UR1987_28

1/18

1987/28. Petroleum geochemistry of a sample of *Tasmanites* oil shale.

P. W. Baillie

Abstract

One sample of *Tasmanites* oil shale from Latrobe has been analysed geochemically. The sample is an extremely rich source rock for oil, containing predominantly aquatic, alga-derived organic matter, and is of low maturity.

INTRODUCTION

The *Tasmanites* oil shale of northern Tasmania (Bacon, 1986) is dominantly telalginite derived from the unicellular alga *Tasmanites*, with minor lamalginite and sporinite (Crisp *et al.*, 1987). Rare vitrinite indicates a reflectance of about 0.4% (Russell, 1980).

Previous geochemical studies have usually been related to hydrogeneration as a possible source of liquid hydrocarbons (Philp *et al.*, 1981; Philp *et al.*, 1982; Russell, 1980). A pyrolysis-gas chromatography and pyrolysis-gas chromatography-mass spectrometry study (Philp and Gilbert, 1983) showed that the kerogen is dominated by alkene/alkane doublets in the C6-C20 range, maximising around C9, and also a very high concentration of tricyclic diterpenoids in the C19 to C23 region and of the type that are typically associated with diterpenoid precursors in marine organisms. Crisp *et al.* (1987) did not detect pristenes in gas chromatographic analyses and noted that extremely low concentrations of aromatic compounds reflected an algal origin for the organic matter in the oil shale.

The present study was carried out by Analabs (Perth) to assess the source potential of the oil shale, and to allow comparison with other Tasmanian hydrocarbon-bearing sequences.

The sample analysed was collected by Ms C.A. Bacon from an outcrop near The Great Bend of the Mersey River [DQ520305].

ANALYTICAL PROCEDURE

The rock was first submitted to screening analyses (Rock-Eval pyrolysis and total organic carbon determination) and then extracted. Saturate, aromatic and NSO fractions of the extract were separated by liquid chromatography, and gas chromatography was performed on the saturate fraction. The branched and cyclic compounds of the saturate fraction were then separated with a molecular sieve, and gas chromatography-mass spectrometry (GC-MS) was carried out on the branched/cyclic fraction.

RESULTS AND DISCUSSION

The analytical results obtained are presented in the following figures and tables:

Type of analysis	*Figure*	*Table*
Total organic carbon		1
Rock-Eval pyrolysis		1
Extraction and liquid chromatography		2
Gas chromatography of saturate fraction	1	3
Gas chromatography-mass spectrometry	2	4

Total organic carbon (TOC), as determined on the unextracted oil shale, is 2.58%, which classifies the sample as an excellent potential source; the high hydrogen index (HI = 748) and low oxygen index (OI = 11) indicate Type-I kerogen, and so the sample has a high source potential for oil (Tissot and Welte, 1984). The value for S1, however, which represents the level of oil already generated by the sample, is low. This observation, together with a resulting production index (S1/S1 + S2) of (almost) zero and a low Tmax value of 436°C, evidence the immaturity of the sample, in agreement with the vitrinite reflectance determination of Russell (1980).

The GC trace (fig. 1) obtained for the sample shows an n-alkane distribution with a maximum at n-C17; only very minor amounts of higher molecular weight compounds are present (fig. 1, Table 3), further suggesting that the organic matter in the oil shale consists predominantly of algal remains (Tissot and Welte, 1984).

The small amount of total extract recovered (Table 2) is believed to be due to the low level of maturity. Low pristane/phytane and pristane/n-C17 ratios, low carbon preference indices in spite of the immaturity of the sample, and a high (C21 + C22)/(C28 + C29) ratio all characterise aquatic organic matter deposited in a reducing depositional environment.

Biomarker distributions were obtained from GC-MS analyses. Sterane distributions (fig. 2a, Table 4) confirm the predominantly marine source of the organic matter (C27/C29 sterane ratio of 0.95), but the presence of C29 steranes might indicate minor contributions from terrestrial sources (Seifert and Moldowan, 1987). C28 steranes are present in the oil shale as well, and are possibly indicators for contribution by lacustrine algae.

The most meaningful biomarker maturity parameters are triterepane and sterane ratios (Seifert *et al.*, 1986; Seifert and Moldowan, 1987). Ts/Tm hopane as well as C29 20S/20R sterane values both confirm a maturity level just before or, at best, at the very beginning of oil generation. The C29 20S/20R sterane ratio of 0.24 is approximately equivalent to about 0.5% Ro, with 0.6% Ro being generally accepted as the beginning of peak oil generation for a Type-I kerogen.

REFERENCES

BACON, C. A. 1986. A summary of the oil shale resources of Tasmania. *Unpubl. Rep. Dep. Mines Tasm.* 1986/61.

CRISP, P. T.; ELLIS, J.; HUTTON, A. C.; KURTH, J.; MARTIN, F. A.; SAXBY, J. D. 1987. *Australian oil shales : a compendium of geological and chemical data.* 109 pp.

PHILP, R. P.; GILBERT, T. D. 1983. Pyrolysis-gas chromatography and pyrolysis-gas chromatography-mass spectrometry studies of Australian oil shales. *Proceedings of the First Australian Workshop on Oil Shale, Lucas Heights, 18-19 March 1983.*

PHILP, R. P.; RUSSELL, N. J.; GILBERT, T. D. 1981. Hydrogeneration of Tasmanian alginite - analysis of hexane-soluble products by thermal distillation-gas chromatography-mass spectrometry. *Fuel* 60:937-944.

PHILP, R. P.; GILBERT, T. D.; RUSSELL, N. J. 1982. Characterisation by pyrolysis-gas chromatography-mass spectrometry of the insoluble organic residues derived from the hydrogeneration of the *Tasmanites* sp. oil shale. *Fuel* 61:221-226.

RUSSELL, N. J. 1980. A batch autoclave study of alginite behaviour in response to heating with metal chlorides. *Coal Geology.* 2:31-52.

SEIFERT, W. K.; MOLDOWAN, J. M. 1987. Use of biological markers in petroleum exploration, *in:* JOHNS, R. (ed.) *Biological markers in the sedimentary record.* 261-290. Elsevier.

SEIFERT, W. K.; MOLDOWAN, J. M.; GALLEGOS, E. J. 1986. Application of mass spectrometry to petroleum exploration, *in:* ACZEL, T. (ed.). *Mass spectrometric characterisation of Shale Oils, ASTM STP 902.* American Society of Testing and Materials, Philadelphia, pp. 121-139.

TISSOT, B.; WELTE, D. H. 1984. *Petroleum formation and occurrence.* Springer-Velag : Berlin. (2nd Edition).

[15 June 1987]

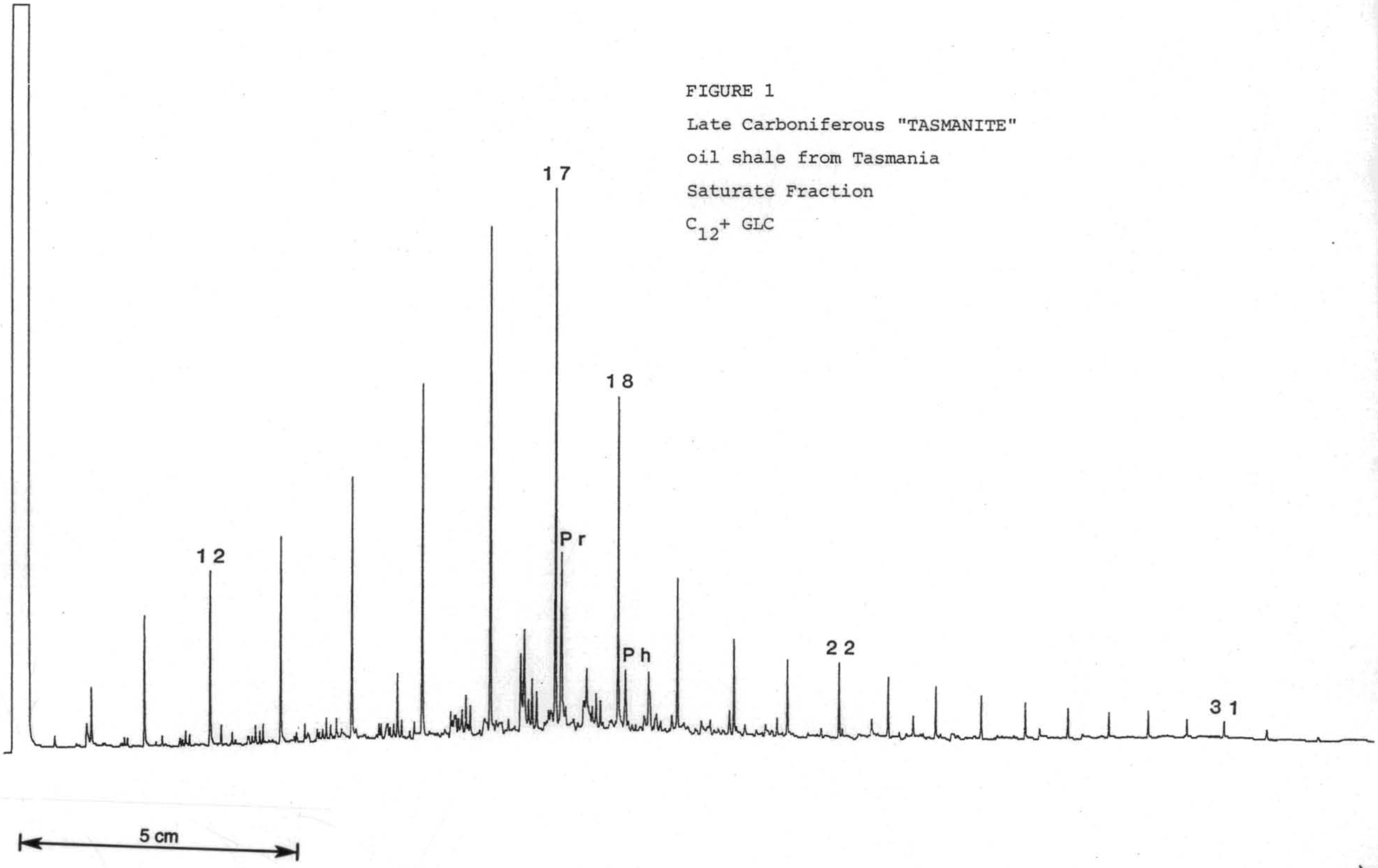


FIGURE 1

Late Carboniferous "TASMANITE"

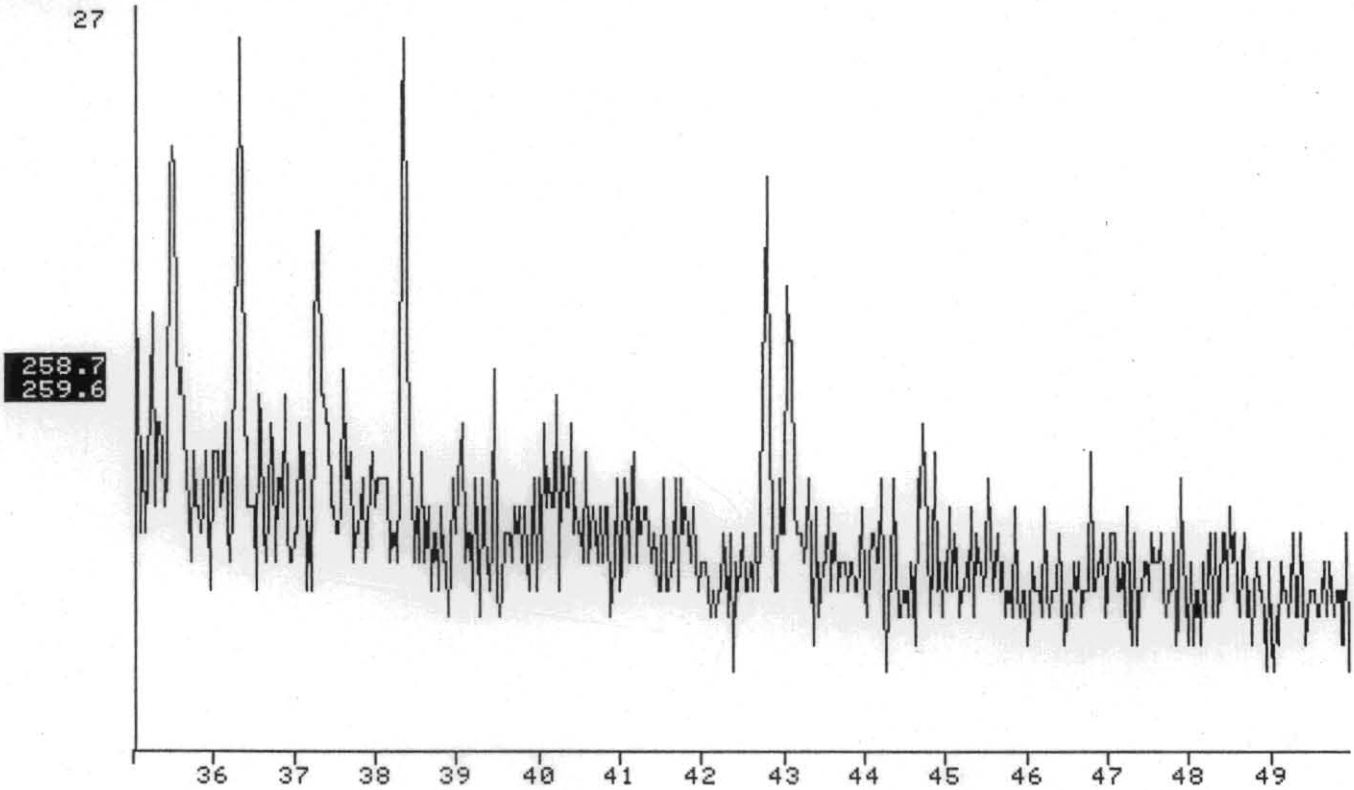
oil shale from Tasmania

Saturate Fraction

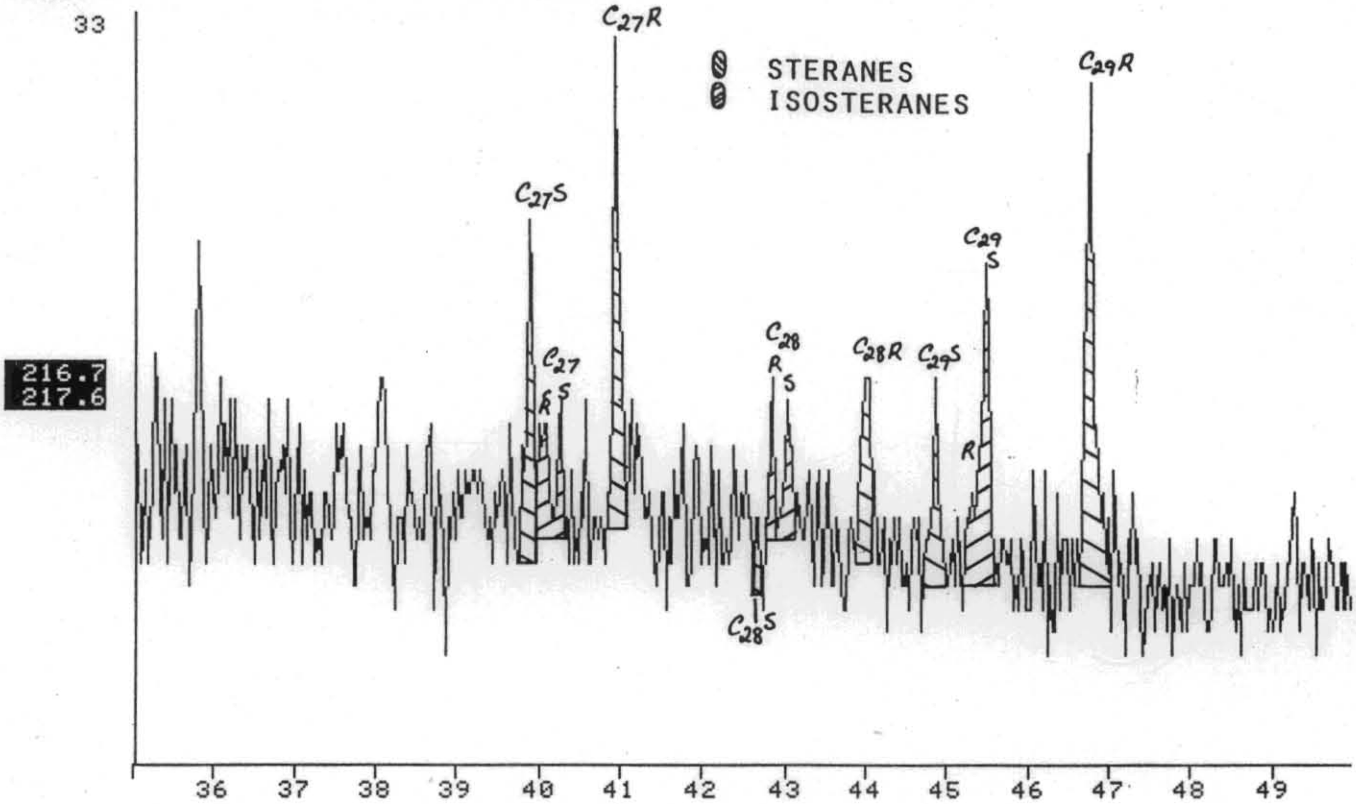
$C_{12}+$ GLC

FIGURE 2A

NAME TASMANITE OIL SHALE. BRANCHED CYCLIC FRAGMENTOGRAM. **FRN** 6305
MISC 18-5-87. GEC. 0.2/20uL. COL#73.



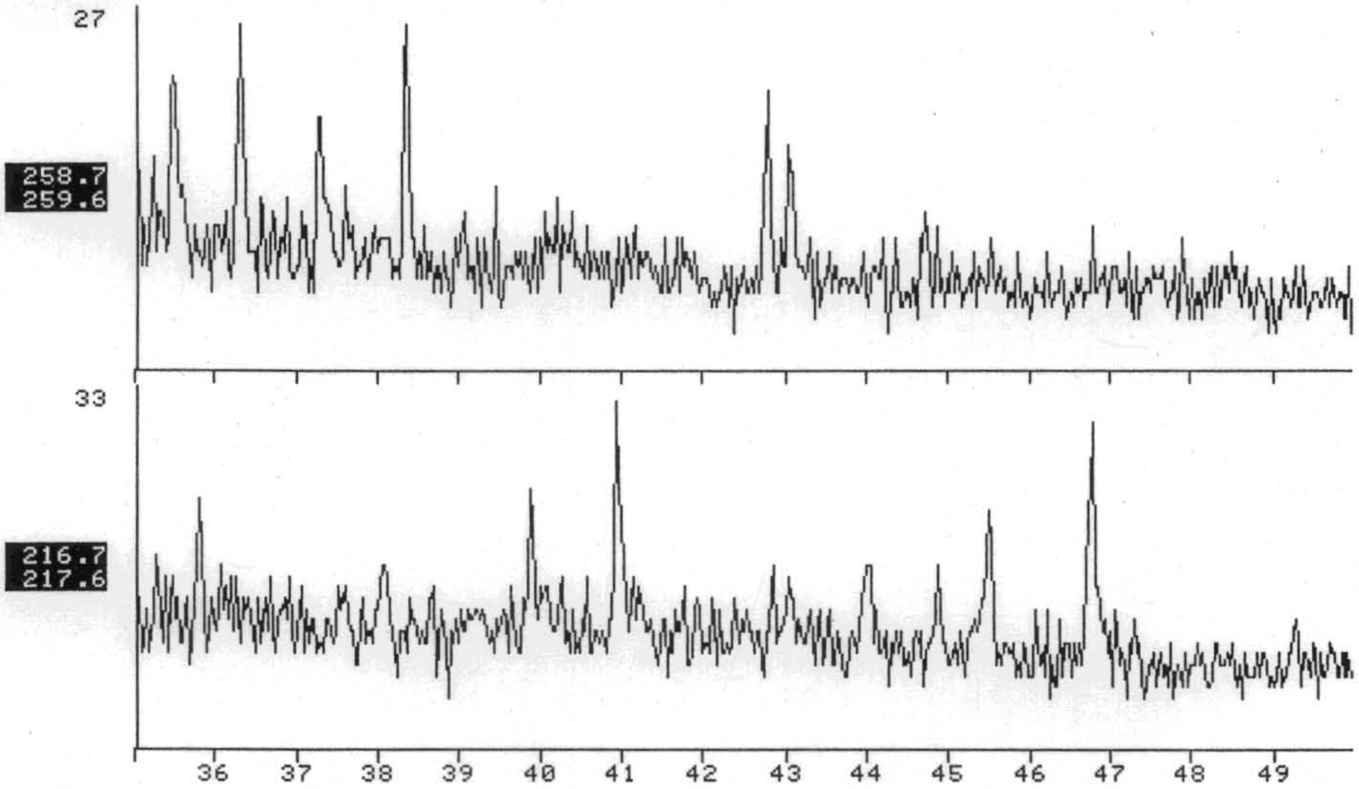
NAME TASMANITE OIL SHALE. BRANCHED CYCLIC FRAGMENTOGRAM. **FRN** 6305
MISC 18-5-87. GEC. 0.2/20uL. COL#73.



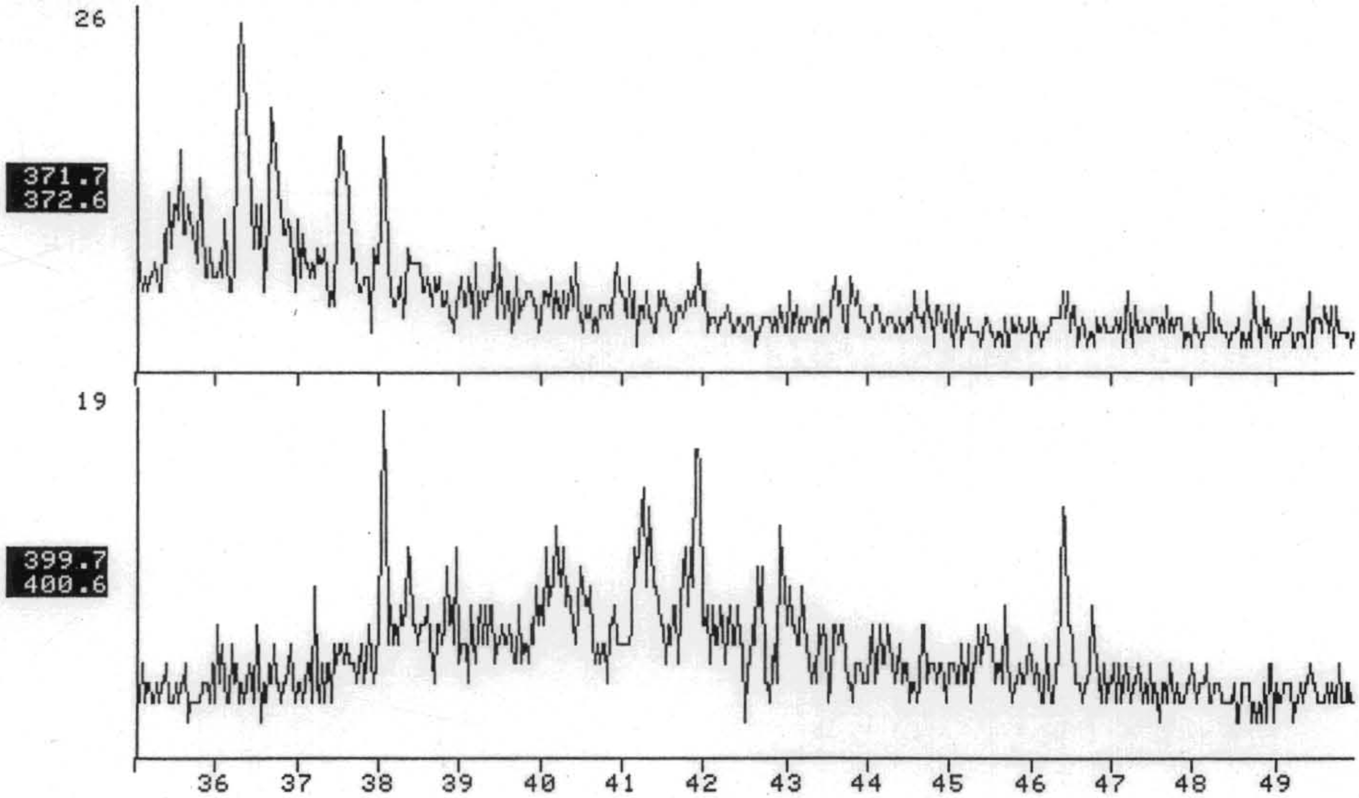
5 cm

FIGURE 2B

NAME TASMANITE OIL SHALE. BRANCHED CYCLIC FRAGMENTOGRAM. **FRN** 6305
MISC 18-5-87. GEC. 0.2/20uL. COL#73.



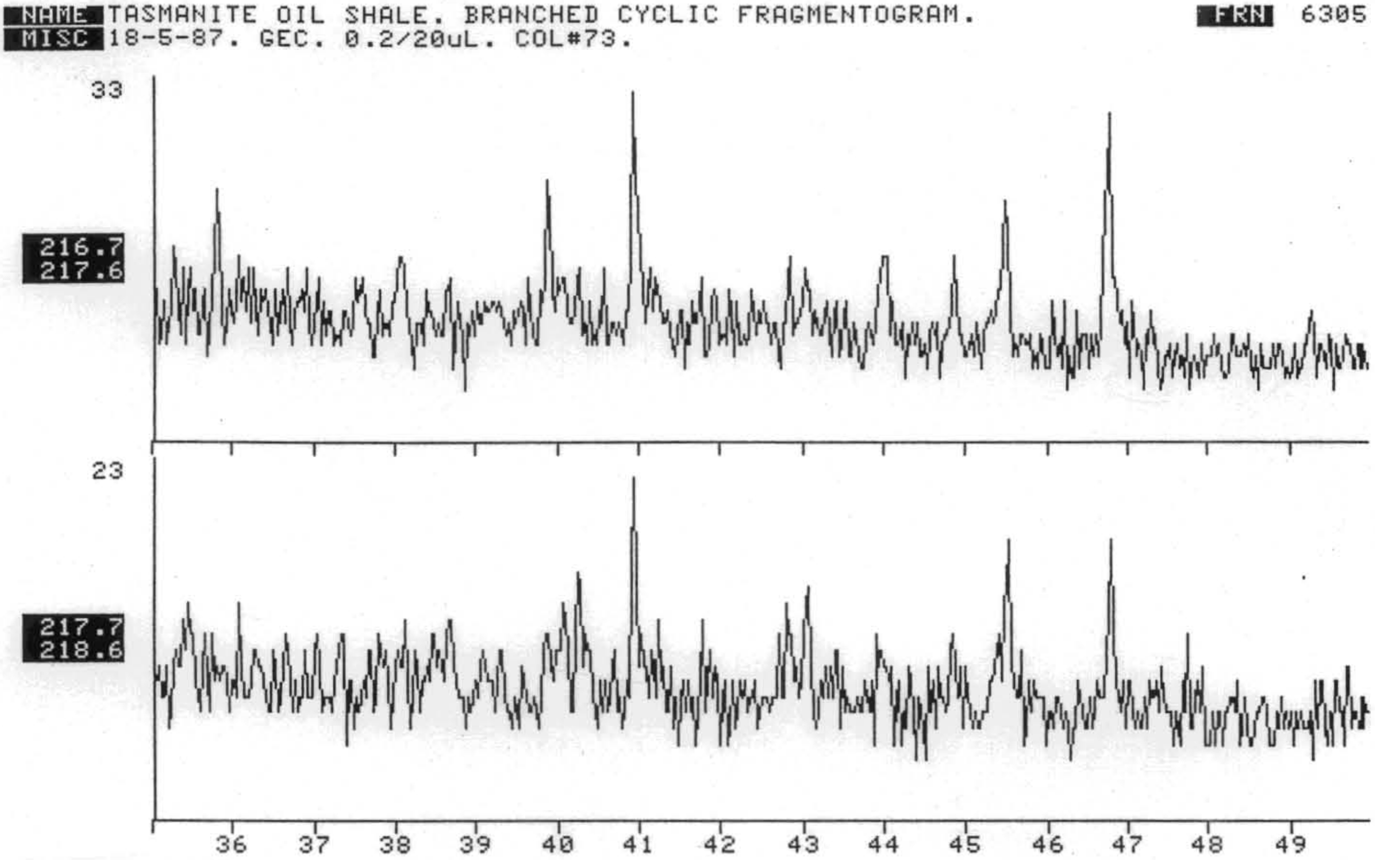
NAME TASMANITE OIL SHALE. BRANCHED CYCLIC FRAGMENTOGRAM. **FRN** 6305
MISC 18-5-87. GEC. 0.2/20uL. COL#73.



5 cm

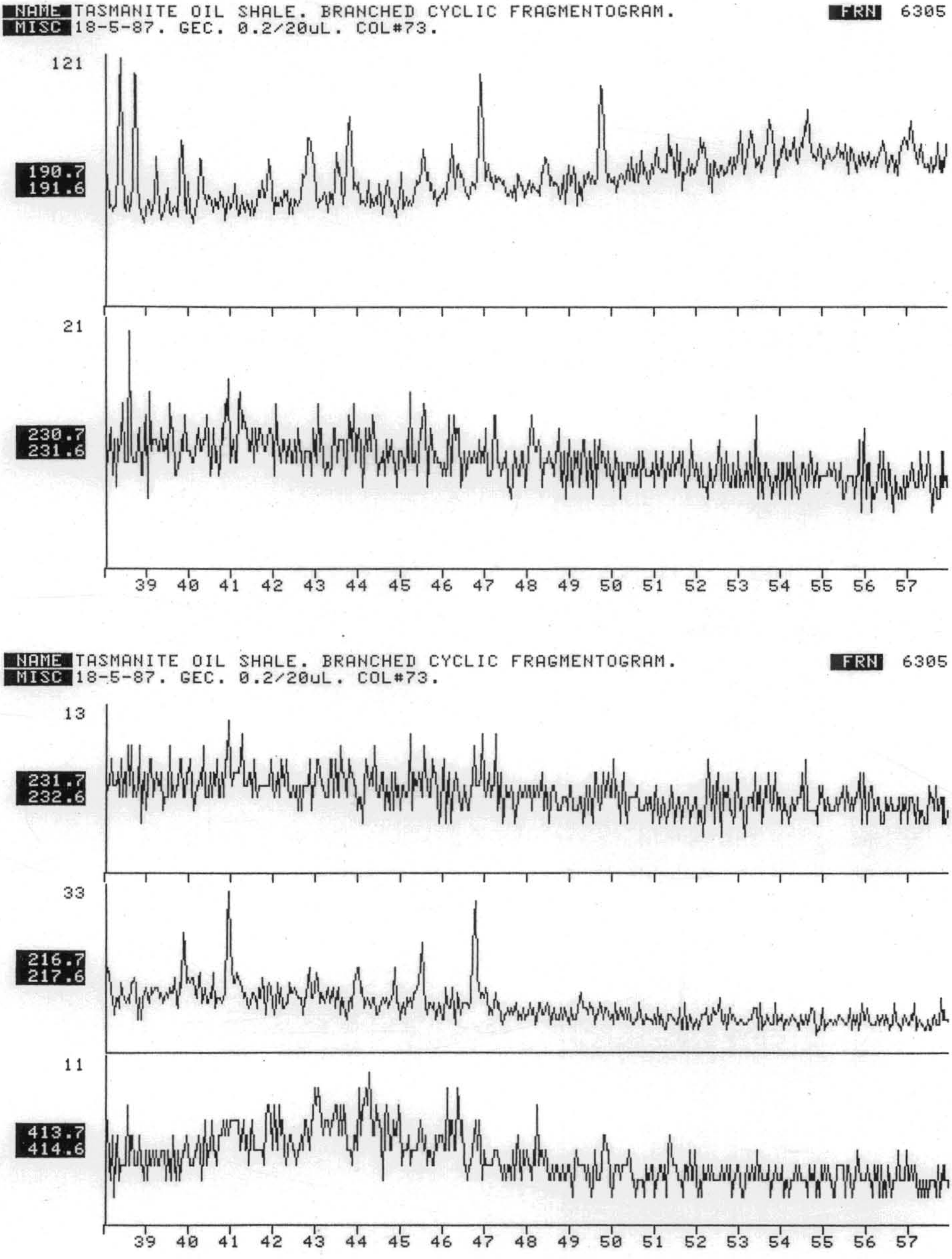
7/18

FIGURE 2C



5 cm

FIGURE 2D


NAME TASMANITE OIL SHALE. BRANCHED CYCLIC FRAGMENTOGRAM.
MISC 18-5-87. GEC. 0.2/20uL. COL#73.
FRN 6305
121
190.7
191.6
21
230.7
231.6
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
NAME TASMANITE OIL SHALE. BRANCHED CYCLIC FRAGMENTOGRAM.
MISC 18-5-87. GEC. 0.2/20uL. COL#73.
FRN 6305
13
231.7
232.6
33
216.7
217.6
11
413.7
414.6
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57

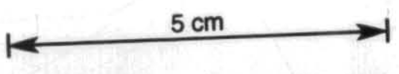
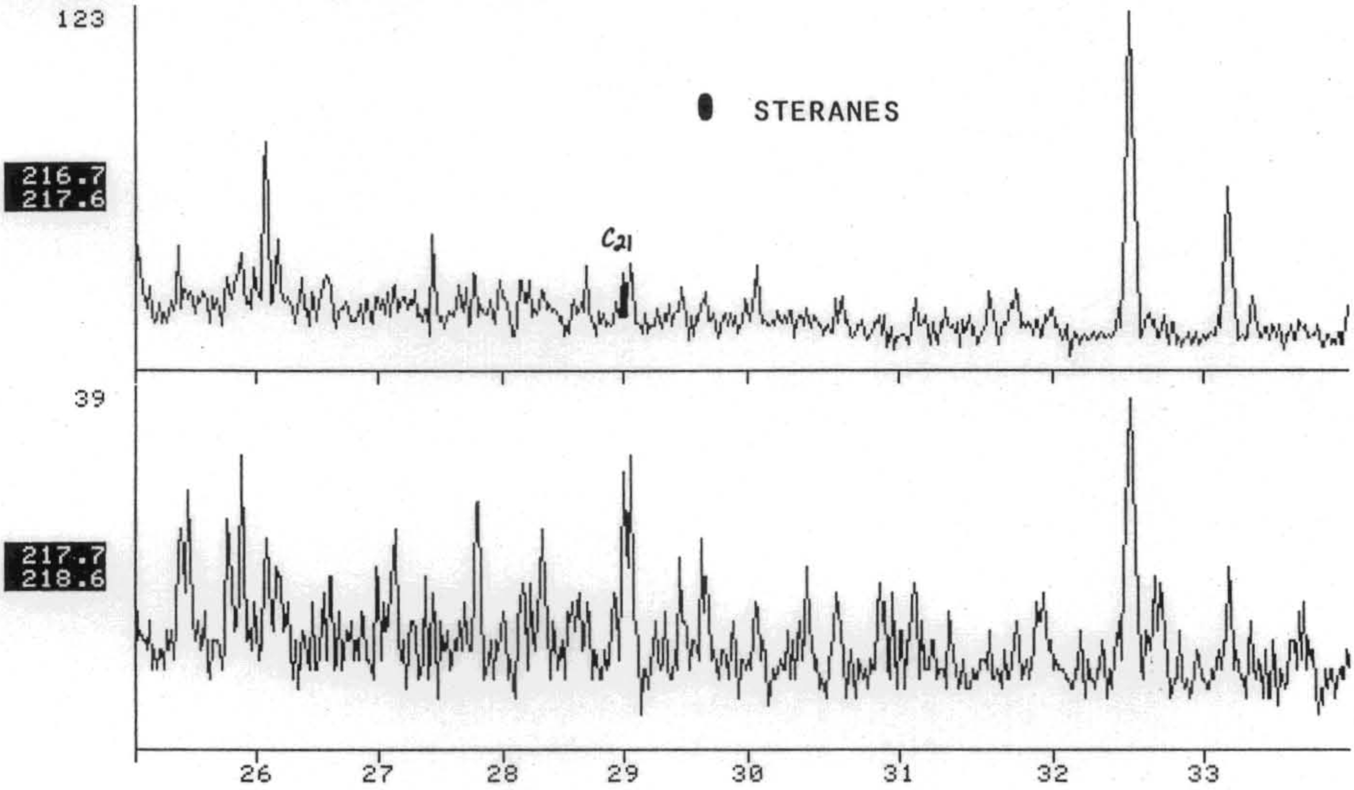
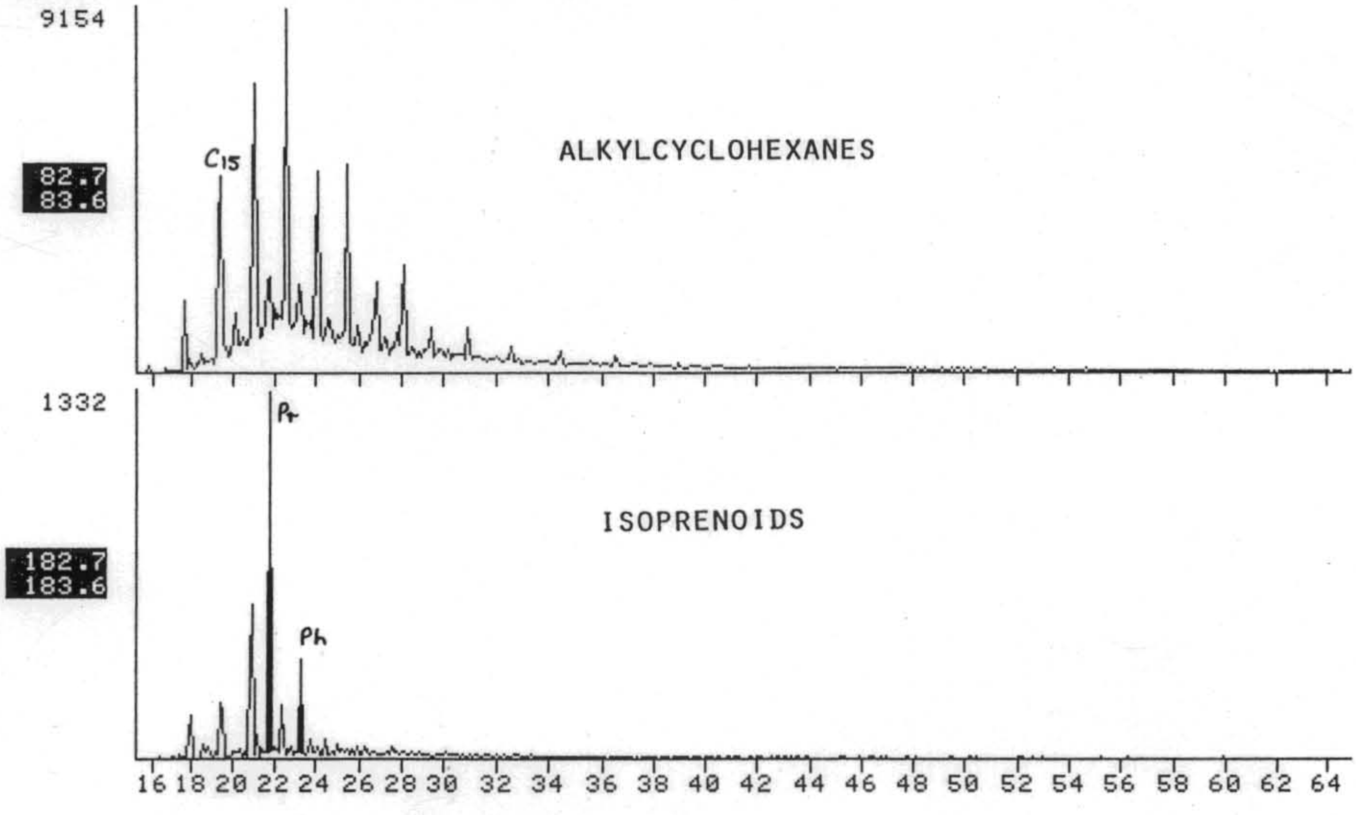

5 cm

FIGURE 2E

NAME TASMANITE OIL SHALE. BRANCHED CYCLIC FRAGMENTOGRAM. **FRN** 6305
MISC 18-5-87. GEC. 0.2/20uL. COL#73.



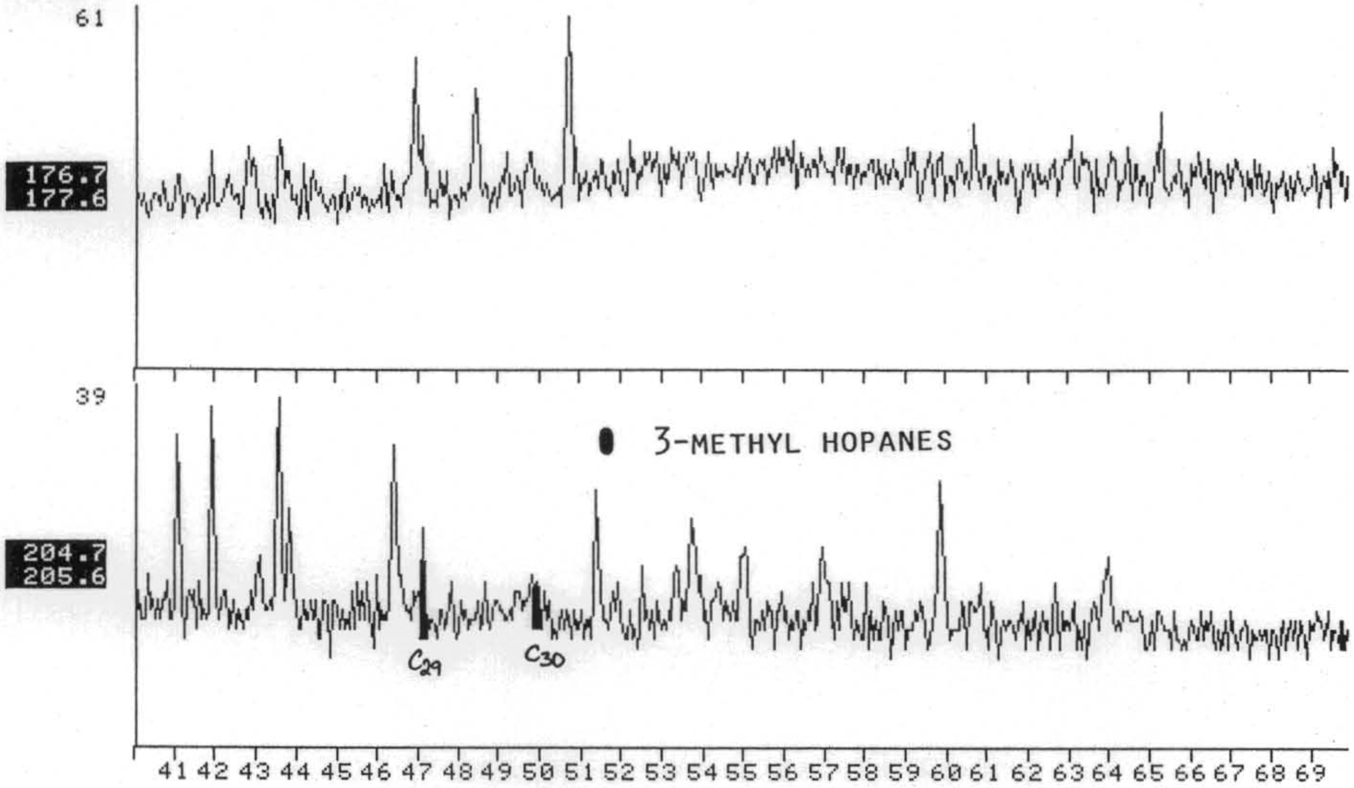
NAME TASMANITE OIL SHALE. BRANCHED CYCLIC FRAGMENTOGRAM. **FRN** 6305
MISC 18-5-87. GEC. 0.2/20uL. COL#73.



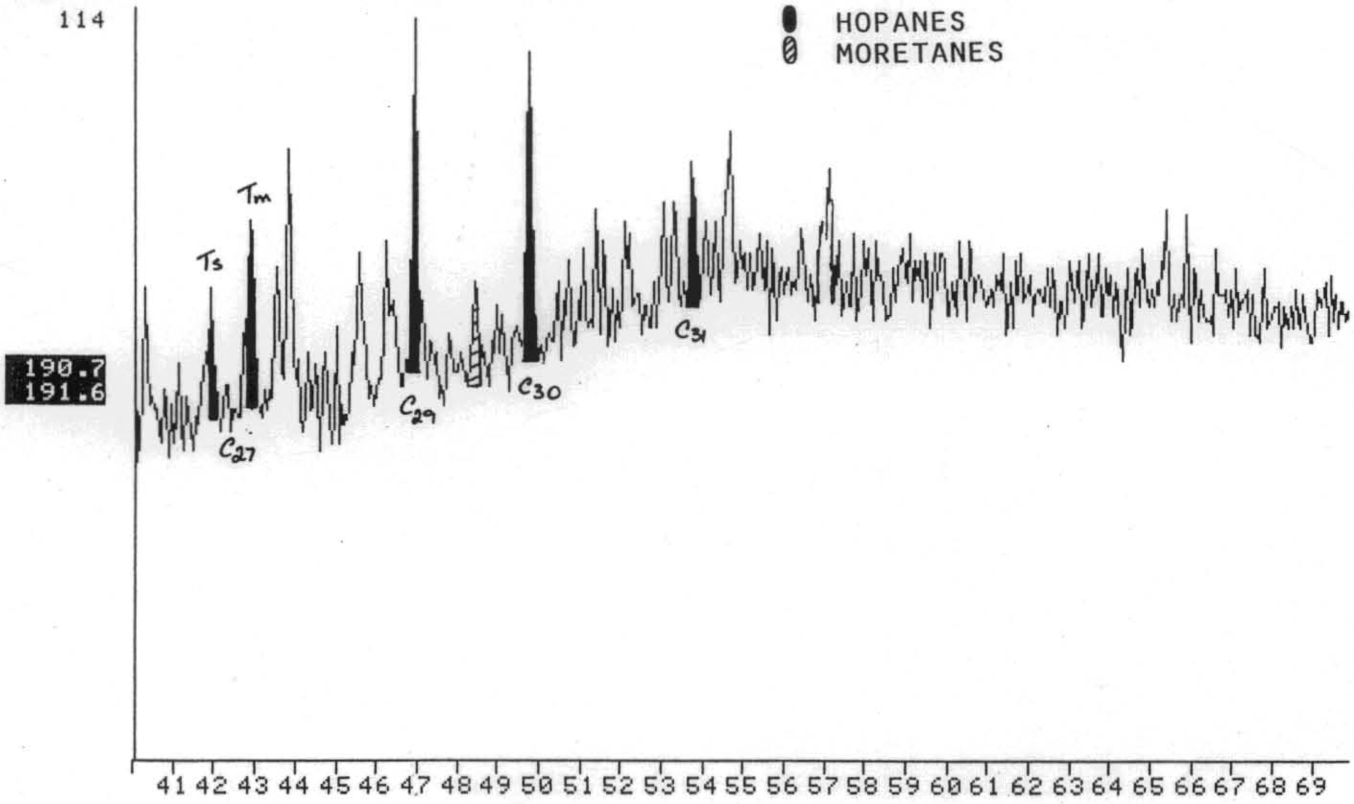
5 cm

FIGURE 2F

NAME TASMANITE OIL SHALE. BRANCHED CYCLIC FRAGMENTOGRAM. **FRN** 6305
MISC 18-5-87. GEC. 0.2/20uL. COL#73.



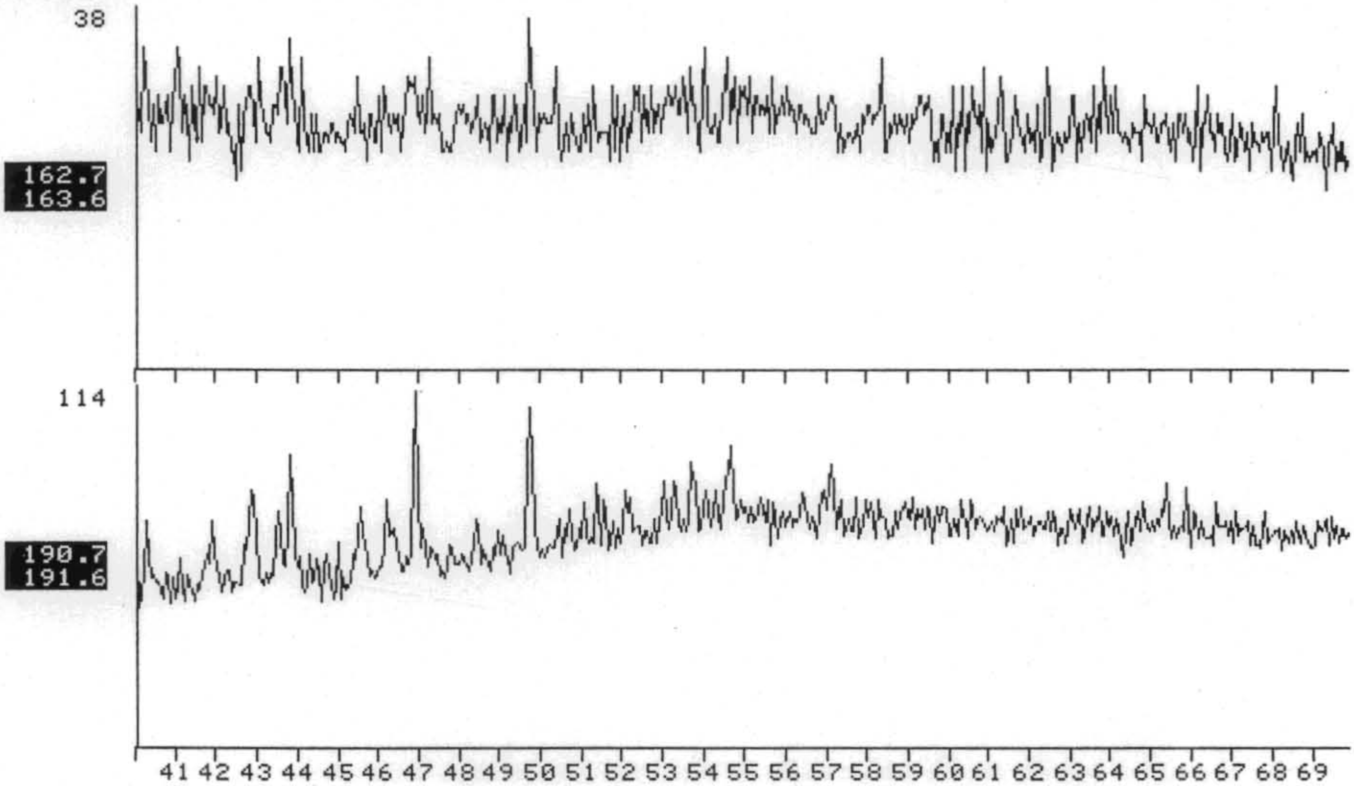
NAME TASMANITE OIL SHALE. BRANCHED CYCLIC FRAGMENTOGRAM. **FRN** 6305
MISC 18-5-87. GEC. 0.2/20uL. COL#73.



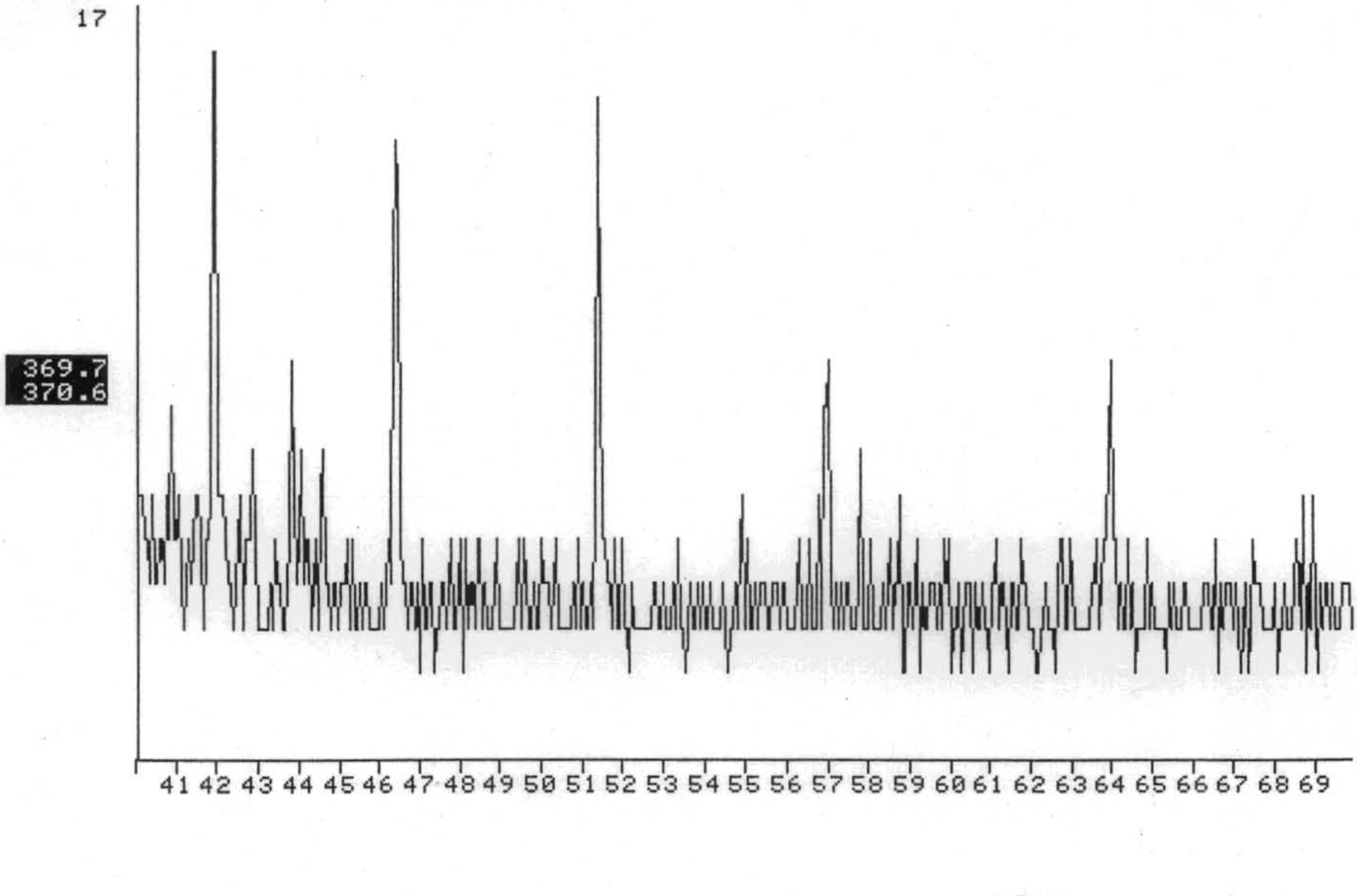
5 cm

FIGURE 2G

NAME TASMANITE OIL SHALE. BRANCHED CYCLIC FRAGMENTOGRAM. **FRN** 6305
MISC 18-5-87. GEC. 0.2/20uL. COL#73.



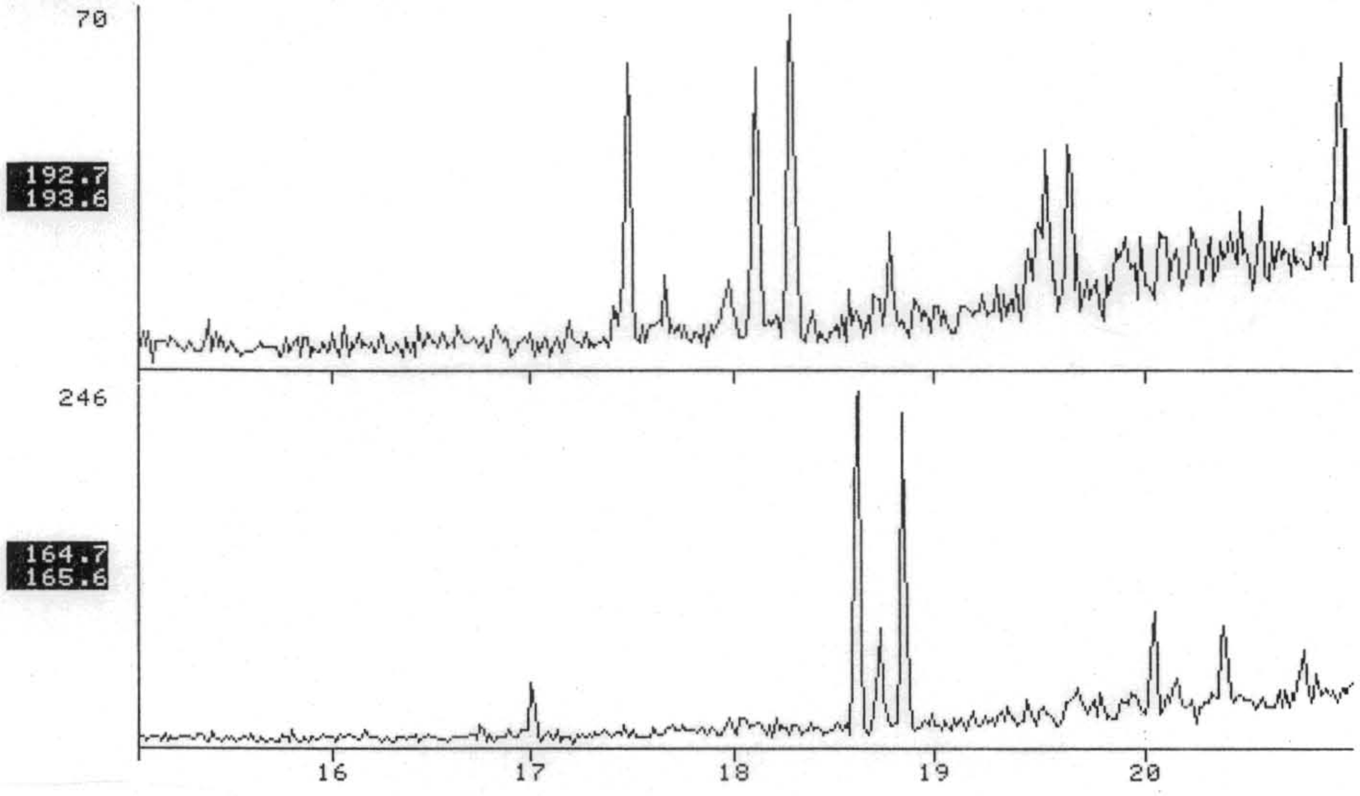
NAME TASMANITE OIL SHALE. BRANCHED CYCLIC FRAGMENTOGRAM. **FRN** 6305
MISC 18-5-87. GEC. 0.2/20uL. COL#73.



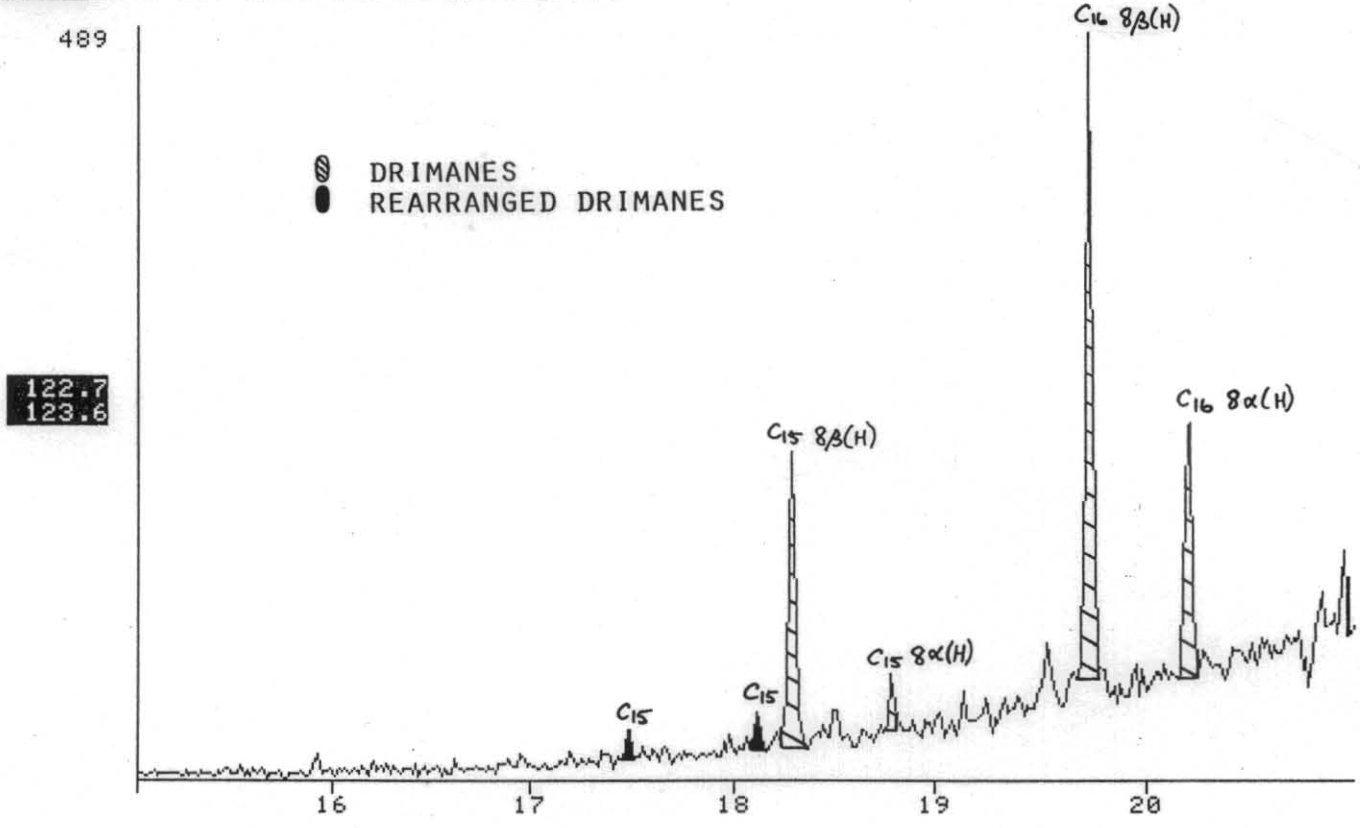
5 cm

FIGURE 2H

NAME TASMANITE OIL SHALE. BRANCHED CYCLIC FRAGMENTOGRAM. **FRN** 6305
MISC 18-5-87. GEC. 0.2/20uL. COL#73.



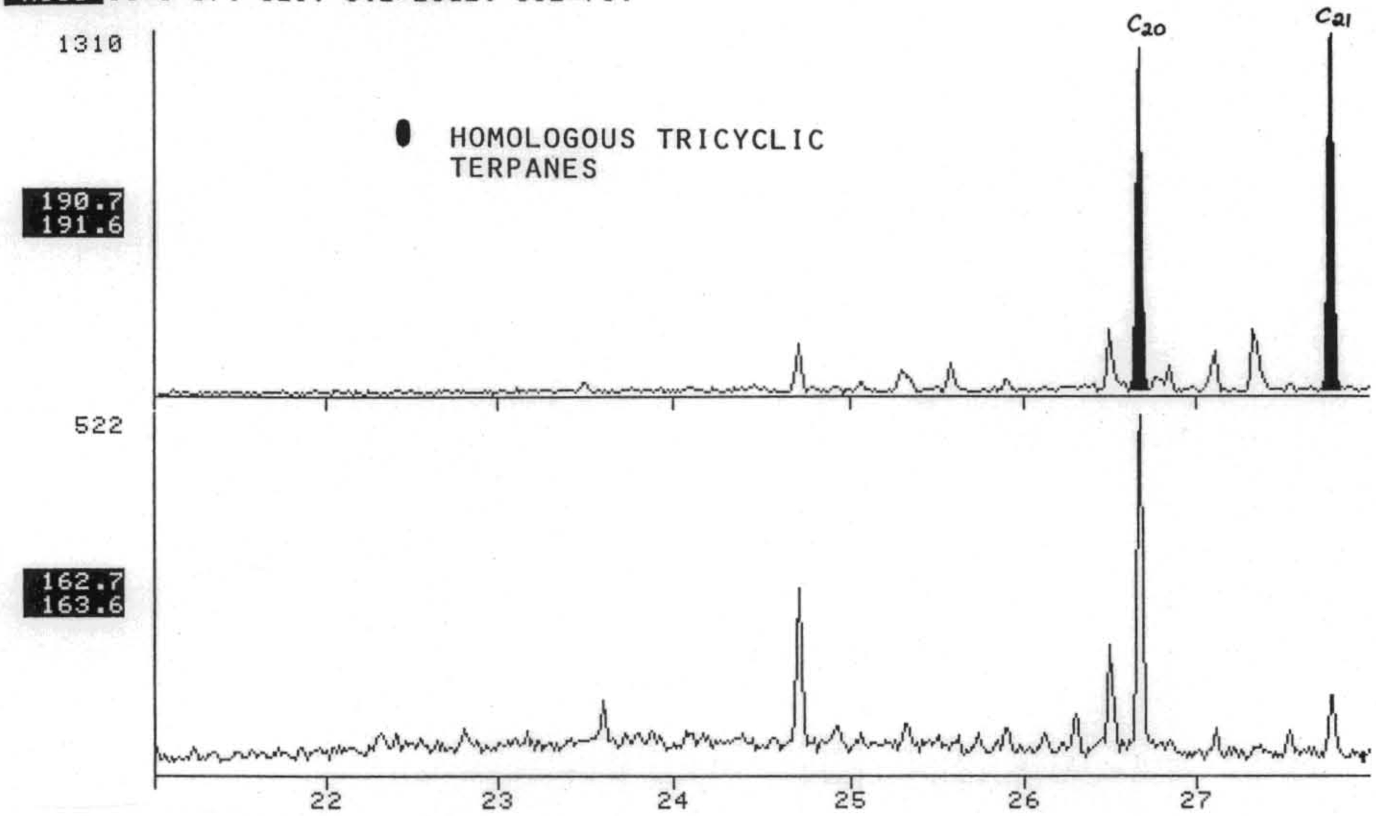
NAME TASMANITE OIL SHALE. BRANCHED CYCLIC FRAGMENTOGRAM. **FRN** 6305
MISC 18-5-87. GEC. 0.2/20uL. COL#73.



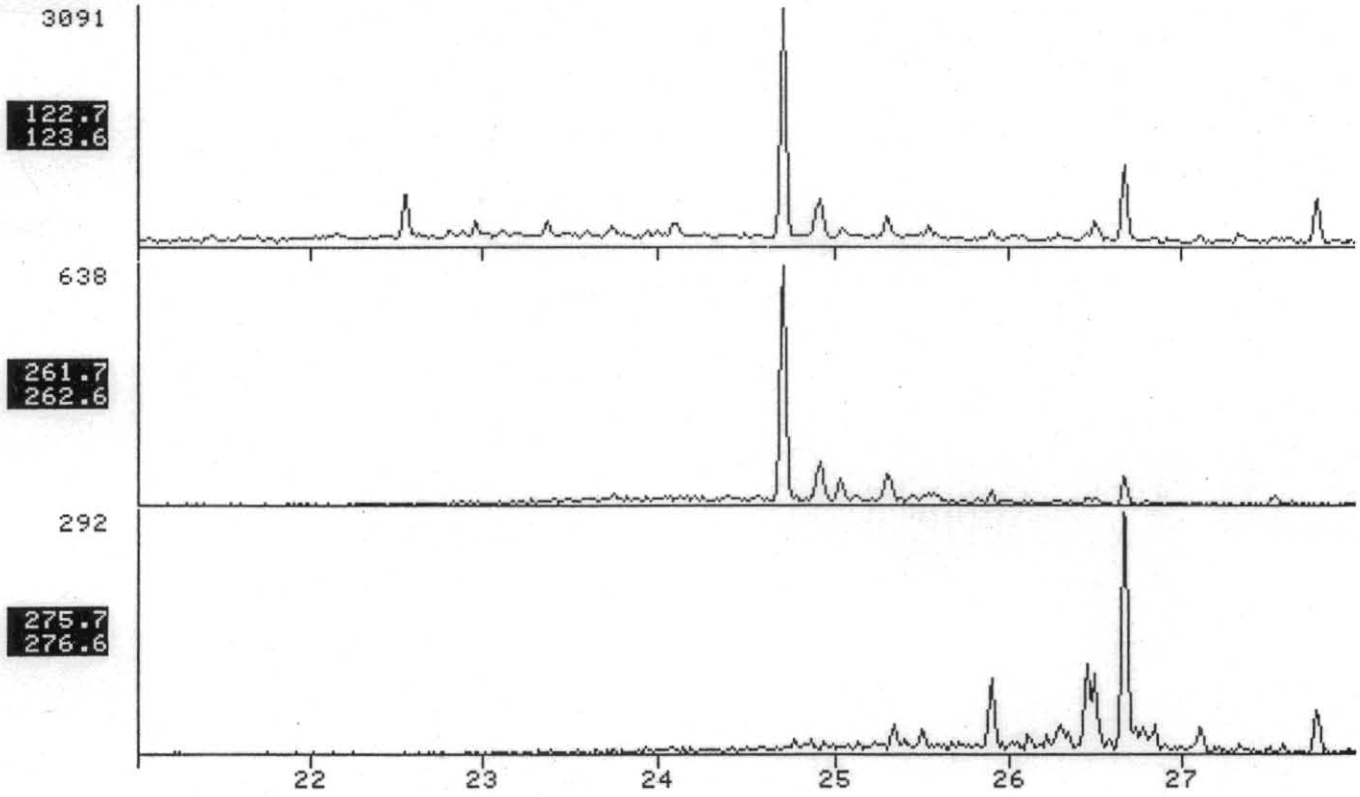
5 cm

FIGURE 2I

NAME TASMANITE OIL SHALE. BRANCHED CYCLIC FRAGMENTOGRAM. **FRN** 6305
MISC 18-5-87. GEC. 0.2/20uL. COL#73.

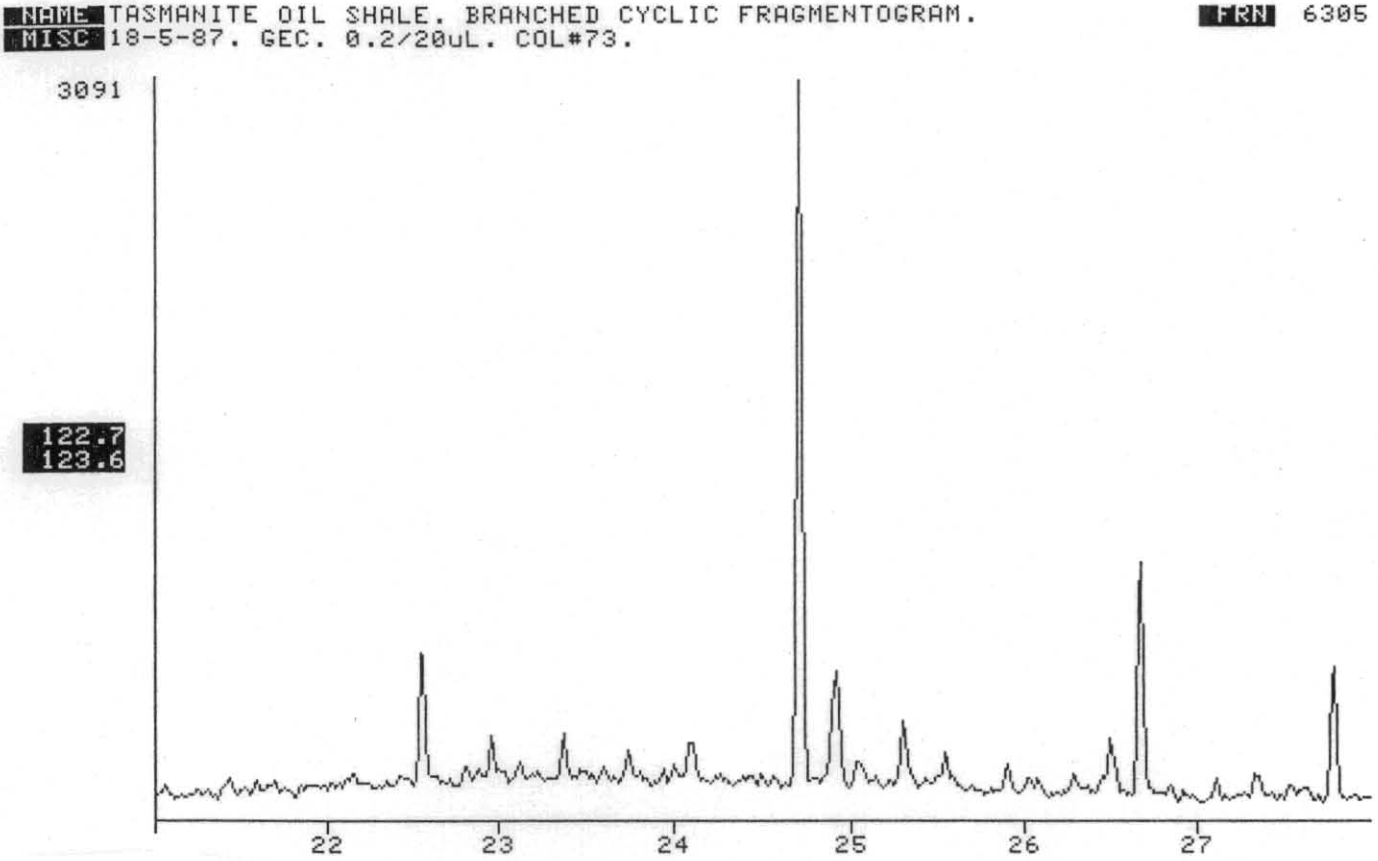


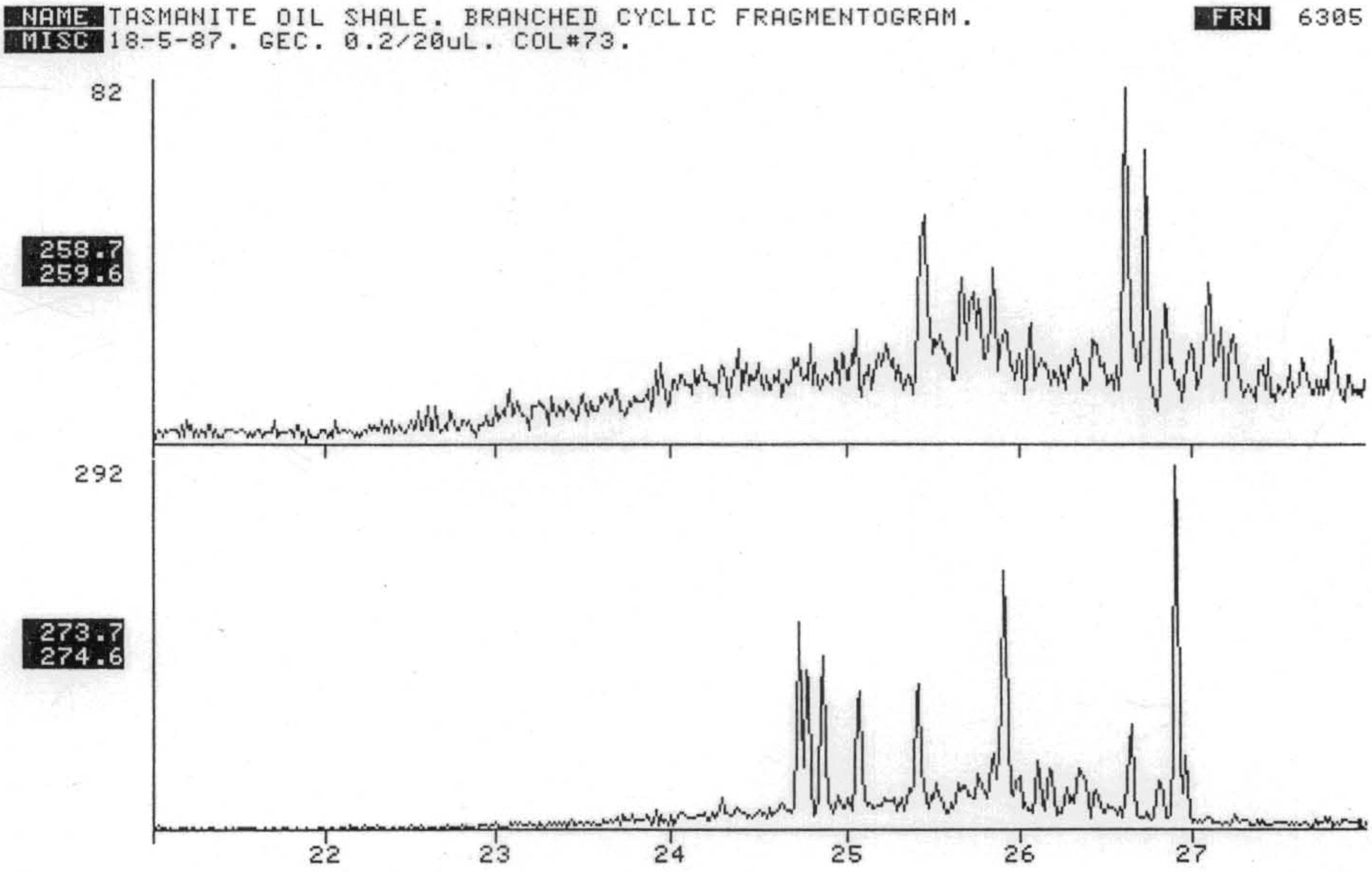
NAME TASMANITE OIL SHALE. BRANCHED CYCLIC FRAGMENTOGRAM. **FRN** 6305
MISC 18-5-87. GEC. 0.2/20uL. COL#73.



5 cm

FIGURE 2J





5 cm

TABLE 1

ROCK-EVAL PYROLYSIS DATA (one run)

TMAX	S1	S2	S3	S1+S2	S2/S3	PI	PC	TOC	HI	OI
436	0.03	19.30	0.30	19.33	64.33	0.00	1.60	2.58	748	11

TMAX = Max. temperature S2
S1+S2 = Potential yield
PC = Pyrolysable carbon
OI = Oxygen Index

S1 = Volatile hydrocarbons (HC)
S3 = Organic carbon dioxide
TOC = Total organic carbon
nd = no data

S2 = HC generating potential
PI = Production index
HI = Hydrogen index

TABLE 2

Summary of Extraction and Liquid Chromatography

A. Concentrations of Extracted Material

			-------Hydrocarbons--------			-----Nonhydrocarbons-----		
Weight of Rock Extd. (grams)	Total Extract (ppm)	Loss on Column (ppm)	Saturates (ppm)	Aromatics (ppm)	HC Total (ppm)	NSO's (ppm)	Asphaltenes (ppm)	NonHC Total (ppm)
50.4	192.5	41.7	45.6	13.9	59.5	91.3	nd	91.3

B. Compositional Data

-----Hydrocarbons------			-----Nonhydrocarbons------							
%SAT.	%AROM.	%HC's	%NSO's	%ASPH.	%Non HC's	EOM(mg) TOC(g)	SAT(mg) TOC(g)	SAT AROM	ASPH NSO	HC Non HC
30.3	9.2	39.5	60.5	nd	60.5	nd	nd	3.29	nd	.7

TABLE 3

Summary of Gas Chromatography Data

A. Alkane Compositional Data

Prist./Phyt.	Prist./n-C17	Phyt./n-C18	CPI(1)	CPI(2)	(C21+C22)/(C28+C29)
2.95	.50	.27	1.07	1.02	2.00

B. n-Alkane Distributions

nC12	nC13	nC14	nC15	nC16	nC17	iC19	nC18	iC20	nC19	nC20	nC21	nC22	nC23	nC24	nC25	nC26	nC27	nC28	nC29	nC30	nC31
5.0	5.5	7.3	9.9	14.2	15.9	8.0	9.8	2.7	4.3	2.6	2.2	2.0	1.7	1.6	1.3	1.2	1.1	1.0	1.1	.7	.9

TABLE 4

SELECTED PARAMETERS FROM GC/MS ANALYSIS

Sample: TASMANITE OIL SHALE

	Parameter	Ion(s)	Value
1.	18α(H)-hopane/17α(H)-hopane (Ts/Tm)	191	0.39
2.	C30 hopane/C30 moretane	191	nd
3.	C31 22S hopane/C31 22R hopane	191	nd
4.	C32 22S hopane/C32 22R hopane	191	nd
5.	C29 20S $\alpha\alpha\alpha$ sterane/C29 20R $\alpha\alpha\alpha$ steranes	217	0.24
6.	$\frac{\text{C29 } \alpha\beta\beta \text{ steranes}}{\text{C29 } \alpha\alpha\alpha \text{ steranes + C29 } \alpha\beta\beta \text{ steranes}}$	217	0.37
7.	C27/C29 diasteranes	259	nd
8.	C27/C29 steranes	217	0.95
9.	18α(H)-oleanane/C30 hopane	191	nd
10.	$\frac{\text{C29 diasteranes}}{\text{C29 } \alpha\alpha\alpha \text{ steranes + C29 } \alpha\beta\beta \text{ steranes}}$	217	nd
11.	$\frac{\text{C30 (hopane + moretane)}}{\text{C29 (steranes + diasteranes)}}$	191/217	1.20
12.	C15 drimane/C16 homodrimane	123	0.45
13.	Rearranged drimanes/normal drimanes	123	0.07
14.	C15 alkylcyclohexane/C30 hopane	83/191	28.71
15.	C15 alkylcyclohexane/C16 homodrimane	83/123	11.63

nd = not detectable