ANNUAL REPORT
CONGA OIL PTY LTD
PROJECT D'ENTRECASTEAUX

LICENCES:
29/84;6/86;7/86;52/86;53/86
8/87;9/87;10/87;11/87;12/87;13/87;14/87;46/87;1/88
CONSOLIDATED AS 1/88

by

Dr. D.E. Leaman

CONGA-8

JUNE 1989

Report prepared for Conga Oil Pty Ltd
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Blackmans Bay. Tas
by Leaman Geophysics
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BASIC AEROMAGNETIC DATA IS IN

89-3065

INTRODUCTION

This is the fourth "annual" report submitted by Conga Oil Pty Ltd in respect of its petroleum exploration of onshore Tasmania. It represents a landmark in Conga's exploration activities and government administration of petroleum exploration in Tasmania.

On the one hand Conga's past activity has established that the exploration is both viable and worthwhile to the general satisfaction of the industry - as suggested by interest in presentations for farm ins - even though Tasmania, as an oil-bearing province, remains a difficult Cinderella.
Past history and skepticism in government circles, as described in previous annual reports, has no plaace in any open minded exploration where success would be of enormous state benefit. Such skepticism has never been expressed at Cabinet level because the exploration, although still basic, is essential and necessary for any primary evaluation of state resources and potential.
On the other hand the Government has recognised that oil exploration is different to mineral or coal exploration and that larger licence areas and lower rents per square kilometre are appropriate. Cabinet-approved regulations in force from July 1, 1988 effectively filled such grey areas in the Mining Act (1929) in the absence of any specific Petroleum legislation.

Conga Oil has been able, therefore, to consolidate its thirteen original licences in SE Tasmania, apply for a larger area in central Tasmania, and consolidate the whole - upon granting - to form EL 1/88. See Figure 1.
Although slight variations in relinquishment conditions apply to the primary consolidation (D'Entrecasteaux area) and the newer central augment a coherent basin-wide evaluation is now possible based on the technical experience of the D'Entrecasteaux region. No further problems related to differential licence acquisitions, renewal dates or fees should now arise in respect of Conga's exploration.

Year 1988-89 has, however, been extremely difficult and the exploration momentum built up in previous years and fully reported in August 1987 and May 1988 collapsed when the orginal D'Entrecasteaux licences were withdrawn from the Mining Act, upon application for renewal, pending a mechanism, or performance of, consolidation. Only licence 46/87 escaped this "limbo" status but all other licences were "outside" the Act for up to nine months. During this uncertain period Conga Oil remained licence holder but conditions of tenure became ill-defined. Expenditure was curtailed pending clarification and renewal-consolidation, originally promised in the period May-June 1988, and exploration activity ceased.
Activity was resumed early in 1989 after renewal and consolidation of the D'Entrecasteaux licences in November, and increased after the Midlands augment was recommended for granting.

This report describes those activities which extended beyond May 1988 and/or were begun after January 1989. Most projects are incomplete and this outline summarises current status.

LICENCES

Held in the name of Conga Oil Pty Ltd, Southern Tasmania.

All are held for oil.

PROJECT D'ENTRECASTEAUX

		applied	originally granted
29/84	Lagoon Hill, North Bruny	190584	100685
6/86	Catamaran	110386	250387
7/86	Southport	120386	250387
52/86	Bruny Island	231286	290487
53/86	Bruny Island	231286	290487
8/87	South Bruny	120287	180987
9/87	South Bruny	120287	180687
10/87	South Arm	120287	180987
11/87	Grove	120287	180987
12/87	Judbury	120287	180987
13/87	Waterloo	120287	180687
14/87	D'Entrecasteaux River	120287	180687
46/87	Boyer	30687	121287

Previous consolidated reporting dates: August 31, 1987
May 5, 1988

The above licences were consolidated as EL 29/84 in November 1988. The original licences had been granted under mineral conditions and this status was changed upon consolidation.

PROJECT MIDLANDS

1/88	Midlands, Tasmania.	220188	210489

Consolidated licence 29/84 and 1/88 will be consolidated to form 1/88 upon granting at the renewal on June 10, 1989.

EXPLORATION HISTORY AND OBJECTIVES

OUTLINE:

The exploration programme outlined in the previous annual report has been severely disrupted due to administrative matters as explained in the Introduction to this report.

Four programmes were reported in progress at May 1988; seep search, extended interpretation of geophysical data, source rock analysis, tillite/breccia basement review. Two other programmes were proposed; regional stratigraphic/palaeontology compilation and processing/assessment of recently acquired marine seismic data.

Due to licence uncertainties only the low cost seep search has been continued, albeit at reduced level, throughout the year. Some independent geochemical research on trace hopanes was extended by Dr. J. Volkman of the CSIRO Marine Laboratories.

Following consolidation of the original D'Entrecasteaux licences , and advice that the Midlands application would succeed, the project was re-activated. However, the ultimate accretion of a very new area - wholly unexplored - required that most new work be heavily biassed toward it in order to generate a reasonably uniform appraisal of the entire licence as soon as possible. It will be appreciated that knowledge of the issues within the D'Entrecasteaux region is now extensive by comparison with the Midlands region.

Work underway is therefore designed to

1 permit finer resolution of issues already defined in the area south of Hobart and perhaps provide for well targetting,
2 provide a regional understanding of the area north of Hobart which is commensurate with that now extant for the southern area,
3 pinpoint any seepage concentrations anywhere in the expanded licence in order to confirm petroleum geochemistry and perhaps suggest foci for detailed exploration.

Seepages and geochemistry:

Seepages have now been reported from the Ross, Brighton, Kempton and Collinsvale areas. Samples from the Brighton occurrence have already been analysed (Appendix 2). This work shows that the material is not similar to samples from the Bruny region and that there are several related paradoxes. It is possible that the curious organic balance may have been generated either by heating of Permian organic material (coal?) by dolerite or by an intense bushfire at the natural tar occurrence. This work poses

many questions which can only be answered by careful sampling and analysis of all sites in the hope that a pattern might emerge.
Further analytical work in the D'Entrecasteaux region has also suggested that much of the marine data may be, at least partly;, contaminated by pollution. See Appendix 1. While the marine data may be suspect the results of onshore sites remain definitive in terms of correlation with local limestone sources - namely Gordon Group.

It is clear, however, that much more research and a bigger family of results is required before any weight should be placed on geochemical exploration, especially since only trace quantities have been recovered from any site to date.

Part of the Quamby Mudstone at Poatina, noted to be "oily" in outcrop has also been analysed. The hydrocarbons present are mature but non-Tasmanites in origin (Appendix 3). They are chemically unlike other occurrences. It is not yet clear whether this material has been generated in-situ or is the result of migration. This may be an important issue as implied by the above discussion or there may prove to be other sources in addition to the Gordon Group. It will be important to separate these and assess which source is responsible for individual occurrences.

Geophysics:

A regional aeromagnetic survey of the enlarged licence has been completed. Specifications were comparable to those of the D'Entrecasteaux survey but the line spacing was increased from 2.5 to 5 km with tie lines at 25 km and a flight elevation of 1600 m.
Provisonal compilations have been received from the contractor (Austirex) but located data tapes and final film versions of maps are still awaited. These will be forwarded when available.

Arrangements have also been made to infill the state gravity data base. This work is being undertaken by the Geophysics Branch of the Mines Department with acquisition costs paid by Conga Oil. At the time of writing some 1500 new stations had been observed in the northern midlands - central plateau region. Work is continuing and all data acquired will be accumulated into the TASGRAV data base after correction and checking.

No interpretation has yet been undertaken of the new or augmented data sets.
No extended interpretation of the D'Entrecasteaux data set has been undertaken since May 1988.

Conductivity data from the northern Midlands has been collated and will be interpreted in association with the magnetics and gravity data recently acquired.

Marine seismic data acquired by the Bureau of Mineral Resources in April 1988 has been partly processed and inspected. Processing is not advanced due to delays in funding approvals pending licence clarifications. Various processing options are now being tested.

Some comments are possible. The data are comparable in form and reflection style to those acquired by Amoco in Storm Bay some twenty years ago. It is of higher quality but appears limited by the same geological issues which blinded the earlier survey - and also affected Conga's Bruny Island test survey as described in the previous annual report.

Tertiary materials are clearly recorded. These often dip steeply and include onlaps and one major unconformity. High velocity bedrock (Permian, Triassic or dolerite) is universally well marked. Sites known to include dolerite then show up to half a second of blind zone. Other areas may exhibit similar properties. It is not yet clear whether processing can resolve these problems and lead to clear display of the Upper Carboniferous unconformity and underlying structures.

Well site location will prove very difficult unless these problems can be solved.

PROGRESS FROM MAY 1988 TO DATE:

1. Further possible seepages have been reported in Midlands Tasmania.

2. Analytical work indicates that some seepage sites may not be true seepages and that others may be the result of contamination. It is also possible that some local heating events have produced petroleum hydrocarbons or that more that one source is available for the material recovered.

3. Gordon Group limestones remain the crucial source and provide a chemical reference for seepages. It is now clear that source separation is practicable.

4. An aeromagnetic survey of central and northern Tasmania has been completed. Sufficient data has been acquired to permit regional structural assesssment.

5. The state gravity data base is being infilled in the northern Midlands. Work is about half completed at this time.

6. Marine seismic data from the southern waterways is being reviewed and processed (BMR).

PROGRAMMES IN PROGRESS:

1. The seep search programme for location of all reported sites and sampling is continuing. If other sites can be confirmed and some patterns established between seepage sites and structural interpretations it is believed that problems of target priorities will be greatly eased.
   This programme will include both sea bed and land searches and complete analyses of recovered samples.

2. Infill of the state gravity data base to a nominal station spacing of perhaps 2 to 2.5 km over large areas.

3. Source rock sampling and analysis. This work is to follow up results reported here and to indicate which members of the stratigraphy are the primary sources. The difference between reefal or back reef members may ultimately be important.

4. Seismic processing tests and evaluation. This work is currently concentrated upon marine data from the southern part of the area.

PROGRAMMES PROPOSED:

1. A regional stratigraphic and palaeontologic compilation to assist well sample identifications.

2. Completion of gravity infill coverage north of Hobart.

3. Regional interpretation of gravity and magnetic data in the area north of Hobart.

4. Detailed gravity and magnetic interpretation of areas of particular interest as determined by (3) or seepage concentrations. Detailed work to be undertaken anywhere within 1/88.

5. Public assisted seepage search. It is hoped that this might lead to reasonable sample volumes and confirmation of source and fluid signatures. Geochemical work to continue in association with the search.

6. Further onshore seismic trials. Since it is clear that any well programme may be limited or forced toward purely stratigraphic objectives in the absence of specific structural controls the problems related to seismic data acquisition must be resolved. Only the coupling of gravity-magnetic implications with seep concentration foci and local seismic survey will lead to viable targetting.

SUMMARY OF EXPLORATION OBJECTIVES

Recent work has demonstrated that the region has petroleum potential and should be explored. The presence or Ordovician-sourced hydrocarbons means that the so - called Tasmania Basin can no longer be considered a post Permian backwater with no potential - especially when it is known that the sourcing limestones possess secondary porosity and could be sealed by the base Permian unconformity.

Issues to be further evaluated include:

SOURCES:
Detailed review of Upper Cambrian to Lower Silurian rocks to identify specific or multiple sources or sourcing members within the Gordon Group. Chemical work by Dr Volkman indicates that much work is required on source-seep chemistries. Current suggestions of multiple sources, local and abnormal sources or contamination must be evaluated.

ASSESS SCALE OF GENERATION OR MIGRATION:
This problem is partly related to the nature of the source. However, any distribution of seepages or source indications defined upon analysis of such seepages will be critical. It is hoped that these indicators might be tied to inferred lithology distribution as suggested from the geophysical or pyroclastic studies.
Although present work is incomplete there appears to be considerable spread in potential seepage sites. This would be most encouraging if it can be shown that old sources free of contamination are implied and the present chemical enigmas can be explained.

PLAY DEFINITION:
Preliminary work to date suggests the possible presence of fold closures, rejuvenated troughs, unconformity seals, shelf deposition, rift margin rise shoulders and dolerite traps. Each of these feature styles will need to be defined, rated and drilled. Rating will be affected by inferred rock distributions and migration considerations and seismic data is likely to be essential to such appraisals. The economics and practicability of seismic methods has been established (although resolution must be further improved) in this environment but the high cost (approx $7000/km) will mean limited coverage and that traverses must be specifically located on other indicators (chemistry, seepages and gravity/magnetics).

OVERALL:
To evaluate the region in such a way as to rationally assess its potential for Conga's purposes or to aid future explorers.

EXPENDITURE SUMMARY

The table below is applied to the set of licences as if consolidated.

The figures provided apply to the reconstituted Conga Oil and cover the period to date from May 5, 1988 and thus refer to a full year of exploration (the problems outlined in the Introduction, notwithstanding).

Geology (regional appraisals, seep search, feeder location, consultants, etc).....$	3628
Geochemistry (analyses).....	4850
Geophysics (regional study, data acquisition interpretation in progress).....	131889
Drilling.....	207814
Administrative overheads (licence fees, accounting, management).....	31691
Other (Drilling engineering, consultants, maps sundries, surveying etc,staff labour.....	40620
Total:	420492

The figures, and categorisation, quoted are as supplied to me by the financial manager of Conga Oil. A complete beakdown is available from the company ledgers.

Report submitted on behalf of
Leaman Geophysics
by

D. Leaman

Dr. D.E. Leaman, B.Sc., Ph.D
M.Aus.I.M.M., M.M.I.C.A

June 3, 1989

5 cm

EL 1/88

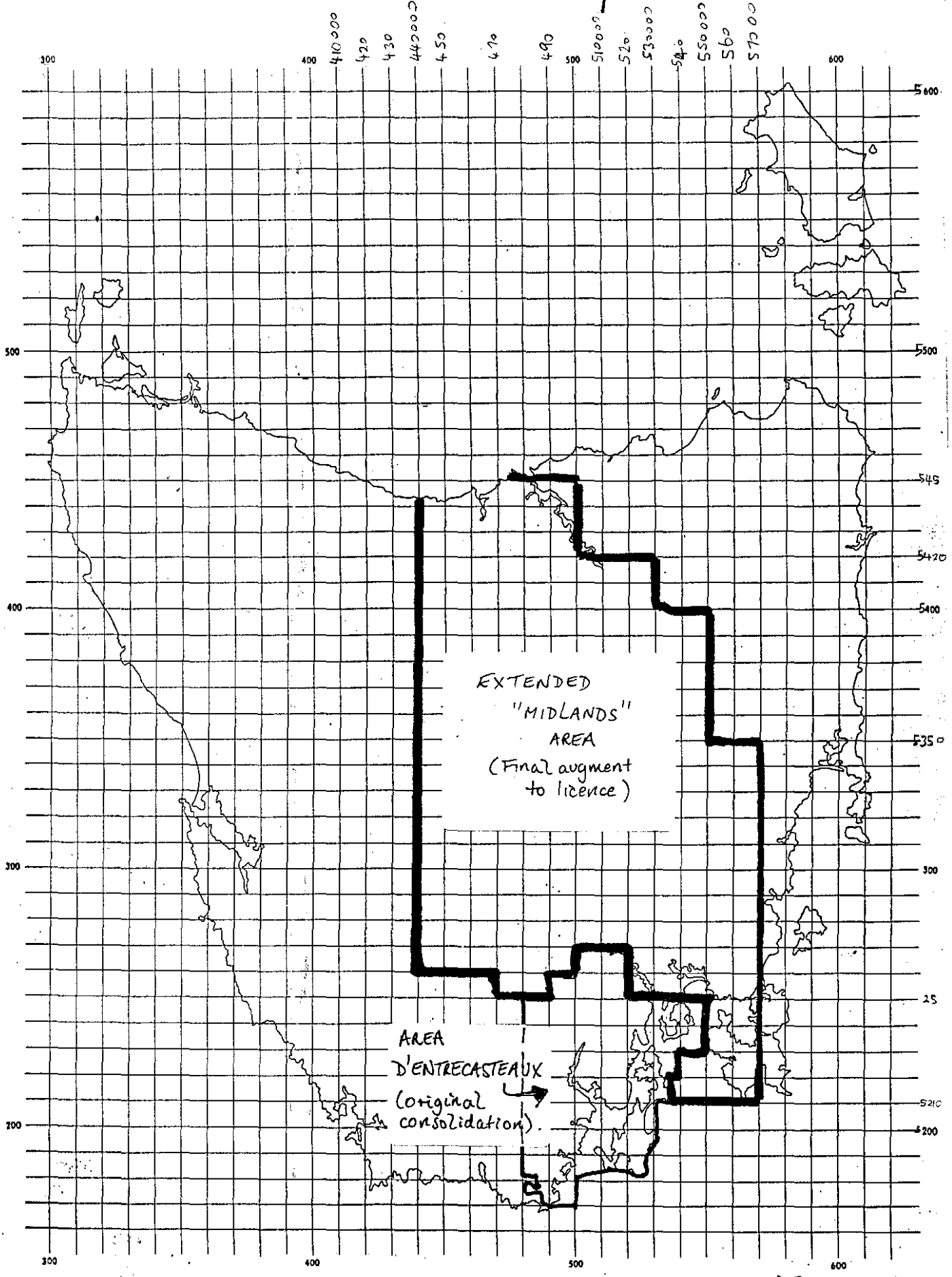

FIGURE 1

APPENDIX 1

CSIRO
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Chief of Division
Dr Angus McEwan, FAA

May 3rd., 1989

Dr D. Leaman
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Dear David

In response to your phone call on Monday, I have put together a few figures comparing the distributions of hydrocarbon biomarkers in sediments from the D'Entrecasteaux Channel and those from Ordovician carbonates from Queenstown. The agreement is quite good after allowance is made for the fact that the surface sediments from the Channel contain some naturally occurring compounds which contribute extra peaks (labelled *) to the m/z 191 and 205 mass fragmentograms.

Our work on the sediments from the D'Entrecasteaux Channel and Ordovician carbonates was carried out in late 1987 and some data were included in my report 88-HC1 to Conga Oil in February, 1988. Since doing that work we have also examined sediments from the Derwent Estuary which contain much higher concentrations of petroleum hydrocarbons having a similar distribution of biomarkers. Most of this work was funded by the Tasmanian Department of Environment so I regret that I cannot release full details at present.

It has always concerned me that the small amounts of petroleum hydrocarbons in the D'Entrecasteaux Channel might be due to pollutant sources, but at the time of doing the work in 1987 there were no obvious sources. However, over the last fortnight we have been conducting a small survey of hydrocarbon distributions in common automotive lubricating oils which are likely sources of pollution in estuarine and coastal areas. These have biomarker distributions which are very similar to those found in sediments from the Channel and Derwent Estuary. I have included a few typical mass fragmentograms for comparison with the earlier work. The similarities are perhaps not too surprising since I understand that in Australia lubricating oils are often derived from Middle East crudes which are also from carbonate source rocks (although of different age).

It is still not possible at this stage to state with any certainty whether the distributions of hydrocarbons in the Channel are due to oil seeps or not, but there is a very real chance that they are due to pollution. It will be difficult to differentiate between seeps of oil from Ordovician carbonates or pollution since the two seem to have very similar biomarker patterns. It might be possible to identify markers that are specific to the Tasmanian carbonates but this would involve a considerable amount of new research with no guarantee of success.

One encouraging feature is that the ratio of diasteranes to steranes is almost identical in the D'Entrecasteaux Channel sediments and Ordovician carbonates, but the few lubricating oils that we have studied contain much lower amounts of diasteranes. These compounds are marked "D" in the m/z 217 mass fragmentograms.

Another way to examine the problem would be to look for changes in hydrocarbon distributions with depth in a core. If the hydrocarbons are from an *in-situ* seep then the petroleum biomarkers should be present at depth, whereas if pollution in recent times is involved they will only be present in surface sediments. I already have some limited data from a core from the Derwent near Bridgewater which showed that the petroleum hydrocarbons are only present in the surface sediment there.

On a more positive note, our earlier work has clearly demonstrated that the Ordovician carbonates in Tasmania do contain distributions of hydrocarbons typical of crude oils. Whether this material is present in sufficient quantities to form commercial accumulations of oil is of course still unknown. The presence of traces of oil on Bruny Island is certainly consistent with some oil seepages, but all of the samples we analysed contained only very small amounts of hydrocarbons. It is a pity that we don't have an unequivocal sample rich in petroleum hydrocarbons from this area to confirm the presence of seeps.

Our analyses of biomarkers in tars from the Midlands are now complete and I am presently preparing a report. The tars contain high concentrations of hydrocarbons but there are also large amounts of polar and non-extractable material which is a surprise. The aliphatic biomarkers are typical of those found in oils of low-moderate maturity and there are significant differences in the biomarker patterns compared with those found in the Ordovician carbonates. In order to get some more information on the possible source of these tars, I undertook a study of the aromatic constituents. Instead of the usual distributions of alkyl naphthalenes, phnenanthrenes etc that one usually associates with a crude oil, I found that the tars contain large amounts of polycyclic aromatic compounds. These are usually associated with high temperature pyrolytic sources, and as far as I am aware they are not found in significant amounts in conventional crude oils. Similar distributions have been reported in the literature for road asphalt, and I hope to examine this possibility very soon.

The sample of Permian rock from Poatina yielded high concentrations of extractable hydrocarbons with a classic petroleum-type distribution. Tricyclic alkanes are not abundant which suggests that *Tasmanites* is not the source of the original organic matter. The biomarker distributions are totally different from those found in the Ordovician carbonates. It would be useful to get some Rock-Eval data for this rock sample to ascertain whether the hydrocarbons were generated *in-situ* or migrated into the mudstone.

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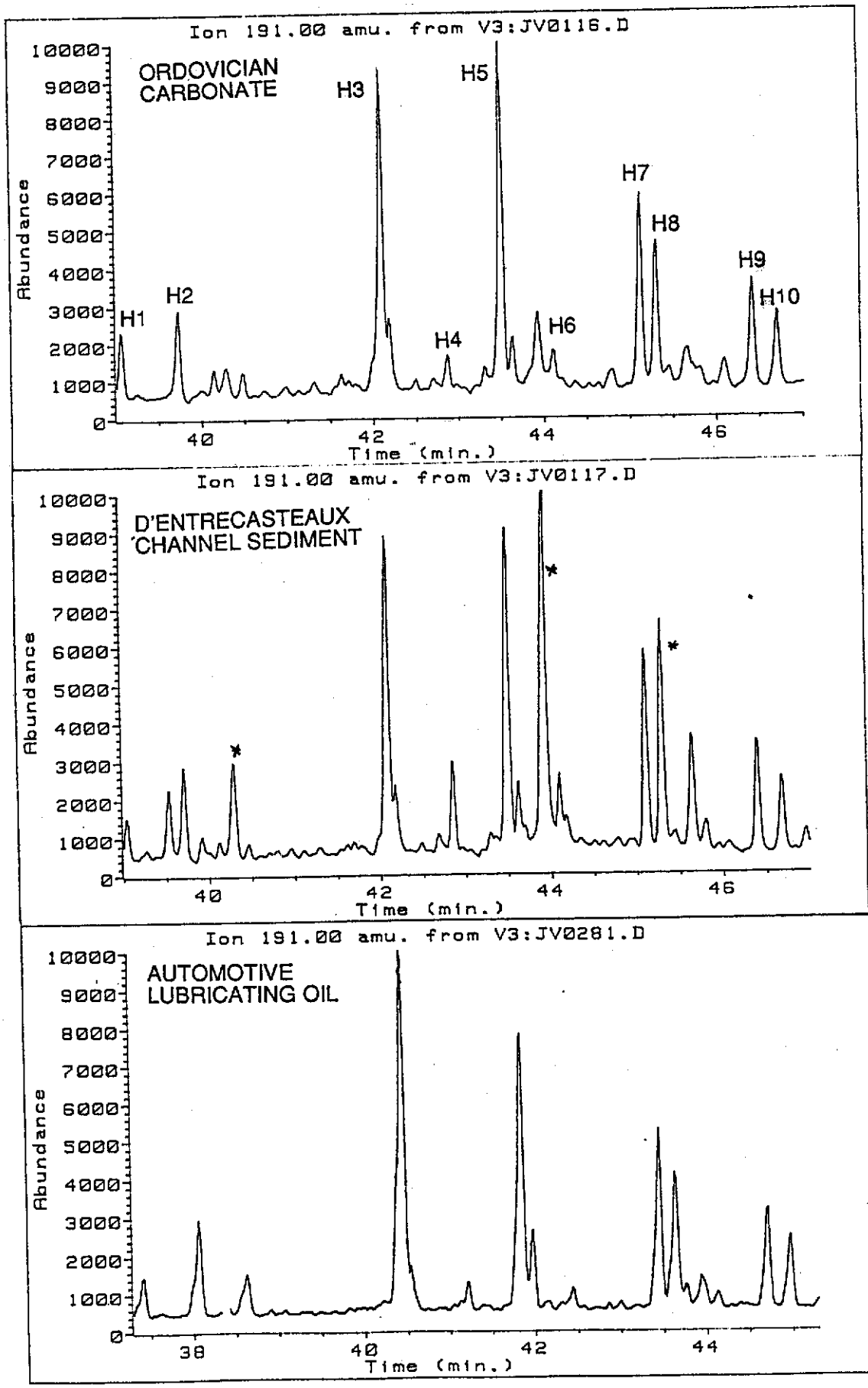
As you can see, much more geochemical work is required to define the source potential of on-shore Tasmania, but there are certainly some tantalising aspects of the present data that are worth further study. One thing that I would like to see is a more detailed geochemical study of possible source rocks using material of well defined provenance. Further studies of sediment cores from the Channel and Estuary may well clarify whether we are dealing with seeps or pollution there.

I hope that this information is of some use to you for your report. I spoke with Malcolm Bendall at the APEA conference and on the phone recently, so he is aware of the analytical data for the tar and Poatina mudstone. He may not be aware of our recent pollution studies, so I will send a copy of this letter to him to bring him up to date.

With best wishes
Yours sincerely

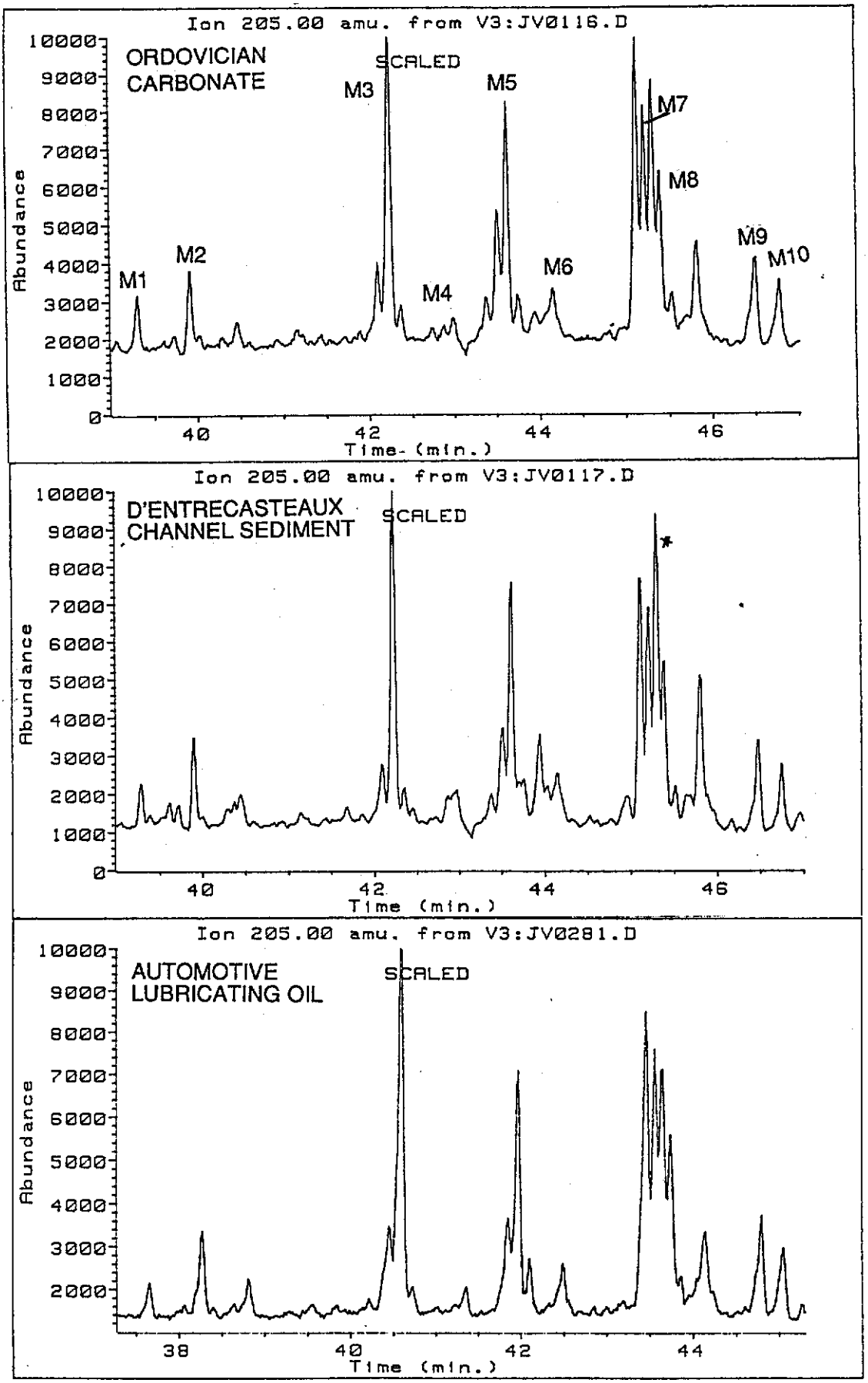
John K. Volkman
Principal Research Scientist

DISTRIBUTIONS OF HOPANES

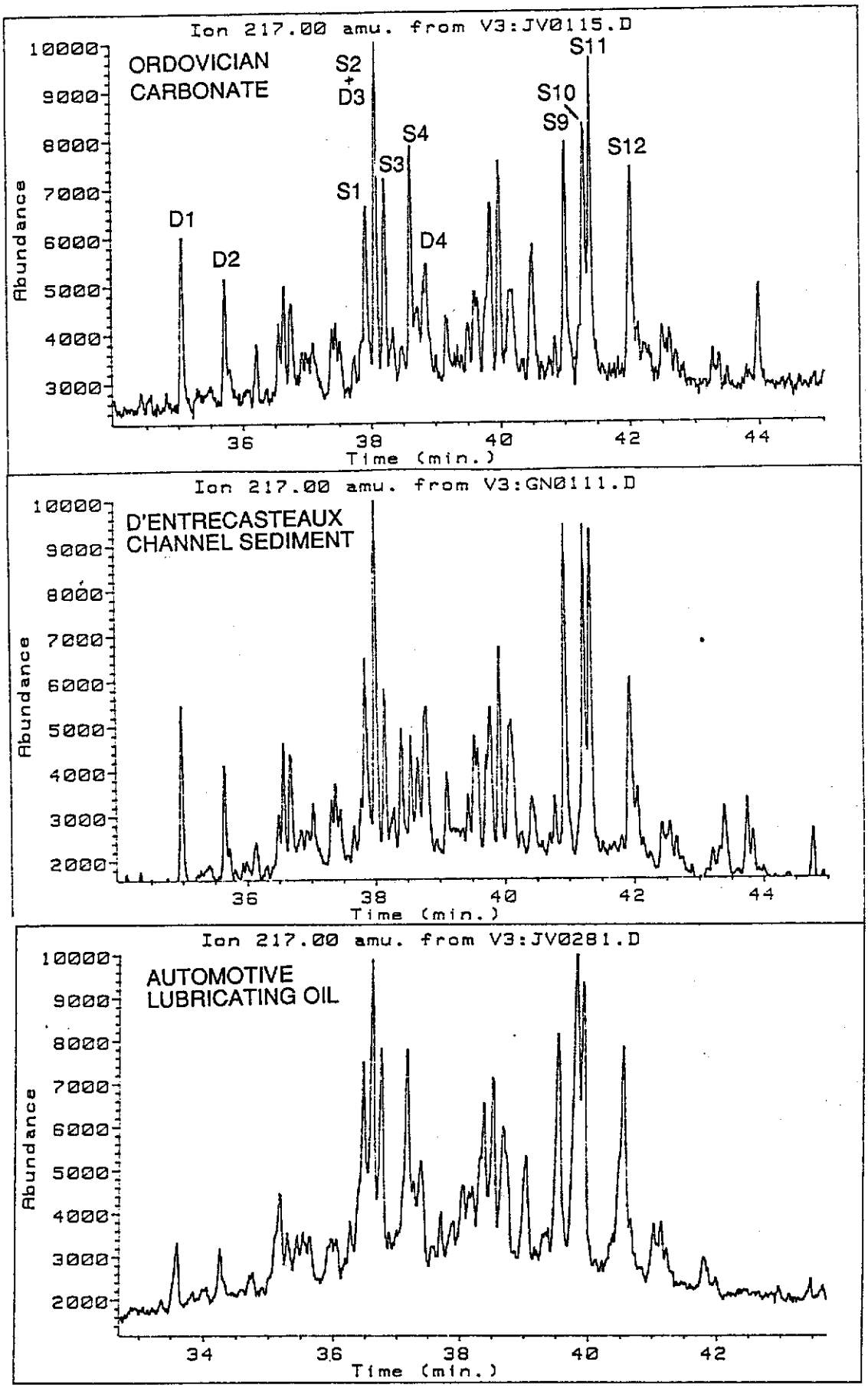


* natural compound

DISTRIBUTIONS OF METHYL HOPANES



DISTRIBUTIONS OF STERANES AND DIASTERANES



Key to identifications of peaks in hopane (m/z 191) and methyl hopane (m/z 205) mass fragmentograms

PEAK		COMPOUND
H1	C_{27}	18α(H)-22,29,30-trisnorneohopane (Ts)
H2	C_{27}	17α(H)-22,29,30-trisnorhopane (Tm)
H3	C_{29}	17α(H),21ß(H)-30-norhopane
H4	C_{29}	17ß(H),21α(H)-30-normoretane
H5	C_{30}	17α(H),21ß(H)-hopane
H6	C_{30}	17ß(H),21α(H)-moretane
H7	C_{31}	(22S)-17α(H),21ß(H)-homohopane
H8	C_{31}	(22R)-17α(H),21ß(H)-homohopane
H9	C_{32}	(22S)-17α(H),21ß(H)-bishomohopane
H10	C_{32}	(22R)-17α(H),21ß(H)-bishomohopane
M1	C_{28}	18α(H)-2-methyl-22,29,30-trisnorneohopane
M2	C_{28}	17α(H)-2-methyl-22,29,30-trisnorhopane
M3	C_{30}	17α(H),21ß(H)-2-methyl-30-norhopane
M4	C_{30}	17ß(H),21α(H)-2-methyl-30-normoretane
M5	C_{31}	17α(H),21ß(H)-2-methylhopane
M6	C_{31}	17ß(H),21α(H)-2-methylmoretane
M7	C_{32}	(22S)-17α(H),21ß(H)-2-methylhomohopane
M8	C_{32}	(22R)-17α(H),21ß(H)-2-methylhomohopane
M9	C_{33}	(22S)-17α(H),21ß(H)-2-methylbishomohopane
M10	C_{33}	(22R)-17α(H),21ß(H)-2-methylbishomohopane

Key to identifications of peaks in sterane (m/z 217) mass fragmentograms.

PEAK		COMPOUND
S1	C_{27}	(20S)-5α(H),14α(H),17α(H)-cholestane
S2	C_{27}	(20R)-5α(H),14ß(H),17ß(H)-cholestane
S3	C_{27}	(20S)-5α(H),14ß(H),17ß(H)-cholestane
S4	C_{27}	(20R)-5α(H),14α(H),17α(H)-cholestane
S5	C_{28}	(20S)-5α(H),14α(H),17α(H)-24-methylcholestane
S6	C_{28}	(20R)-5α(H),14ß(H),17ß(H)-24-methylcholestane
S7	C_{28}	(20S)-5α(H),14ß(H),17ß(H)-24-methylcholestane
S8	C_{28}	(20R)-5α(H),14α(H),17α(H)-24-methylcholestane
S9	C_{29}	(20S)-5α(H),14α(H),17α(H)-24-ethylcholestane
S10	C_{29}	(20R)-5α(H),14ß(H),17ß(H)-24-ethylcholestane
S11	C_{29}	(20S)-5α(H),14ß(H),17ß(H)-24-ethylcholestane
S12	C_{29}	(20R)-5α(H),14α(H),17α(H)-24-ethylcholestane
D1	C_{27}	(20S)-13ß(H),17α(H)-diasterane
D2	C_{27}	(20R)-13ß(H),17α(H)-diasterane
D3	C_{29}	(20S)-13ß(H),17α(H)-diasterane
D4	C_{29}	(20R)-13ß(H),17α(H)-diasterane

APPENDIX 2

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Chief of Division
Dr Angus McEwan, FAA

May 5th., 1989

Dr D. Leaman
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Dear David

I enclose my report 89-HC1to Conga Oil on the hydrocarbon compositions of the tar samples from the Midlands. I have also sent a copy to Malcolm Bendall.

The results are a bit of a puzzle and certainly don't fit conventional notions about what a seep-derived bitumen should look like. The hydrocarbons include all the usual biomarkers found in crude oils but the distributions are very different from those in the Ordovician carbonates. The relatively small amounts of hydrocarbons and large amounts of polar compounds present are of concern. Also, much of the tar wasn't extractable and there are large amounts of polycyclic aromatic hydrocarbons present which one normally associates with pyrolysis of fossil fuels.

It would help if I could get some more details of where these samples were obtained from, so that we can exclude man's activities as a source. There is a slim possibility that the unusual features of the hydrocarbon distributions were produced by dolerite sills intruding into an organic-rich sediment. Alternatively, could the tar have been subjected to intense heating such as a bushfire?

My report on the Poatina mudstone will follow in a few days.

With best wishes
Yours sincerely

John K. Volkman
Principal Research Scientist

CSIRO
Marine Laboratories

REPORT 89-HC1

HYDROCARBONS IN TWO TAR SAMPLES FROM THE MIDLANDS, TASMANIA

Prepared by: J. K. Volkman and D.G. Holdsworth
CSIRO Division of Oceanography

Prepared for: Conga Oil Pty. Ltd.
84 Wells Parade
Blackmans Bay
Tasmania

Attention: Mr Malcolm Bendall

May 3rd, 1989

CSIRO
AUSTRALIA

SAMPLES

Analytical data for two tars and an underlying rock sample are presented in this report.

BARNES BAY. also Brighton North and

BIT#1 A small sample of black tar from the Midlands area of Tasmania. 0.523 g of bitumen was extracted with chloroform to give a strong yellow-green extract having a very strong "oily" smell. The residue was further extracted with chloroform-hexane which produced additional extractable material.

(BRIDGEWATER - TAR) Brighton Nth

M1 A small sample of black tar from the same area of Tasmania. The tar was quite difficult to break and had a strong aromatic smell. Several of the samples supplied had a domed appearance and still had soil attached to the underside. 0.51 gram of crushed tar was extracted with chloroform.

(BRIDGEWATER - ROCK) Brighton Nth

M2 Small pieces of rock from immediately below the tar. The sample was wire brushed before crushing to ensure that all soil and tar fragments were removed. Small black particles were present in the rock and it was thought that these might be remnants of oil that had percolated up through the rock. 300 grams of crushed sediment were extracted.

Samples M1 and M2 were provided by Mr Malcolm Bendall of Conga Oil on January 10th., 1989. Sample BIT#1 was provided by Dr David Leaman in 1988.

Samples M1 and M2 were crushed using crushers at the University of Tasmania on January 15th., 1989. Hydrocarbon data were to be compared with the distributions of hydrocarbons found in suspected seeps from Bruny Island (Volkman, 1987) and hydrocarbons in sediments from the D'Entrecasteaux Channel and Ordovician carbonates from Queenstown and Ida Bay (Volkman, 1988).

locations:
DLeaman

METHODS AND RESULTS

TOTAL LIPID CONTENT

Portions of the extracts of M1 and M2 were analysed by Iatroscan thin-layer chromatography-flame ionisation detection (Volkman *et al.*, 1986) to determine the content of hydrocarbons.

TLC-FID chromatograms are shown in Figure 1. The hydrocarbon and polar lipid contents are shown below:

TABLE 1: CONCENTRATIONS OF HYDROCARBONS AND POLAR COMPOUNDS IN TAR AND ROCK SAMPLE

SAMPLE	HYDROCARBONS mg/g (dry weight)	POLAR COMPOUNDS mg/g (dry weight)
BIT#1:	nd	nd
M1	40	245
M2	0.13	0.0047

nd: not determined since extract was not quantitative.

Hydrocarbons comprised the major part of the extractable organic matter in rock sample M2 and there was no evidence for appreciable amounts of oxygenated lipids, such as free fatty acids or sterols, which are commonly found in immature sediments, in any sample.

Although the concentration of hydrocarbons in the tar sample was very much greater than in the underlying rock (Table 1), most of the extractable material was in fact polar compounds (Fig. 1) and more than half of the tar was not extractable into organic solvents at all.

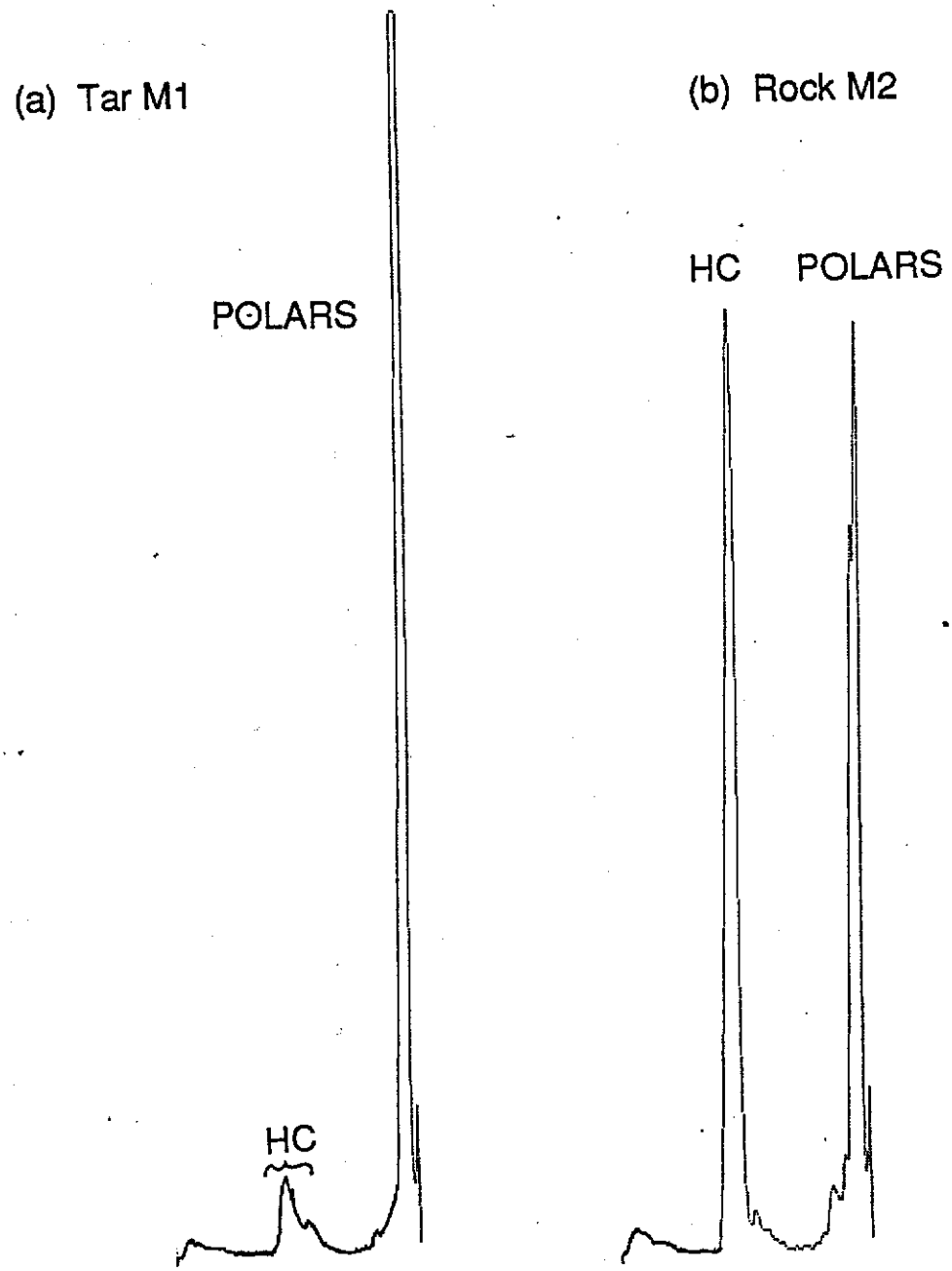


Figure 1. Iatroscan thin layer chromatography-flame ionisation detection (TLC-FID) chromatograms of extracts from samples M1 and M2. POLARS-polar lipids; HC-hydrocarbons. Solvent system: hexane:diethyl ether 94:6.

TOTAL HYDROCARBONS

Total hydrocarbons were separated by applying an aliquot of the total extract to a column of silica gel and eluting with hexane (10 ml) to obtain the aliphatic hydrocarbon fraction. A second fraction containing aromatic hydrocarbons was obtained by eluting with hexane-toluene (10 ml).

Each fraction was analysed by capillary gas chromatography on a 50 meter non-polar methyl silicone fused silica capillary column. Gas chromatograms of the aliphatic hydrocarbons are shown in Figure 2. Distributions of aromatic hydrocarbons are shown in Figures 5 and 8.

ALIPHATIC HYDROCARBONS

Hydrocarbons in sample BIT#1 consisted mainly of long-chain ($>C_{20}$) n-alkanes having a very slight odd over even predominance (Fig. 2 a). Hydrocarbons with chain-lengths less than C_{16} were very minor constituents: unaltered crude oils usually contain an abundance of such components. Polycyclic compounds are major constituents in the time window 40-48 minutes of the chromatogram.

The distribution of hydrocarbons in tar sample M1 is remarkably similar to that in BIT#1 except that very long-chain alkanes are relatively more abundant (Fig. 2 b). M1 also shows a significant "unresolved complex mixture" (UCM or hump) throughout the chain-length range. This UCM consists of a very complex mixture of branched and cyclic alkanes that cannot be resolved into individual components, even by the high resolution capillary columns used in this study. This UCM is less obvious in BIT#1, possibly because this sample was not extracted as exhaustively as M1.

The hydrocarbon distribution in the rock underlying the tar M1 is quite different. n-Alkanes show a bimodal distribution with a maximum at n-C_{17} as well as at higher carbon numbers. The UCM is very pronounced and continues to very high carbon numbers. The distribution above C_{20} is very complex and consists of numerous branched and cyclic components with only small amounts of n-alkanes.

Pristane and phytane are conspicuous constituents in the rock sample M2 (Figs. 2 c), but not in the two tar samples BIT#1 and M1.

029

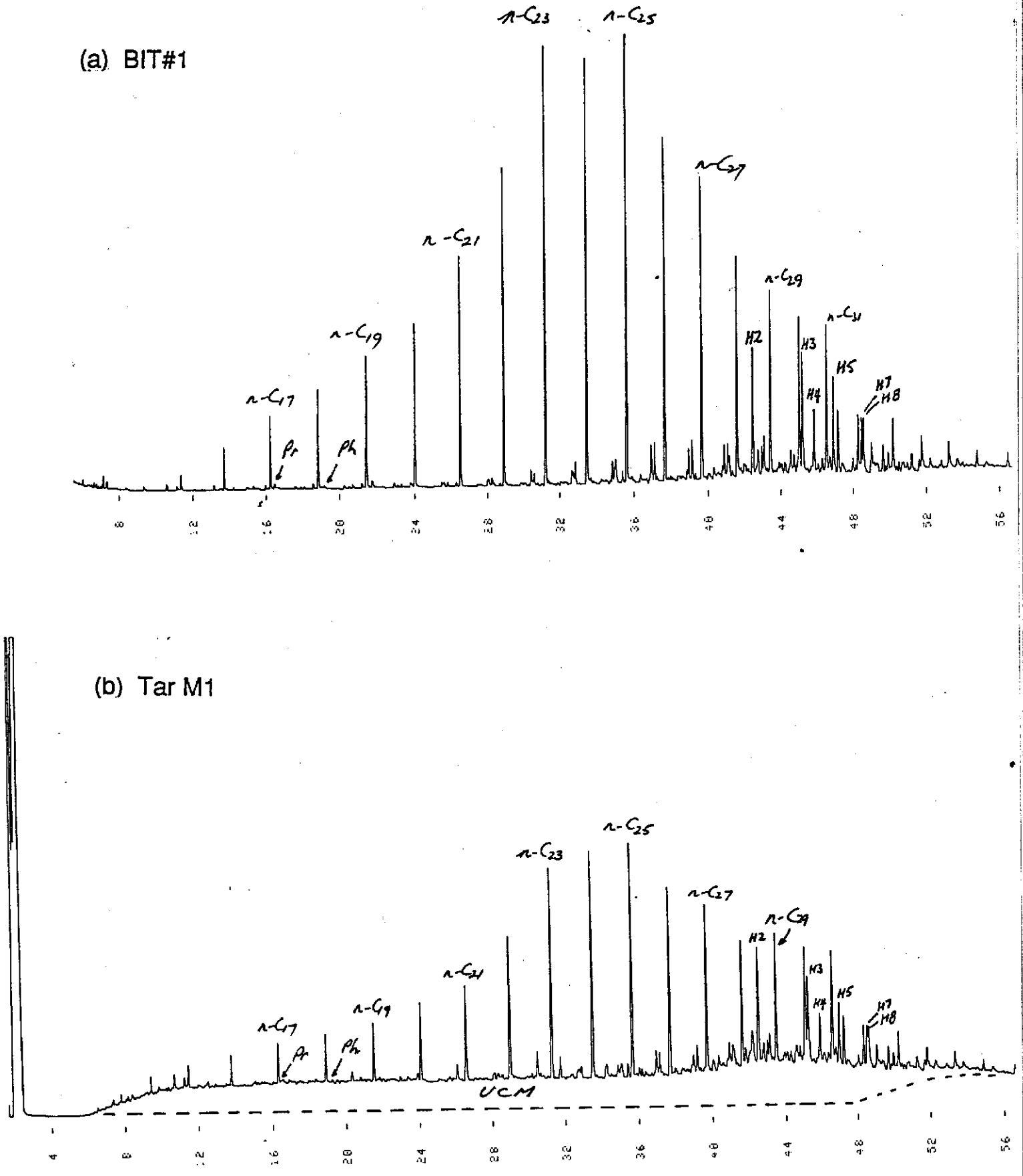


Figure 2. Capillary gas chromatogram of aliphatic hydrocarbons in (a) tar sample Bit#1 and (b) tar sample M1. High molecular weight cyclic compounds are hopanes.

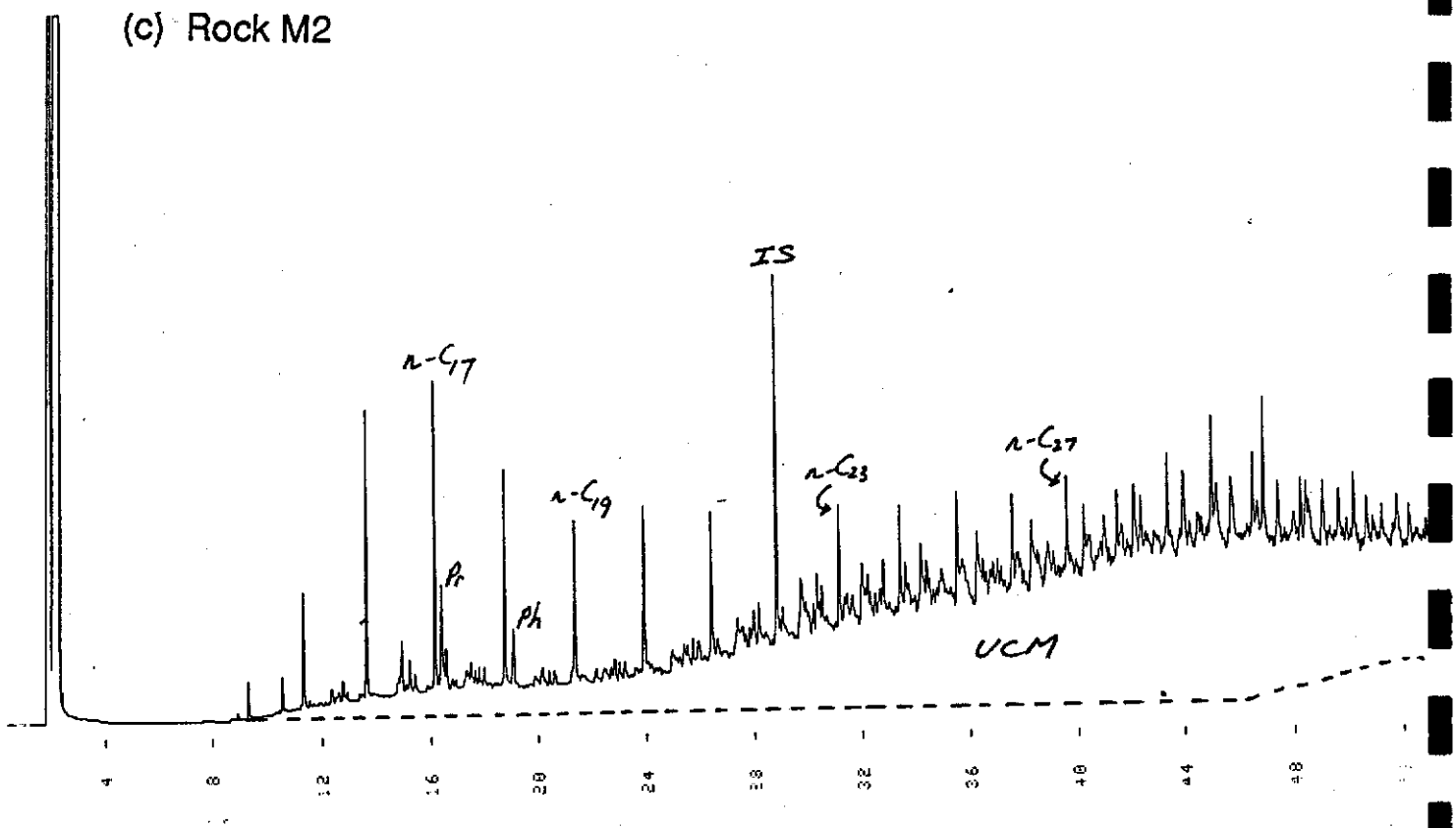


Figure 2c. Capillary gas chromatogram of aliphatic hydrocarbons in underlying rock sample M2.

BIOMARKERS

To obtain more detailed information about the composition of the hydrocarbons in the tars and rock samples, the aliphatic hydrocarbon fractions were analysed by gas chromatography-mass spectrometry in selected ion monitoring mode (SIM) and full data acquisition modes.

Distributions of polycyclic biomarkers characteristic of crude oils were determined using the selected ion monitoring facility of the mass spectrometer. Data for ions m/z 217 and 218 (steranes), m/z 259 (diasteranes), m/z 191 (hopanes), m/z 177 (demethylated hopanes), m/z 205 (methyl hopanes), m/z 113 and 183 (acyclic isoprenoids) and various molecular ions were acquired.

Representative mass fragmentograms are shown in Figures 3 and 4.

Hopanes

The tar samples BIT#1 and M1 contain almost identical distributions of biomarkers (Figs. 3 a,c). The proportions of various isomers suggest a maturity level equivalent to the beginning of the oil window. The distribution in the underlying rock M2 is quite different, and appears to be at a much higher level of thermal maturity (Fig. 3 e). Biogenic hydrocarbons were not detected in any of the samples. Hopanes are particularly abundant in the tars and are responsible for the extra peaks in the high molecular weight region of aliphatic hydrocarbon capillary gas chromatogram (Figs. 2 a,b). They are relatively less abundant in M2.

Several features of the hopane distributions can be used to ascertain the degree of thermal maturity of the sample. These show that the tar distributions (Figs. 3 a,c) are typical of those found in moderately mature sediments at the beginning of the oil window, whereas those in M2 indicate a higher maturation level. Hopanes having an "immature" ßß stereochemistry were minor components and unsaturated hopenes were not detected in any sample.

(a) In the extended hopanes (i.e. >C_{30}) the 22S epimer is more abundant than the 22R epimer and their ratio is typical of mature sediments. These isomers isomerise to an equilibrium mixture at maturities before the oil window and so are of little value for comparing mature samples. The low abundance of these extended hopanes relative to C_{29} and C_{30} hopanes distinguishes the distributions in the tar from those found in many oils. Note that extended hopanes are relatively more abundant in the rock M2.

(b) Moretanes (peaks H4 and H6) are about half as abundant as 17 (H),21ß(H)-hopanes in the m/z 191 mass fragmentograms for the tars (peaks H3 and H5; Figs 3 a,c) which indicates that these hydrocarbons are not derived from a high maturity oil. In contrast, the distribution in M2 shows low abundance of moretanes indicating a higher maturity.

(c) An unusual characteristic of the tars is the high abundance of the C_{27} hopane Tm. The ratio of the two C_{27} hopanes Ts and Tm is a sensitive indicator of thermal maturity. Ts is a very minor constituent of both tars again indicating that these hydrocarbons were produced at a low thermal maturity. It is difficult to put an equivalent vitrinite reflectance value on this, but it is probably near 0.5. In M2, Ts is much more abundant although still less than Tm.

Key 1. Identifications of peaks in hopane (m/z 191) and methyl hopane (m/z 205) mass fragmentograms

PEAK		COMPOUND
H1	C_{27}	18∝(H)-22,29,30-trisnorneohopane (Ts)
H2	C_{27}	17∝(H)-22,29,30-trisnorhopane (Tm)
H3	C_{29}	17∝(H),21ß(H)-30-norhopane
H4	C_{29}	17ß(H),21∝(H)-30-normoretane
H5	C_{30}	17∝(H),21ß(H)-hopane
H6	C_{30}	17ß(H),21∝(H)-moretane
H7	C_{31}	(22S)-17∝(H),21ß(H)-homohopane
H8	C_{31}	(22R)-17∝(H),21ß(H)-homohopane
H9	C_{32}	(22S)-17∝(H),21ß(H)-bishomohopane
H10	C_{32}	(22R)-17∝(H),21ß(H)-bishomohopane
H11	C_{33}	(22S)-17∝(H),21ß(H)-trishomohopane
H12	C_{33}	(22R)-17∝(H),21ß(H)-trishomohopane
H13	C_{34}	(22S)-17∝(H),21ß(H)-tetrakishomohopane
H14	C_{34}	(22R)-17∝(H),21ß(H)-tetrakishomohopane
H15	C_{35}	(22S)-17∝(H),21ß(H)-pentakishomohopane
H16	C_{35}	(22R)-17∝(H),21ß(H)-pentakishomohopane
M1	C_{28}	18∝(H)-2-methyl-22,29,30-trisnorneohopane
M2	C_{28}	17∝(H)-2-methyl-22,29,30-trisnorhopane
M3	C_{30}	17∝(H),21ß(H)-2-methyl-30-norhopane
M4	C_{30}	17ß(H),21∝(H)-2-methyl-30-normoretane
M5	C_{31}	17∝(H),21ß(H)-2-methylhopane
M6	C_{31}	17ß(H),21∝(H)-2-methylmoretane
M7	C_{32}	(22S)-17∝(H),21ß(H)-2-methylhomohopane
M8	C_{32}	(22R)-17∝(H),21ß(H)-2-methylhomohopane
M9	C_{33}	(22S)-17∝(H),21ß(H)-2-methylbishomohopane
M10	C_{33}	(22R)-17∝(H),21ß(H)-2-methylbishomohopane
M11	C_{34}	(22S)-17∝(H),21ß(H)-2-methyltrishomohopane
M12	C_{34}	(22R)-17∝(H),21ß(H)-2-methyltrishomohopane
M13	C_{35}	(22S)-17∝(H),21ß(H)-2-methyltetrakishomohopane
M14	C_{35}	(22R)-17∝(H),21ß(H)-2-methyltetrakishomohopane
M15	C_{36}	(22S)-17∝(H),21ß(H)-2-methylpentakishomohopane
M16	C_{36}	(22R)-17∝(H),21ß(H)-2-methylpentakishomohopane

BIT #1

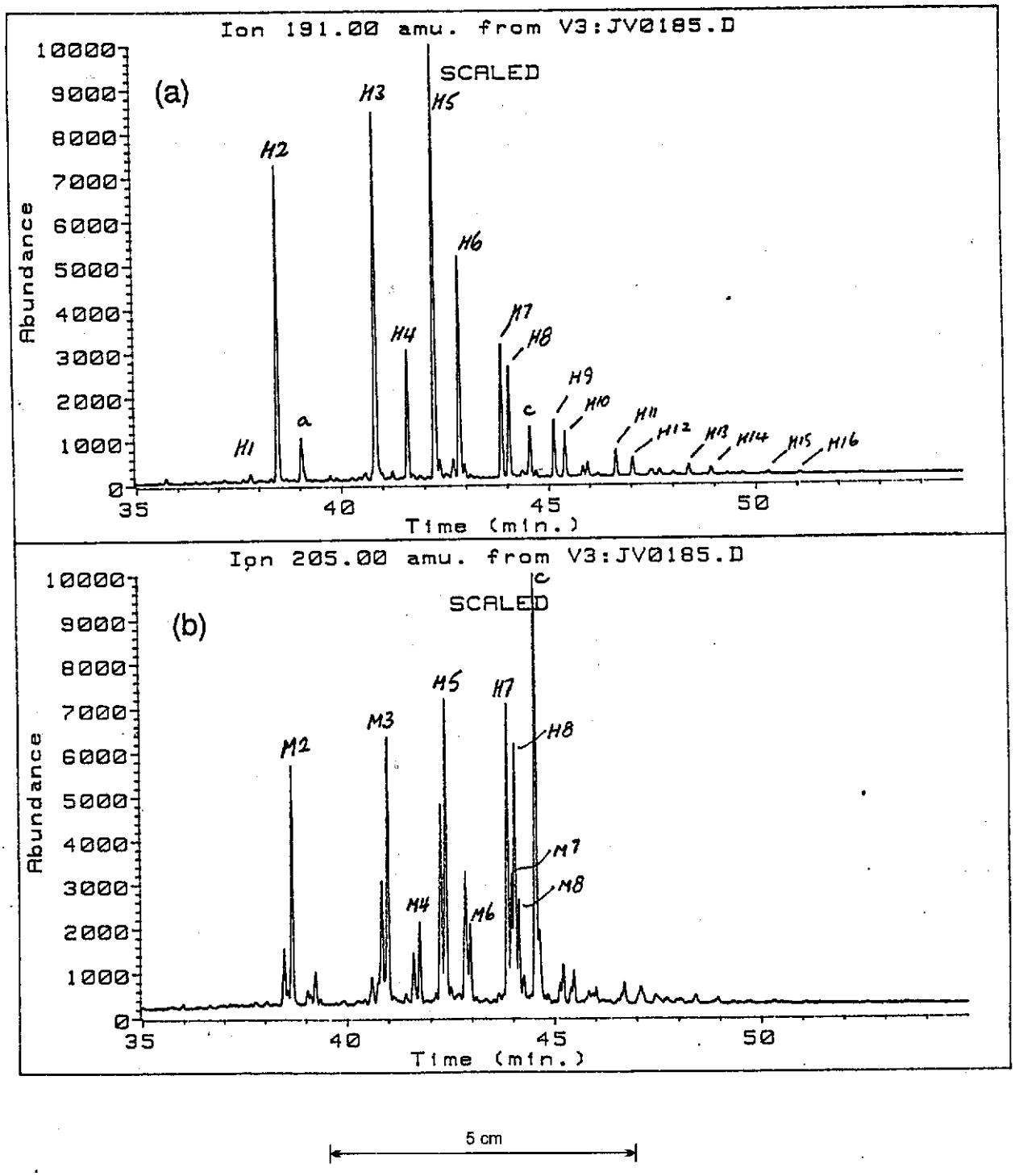


Figure 3. Mass fragmentograms for (a) m/z 191 and (b) m/z 205 showing distributions of hopanes and methyl hopanes respectively in tar sample BIT#1. See accompanying key for peak identifications.

TAR M1

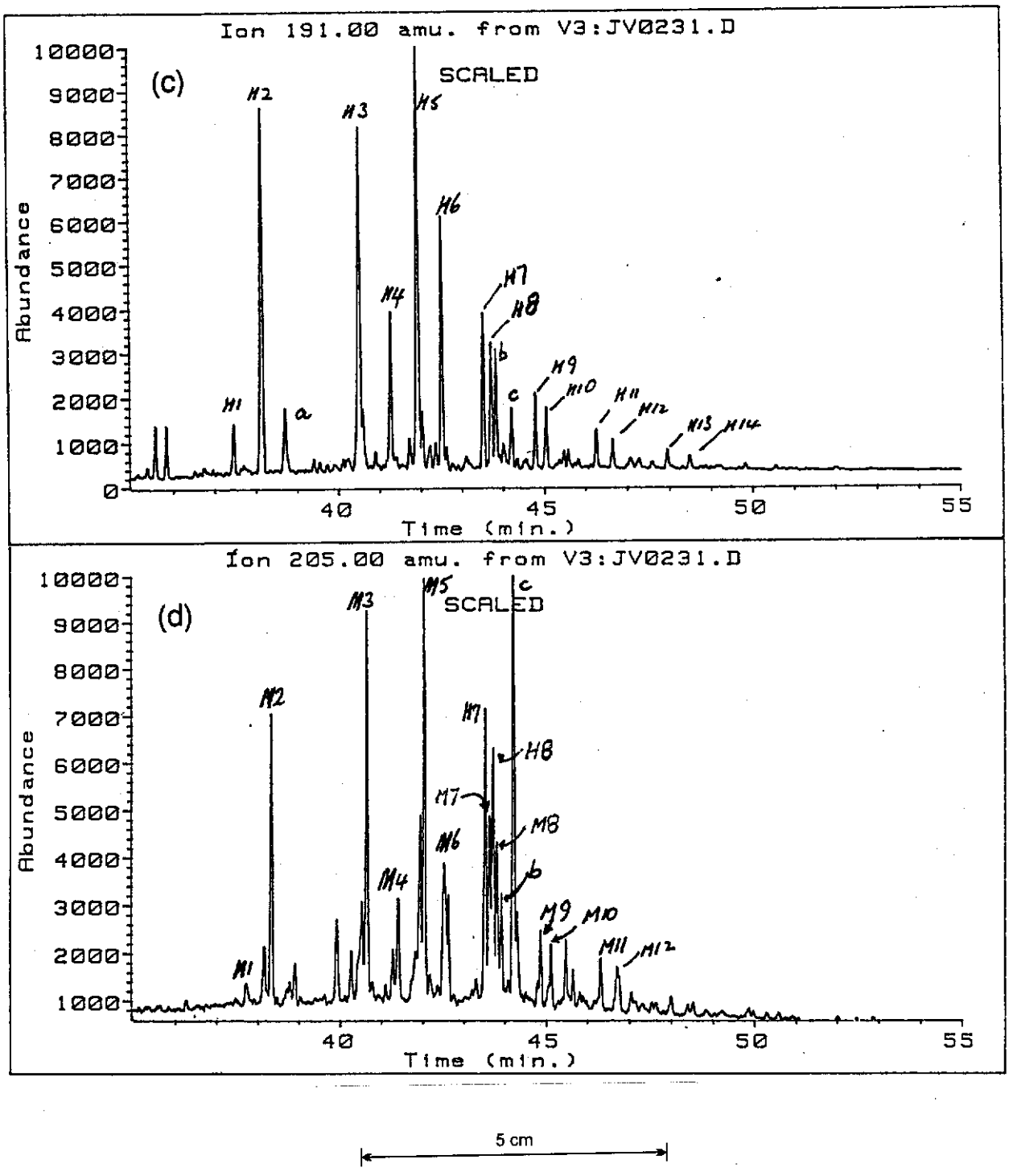
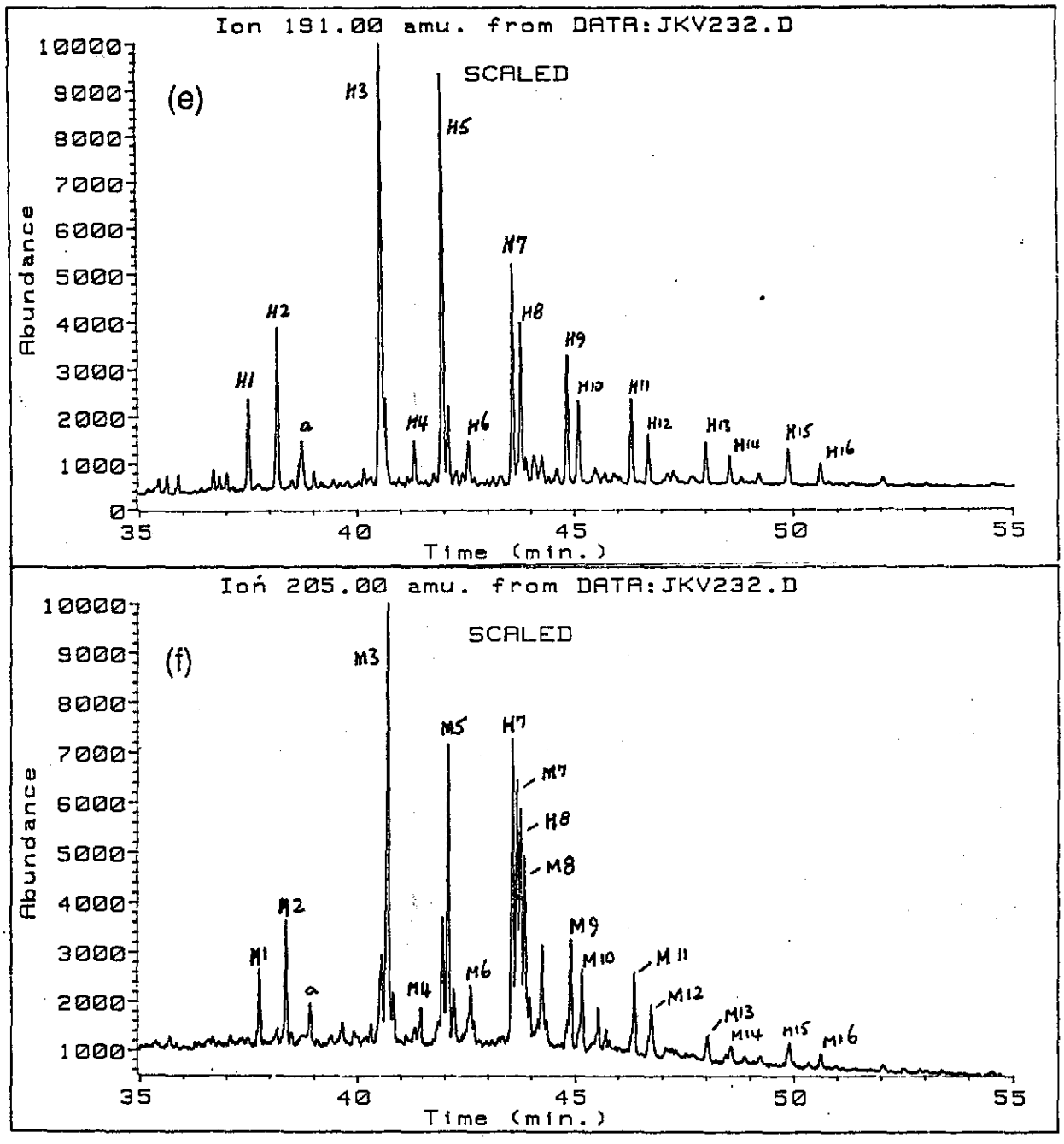


Figure 3. Mass fragmentograms for (c) m/z 191 and (d) m/z 205 showing distributions of hopanes and methyl hopanes respectively in tar sample M1. See accompanying Key 1 for peak identifications.

ROCK M2



5 cm

Figure 3. Mass fragmentograms for (e) m/z 191 and (f) m/z 205 showing distributions of hopanes and methyl hopanes respectively in underlying rock sample M2. See accompanying Key 1 for peak identifications.

036

In summary, the hopane distributions are very different from those found in suspected seep samples from Bruny Island (Volkman, 1987) or in Ordovician limestones from Queenstown and Ida Bay (Volkman, 1988). However, the hopane distribution in the underlying rock M2 is very similar to that found in the carbonates (Fig. 3e). The hydrocarbons in the tar are much less mature than those in the underlying rock and the data do not support the idea that the tar hydrocarbons have migrated through this sediment.

Demethylated hopanes

Demethylated hopanes were not detected in the tar samples using a m/z 177 mass fragmentogram (data not shown). These are commonly associated with highly biodegraded residues of crude oil (Volkman *et al.*, 1983) and their absence suggests that the unusual composition of the tars is probably not due to biodegradation.

Methyl hopanes

The tars contain relatively high concentrations of 2-methyl hopanes. These hopanes contain an additional methyl group in the A ring which results in a major fragment ion at m/z 205 instead of m/z 191. Mass fragmentograms are shown in Figure 3. Methyl hopanes are abundant in oils derived from carbonate source rocks although they are not restricted to this source facies. They are also abundant in the Ordovician limestones, but the isomer distributions are quite different to those found here.

A convenient parameter to measure their relative abundance is the ratio of C_{31} hopanes (peaks H7 and H8) to C_{32} methyl hopanes (M7 and M8) determined from the m/z 205 mass fragmentogram since both compounds give a m/z 205 ion. There is a small difference in this ratio for the two tar samples, with the M1 tar containing a slightly higher proportion of methyl hopanes.

Methyl hopanes are also abundant in the underlying rock M2, but the distribution of homologues is different as is the hopane/methyl hopane ratio. This distribution is very similar to that found in the Ordovician carbonates.

Tricyclic alkanes

Tricyclic alkanes were very minor constituents of the tars and M2 as judged by peak areas in the m/z 191 mass fragmentograms. These compounds dominate the m/z 191 mass fragmentograms obtained from Tasmanites (unpublished data).

Steranes

Distributions of steranes can provide information about the maturity and source of a crude oil. Mass fragmentograms for m/z 217 and m/z 218 are shown in Figure 4.

The tar samples BIT#1 and M1 contains only small quantities of steranes relative to hopanes and the distribution of isomers is quite unusual. C_{29} steranes are major constituents (Figs. 4 a-d) whereas C_{27} steranes and C_{28} steranes are very minor. This distribution is unlike any found previously in samples from Bruny Island. High concentrations of C_{29} steranes are common in oils derived mainly from higher plant (coaly) material.

The sterane distribution in M2 is very different from that in the tars with C_{27} steranes only slightly less abundant than C_{29} steranes. C_{28} steranes are also present in moderate amounts (Fig. 4 e,f). These data make it very unlikely that the two hydrocarbon distributions have the same source. Sterane maturity parameters for the tars are consistent with the low maturity inferred from the hopane parameters, whereas the hydrocarbons in M2 are much more mature. This is readily apparent from the low abundance of peaks S10 and S11 relative to S9 and S12 in the tars, and reverse result for M2 (Fig. 4).

C_{27} diasteranes (rearranged steranes) are barely detectable in the tars and C_{29} diasteranes (D3 and D4) dominate the distribution. This is analogous to the dominance of C_{29} steranes in the sterane profile and indicates that the original source material contained abundant C_{29} sterols. The diasterane/sterane ratio is much higher in M2 and the proportions of C_{27} and C_{29} components is also quite different. Diasteranes are typically abundant where the source rocks contain large amounts of clays which catalyse the steroid backbone rearrangement.

In summary, the sterane and diasterane data confirm the relatively low maturity of the tar hydrocarbons. They do not support the idea that the tar hydrocarbons migrated through the underlying rock M2. The distribution of steroidal alkanes in M2 is similar to that in the Ordovician carbonates, as is the distribution of hopanoid alkanes.

Key 2. Identifications of peaks in sterane and diasterane (m/z 217 and 218) mass fragmentograms.

PEAK	COMPOUND
S1	C_{27} (20S)-5α(H),14α(H),17α(H)-cholestane
S2	C_{27} (20R)-5α(H),14ß(H),17ß(H)-cholestane
S3	C_{27} (20S)-5α(H),14ß(H),17ß(H)-cholestane
S4	C_{27} (20R)-5α(H),14α(H),17α(H)-cholestane
S5	C_{28} (20S)-5α(H),14α(H),17α(H)-24-methylcholestane
S6	C_{28} (20R)-5α(H),14ß(H),17ß(H)-24-methylcholestane
S7	C_{28} (20S)-5α(H),14ß(H),17ß(H)-24-methylcholestane
S8	C_{28} (20R)-5α(H),14α(H),17α(H)-24-methylcholestane
S9	C_{29} (20S)-5α(H),14α(H),17α(H)-24-ethylcholestane
S10	C_{29} (20R)-5α(H),14ß(H),17ß(H)-24-ethylcholestane
S11	C_{29} (20S)-5α(H),14ß(H),17ß(H)-24-ethylcholestane
S12	C_{29} (20R)-5α(H),14α(H),17α(H)-24-ethylcholestane
D1	C_{27} (20S)-13ß(H),17α(H)-diasterane
D2	C_{27} (20R)-13ß(H),17α(H)-diasterane
D3	C_{29} (20S)-13ß(H),17α(H)-diasterane
D4	C_{29} (20R)-13ß(H),17α(H)-diasterane

038

BIT#1

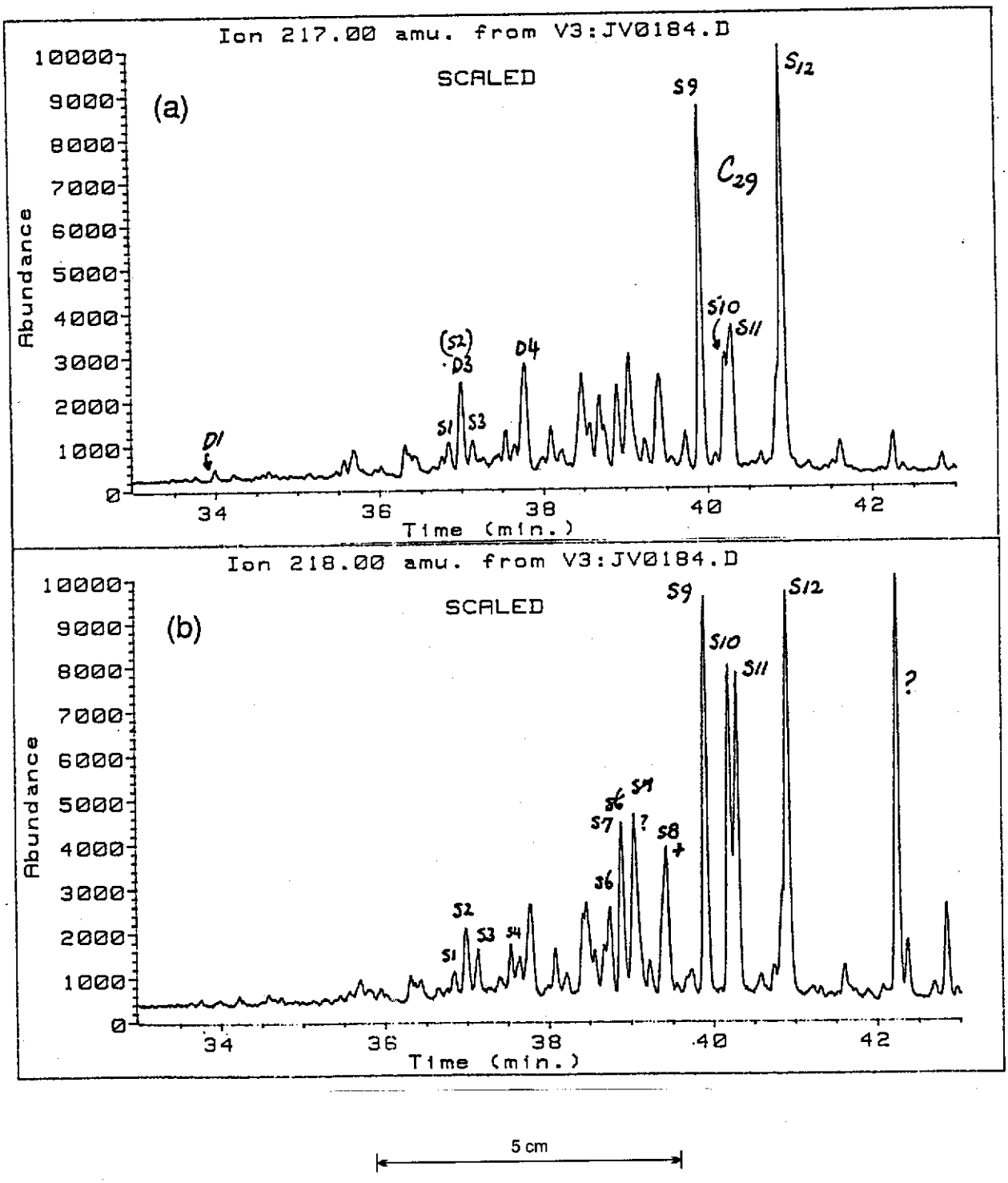


Figure 4. Mass fragmentograms for (a) m/z 217 and (b) m/z 218 showing distribution of C_{26}-C_{30} steranes and diasteranes in tar sample BIT#1. See accompanying Key 2 for peak identifications.

TAR M1

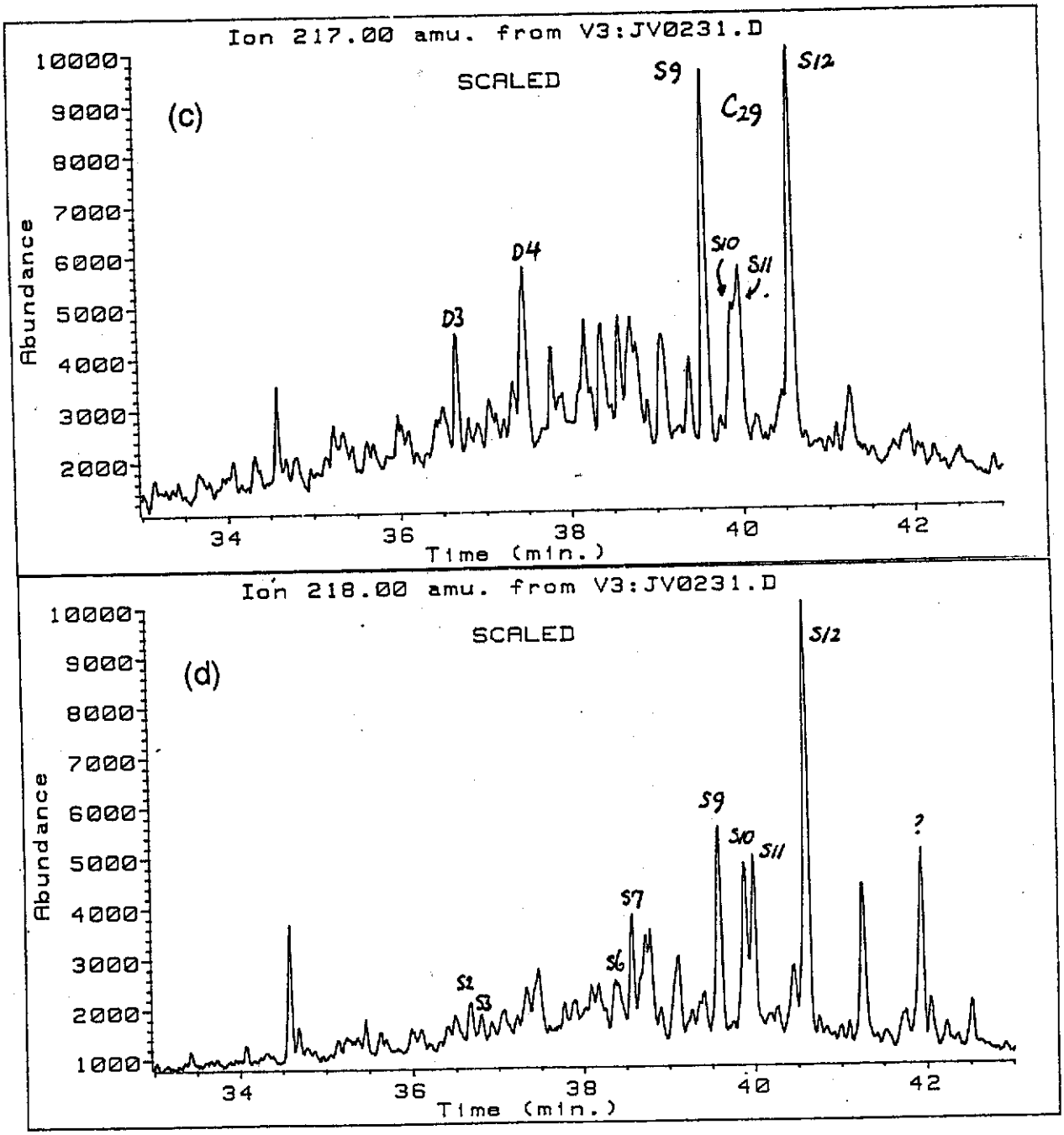


Figure 4. Mass fragmentograms for (c) m/z 217 and (d) m/z 218 showing distribution of C_{26}-C_{30} steranes and diasteranes in tar sample M1. See accompanying Key 2 for peak identifications.

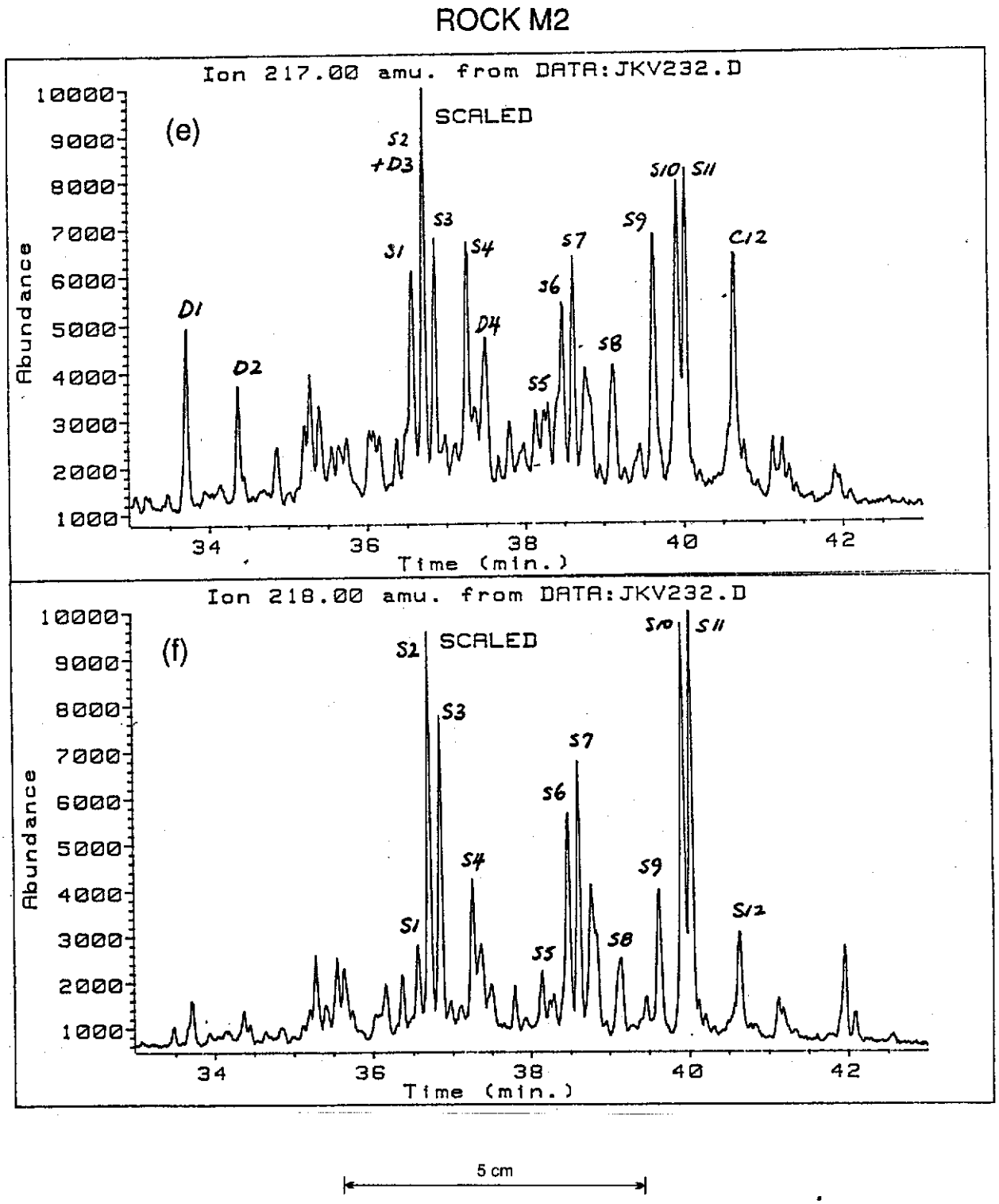


Figure 4. Mass fragmentograms for (e) m/z 217 and (f) m/z 218 showing distribution of C_{26}-C_{30} steranes and diasteranes in underlying rock sample M2. See accompanying Key 2 for peak identifications.

AROMATIC HYDROCARBONS IN THE TARS

The unusual compositional features of the aliphatic hydrocarbons in the tars prompted a study of the aromatic constituents to see whether they might provide further data on the source of the tars. Capillary gas chromatograms of the total aromatic hydrocarbon fractions are shown in Fig. 5.

Both tars contained a very similar distribution of aromatic components. Analysis by capillary gas chromatography-mass spectrometry in full scan mode showed that all of the major peaks were polycyclic aromatic hydrocarbons. These compounds are not common constituents of crude oils and are more usually associated with high temperature pyrolysis or burning of fossil fuels, particularly coals.

A search of the literature revealed that Wakeham *et al.* (1980) had identified very similar distributions of PAH in sediments from several Swiss lakes (Fig. 6). They also found similar distributions in street dust and road asphalt (Fig. 7) which led them to conclude that urban run-off was the most probable source of the aromatic hydrocarbons found. Peaks in tar aromatic hydrocarbon chromatograms (Fig. 5) have been labelled according to the same scheme as Wakeham *et al.* (1980) to highlight the similarity in these distributions.

The presence of such high concentrations of PAH is not consistent with the tar samples being sourced from petroleum seeps unless one can invoke some additional mechanism for altering the original petroleum composition. Forest fires have been proposed as a source of PAH (Youngblood and Blumer, 1975), but others have argued against this (Hase and Hites, 1976).

The aromatic hydrocarbon fraction in the underlying sediment M2 lacks significant amounts of PAH (Fig. 8).

042

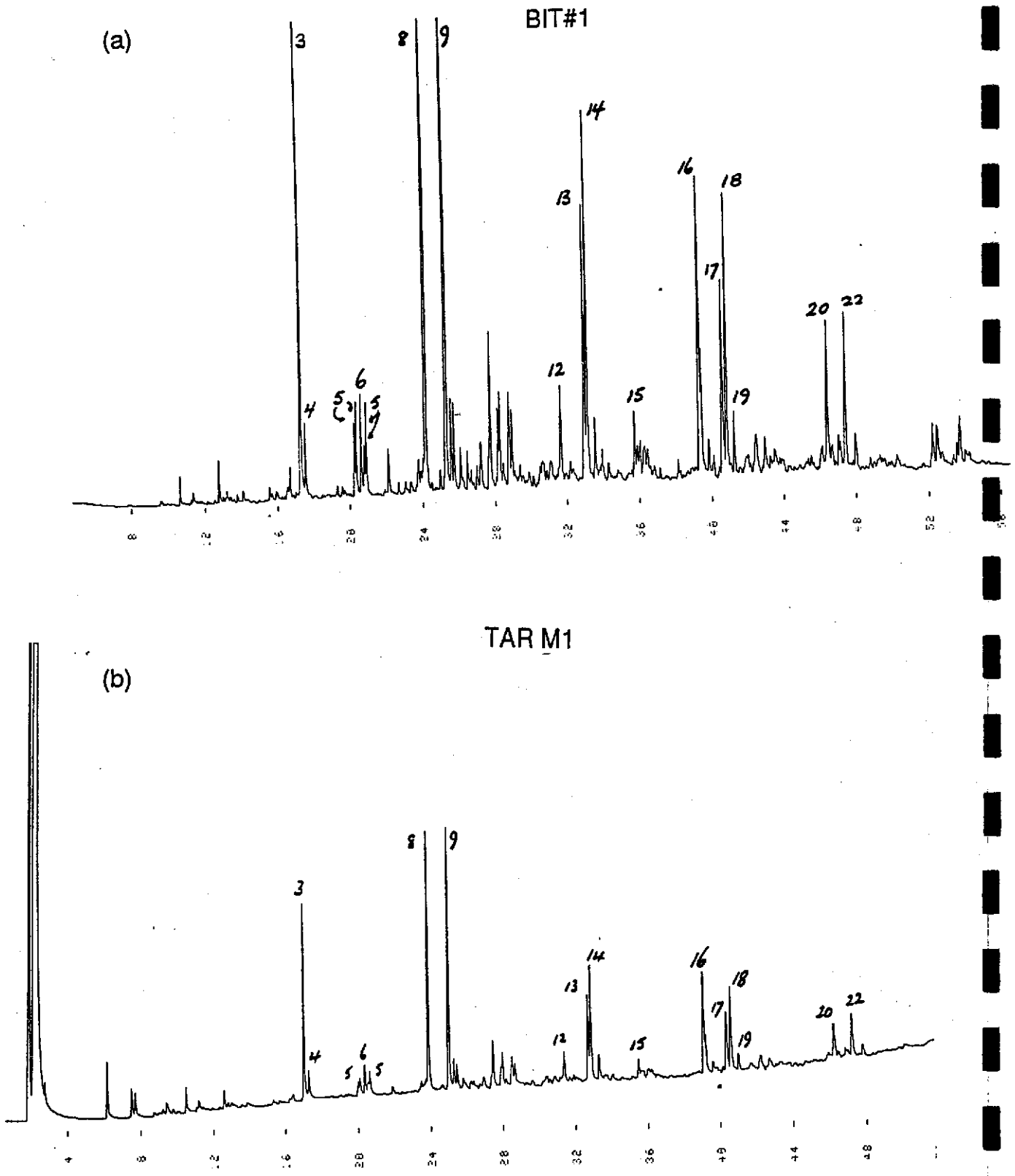


Figure 5. Capillary gas chromatograms showing distribution of aromatic hydrocarbons in (a) tar sample BIT#1 and (b) tar sample M1. Peak identifications are given in Fig. 7.

Polycyclic aromatic hydrocarbons in Recent lake sediments

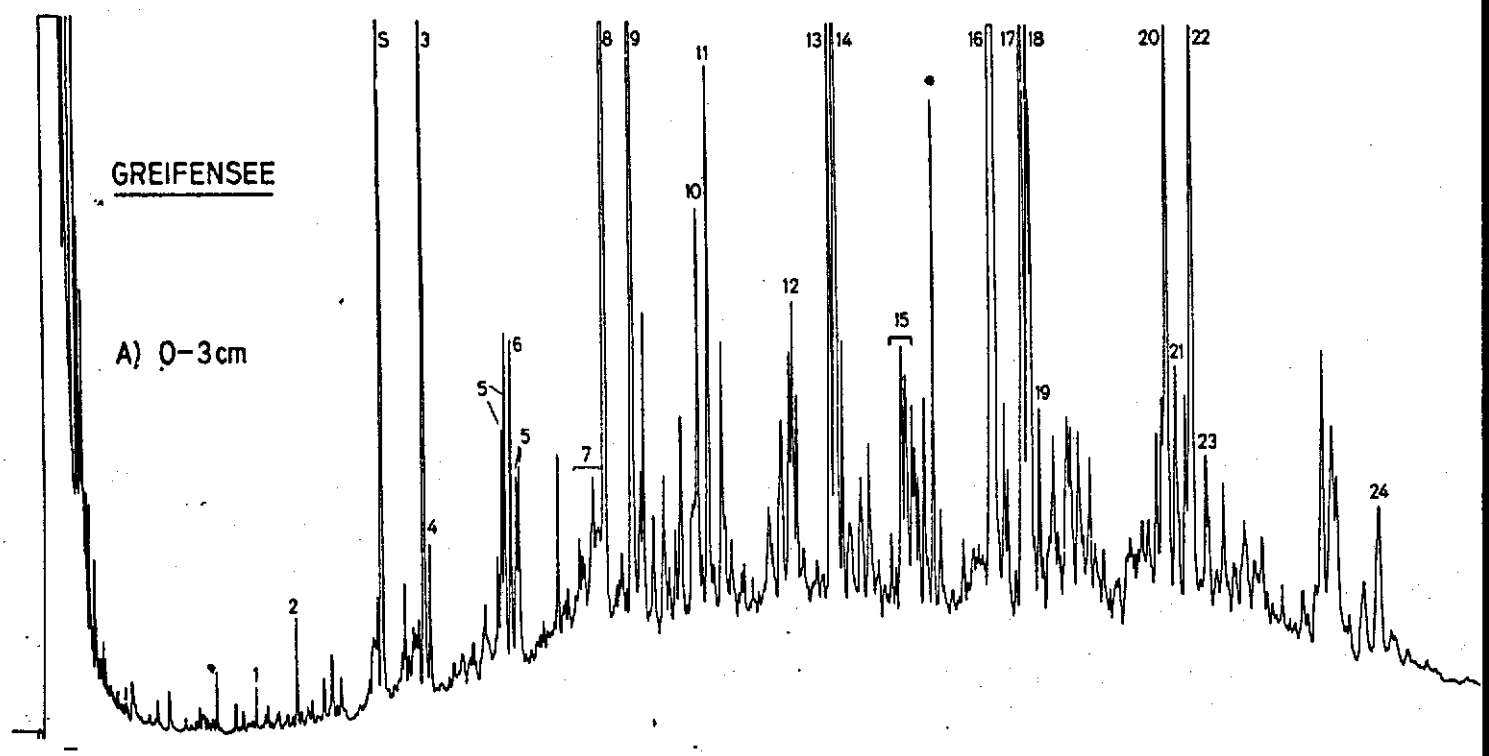


Figure 6. Capillary gas chromatogram showing distribution of aromatic hydrocarbons in a polluted lake sediment from Switzerland (from Wakeham *et al.*, 1980). Note the close similarity with the tar distributions. Peak identifications are given in Fig. 7.

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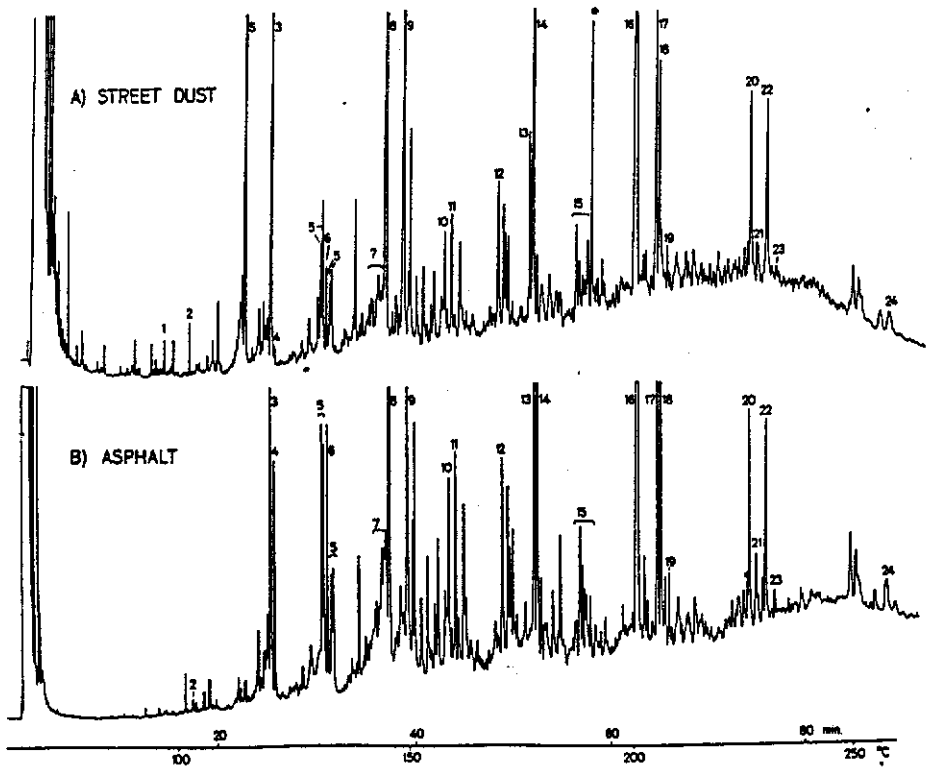
Polycyclic aromatic hydrocarbons in Recent lake sediments—I. Compounds having anthropogenic origins

STUART G. WAKEHAM,* CHRISTIAN SCHAFFNER and WALTER GIGER

Polycyclic aromatic hydrocarbons identified in lake sediments

Peak Number	Compound
1	Acenaphthene
2	Fluorene
3	Phenanthrene
4	Anthracene
5	Methylphenanthrenes[a]
6	4,5-Methylenephenanthrene
7	Dimethyl/ethylphenanthrenes
8	Fluoranthene
9	Pyrene
10	1,2-Benzofluorene
11	2,3/3,4-Benzofluorenes
12	1,2-Benzofluoranthene
13	1,2-Benzanthracene
14	Chrysene/triphenylene
15	Methylchrysenes
16	Benzofluoranthenes
17	1,2-Benzopyrene
18	3,4-Benzopyrene
19	Perylene
20	Indeno (1,2,3-cd)pyrene
21	1,2,3,4/1,2,5,6-Dibenzanthracenes
22	1,12-Benzoperylene
23	Anthanthrene
24	Coronene
S	Internal Standard

[a] In order of elution: 3-Methylphenanthrene, 2-Methylphenanthrene, 9-Methylphenanthrene, 1-Methylphenanthrene.



Capillary gas chromtograms of PAH isolated from a street dust (A) and weathered asphalt (B). Numbers refer to identified compounds in Table 2. GC conditions as for Fig. 2. In A, the phthalate (●) is present (see Fig. 2), while in B it is absent.

Figure 7. Capillary gas chromatograms showing distribution of aromatic hydrocarbons in street dirt and road asphalt, together with a Table of peak identifications (from Wakeham

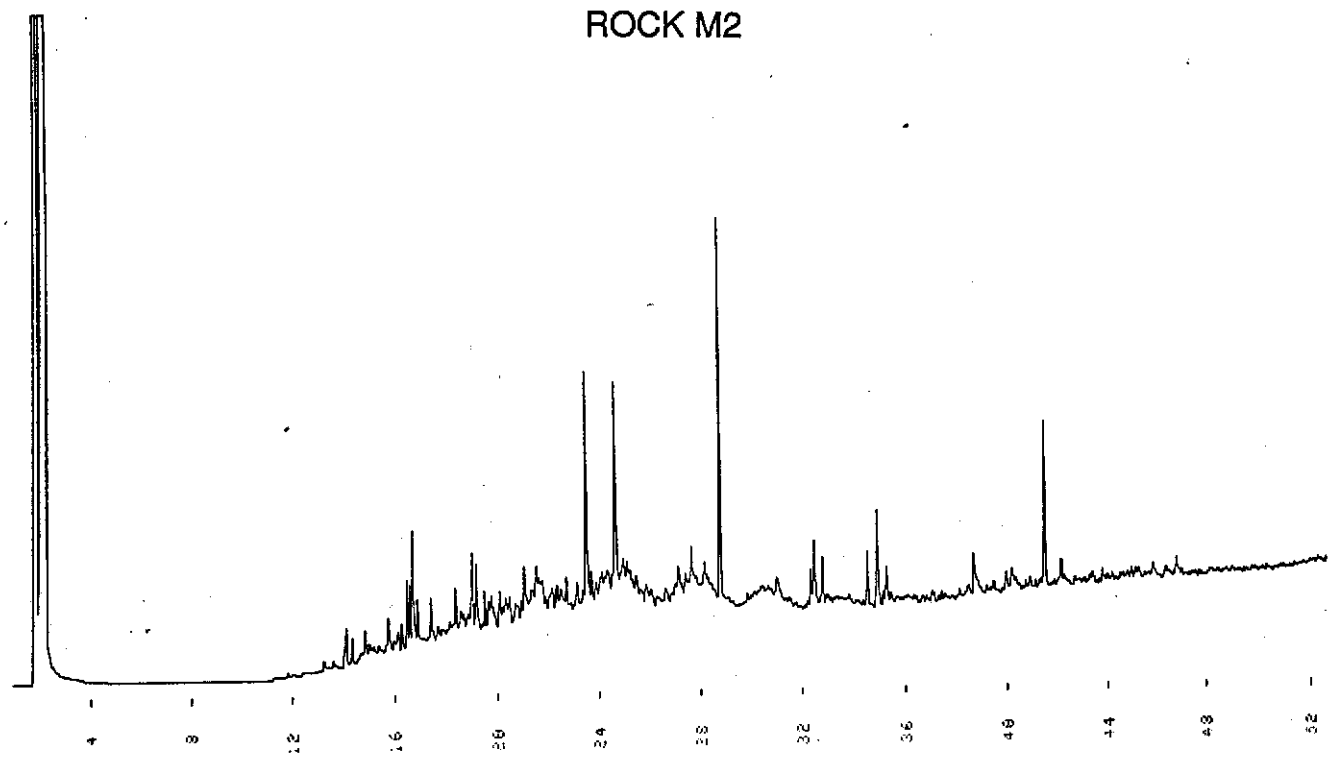


Figure 8. Capillary gas chromatogram showing distribution of aromatic hydrocarbons in underlying rock sample M2. Individual peaks not identified. Note the lack of PAH.

046

CONCLUSIONS

The two tar samples have very similar hydrocarbons compositions and can be considered to have had the same source. The aliphatic hydrocarbons have features similar to those in crude oils generated at relatively low thermal maturity (vitrinite relectance about 0.5).

The tars contain large amounts on non-extractable material and most of the compounds that can be extracted are polar components which is not a typical of an unaltered crude oil.

There is no evidence to suggest that the hydrocarbons in the tar and underlying rock are related. Source and maturation paramters are quite different which makes it unlikely that the tar hydrocarbons have migrated through the rock.

The biomarker patterns of the tars are quite unlike any of the suspected seep samples analysed from Bruny Island or D'Entrecasteaux Channel. It seems unlikely therefore that they may have been sourced from a seepage of petroleum generated from Ordovician carbonates. They have definitely not been sourced from Tasmanites.

The biomarker characteristics of the hydrocarbons in the underlying rock are however remarkably similar to those in the Ordovician carbonates.

The tars lack low molecular weight hydrocarbons that are characteristic of unaltered crude oils. These may have been lost by weathering or alternatively may not have been there in the first place as would be the case for a refined petroleum product or road tar. There is no evidence that this effect could be due to biodegradation.

The high proportion of C_{29} steranes and diasteranes in the tar is suggestive of material derived from higher plants (such as a coal), but the presence of such high amounts of methyl hopanes which are more commonly associated with petroleum from carbonate source rocks argues against this.

The presence of very high concentrations of polycyclic aromatic hydrocarbons (PAH) indicates that the tar is not simply an unaltered native oil seep. Their presence suggests that at some stage the tar organic matter has been subjected to high temperature burning. These PAH could not be associated with the original formation of the petroleum-like hydrocarbons since the biomarker maturity parameters indicate generation at a relatively low thermal maturation.

On balance, the geochemical data provide little support for the hypothesis that the tars are the result of *in situ* petroleum seepages unless reasonable mechanisms can be found to account for the unusual biomarker and aromatic hydrocarbon compositions and high proportion of polar and non-extractable material. It would be useful to analyse the tars by microscopy and to determine their carbon content and elemental composition.

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APPENDIX 3

CSIRO
Marine Laboratories

REPORT 89-HC2

HYDROCARBONS IN A LOWER PERMIAN MUDSTONE FROM POATINA, TASMANIA

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Attention: Mr Malcolm Bendall

May 9th, 1989

CSIRO
AUSTRALIA

SAMPLES

This report presents analytical data for the hydrocarbon composition of a Lower Permian mudstone from Poatina, Tasmania. This sample is thought to be stratigraphically related to the Quamby mudstone (D. Leaman, pers. comm.), which contains *Tasmanites*. The rock sample was provided by Mr Malcolm Bendall of Conga Oil on January 10th., 1989 together with samples of tar from the Midlands. Analytical data for the tar samples are presented in a separate report (Volkman and Holdsworth, 1989).

The sample provided was a single rock fragment. It was grey in colour and had a noticeable petroleum-like smell when broken open. The sample was wire brushed to ensure that no surface contamination was present and crushed using the crushers at the University of Tasmania on January 15th., 1989. 420 grams of crushed sediment were extracted with chloroform to give a yellow-green extract having a strong "oily" smell.

METHODS AND RESULTS

TOTAL LIPID CONTENT

A portion of the chloroform extract was analysed by Iatroscan thin-layer chromatography-flame ionisation detection (Volkman *et al.*, 1986) to determine the total hydrocarbon concentration in the rock. A TLC-FID chromatogram is shown in Figure 1.

Hydrocarbons were the major constituent of the solvent extract and there was only a small amount of polar lipid present. No sterols, alcohols or fatty acids were detectable.

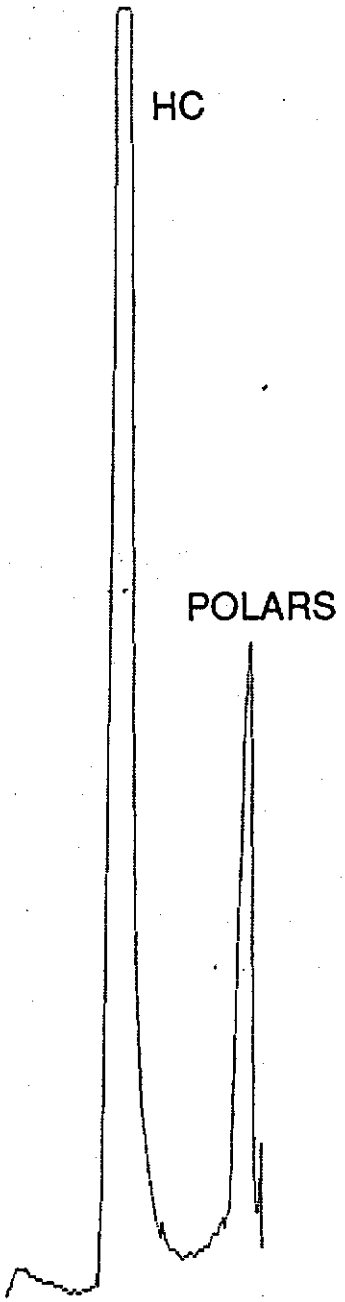

Figure 1. TLC-FID

POLARS-polar lipids

HC- hydrocarbons.

Solvent system: hexane:diethyl ether 94:6.

TABLE 1: CONCENTRATIONS OF HYDROCARBONS AND POLAR COMPOUNDS IN PERMIAN MUDSTONE

HYDROCARBONS	120 μg/g (dry weight)
POLAR COMPOUNDS	4.8 μg/g (dry weight)

The total amount of hydrocarbons is not particularly high, but it must be noted that volatile hydrocarbons (<n-C_{10}) are not be measured by this technique. These are probably quite abundant in this sediment judging from the gas chromatogram of the aliphatic hydrocarbons (Fig. 2).

For comparison, the Permian Inglis siltstone from Oonah has about twice the concentration of extractable hydrocarbons (>n-C_{10}: 270-290 μg/g; Denwer, 1986), and Tasmanite from the same section has 20 times as much (4.25 mg/g; Denwer, 1986).

TOTAL HYDROCARBONS

Total hydrocarbons were separated by applying an aliquot of the total extract to a column of silica gel and eluting with hexane (10 ml) to obtain the aliphatic hydrocarbon fraction. A second fraction containing aromatic hydrocarbons was obtained by eluting with hexane-toluene (10 ml).

Each fraction was analysed by capillary gas chromatography on a 50 meter non-polar methyl silicone fused silica capillary column. A gas chromatogram of the aliphatic hydrocarbons is shown in Figure 2. The distribution of aromatic hydrocarbons is shown in Figure 7.

ALIPHATIC HYDROCARBONS

The aliphatic hydrocarbons show the complete range of homologues that is typical of a mature crude oil. Short-chain (<n-C_{15}) alkanes are particularly abundant, but homologues extended at least to n-C_{36} (Fig. 2). Note that hydrocarbons smaller less than n-C_{10} would have been lost in the extraction procedure.

Branched and cyclic compounds are relatively minor constituents in the gas chromatogram due to the overwhelming predominance of n-alkanes.

The chromatogram also shows a small "unresolved complex mixture" (UCM or hump) throughout the chain-length range. This UCM consists of a very complex mixture of branched and cyclic alkanes that cannot be resolved into individual components, even by the high resolution capillary columns used in this study.

Pristane and phytane are conspicuous constituents in the mudstone (Fig. 2). The pristane/phytane ratio is 2.2; in the Inglis siltstone it is 3.5 (Denwer, 1986). Values greater than 1 are usually associated with an oxic depositional environment.

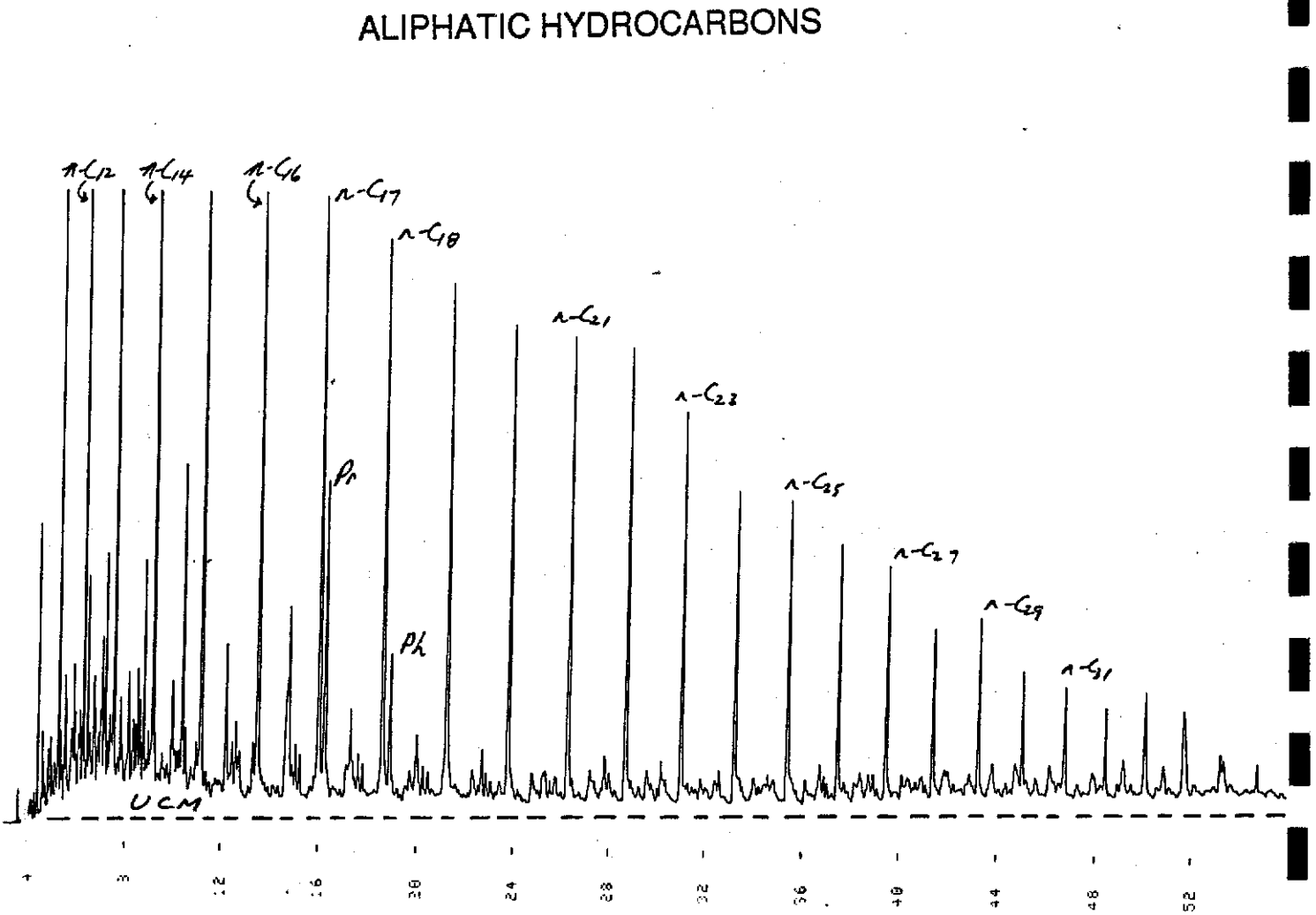

Figure 2. Capillary gas chromatogram of aliphatic hydrocarbons in the mudstone. Pr: pristane; Ph: phytane. n-Alkanes are denoted by n-C_X where "x" is the number of carbon atoms.

BIOMARKERS

To obtain more detailed information about the hydrocarbon composition, the aliphatic hydrocarbon fraction was analysed by gas chromatography-mass spectrometry in selected ion monitoring mode (SIM) and full data acquisition modes.

Distributions of polycyclic biomarkers that are commonly found in crude oils were determined using the selected ion monitoring facility of the mass spectrometer. Data for ions m/z 217 and 218 (steranes), m/z 259 (diasteranes), m/z 191 (hopanes), m/z 177 (demethylated hopanes), m/z 205 (methyl hopanes), m/z 113 and 183 (acyclic isoprenoids) and various molecular ions were acquired.

Tricyclic alkanes

Tricyclic alkanes dominate the m/z 191 mass fragmentograms over most of the carbon-number range (Figure 3), but longer-chain tricyclics are less abundant than hopanes in the higher molecular weight region of the m/z 191 mass fragmentograms (Fig. 4a), as shown by the small peaks eluting between the hopanes.

Tricyclic alkanes are very abundant in Tasmanites (Denwer, 1986; Simoneit *et al.*, 1986), and the distribution is similar to that found in the mudstone (Fig. 3) although the latter contains less of the tricyclic alkanes lower than C_{23}. Isomer ratios also differ probably due to differences in thermal maturity.

Total amounts of tricyclic alkanes in the mudstone are very much less than in Tasmanites. In Tasmanites, the lower molecular weight tricyclic alkanes are more abundant than n-alkanes, but in the mudstone the n-alkanes greatly predominate as shown by the small size of the peaks due to cyclic compounds eluting between the n-alkanes (Fig. 2).

Hopanes

Hopane distributions as represented by mass fragmentograms of the major fragment ion m/z 191 are shown in Figure 3 and 4a (C_{26}-C_{36} hopane range).

The hopane distribution in the mudstone is quite distinctive with a high predominance of the C_{30} hopane (peak H5; Fig. 4a), and comparatively low abundance of extended (>C_{30}) hopanes. The C_{29} hopane (peak H3) is surprisingly low in abundance. Hopanes having an "immature" ßß stereochemistry and unsaturated hopenes were not detected. Moretanes (peaks H4 and H5) are present in very minor amounts.

Hopane distributions can be used to ascertain the degree of thermal maturity from the relative proportions of key isomers.

(a) In the extended hopanes (i.e. >C_{30}) the 22S epimer is more abundant than the 22R epimer (e.g. peaks H7 and H8) which is typical of mature sediments. These isomers isomerise to an equilibrium mixture at maturities before the oil window.

(b) Moretanes (peaks H4 and H6) are very minor components compared with 17∝(H),21ß(H)-hopanes of the same chain-length (peaks H3 and H5). Similar ratios are found in mature crude oils.

Key 1. Identifications of peaks in hopane (m/z 191) and methyl hopane (m/z 205) mass fragmentograms

PEAK		COMPOUND
H1	C_{27}	18α(H)-22,29,30-trisnorneohopane (Ts)
H2	C_{27}	17α(H)-22,29,30-trisnorhopane (Tm)
H3	C_{29}	17α(H),21ß(H)-30-norhopane
H4	C_{29}	17ß(H),21α(H)-30-normoretane
H5	C_{30}	17α(H),21ß(H)-hopane
H6	C_{30}	17ß(H),21α(H)-moretane
H7	C_{31}	(22S)-17α(H),21ß(H)-homohopane
H8	C_{31}	(22R)-17α(H),21ß(H)-homohopane
H9	C_{32}	(22S)-17α(H),21ß(H)-bishomohopane
H10	C_{32}	(22R)-17α(H),21ß(H)-bishomohopane
H11	C_{33}	(22S)-17α(H),21ß(H)-trishomohopane
H12	C_{33}	(22R)-17α(H),21ß(H)-trishomohopane
H13	C_{34}	(22S)-17α(H),21ß(H)-tetrakishomohopane
H14	C_{34}	(22R)-17α(H),21ß(H)-tetrakishomohopane
H15	C_{35}	(22S)-17α(H),21ß(H)-pentakishomohopane
H16	C_{35}	(22R)-17α(H),21ß(H)-pentakishomohopane
M1	C_{28}	18α(H)-2-methyl-22,29,30-trisnorneohopane
M2	C_{28}	17α(H)-2-methyl-22,29,30-trisnorhopane
M3	C_{30}	17α(H),21ß(H)-2-methyl-30-norhopane
M4	C_{30}	17ß(H),21α(H)-2-methyl-30-normoretane
M5	C_{31}	17α(H),21ß(H)-2-methylhopane
M6	C_{31}	17ß(H),21α(H)-2-methylmoretane
M7	C_{32}	(22S)-17α(H),21ß(H)-2-methylhomohopane
M8	C_{32}	(22R)-17α(H),21ß(H)-2-methylhomohopane
M9	C_{33}	(22S)-17α(H),21ß(H)-2-methylbishomohopane
M10	C_{33}	(22R)-17α(H),21ß(H)-2-methylbishomohopane
M11	C_{34}	(22S)-17α(H),21ß(H)-2-methyltrishomohopane
M12	C_{34}	(22R)-17α(H),21ß(H)-2-methyltrishomohopane
M13	C_{35}	(22S)-17α(H),21ß(H)-2-methyltetrakishomohopane
M14	C_{35}	(22R)-17α(H),21ß(H)-2-methyltetrakishomohopane
M15	C_{36}	(22S)-17α(H),21ß(H)-2-methylpentakishomohopane
M16	C_{36}	(22R)-17α(H),21ß(H)-2-methylpentakishomohopane

Key 2. Identifications of peaks in sterane and diasterane (m/z 217 and 218) mass fragmentograms.

PEAK		COMPOUND
S1	C_{27}	(20S)-5α(H),14α(H),17α(H)-cholestane
S2	C_{27}	(20R)-5α(H),14ß(H),17ß(H)-cholestane
S3	C_{27}	(20S)-5α(H),14ß(H),17ß(H)-cholestane
S4	C_{27}	(20R)-5α(H),14α(H),17α(H)-cholestane
S5	C_{28}	(20S)-5α(H),14α(H),17α(H)-24-methylcholestane
S6	C_{28}	(20R)-5α(H),14ß(H),17ß(H)-24-methylcholestane
S7	C_{28}	(20S)-5α(H),14ß(H),17ß(H)-24-methylcholestane
S8	C_{28}	(20R)-5α(H),14α(H),17α(H)-24-methylcholestane
S9	C_{29}	(20S)-5α(H),14α(H),17α(H)-24-ethylcholestane
S10	C_{29}	(20R)-5α(H),14ß(H),17ß(H)-24-ethylcholestane
S11	C_{29}	(20S)-5α(H),14ß(H),17ß(H)-24-ethylcholestane
S12	C_{29}	(20R)-5α(H),14α(H),17α(H)-24-ethylcholestane
D1	C_{27}	(20S)-13ß(H),17α(H)-diasterane
D2	C_{27}	(20R)-13ß(H),17α(H)-diasterane
D3	C_{29}	(20S)-13ß(H),17α(H)-diasterane
D4	C_{29}	(20R)-13ß(H),17α(H)-diasterane

TRICYCLIC HYDROCARBONS AND HOPANES

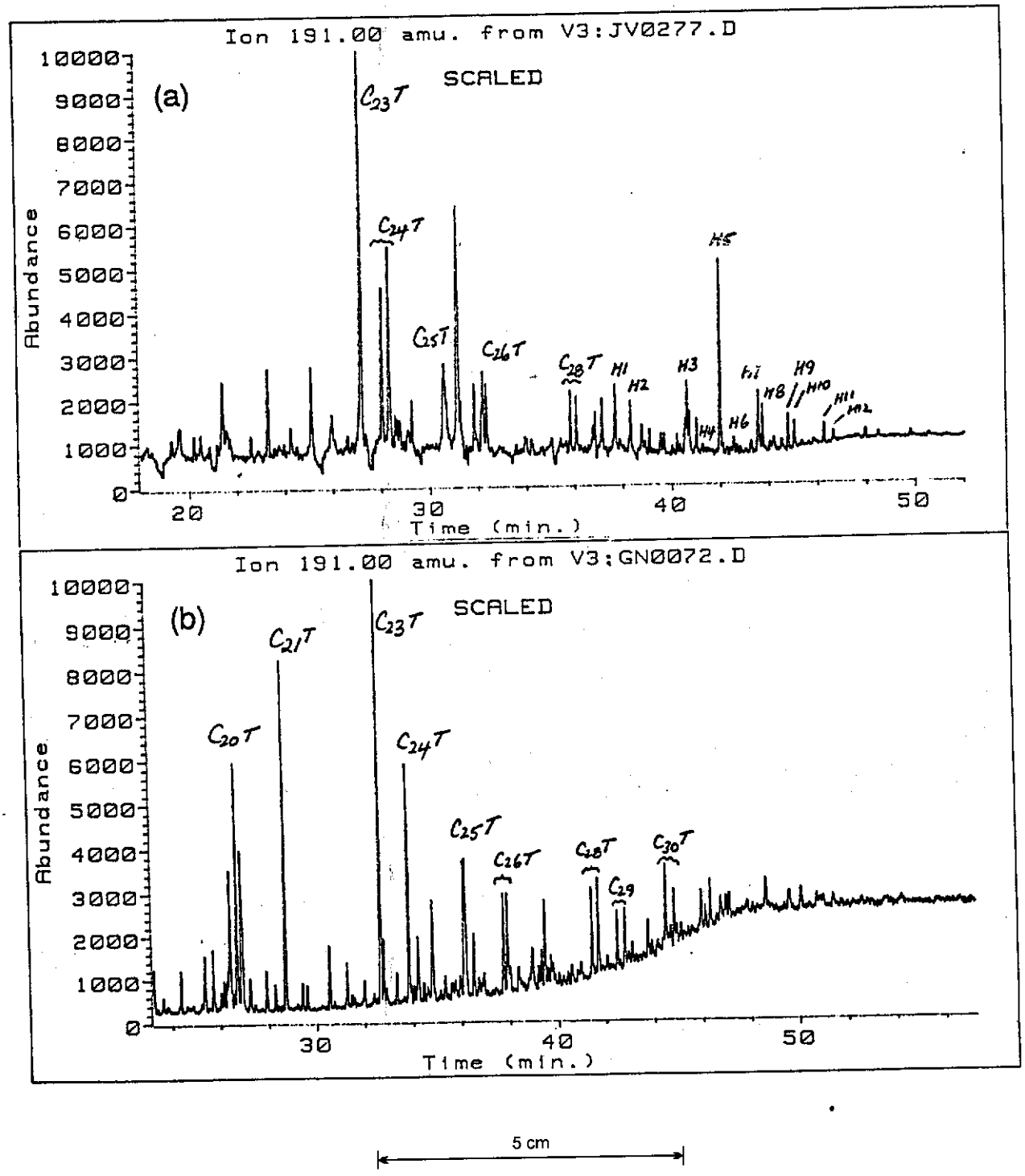

Figure 3. Mass fragmentograms for m/z 191 in (a) Permian mudstone and (b) Tasmanite. Tricyclic alkanes are denoted by C_XT where "x" is the number of carbon atoms. Note the general similarities of the tricyclic alkane distributions and higher relative abundance of hopanes (labelled H) in the mudstone. The mudstone has much smaller amounts of C_{20} and C_{21} tricyclic alkanes than Tasmanite.

HOPANES AND METHYL HOPANES

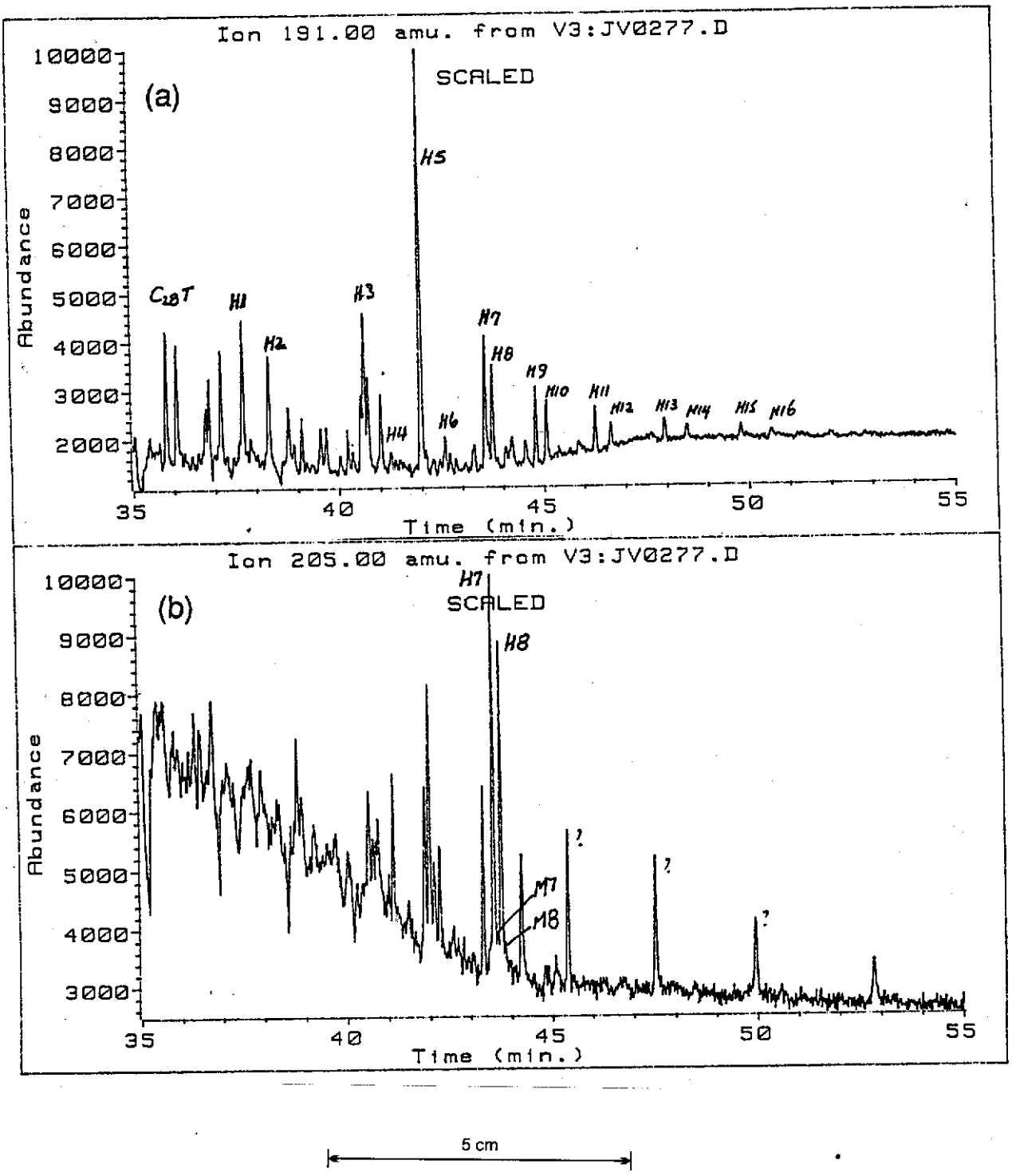

Figure 4. Mass fragmentograms for (a) m/z 191 and (b) m/z 205 showing distributions of hopanes (labelled H) and methyl hopanes (labelled M). See accompanying Key 1 for peak identifications. Note the lack of significant amounts of methyl hopanes. Tricyclic alkanes are denoted by T.

(c) The ratio of the two C_{27} hopanes Ts (peak H1) and Tm (peak H2) is a sensitive indicator of thermal maturity. Ts is almost as abundant as Tm indicating that these hydrocarbons were produced at a high thermal maturity. The equivalent vitrinite reflectance would be in excess of 0.7.

The hopane distributions are very different from those found in suspected seep samples from Bruny Island (Volkman, 1987) or in Ordovician carbonates from Queenstown and Ida Bay (Volkman, 1988). The hopane distributions of the latter contain the C_{29} hopane as a major component, and extended hopanes are relatively more abundant.

Demethylated hopanes

A m/z 177 mass fragmentogram (data not shown), showed that demethylated hopanes were not present in the mudstone. These are commonly associated with highly biodegraded residues of crude oil (Volkman *et al.*, 1983).

Methyl hopanes

The mudstone contains only trace amounts of 2-methyl hopanes as shown by the m/z 205 mass fragmentogram (Fig. 4b). Methyl hopanes are abundant in the Ordovician carbonates (Volkman, 1988), and in most oils derived from carbonate source rocks although they are not restricted to this source facies.

Steranes

Distributions of steranes can provide information about the maturity and source of a crude oil. Mass fragmentograms for m/z 217 and m/z 218 are shown in Figure 5.

C_{27} steranes are only slightly more abundant than C_{29} steranes; C_{28} steranes are also present in moderate amounts (Fig. 5). Sterane maturity parameters are consistent with a fairly high maturity which is consistent with the hopane parameters. Note the higher abundance of αββ isomers (peaks S10 and S11) compared with ααα isomers (peaks S9 and S12) (Fig. 5).

C_{27} and C_{29} diasteranes (rearranged steranes) are very abundant (peaks labelled D in Fig. 5). Diasteranes are typically abundant where the source rocks contain large amounts of clays which catalyse the steroid backbone rearrangement.

The m/z 217 mass fragmentogram over the entire carbon number range shows an abundance of lower molecular weight steranes (Fig. 6). Individual components have not been identified, but such compounds are usually associated with thermal cracking of higher molecular weight steranes and diasteranes in oils of higher maturity.

Steranes in Tasmanites show a much higher predominance of C_{29} components and the diasterane/sterane ratio is much less than in the mudstone (Denwer, 1986).

STERANES AND DIASTERANES

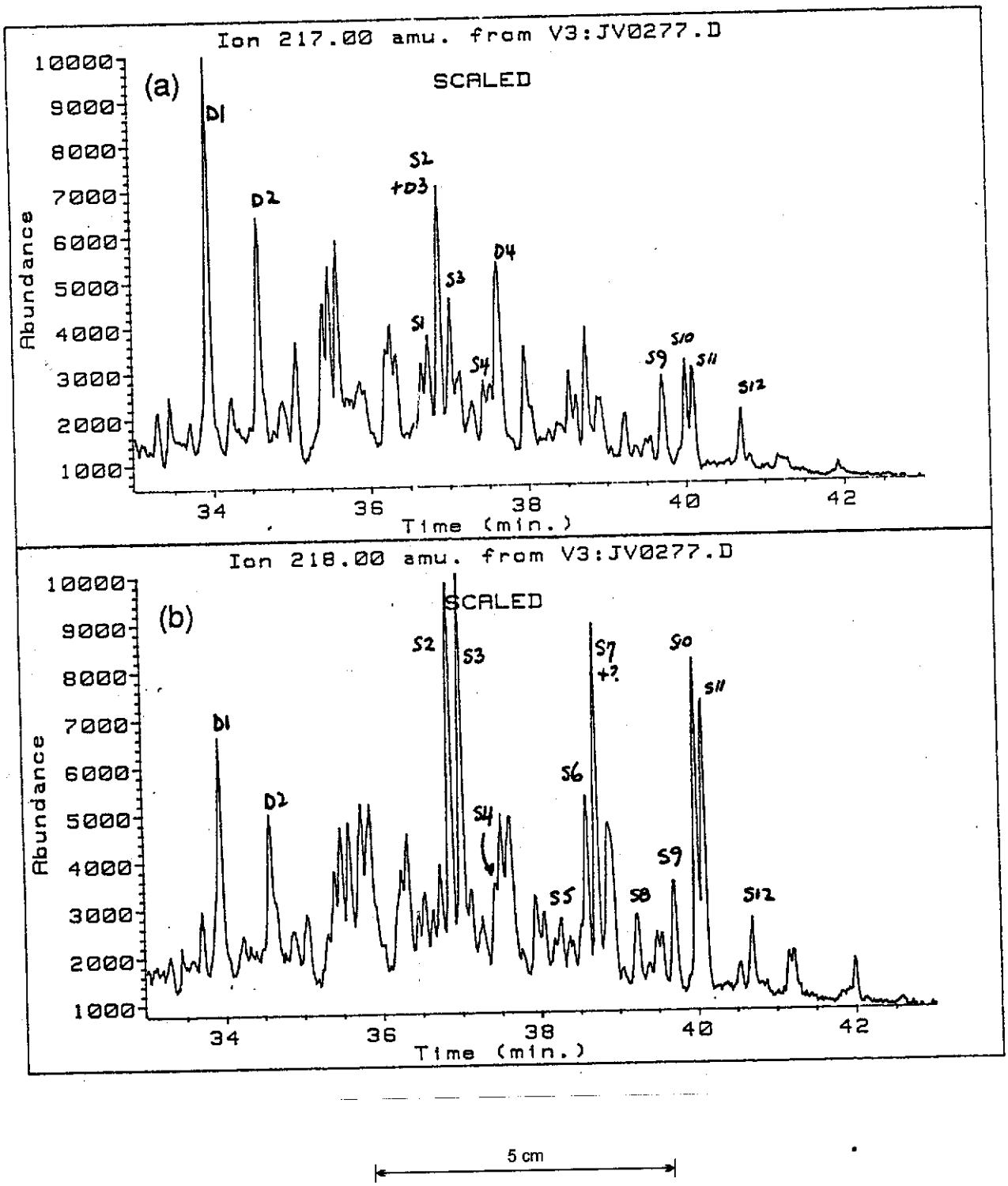

Figure 5. Mass fragmentograms for (a) m/z 217 and (b) m/z 218 showing distribution of C_{26}-C_{30} steranes (labelled S) and diasteranes (labelled D). See accompanying Key 2 for peak identifications. Note the high abundance of diasteranes which is often associated with sediments containing a high clay content.

STERANES AND DIASTERANES

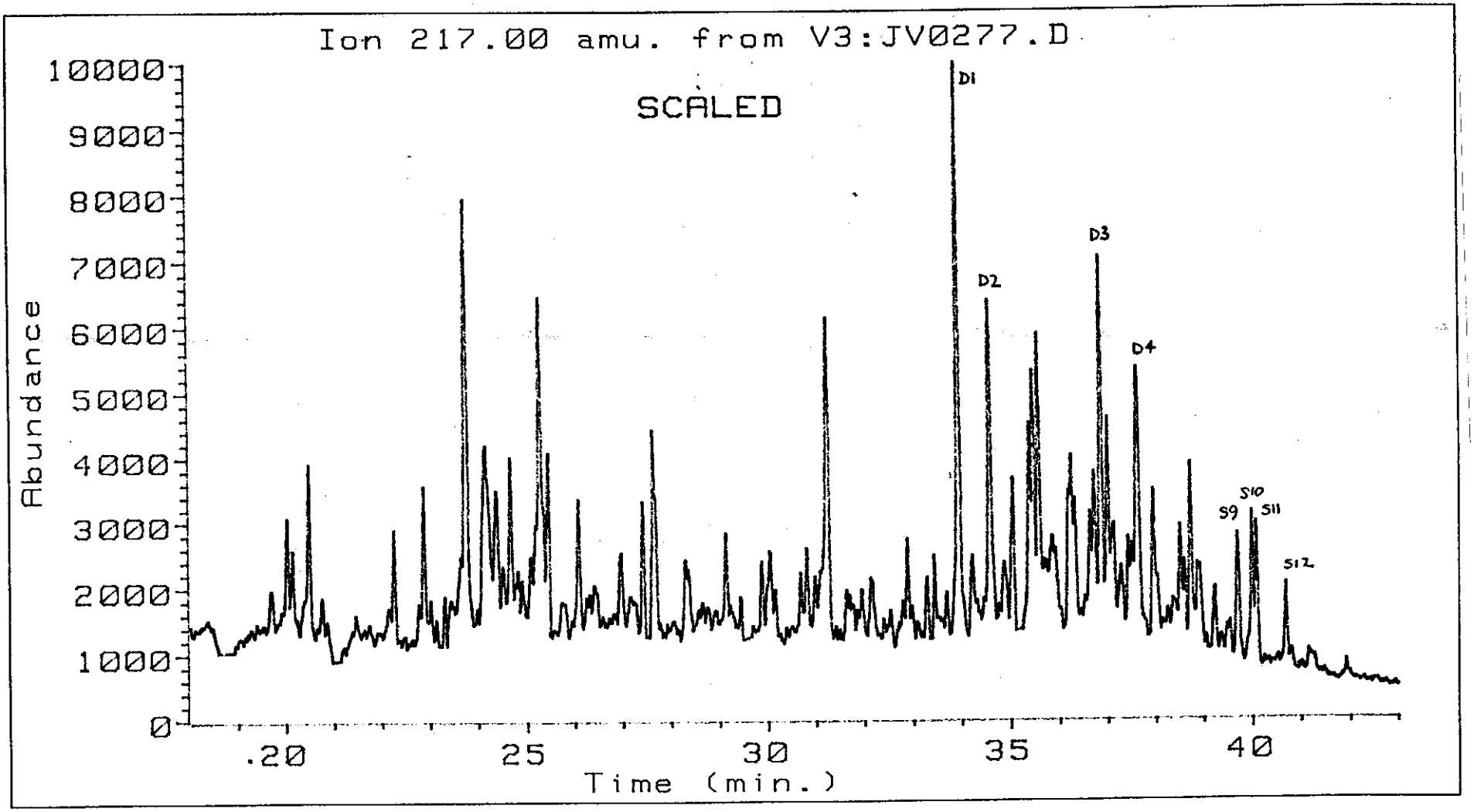

Figure 6. Mass fragmentogram for m/z 217 showing the distribution of C_{20}-C_{30} steranes and diasteranes. See accompanying Key 2 for peak identifications. Note the high abundance of shorter-chain steranes (isomers not identified).

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AROMATIC HYDROCARBONS

A preliminary investigation was carried out on the aromatic hydrocarbon fraction since the extract had a distinctly "aromatic" smell. A capillary gas chromatogram of the total aromatic hydrocarbon fraction is shown in Fig. 7. Analysis by capillary gas chromatography-mass spectrometry in full scan and selected ion monitoring modes was used to identify major constituents.

The aromatic fraction contains an abundance of low molecular weight components (mainly alkyl naphthalenes) which is typical of a mature crude oil. Naphthalene and more volatile aromatic hydrocarbons would have been lost in the extraction procedures.

Distributions of methyl naphthalenes, dimethyl naphthalenes, and trimethyl naphthalenes are shown in Fig. 8 as mass fragmentograms of the corresponding molecular ions (m/z 142, 156 and 170 respectively).

Phenanthrene and alkyl phenanthrenes are less abundant, but still represent significant components of the aromatic fraction. Distributions of phenanthrene, methyl phenanthrenes and dimethyl phenanthrenes are shown in Fig. 9 as mass fragmentograms of the corresponding molecular ions (m/z 178, 192 and 206 respectively).

The methyl phenanthrene index calculated from the abundance of phenanthrene and methyl phenanthrene isomers according to Radke *et al.* (1983) was 0.66 corresponding to a vitrinite reflectance of about 0.75. This value must be treated with some caution, but it usually gives a reasonable indication of the degree of thermal maturation to which the source rock has been subjected.

The aromatic hydrocarbon fraction contains a major compound eluting at 32 minutes (Fig. 7). The mass spectrum is shown in Fig. 10b. A mass fragmentogram for the base peak m/z 159 (Fig. 11) showed that this compound was not part of a series, but a related compound with a base peak at m/z 145 was also detected in small amounts. A mass spectrum is shown in Fig. 10a. The identity of these compounds has not been established but they may be aromatic sulphur compounds.

Aromatic steroid hydrocarbons were present in very small amounts. Mass fragmentograms for m/z 231 (triaromatic sterids) and m/z 253 (monoaromatic steroids) are shown in Fig. 12. Both distributions are dominated by shorter-chain components which lack the side-chains of the parent sterols due to thermal cracking reactions. Such distributions are typical of mature crude oils.

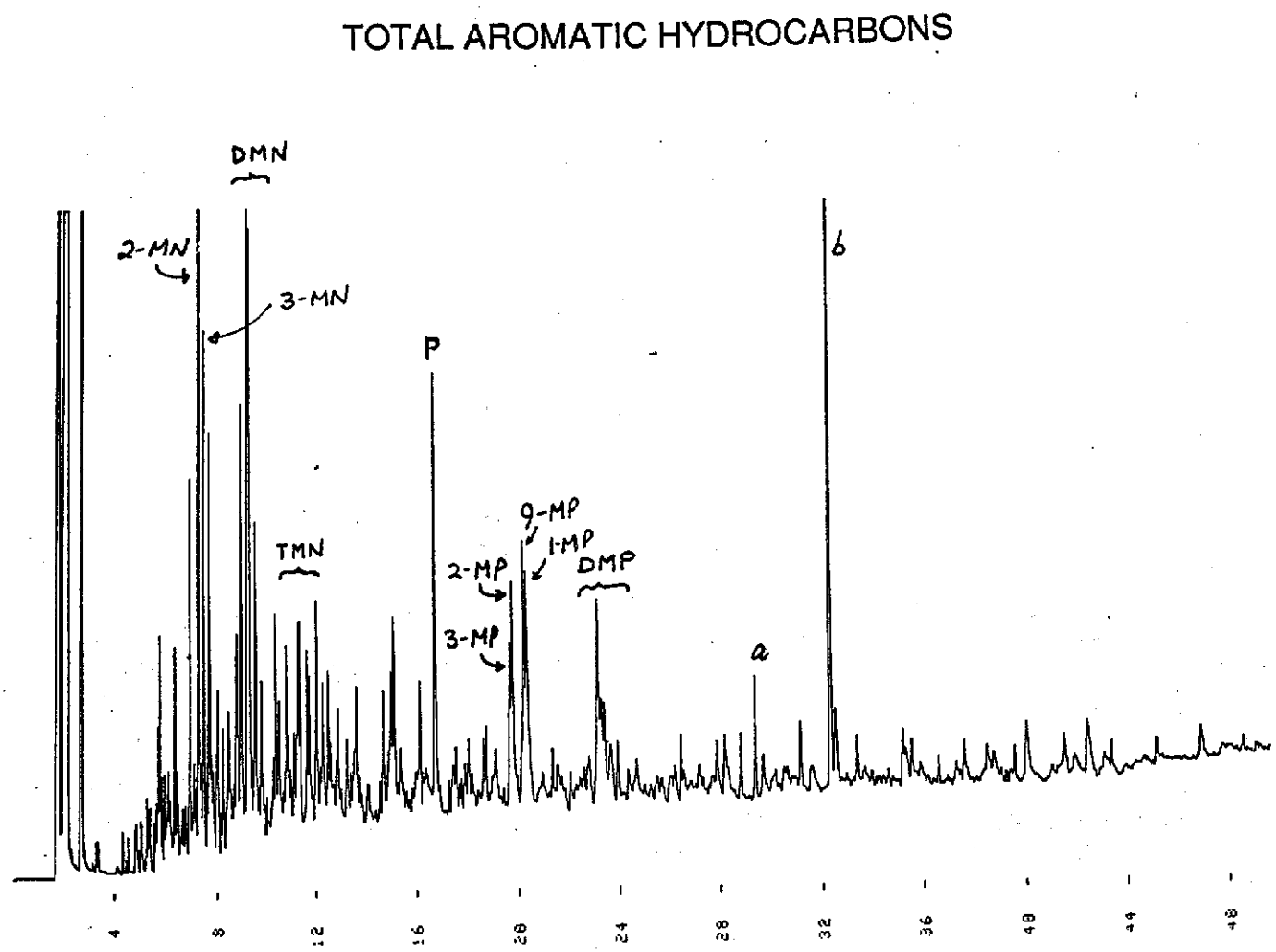

Figure 7. Capillary gas chromatogram showing the distribution of aromatic hydrocarbons. MN: methyl naphthalenes, DMN: dimethyl naphthalenes, TMN: trimethyl naphthalenes; P: phenanthrene, MP: methyl phenanthrenes, DMP: dimethyl phenanthrenes. Peaks a and b are unknown (see text; mass spectra are shown in Fig. 10).

MASS FRAGMENTOGRAMS FOR ALKYL NAPHTHALENES

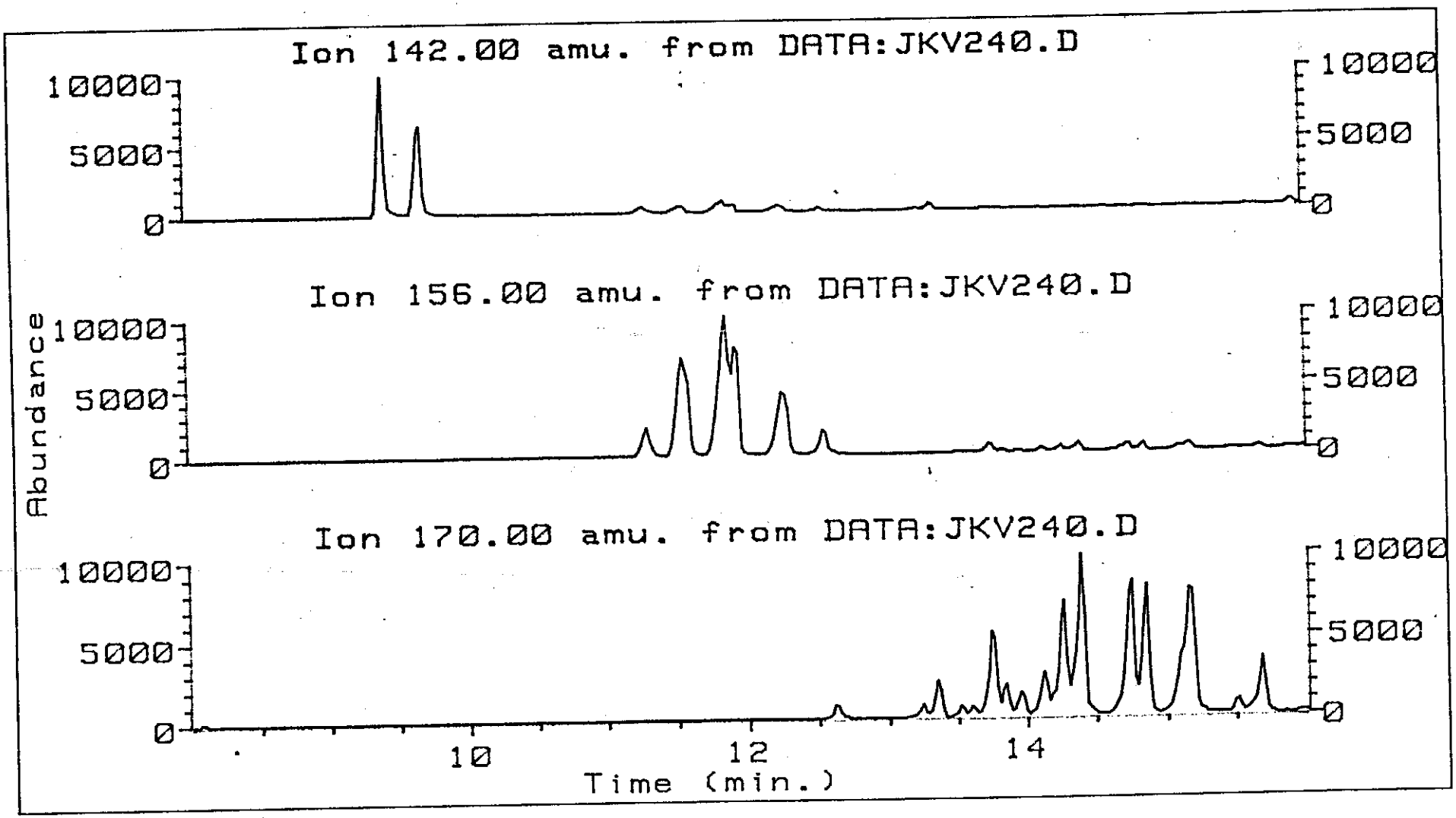

Figure 8. Mass fragmentograms for m/z 142 (methyl naphthalenes), m/z 156 (dimethyl naphthalenes) and m/z 170 (trimethyl naphthalenes).

MASS FRAGMENTOGRAMS FOR ALKYL PHENANTHRENES

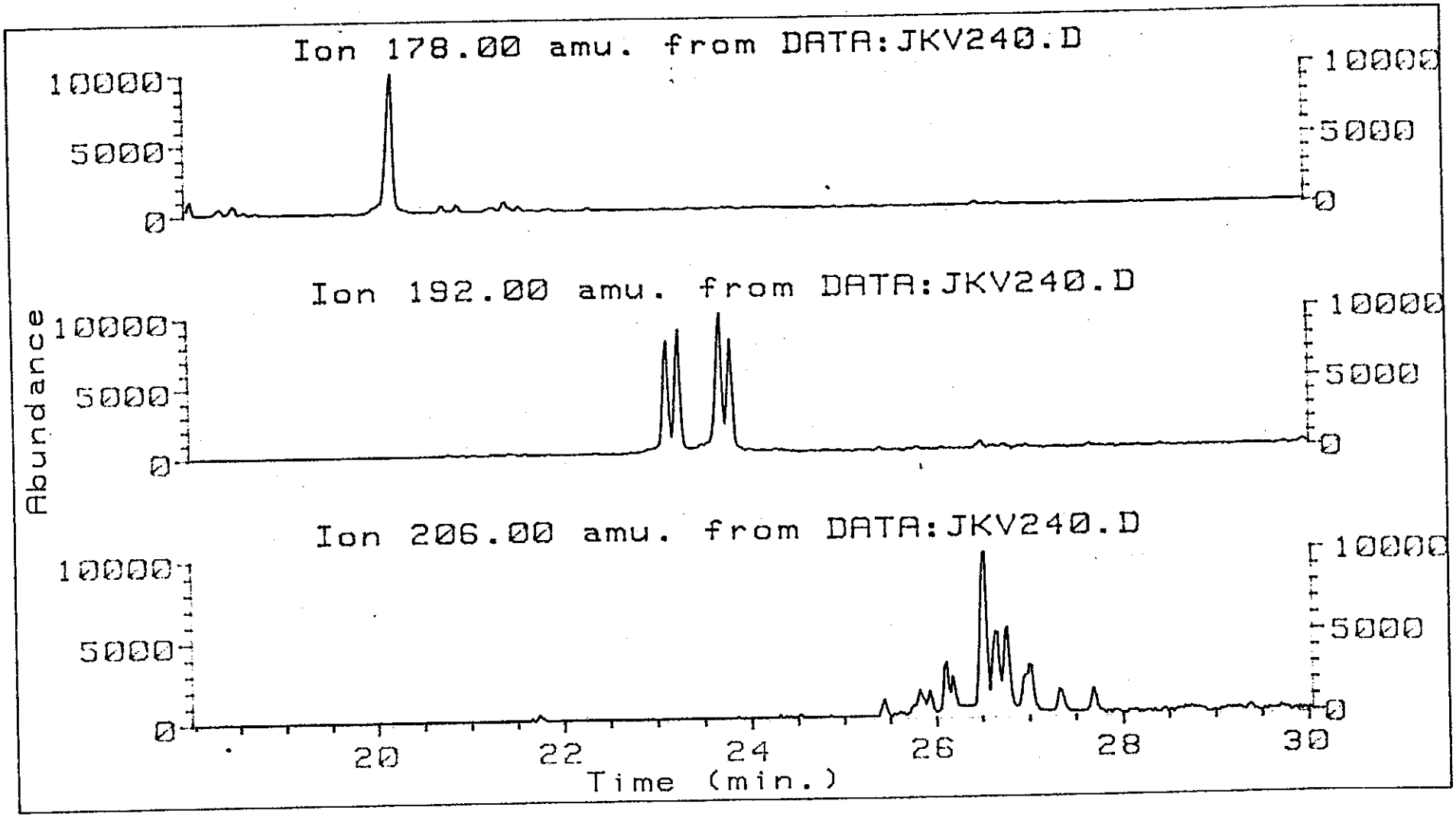

Figure 9. Mass fragmentograms for m/z 178 (phenanthrene), m/z 192 (methyl phenanthrenes) and m/z 206 (dimethyl phenanthrenes).

MASS SPECTRA OF UNKNOWN AROMATIC HYDROCARBONS

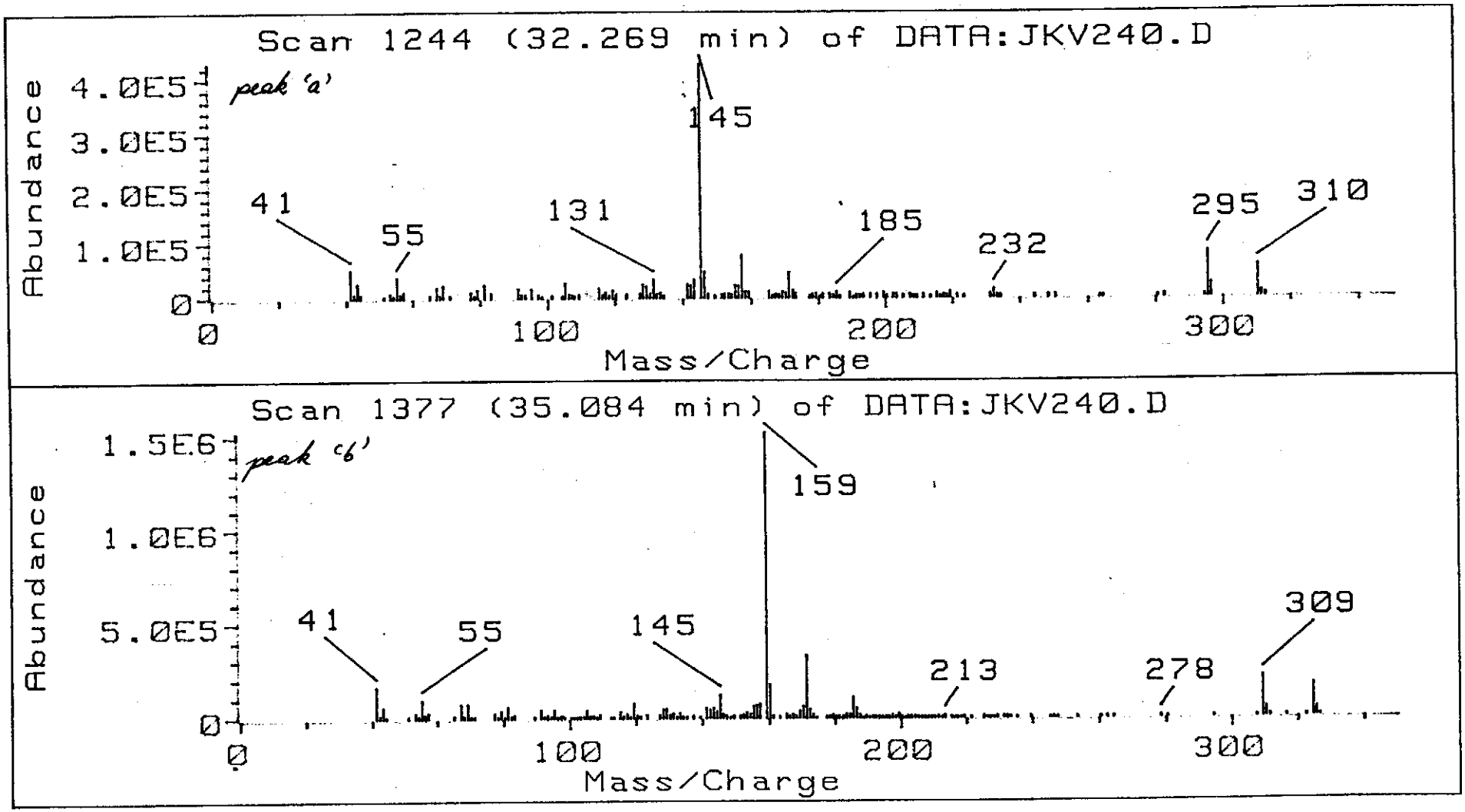

Figure 10. Mass spectra of two unknown compounds in the aromatic hydrocarbon fraction.

UNKNOWN AROMATIC HYDROCARBONS

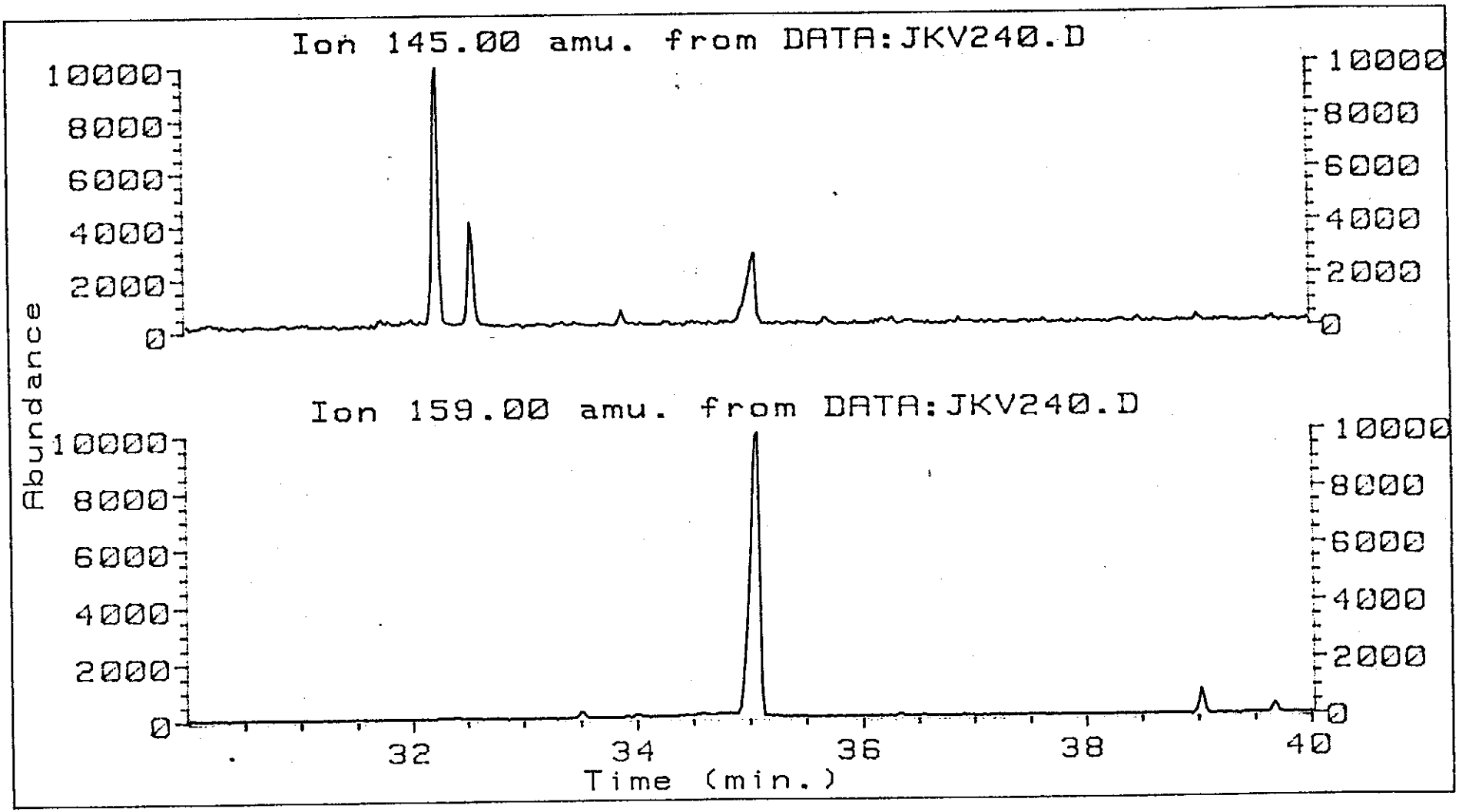

Figure 11. Mass fragmentograms for m/z 145 and m/z 159 showing distribution of unknown compounds in the aromatic fraction.

ARCMATIC STEROIDAL HYDROCARBONS

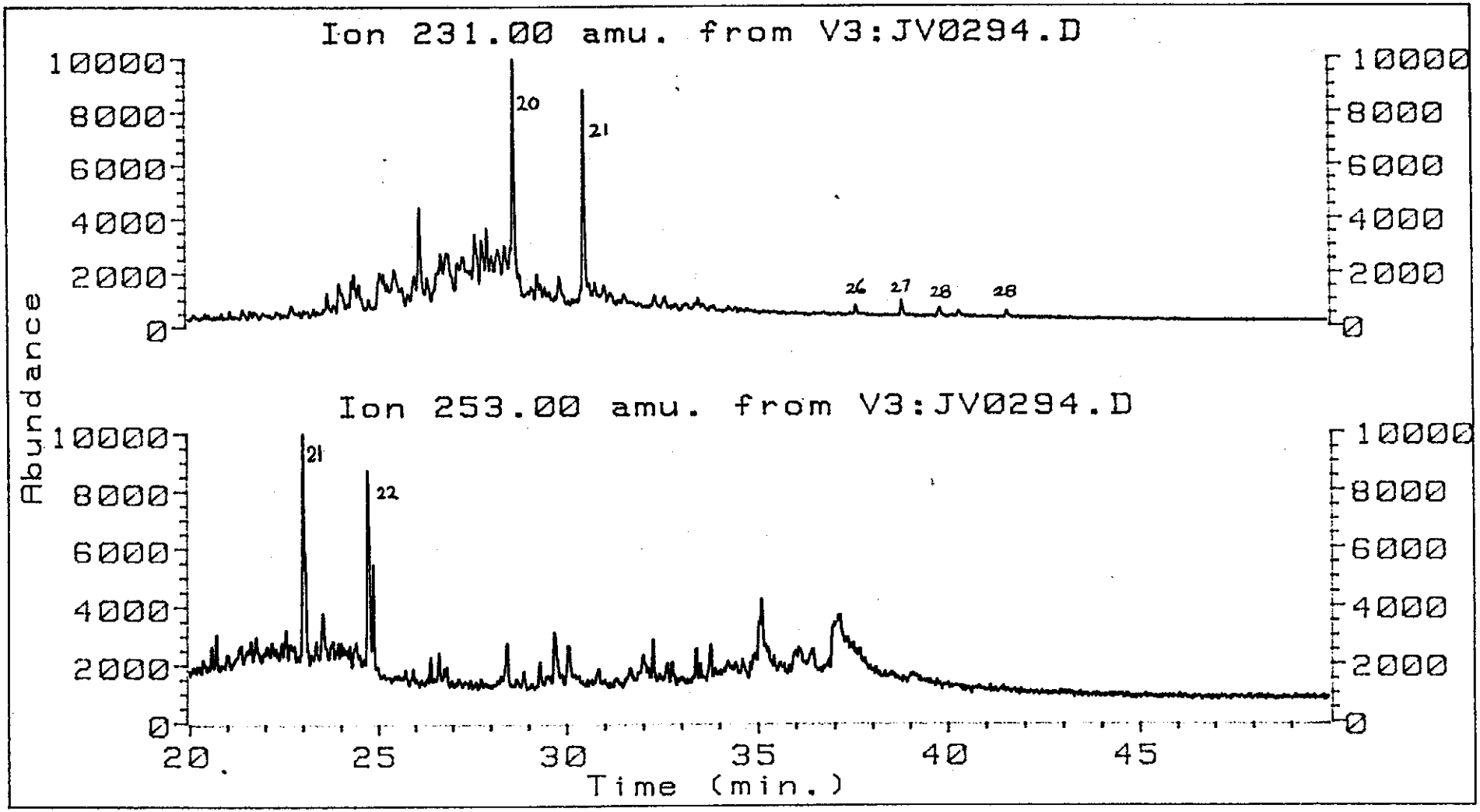

Figure 12. Mass fragmentograms for m/z 231 and m/z 253 showing distribution of triaromatic and monoaromatic steroid hydrocarbons respectively. Numerals indicate the total number of carbon atoms.

CONCLUSIONS

The mudstone contains appreciable amounts of hydrocarbons having the characteristic distributions found in a mature crude oil. n-Alkanes and low molecular weight aromatic hydrocarbons are abundant constituents which is typical of petroleum.

The biomarker distributions are distinctly different from those found in Ordovician carbonates. Methyl hopanes are very minor constituents and diasteranes (which are commonly associated with sediments containing a high content of clays) are abundant.

The total amount of extractable hydrocarbons determined by TLC-FID is at least 120 ppm. This value is likely to be a significant underestimate due to losses of volatile components in the extraction steps.

The methyl phenanthrene ratio suggest that the hydrocarbons were generated at a thermal maturity equivalent to a vitrinite relectance of about 0.75 i.e. well into the oil window. Aliphatic biomarker parameters suggest a similar level of maturity.

The presence of tricylic alkanes suggest that *Tasmanites* may have been the source of some of the hydrocarbons, but their low abundance relative to n-alkanes indicates that other sources are probably more important.

These data do not exclude the possibility that the hydrocarbons have migrated into the rock rather than the result of *in situ* production. However, there was no sign of staining and the general similarity of the distributions to those in stratigraphically related Inglis siltstone suggest that they are indigenous to the rock.

I recommend that if further studies are considered then a high priority be given to obtaining Rock Eval data to assess the source potential of the mudstone. It would also be of interest to identify whether *Tasmanites* was present from microscopic examination.

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