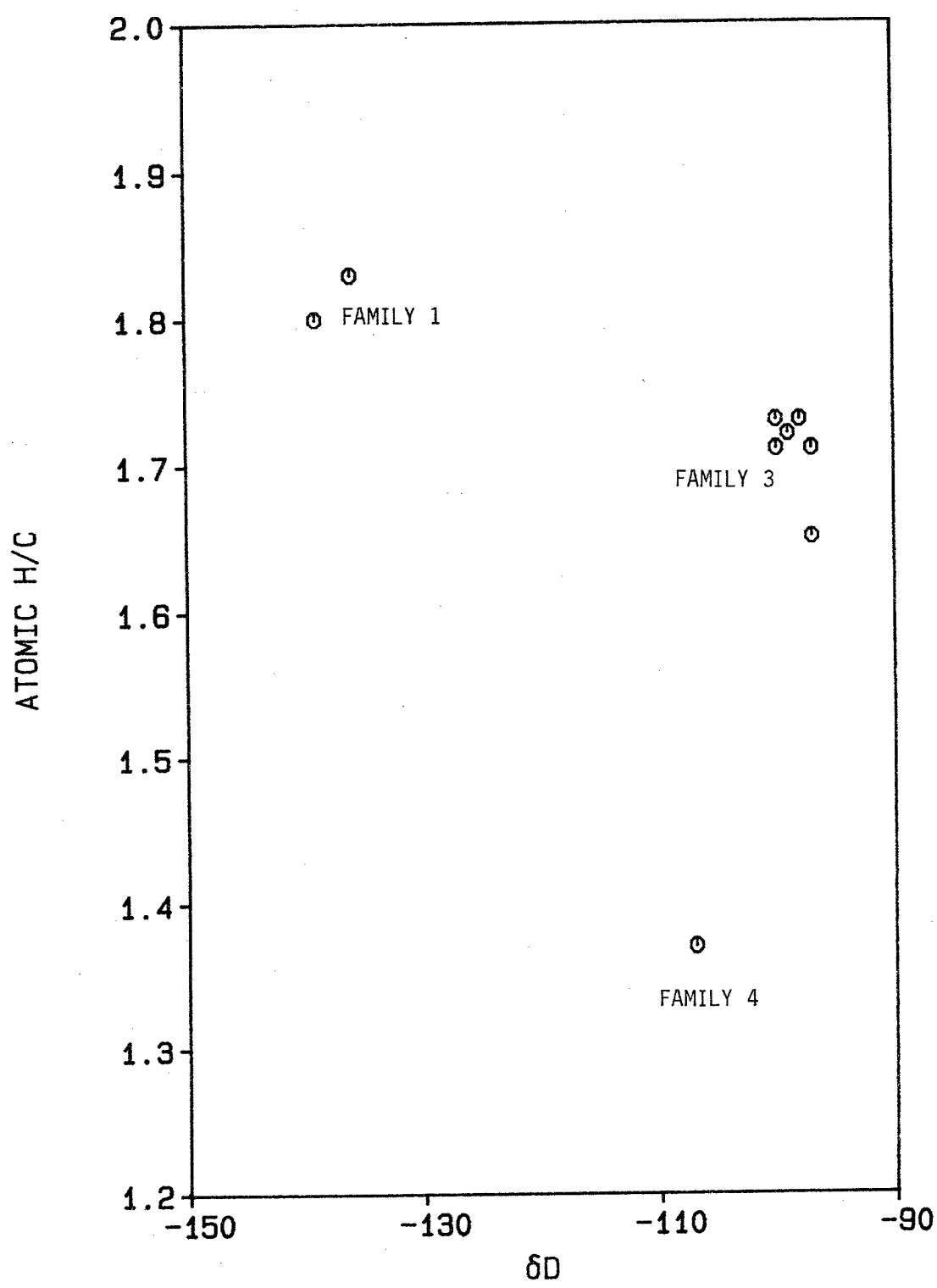


FIGURE 16

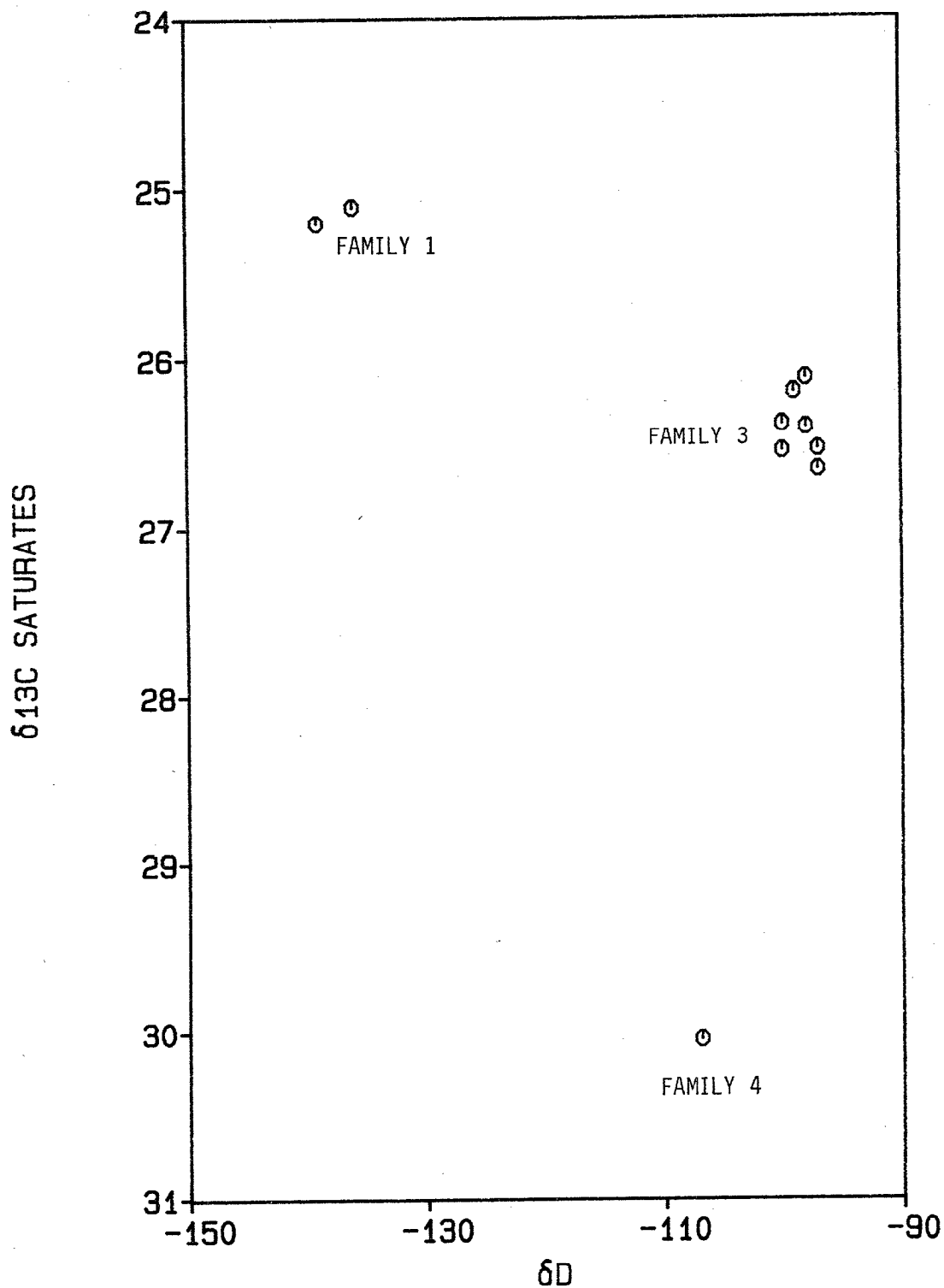
CARBON AND HYDROGEN ISOTOPIC COMPOSITION OF
OTWAY BASIN COASTAL BITUMENS

FIGURE 17

SULPHUR CONTENT AND ISOTOPIC COMPOSITION OF
OTWAY BASIN COASTAL BITUMENS

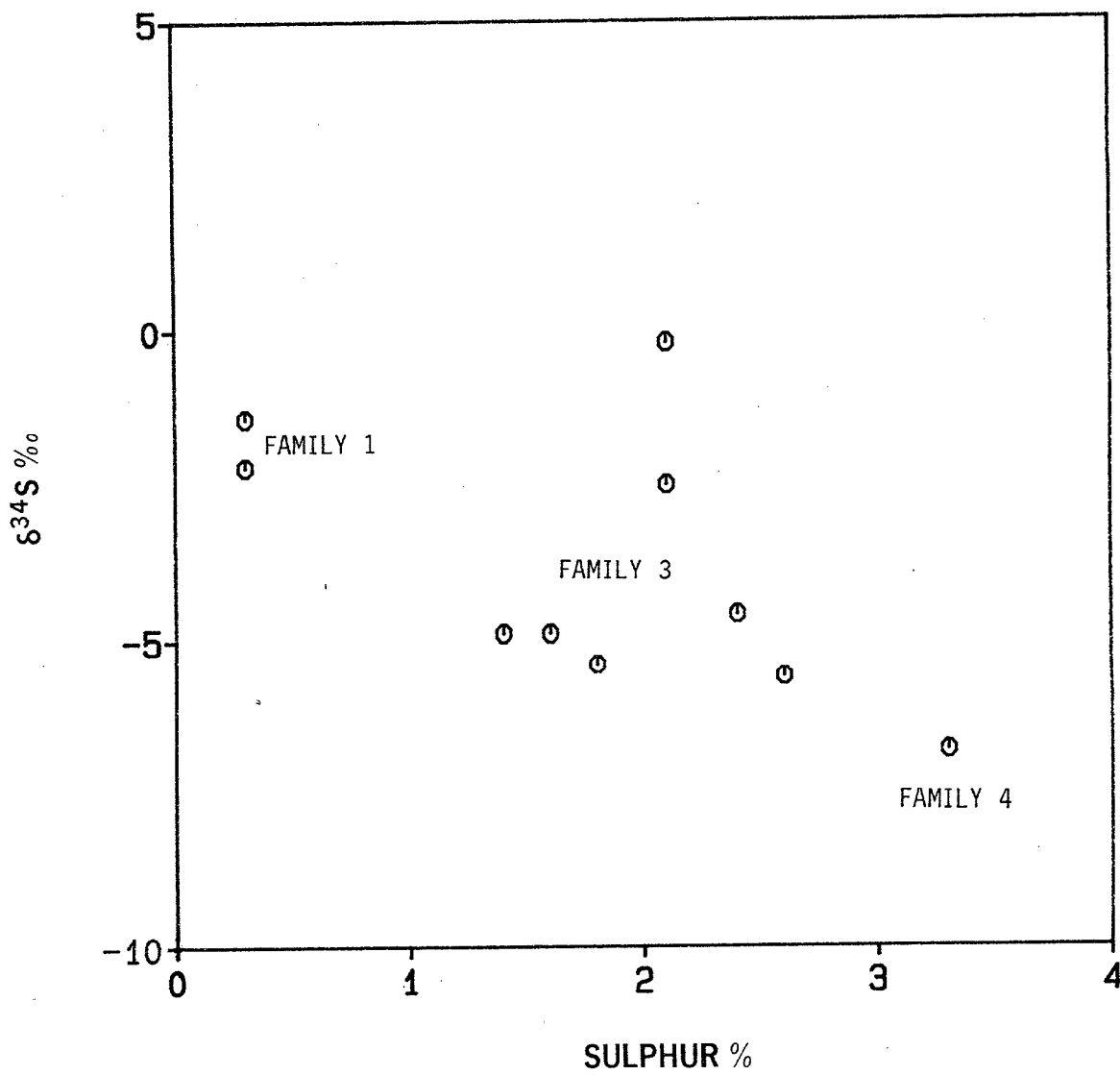


FIGURE 18

OTWAY BASIN

ENVIRONMENT/AGE	KEROGEN	BIOTA
Deep, stratified, rift-associated lake	? Type 1	<i>Botryococcus</i>
Highly productive epilimnion		Dinoflagellates
Hypolimnion anoxic, freshwater to saline		Methanogenic bacteria
Temperate climate		Sulphate- reducing bacteria
?Late Jurassic—?Late Cretaceous		



APPENDIX 1

ANALYTICAL TECHNIQUES

1. SAMPLE PREPARATION

The bitumen as received in the laboratory was mixed with variable amounts of sand and other foreign matter. Bitumen was dissolved in excess methylene chloride at ambient temperature using ultrasonication and the solution filtered through a bed of florosil in a sintered glass funnel. Solvent was removed by evaporation on a steam bath.

2. API GRAVITY AND POUR POINT

Specific gravity was determined by the pycnometer method, and converted to the equivalent API gravity. Pour point was estimated using a scaled-down version of the standard technique.

3. ELEMENTAL ANALYSIS

Carbon, hydrogen, nitrogen and ash were determined by standard microanalytical methods.

Total sulphur was determined by inductively coupled plasma (ICP) atomic emission spectroscopy with di-isobutylketone as solvent.

4. HYDROGEN AND SULPHUR ISOTOPIC ANALYSES

Aliquots of mineral-matter-free bitumen were submitted to Global Geochemistry Corporation, Canoga Park, California for measurement of δD and $\delta^{34}S$.

5. LIQUID CHROMATOGRAPHY

Asphaltenes were precipitated from the extract/topped oil by refluxing with petroleum ether prior to liquid chromatography. The asphaltene-free fraction was separated into hydrocarbons (saturates and aromatics) and polar compounds (resins) by liquid chromatography on activated alumina (sample: adsorbent ratio = 1:100). Hydrocarbons were eluted with petroleum ether/dichloromethane (50:50) and resins with methanol/dichloromethane (65:35). The saturated and aromatic hydrocarbons were then separated by liquid chromatography on activated silica gel (sample: adsorbent ratio = 1:100) eluting in turn with petroleum ether and petroleum/dichloromethane (91:9).

6. GAS CHROMATOGRAPHY (GC)

The saturated hydrocarbons (alkanes) were examined by gas chromatography using the following instrumental parameters:

A1.2

Gas chromatograph: Perkin Elmer Sigma 2 fitted with on-column injector

Column: 25 m x 0.3 mm fused silica, SGE QC3/BP1

Detector temperature: 300°C

Carrier Gas: He at 85 kPa

Column temperature: 100-290°C at 5° per minute and held at 290°C until all peaks eluted

Quantification: Relative concentrations of individual normal and isoprenoid alkanes obtained by measurement of peak areas with a Hewlett Packard 3392A integrator

7. GAS CHROMATOGRAPHY-MASS SPECTROMETRY (GC-MS)

Naphthenes (branched/cyclic alkanes) were isolated from the bitumen by urea adduction of its saturates fraction.

GC-MS analysis of the naphthenes (urea non-adduct) was undertaken in the selected ion detection (SID) mode. The instrument and its operating parameters were as follows:

System: Hewlett Packard (HP) 5790 GC coupled with a HP5970A mass mass selective detector and HP9816S data system

Column: 25 m x 0.34 mm i.d. HP Ultra Performance cross-linked methylsilicone phase fused silica, interfaced directly to source of mass spectrometer

Injector: Carlo Erba on-column injector

Carrier gas: He at 0.2 kg/cm² head pressure

Column temperature: 35-290°C/min.

Mass spectrometer conditions: 70 eV EI; 9-ion selected ion monitoring, 50 millisecc dwell dwell time for each ion

The following mass fragmentograms were recorded:

<u>m/z</u>	<u>Compound Type</u>
123	sesquiterpanes (incl. drimanes), diterpanes
177	demethylated triterpanes
183	acyclic alkanes (incl. isoprenoids)
191	triterpanes (incl. hopanes, moretanes)
205	methyl triterpanes
217	steranes
218	steranes
231	4-methyl steranes
259	diasteranes, diterpanes

Integration of the m/z 183, 191, 217 and 231 mass fragmentograms allowed calculation of the biomarker ratios in Tables 5 and 6.

8. CARBON ISOTOPIC ANALYSIS

Aliquots of the saturated and aromatic hydrocarbon fractions (≈4 mg) were heated at 900°C for 4 hours over CuO and Ag wire in evacuated quartz combustion tubes. Following separation from the co-produced H₂O on a vacuum line, the CO₂ was collected in a sample bulb for introduction to the mass spectrometer. The ¹³C/¹²C isotope ratios were measured on a VG602 Isotope Mass Spectrometer at the CSIRO Soils Division, Glen Osmond. Appropriate corrections were made for the ¹⁷O contribution. Although an anthracite standard was used, all data are expressed in δ¹³C units relative to the PDB standard, where:

$$\delta^{13}\text{C} = \left[\frac{^{13}\text{C}/^{12}\text{C sample}}{^{13}\text{C}/^{12}\text{C standard}} - 1 \right] \times 10^3$$