CSIRO Marine Laboratories

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HYDROCARBON ANALYSIS OF BRUNY ISLAND FAULT BRECCIA

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HYDROCARBON ANALYSIS OF BRUNY ISLAND FAULT BRECCIA

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INTRODUCTION

On May 2, 1995 a sample was received at the Marine Laboratories from Tasmania Development and Resources, Industry Safety and Mines Division. The sample was wrapped in aluminium foil and stored in a glass jar although the sample apparently had originally been stored in a plastic container.

The sample, thought to be a fault breccia, was stated to have been taken from a drill hole (Shittem-1) on Bruny Island at a depth of 810 m and was reported to have a slight "diesel" odour. The CSIRO Division of Oceanography was contracted by Industry Safety and Mines to fingerprint any hydrocarbons present in the sample and comment on their possible origins.

EXPERIMENTAL

The sample was crushed using a pestle and mortar and 54 g was transferred to a centrifuge tube. Extraction was then performed by adding chloroform:methanol (2:1, 60 ml) and sonicating in a water bath for 15 minutes, stirring and sonicating for a further 15 minutes. The sample was then centrifuged at 1800 r.p.m. for 10 minutes and the supernatant transferred to a separating funnel containing water (Milli Q, 100 ml). The extraction was then repeated as above and the combined extracts partitioned against the water. The chloroform layer was collected in a round bottom flask and the water re-extracted with further chloroform (30 ml) which was then added to the extract. The solvent was reduced under vacuum and the extract transferred directly to a micro-silica gel column and the aliphatic hydrocarbons eluted with hexane (2 ml).

The sample was then analysed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) by injecting 0.5 µl on-column from a volume of 100 µl. GC was performed using a Shimadzu GC-9A fitted with an apolar capillary column (HP-1, 50 m x 0.32 mm, 0.17 µm phase thickness) and SGE on-column injector. Hydrogen was the carrier gas and the oven programmed at 40 °C for 1 minute and then at 30°C/minute to 120°C followed by 4°C/minute to 310°C and then held isothermally for 15 minutes. Data was collected using DAPA chromatographic software.

GC-MS analysis used a Fisons Instruments MD800 operating in the Selected Ion Recording (SIR) mode. GC conditions were similar to those above except a Fisons GC8000 was used and helium was the carrier gas. Typical operating conditions are: transfer line 310 °C; electron impact energy 70 eV; source 250 °C; dwell time 0.08 s and inter channel delay 0.02 s.

RESULTS and DISCUSSION

The rock sample was found to contain approximately 30 ppm (w/w) of hydrocarbons. This is a relatively low concentration and not typical of sediments containing significant amounts of migrated hydrocarbons. Figure 1 shows the gas chromatogram of the aliphatic hydrocarbon fraction isolated from the rock sample. The chromatogram exhibits two interesting features:

1. A relatively narrow *n*-alkane distribution with no odd over even predominance, extending from C_{12} to C_{25}, maximising at C_{15}.

2. A relatively high pristane/phytane ratio (*ca.* 6.6)

The relatively narrow carbon number range could be indicative of either a light high maturity petroleum or a refined petroleum product. The high pristane/phytane ratio is a common characteristic of Bass Strait terrestrially derived crude oils, though these would normally be expected to have *n*-alkanes extending to higher carbon numbers.

Figure 2 shows the *m/z* 191 mass fragmentogram highlighting the presence of hopanes in the aliphatic fraction. This exhibits a Ts/Tm ratio of C_{27} hopanes of approximately 1 and $C_{29} > C_{30}$, both of which can be indicative of a carbonate source for the hydrocarbons although the Ts/Tm ratio is affected by thermal maturity. The peak annotated with a * is an unknown which is assumed to be a contaminant. It corresponds to the peak similarly annotated in the GC chromatogram (Fig. 1). In addition, the sample contains relatively abundant methyl hopanes (Fig. 3) which are usually found in carbonate sourced oils. This is contradictory to the pristane/phytane data which suggests a shale source rock containing terrigenous organic matter.

The sterane distribution (Fig. 4) is consistent with the hopane data. The C_{27} and C_{29} steranes are present in approximately equal proportions along with slightly smaller amounts of C_{28} compounds and relatively low concentrations of diasteranes (Fig. 5), all of which is consistent with a carbonate source.

The most common source of carbonate derived oils is the Middle East oils which are imported into Australia for refining, but a possible Tasmanian origin for carbonate sourced hydrocarbons could be the Ordovician limestones, which have been analysed previously (Volkman, 1988). A comparison of the data from those samples and that analysed here is given in Table 1 which also includes data for a Kuwait and a Bass Strait crude oil. From these data it is clear that there are some significant differences between the Bruny Island sample and the Ordovician limestones, importantly the C_{29} norhopane/C_{30} hopane ratio (parameter 7) C_{27}/C_{29} steranes (parameter 8), the relative proportions of C_{27}/C_{29} diasteranes (parameter 9) and the pristane/phytane ratio (parameter 10).

The possibilities are therefore:

i. there is an input of contamination such as a refined Bass Strait oil overprinting the indigenous signature, or
ii. that the hydrocarbon distributions represent a true indication of the organic matter, or
iii. the distributions represent an input of a contaminant mixture, such as fuel and/or lubricants.

If in fact the *n*-alkanes are associated with a Bass Strait origin (as suggested by the pristane/phytane ratio) then it may be reasonable to expect some influence on the biomarker data unless the hydrocarbons have been refined. If this was the case and these hydrocarbons were contributing to the biomarker data, there would be a noticeable enhancement of the C_{29} steranes and diasteranes. It is worth noting that the core section could not be washed to remove peripheral contamination due to the fragmented nature of the sample.

The fact that there appears to be no noticeable effect on the sterane and diasterane distributions would suggest that this is a refined product and the biomarkers have been excluded. Alternatively, the source of the *n*-alkanes would need to be so over-mature that

polycyclic biomarker abundances are extremely low. It is conceivable that the organic matter producing the carbonate signature is the source of the *n*-alkanes, but none have been previously reported with such a pristane/phytane ratio. However, the lack of any source rock data for this area prevents any firmer conclusions being drawn.

Which of these possibilities is the origin for the hydrocarbons in the sample can only be determined by a thorough investigation of the possible source rocks and of the fuels and lubricants used at the drill site.

CONCLUSIONS

- The rock sample contains a low concentration (30 ppm) of hydrocarbons, predominantly over an *n*-alkane range from C_{12} - C_{25}.
- The biomarker profiles indicate a mature hydrocarbon distribution, probably from mixed sources. These have biomarker signatures which are generally associated with Bass Strait and carbonate derived oils. It is difficult to tell if these represent a true indication of indigenous organic matter or contamination.
- To establish which interpretation is correct it would be necessary to analyse possible source rocks and fuels and lubricants from the drill site.

REFERENCES

Volkman, J.K (1988) Hydrocarbons in Ordovician Limestones From Queenstown and Lune River, Tasmania. CSIRO Division of Oceanography Report 88-HC1 for Conga Oil Pty. Ltd.

Table 1: Comparison Of Biomarker Data for Tasmanian Ordovician Limestones, Bruny Island sample and Representative Middle East and Bass Strait Oils

	Parameter	Limestones*	Bruny Is. Sample	Kuwait	Bass Strait
1	Ts/Tm	0.77	0.96	0.3	0.70
2	hopane/moretane	10.1	7.1	15.4	6.1
3	C_{31} hopanes	57	55	56	54
4	C_{32} hopanes	60	58	59	58
5	ααα steranes	1.03	0.87	1.2	1.7
6	20R steranes	1.11	1.01	1.3	1.55
7	C_{29}/C_{30} hopane	1.00	1.23	1.28	0.45
8	C_{27}/C_{29} steranes	1.17	0.60	0.6	0.3
9	C_{27}/C_{29} diasteranes	1.11	0.87	n.d.	0.4
10	pristane/phytane	1.60	6.6	1.04	6.19
11	pristane/*n*-C_{17}	0.40	0.66	0.31	0.78

* Average of values for Ida Bay and Queenstown Ordovician limestones (Volkman, 1988)

Explanation of parameters:

1. C_{27} 18α(H)-22,29,30-trisnorneohopane (Ts)/C_{27} 17α(H)-22,29,30-trisnorneohopane (Tm)
2. C_{30} 17α(H),21β(H) hopane/C_{30} 7β(H),21α(H) hopane
3. C_{31} 22S hopane/(C_{31} 22R + 22S hopanes) x 100
4. C_{32} 22S hopane/(C_{32} 22R + 22S hopanes) x 100
5. C_{29} ααα-steranes: 20S/20R
6. C_{29} 20R steranes: αββ/ααα
7. C_{29} 17α(H),21β(H) norhopane/C_{30} 7α(H),21β(H) hopane
8. Sum C_{27} steranes/Sum C_{29} steranes
9. Sum C_{27} diasteranes/Sum C_{29} diasteranes

n.d. = not detected

1-4,7 calculated from m/z 191 (Fig. 2)
5-6,8 calculated from m/z 217 (Fig. 4)
9 calculated from m/z 259 (Fig. 5)
10-11 calculated from GC chromatogram

Note: Parameters 1-6 are affected by thermal maturity.

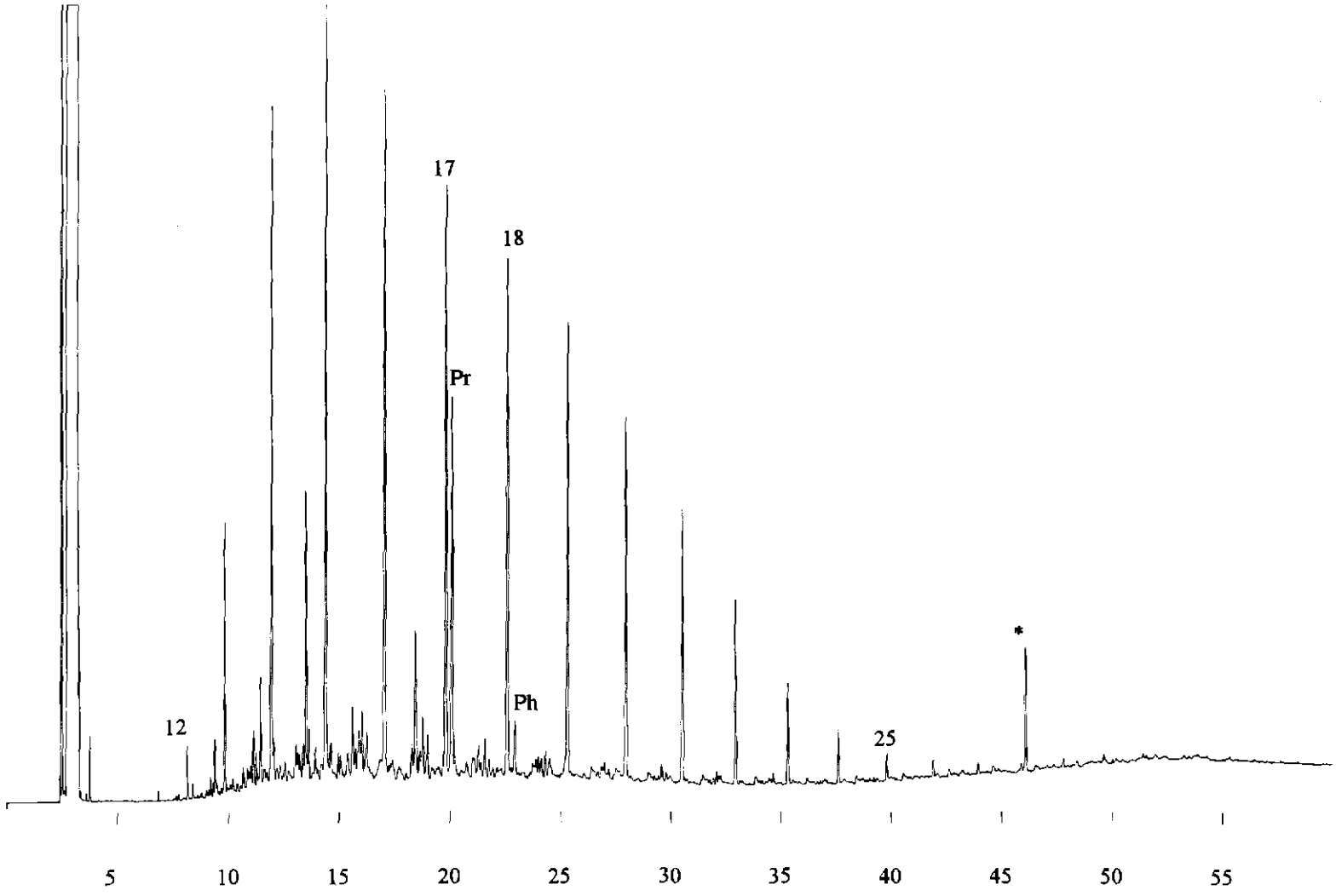

Figure 1: GC Chromatogram of the Aliphatic hydrocarbons Isolated From the Bruny Island Rock Sample
(Numbers refer to carbon number; Pr = pristane, Ph = phytane, * = an unknown)

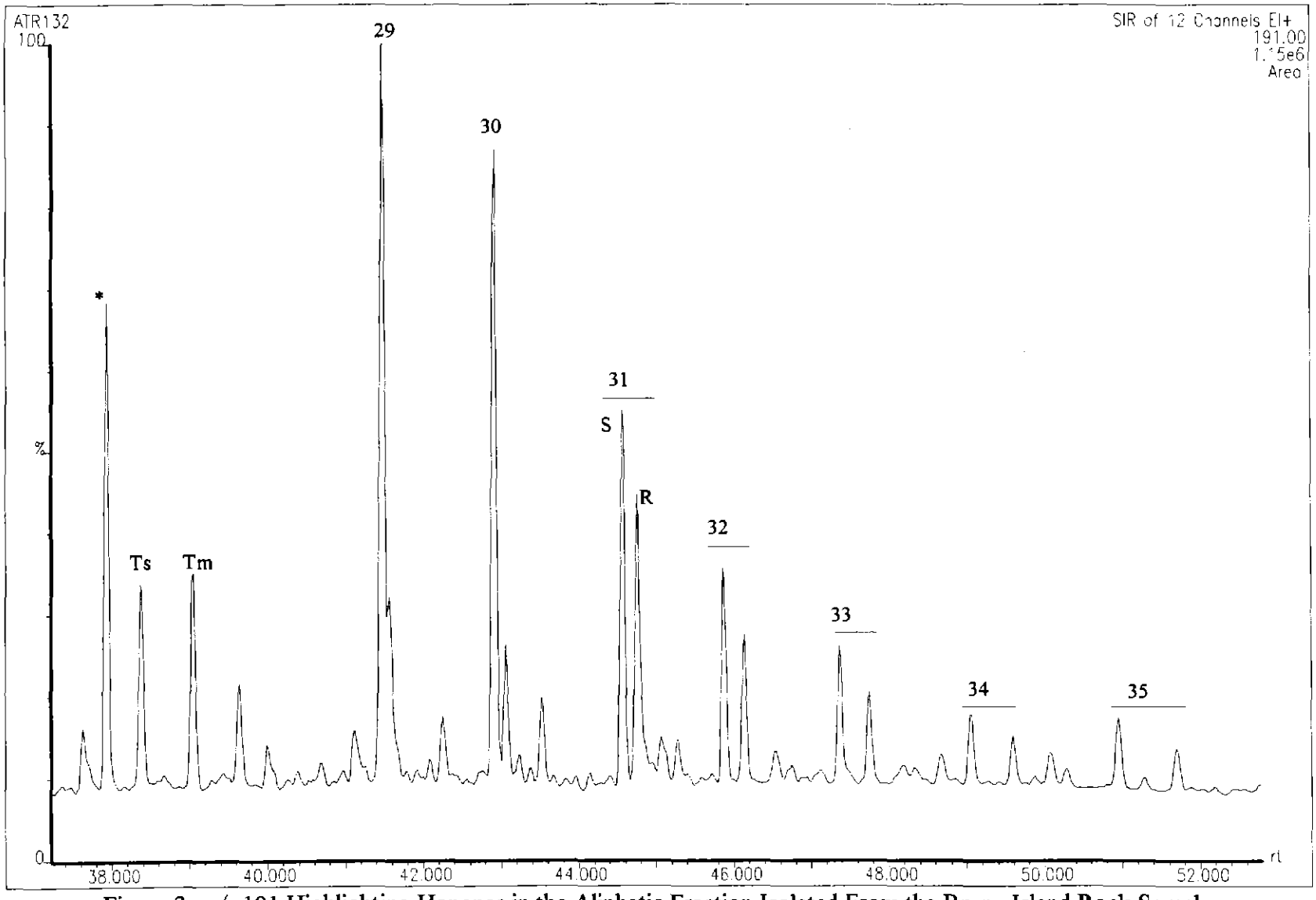

Figure 2: *m/z* 191 Highlighting Hopanes in the Aliphatic Fraction Isolated From the Bruny Island Rock Sample
(Numbers refer to carbon number, Ts and Tm are C_{27} Trisnorhopanes, S and R refer to stereochemistry at carbon 22, * = an unknown)

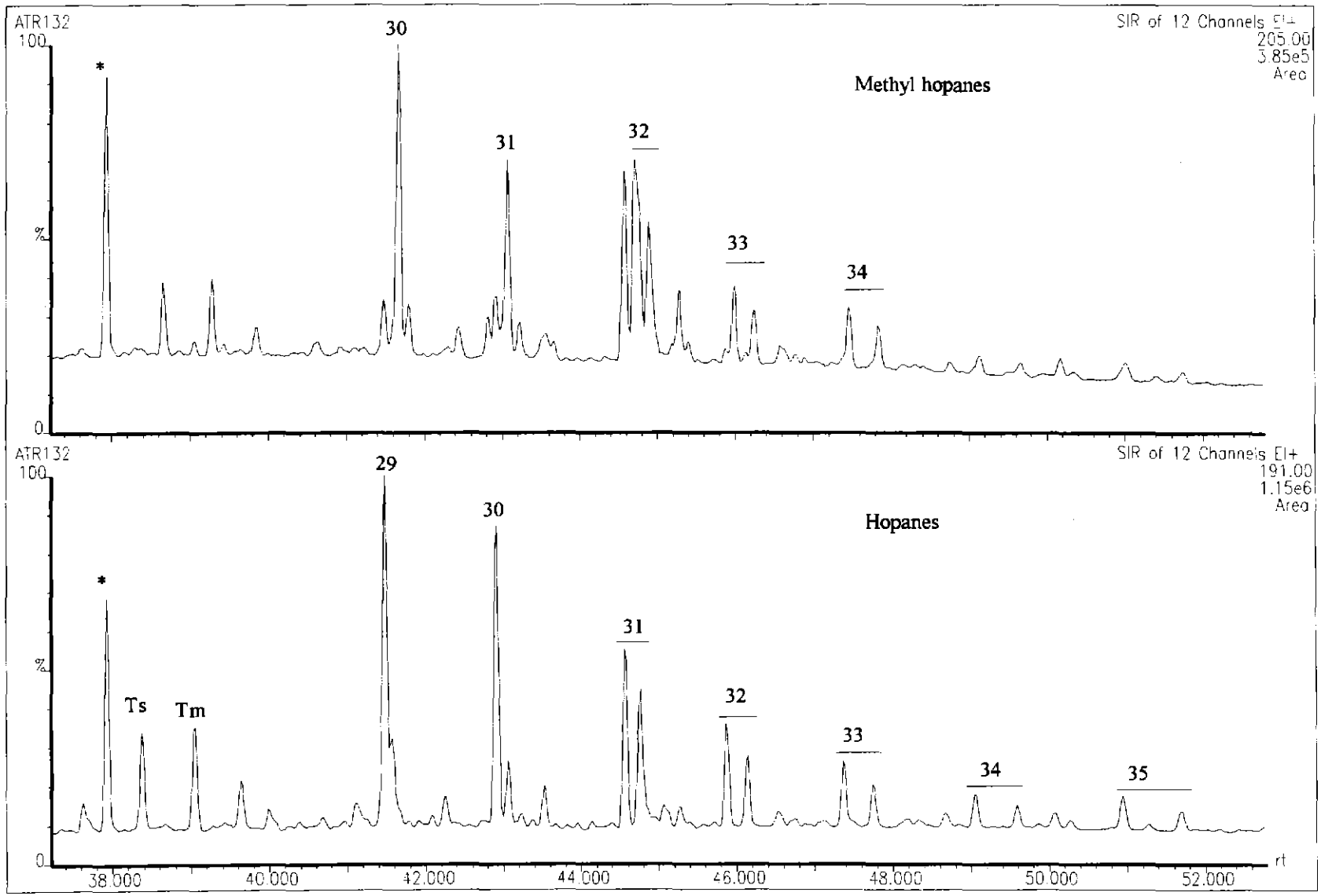

Figure 3: *m/z* 205 Highlighting Methyl Hopanes in the Aliphatic Fraction Isolated From the Bruny Island Rock Sample
(Numbers refer to carbon number, Ts and Tm are C_{27} Trisnorhopanes, * = an unknown)

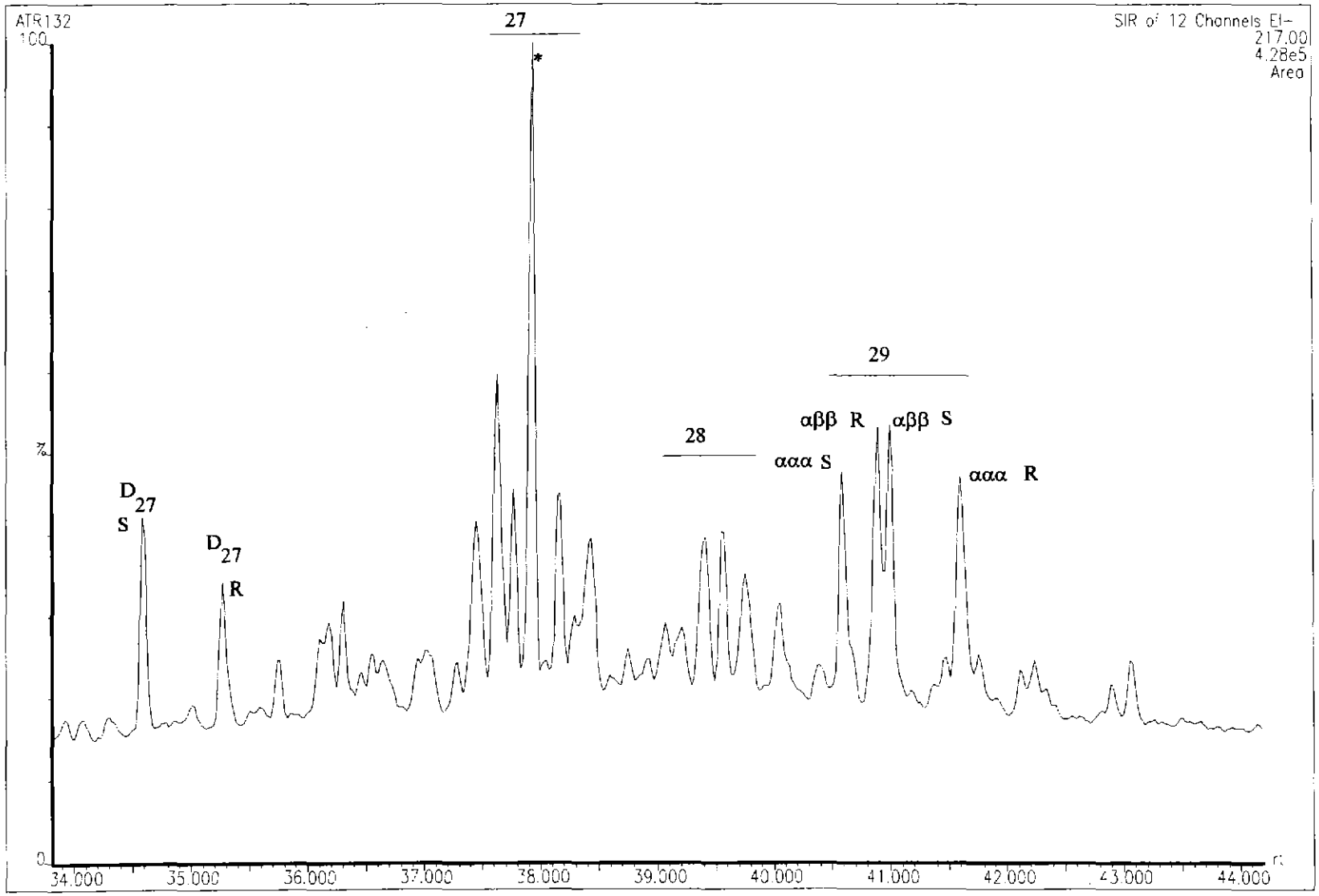

Figure 4: *m/z* 217 Highlighting Steranes in the Aliphatic Fraction Isolated From the Bruny Island Rock Sample

(numbers refer to carbon number, D = diasterane, S and R refer to stereochemistry at carbon 20, a and B refer to hydrogen stereochemistry at carbons 5,14 and 17, * = an unknown)

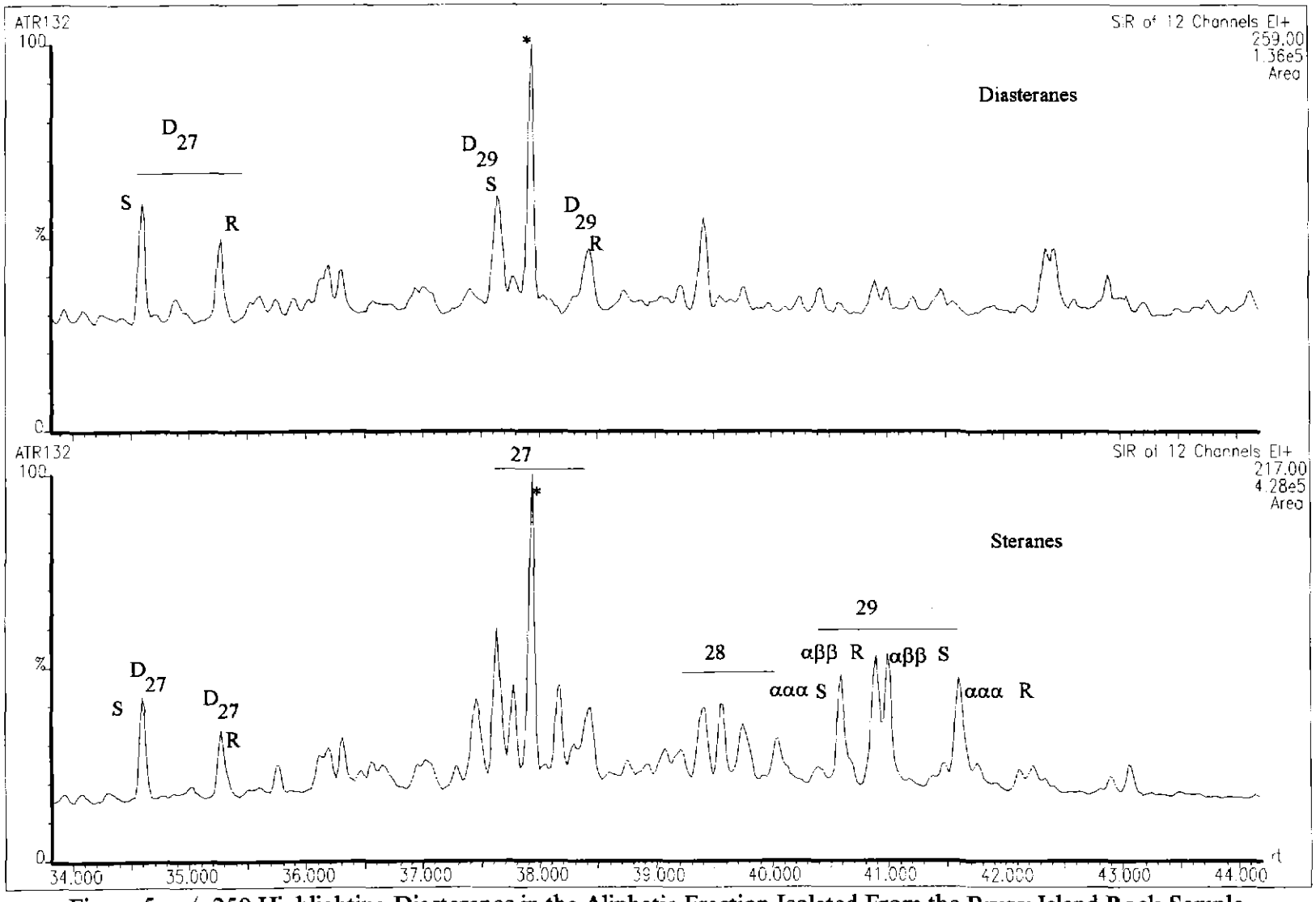

Figure 5: *m/z* 259 Highlighting Diasteranes in the Aliphatic Fraction Isolated From the Bruny Island Rock Sample

(numbers refer to carbon number, D = diasterane, S and R refer to stereochemistry at carbon 20, α and B refer to hydrogen stereochemistry at carbons 5,14 and 17, * = an unknown presumed to be a contaminant)

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SCHEDULE

Data Description

Hydrocarbon analysis of Bruny Island sample and interpretation of the results