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RESTRICTED INVESTIGATION REPORT 991R

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MINERALS RESEARCH LABORATORIES

TASMANITE OIL SHALE

- *First Quarterly Report*

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OPEN FILE

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INTRODUCTION

Following a preliminary study (Investigation Report 951R) the CSIRO Fuel Geoscience Unit commenced a twelve months program of studies on behalf of Endeavour Resources Limited on October 1, 1978. The aim of the study is to characterize the deposit and carry out small scale tests in order to identify the most feasible means of obtaining useful products from tasmanite shale. This report covers work carried out during the first quarter (to December 31, 1978); much of this work has necessarily been of a preliminary nature, especially since some sample material was received only at the end of the period. Work to be included in the study falls in the following categories:

- (a) microscopic observations (including fluorescence and electron microscopy) supported by X-ray diffraction;
- (b) chemical analyses and assays, with attention to structure of organic matter;
- (c) comminution and the liberation of organic matter by various methods;
- (d) solvent extraction tests; and
- (e) characterization of any products.

HISTORICAL

Oil shale in Tasmania was discovered along the Mersey River in the 1800's. About 1861 the first company associated with the oil shale was formed. However, it was not until 1901 that extensive laboratory examinations were made on the shale. In 1910 several retorts were built to process the shale, and during the next five years the production of crude oil from the oil shale increased. In 1927 after a lapse in interest, crude oil production started again and continued until 1934. Between 1935 and 1940 investigations were made into the viability of

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of producing asphalt from the oil shale. Bitumen production was also looked into but Government aid was not made available, and the project did not proceed.

In the 1970's, with the increasing cost of imported crude oil, there has been renewed interest in oil shale and products which could be prepared from it. It now seems possible that useful materials will be produced economically from oil shale in the future, one such material perhaps being bitumen for road-making

SAMPLES

Apart from small samples held by the Unit, the samples at present available for the study are as follows:

Four samples of lump shale specimens were received prior to the commencement of the project.

A 10 Kg sample of tasmanite concentrate was received on October 3, 1978.

A batch of core samples from the Tasmanian Department of Mines was received on December 11, 1978.

Since only the lump shale specimens and the tasmanite concentrate were available for most of the period, the observations made here refer to them. It is expected that the core samples, which are now being processed, will be the focus for most study during the second quarter.

PETROLOGY

A short petrological description was given in Investigation Report 951R. There is nothing of significance to add at the present stage.

INORGANIC MATTER

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No great difference has been noted between minerals in the Tasmanites-rich bands and those in bands intermediate between layers rich in organic matter. The grain sizes of minerals range from sub-microscopic to 250 μ ; the most common grain sizes observed in the lump samples are 50 - 100 μ .

X-ray diffraction examinations were made of minerals in the kerogen concentrate and in the four lump samples; the results are given in Table 1. There is a high degree of consistency in the results, which suggest that acid igneous rocks or high-grade metamorphics of acid composition have contributed substantially to the sediments which formed the shales. The presence of various carbonates is interesting; if, as seems likely, these were deposited at, or soon after deposition, the acidity of humic material must have been neutralized. Perhaps this accounts in part for the rarity of humic (i.e. vitrinitic) material in the shales, and the abundance of algal remains, which would not have been associated with abundant acid groups.

Volumetric point count analyses were also made on the four lump samples, although in each case there was a high proportion of fine-grained material ("matrix") which could not be positively identified. The results are given in Table 2. Some characteristics of the different minerals are as follows:-

The quartz grains are generally sub-rounded, with the smaller grains tending to be angular. The quartz in some grains also shows undulose extinction, a feature of strain which probably occurred before the deposition of the shale. The chlorite and muscovite, in most cases, have retained their elongate sections (010). There also appears to be some sericite associated with the muscovite.

Kaolinite occurs as apparent veins of mosaic-like crystal masses, which were observed in both transverse and elongate orientation.

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TABLE 1

MINERALS DETECTED BY X-RAY DIFFRACTION ANALYSIS
OF TASMANITE SAMPLES

- LN 77591 - (kerogen concentrate)
quartz, muscovite, kaolinite/chlorite, gypsum,
probably feldspar.

- LN 61388 - (lump sample)
quartz, muscovite, kaolinite/chlorite, probably
feldspar, possibly dolomite and Mg calcite.

- LN 61389 - (lump sample)
quartz, muscovite, kaolinite/chlorite, probably
dolomite, feldspar, pyrite, possibly Mg calcite,
siderite.

- LN 61390 - (lump sample)
quartz, muscovite, kaolinite/chlorite, gypsum,
probably dolomite, Mg calcite, feldspar, pyrite.

- LN 61391 - (lump sample)
quartz, muscovite, kaolinite/chlorite, gypsum
probably feldspar, possible dolomite and Mg calcite.

The pyrite in the rocks usually has one of two forms: as roughly spherical single particles from 5 μm to 25 μm on average in size, or in framboidal form. The pyrite commonly appears to have concentrated along the outside edges of some of the "Tasmanites" bodies, and at the margins of other minerals. Some of the pyrite has altered partly or completely to iron oxides. This oxidation of the pyrite may be a natural feature, or may have occurred after the original sample was taken. The oxidation is irregular in occurrence and further work on this aspect will be needed. (The same is true of the gypsum detected by X-ray diffraction which could be original, but may well have formed during oxidation of the shale.)

Carbonates, the other major mineral group, consist mainly of dolomite and of calcite, and are amongst the larger sized grains that are recognizable. The grains are generally anhedral with some euhedral and subhedral shapes. They range in size from 25 μm to 75 μm . They lack well-defined cleavage.

ORGANIC MATERIAL

There are at least three types of organic material to be found in these samples. They are tasmanite, and the coal macerals vitrinite and inertinite. The tasmanite is the most abundant of these, since it averages 40 - 50% by volume of the oil shale (Table 2).

The Tasmanites bodies are typically disc-shaped, about 300 to 400 μm across and 30 to 50 μm thick on average. Some of the largest sized bodies may be over 500 μm across. It appears that the disc-shapes have been formed by the flattening of spheroidal shaped bodies during deposition and compaction. A few of the rounded shapes have been preserved by infilling of other minerals into the central cavity before compression could take place. No original internal structures in these

TABLE 2

MINERAL AND SPORE ANALYSIS OF TASMANITE SAMPLES

(Results are given as percentages by volume)

Lab No.	Tasman -ites bodies	Quartz	Musc.	Matrix*	Carbon ates	Kaolin ite	Chlor ite	Pyrite [†]	Felds.	Gyp.	Total No of counts
61388	44.2	4.3	1.4	39.9	7.7	1.5	0	0.3	0	0.7	719
61389	43.2	3.2	2.5	37	5.6	2.6	0.3	5.6	0	0	683
61390	54	6.4	1.1	31	2.5	0	0.7	2.7	0.2	1.4	559
61391	47.8	4.7	2	34.6	4.2	2.4	1.1	2.7	0	0.5	789

* Matrix - When the mineral matter is micro-crystalline and unidentifiable with certainty by optical means (includes inorganic and organic matter).

† Pyrite - The readings also include partly oxidised pyrite.

Relative Predominance of the Minerals:

This estimation is taken from X-ray diffraction graphs and is an overall assessment.

Quartz is the most predominant mineral followed by muscovite, the clay minerals, the carbonates, the pyrite and other accessory minerals.

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bodies have been preserved. The single walls of the discs range in thickness from 5 μ m to 25 μ m; in thin-section these walls show well-formed pore structures which are continuous through the wall. The pores are from less than 1 μ m to 1 μ m wide.

Tasmanites is now widely accepted as being of algal origin, although to which genus it belongs is still an outstanding question.

The very concentrated beds of algal bodies are usually comparatively free of minerals.

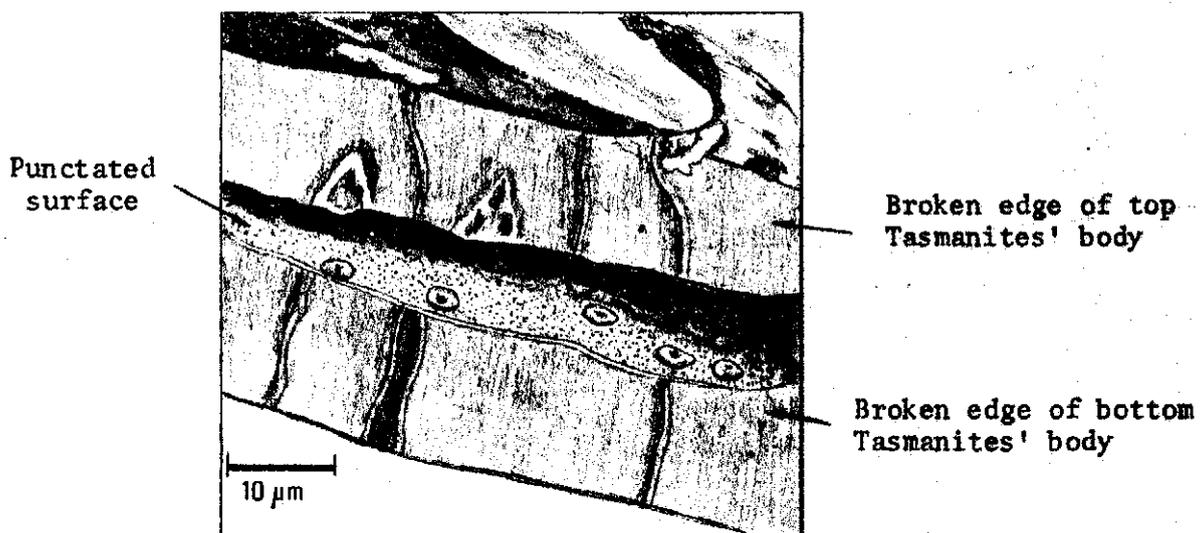
The areas which are dominated by mineral matter also contain a scattering of algal bodies in amongst the matrix. The size of individual algal bodies within the bed varies greatly, so that there do not seem to be concentrations of any particular size of algal body anywhere. The different sizes of algal bodies may indicate a population composed of different stages of maturity.

The preservation of the algal bodies is very good. Most are complete, with very few that are highly fragmented. This probably reflects their tough, leathery consistency.

There are some signs of abrasion, such as pitting and rough surfaces on the algal bodies, which indicates that there was some 'wear' before deposition.

Under the scanning electron microscope a great amount of detail can be seen, especially of the algal body surface. It can be noted that the surface is punctated all over with very small pores less than $\frac{1}{2}$ μ m across, which do not appear to penetrate very deeply below the surface. However, there are larger pores, about 1 to $1\frac{1}{2}$ μ m across, which are fewer in number and scattered, with no regular pattern. These pores are presumably those that completely penetrate the body wall perpendicular to the surface, as seen in thin section (Fig. 1).

Sketch from Electron Scanning Microscope
photograph of Tasmanites' wall



Minor punctations on Tasmanites surface do not extend below surface,
but large, more obvious pores penetrate through the full thick-
ness of the wall.

FIGURE 1.

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Microscopically, tasmanite is yellow to orange-brown, translucent and optically anisotropic. In transmitted light with crossed nicols it has an olive green and dark striated appearance with mottled extinction. Under blue light, the tasmanite shows a very bright yellow-green fluorescence.

The other types of organic matter are the coal macerals vitrinite and inertinite. These macerals are only found as traces, and therefore are not very significant in relation to the nature and properties of the organic matter. One interesting point, however, (mentioned in Investigation Report 951R) is the low reflectance of the vitrinite which would place it in a low "rank" in coal terms. This low "rank" is confirmed by the bright fluorescence of the tasmanite.

CHEMISTRY OF ORGANIC MATTER

Various analyses were carried out on the concentrate (Table 3). These show the expected very high yield of volatile matter, high hydrogen-to-carbon ratio, and a high sulfur content, most of which is organic sulfur. The high proportion of sulfate sulfur again raises the question as to how much of this results from the post-sampling oxidation of other forms of sulfur. This whole matter of sulfur distribution is very important since it will obviously influence the subsequent processing of the tasmanite.

The Gray-King Assay at 600°C gives a useful picture of the products to be obtained from pyrolysis under a particular set of conditions. These results will be compared with Fischer Assays which have now commenced and will be included in the next report.

TABLE 3

TASMANITE OIL SHALE:
ANALYSES OF THE KEROGEN CONCENTRATES

(Results are given as percentages unless otherwise stated)

Lab No.		77591	
		<u>Air-Dried</u>	<u>D.A.F.</u>
Moisture		3.5	-
Ash		32.6	-
Volatile Matter		60.2	94.3
Fixed Carbon		3.7	5.7
<hr/>			
Specific Energy	(MJ/Kg)	23.69	37.11
<hr/>			
Sulfur - Total		3.32	-
Pyritic		0.11	-
Sulfate		1.15	-
Organic (difference)		2.06	-
<hr/>			
Carbon (uncorr. for CO ₂)		48.2	75.5
Hydrogen		6.4	10.0
Nitrogen		0.5	0.8
Sulfur (organic)		2.1	3.2
Oxygen (difference)		6.7	10.5

H/C = 1.58

Carbon dioxide = 0.10

Relative density = 1.38

Gray-King Assay (600°C)

(Results given as percentages)

Coke (including mineral matter) 41.9

Tar 43.6

Liquor 7.3

Gas (difference) 7.2

* D.A.F. = Dry, ash-free

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An analysis of the ash resulting from an ashing of the kerogen concentrate is included in Table 4. This gives the percentage of the oxides found in the ash. This analysis does not include sodium, however, as the technique does not read this element for analysis. This means that the 2.8% not accounted for in the total figure, probably includes some amount of sodium oxide. Further testing will be done to estimate the sodium oxide content of this ash.

TABLE 4

XRF MAJOR ELEMENT ANALYSIS (Kerogen concentrate)

Lab No.		77591
Constituent	expressed as	%
Silica	SiO ₂	68.52
Alumina	Al ₂ O ₃	10.30
Iron Oxide	Fe ₂ O ₃	7.24
Titanium Oxide	TiO ₂	0.88
Manganese Oxide	Mn ₃ O ₄	0.05
Calcium Oxide	CaO	1.62
Magnesium Oxide	MgO	1.56
Potassium Oxide	K ₂ O	2.53
Phosphate	P ₂ O ₅	0.36
Sulfate	SO ₃	2.85
Loss (moisture, etc)		1.30
TOTAL		97.20

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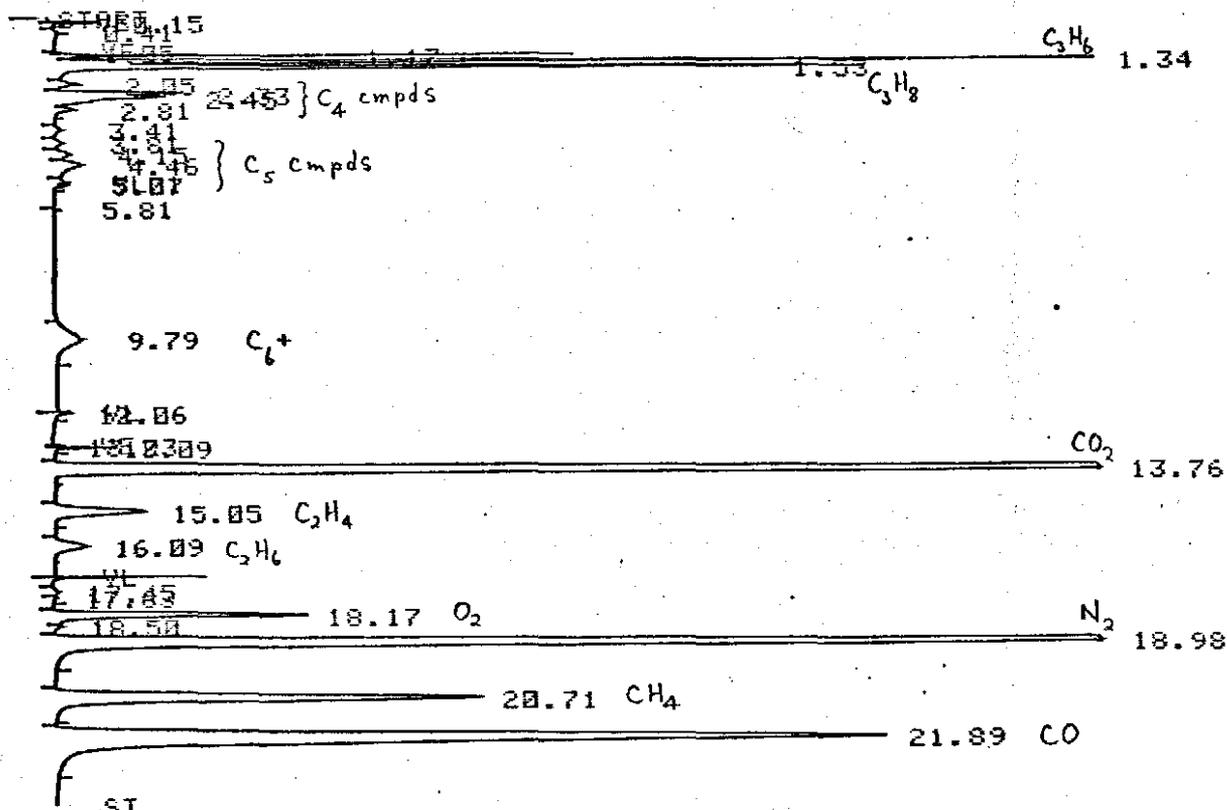
Gas chromatography was used to analyse the gas given off in the Gray-King Assay test at 600°C. The chromatogram and resulting analysis are in Figure 2.

The occurrence of the oxygen peak in the chromatogram may be partly due to air entering the system while sampling of the gas took place. The nitrogen content is very high and cannot be wholly accounted for in the fractionation of air, since it is not in proportion with the oxygen peak.

Another preliminary test done was analysis by Curie point pyrolysis-gas chromatography. The pyrogram (Figure 3), is dominated by n-hydrocarbons of carbon number 18 and below. The doublets are due to the presence of an alkane and an alkene at each carbon number. This technique will be used to monitor changes that occur in tasmanite as it is being hydrogenated; comparisons of these tests will be made at a later date.

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GAS CHROMATOGRAM OF TASMANITE CONCENTRATE - 600°C



NP 5830A
NORM

RT	EXP RT	AREA	CAL #	% by volume AMT	
1.34	1.34	162400	1	4.446	C ₃ H ₆
1.53	1.53	149900	2	4.085	C ₃ H ₈
2.33	2.33	28770	3	0.595	C ₄
2.45	2.45	33770	4	0.698	
4.46	4.46	16230	5	0.274	C ₅
9.79	9.79	23980	6	0.344	
13.76	13.76	679200	7	25.485	C ₆ ⁺
15.85	15.85	42030	8	1.550	CO ₂
16.89	16.89	16230	9	0.563	C ₂ H ₄
18.17	18.17	83080	10	3.736	C ₂ H ₆
18.98	18.98	618100	11	26.065	O ₂
20.71	20.71	199500	12	9.786	N ₂
21.89	21.89	538500	13	22.534	CH ₄

XF: 1.0000 E+ 0

FIGURE 2.

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CURIE-POINT PYROLYSIS - GAS CHROMATOGRAM
OF TASMANITE SAMPLE

Operator RPP Date 5/978
 COLUMN No. length Dia
 Coating SP2100 Cones.
 Support SCOT Alch.
 TEMP. Col. Inlet 0 °C Final 220 °C
 Rate 4 °C/min Det. C. Inp. °C
 CARRIER GAS 6-6 Rate ml/min.
 Pressures: Inlet Outlet
 Hydrogen ml/min. Air ml/min.
 DETECTOR: Rate ml/min.
 Scavenger Rate ml/min.
 Sens. Rec. range
 SAMPLE TASMANITE Size
 Solvent 60° 10 sec Concn.

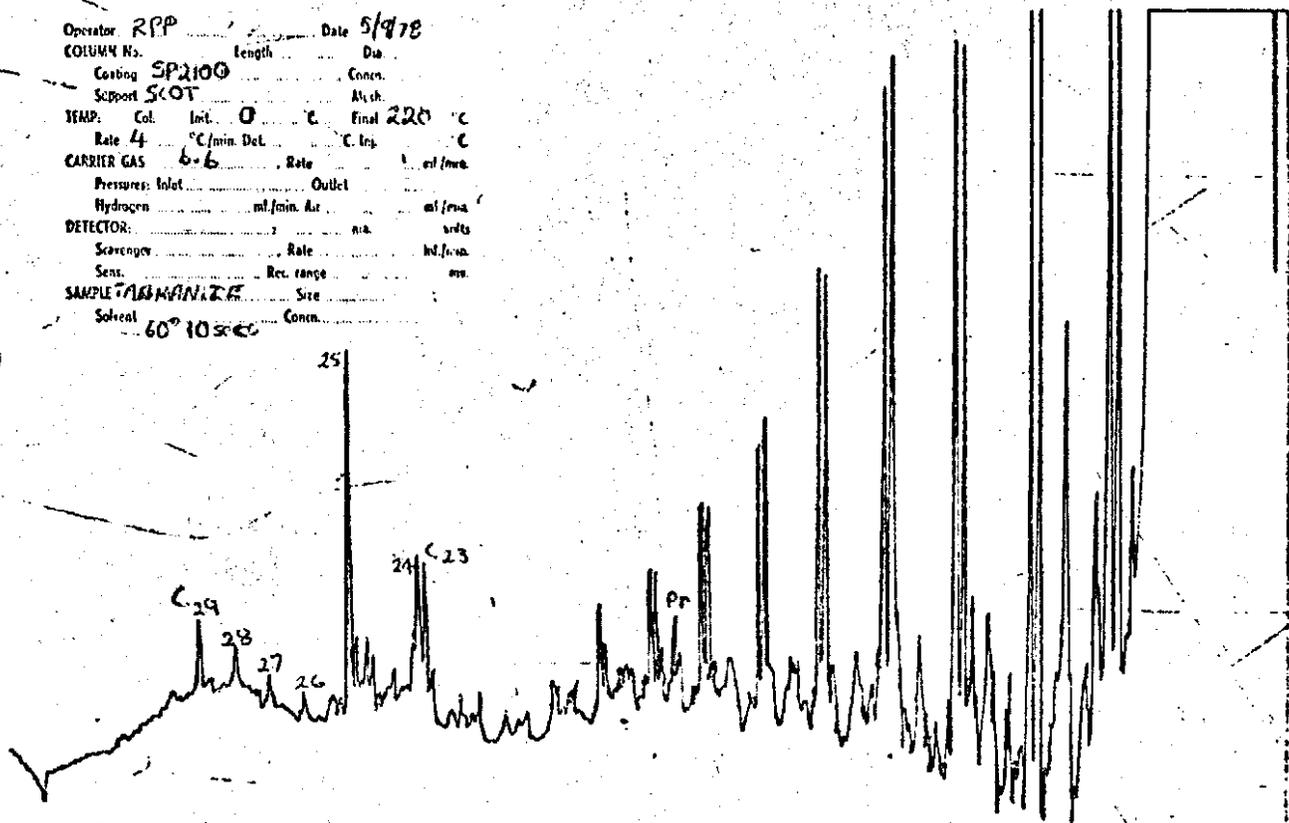


FIGURE 3.

FUTURE WORK

- (1) Further microscopical examinations on incoming core samples to determine the characteristics of the rocks and mineral make-up, and to evaluate the stratigraphical variation.
- (2) Chemical assessment of organic content and composition of different core samples.
- (3) Study of chemical nature of tasmanite, using small-scale concentrates.
- (4) Search for the best means of concentrating the tasmanite from the shale so that efficient processing can proceed. Methods such as froth flotation, density separation and screening will be investigated if enough sample material is available.
- (5) Small-scale pyrolysis tests will be carried out shortly on the kerogen concentrate and possibly on samples received in the future.
- (6) Small-scale hydrogenation tests will be carried out, using different temperatures and pressures, to test the effect on the tasmanite, and to see what products can be produced. Curie point pyrolysis-gas chromatography will be used to monitor the changes that occur under hydrogenation.

Most of the above work can be carried out, or at least begun, on the samples now in hand. However, we would re-emphasize the need for freshly drilled samples when these can be made available.

ACKNOWLEDGEMENTS:

Thanks are due to Dr J. Saxby for gas chromatography, Dr R.P. Philp for Curie point pyrolysis, A. Horne for X-ray diffraction, S. Goadby and Dr M. Hough for ash analysis and to N.C. Watson's group for chemical analysis.

CAPTIONS TO PHOTOGRAPHS

(Figures 4 to 11 inclusive)

Figures 4 to 7 are photographs which have been taken in reflected plane polarized light in air. Figure 8 is of a thin section in transmitted light. Figures 9 to 11 are coloured photographs, 9 and 10 having been taken in reflected light with crossed nicols; 11 was made using blue light fluorescence.

Figure:

4. Tasmanites in a band, showing moulding of algal bodies into conformational shapes.
(Tasmanites = grey, flattened shapes; inertinite = white)
(X165)
5. Large algal body, centre. Degraded algal body, lower left-hand corner (X410).
6. Concentrated Tasmanites band. (Single pyrite grains = small, white.) (X410).
7. Tasmanites bed, showing different sizes of algal bodies
(Inertinite = white) (X165)
8. Tasmanites body showing transverse pores in the wall (X165).

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9. Mineral matter between the larger brown coloured Tasmanites bodies with smaller ones interspersed between. (X170)
10. Mineral matter between small Tasmanites' bands. (Small red-brown spheres are oxidized pyrite grains.) (X170)
11. Yellow-green fluorescence of the algal bodies. (X425)

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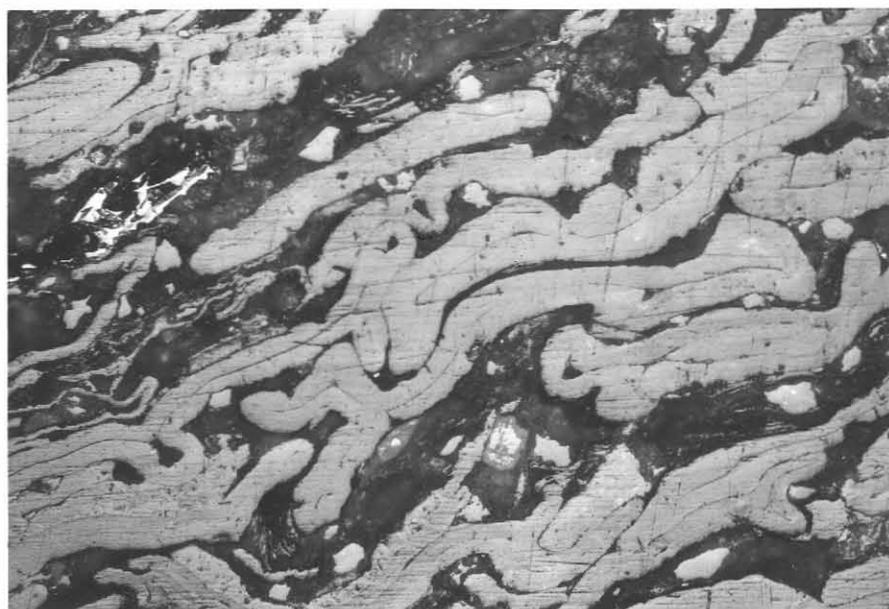


FIGURE 4.



FIGURE 5.

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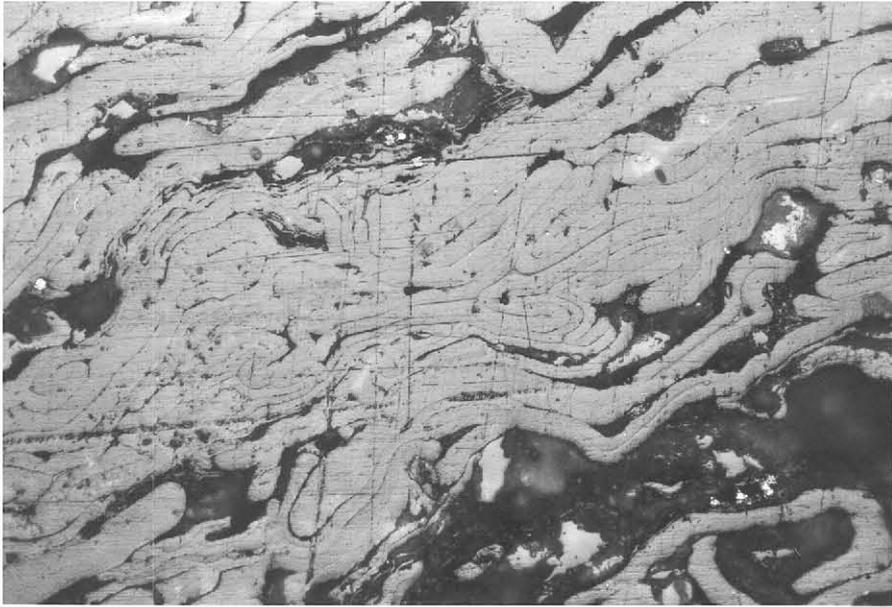


FIGURE 6.

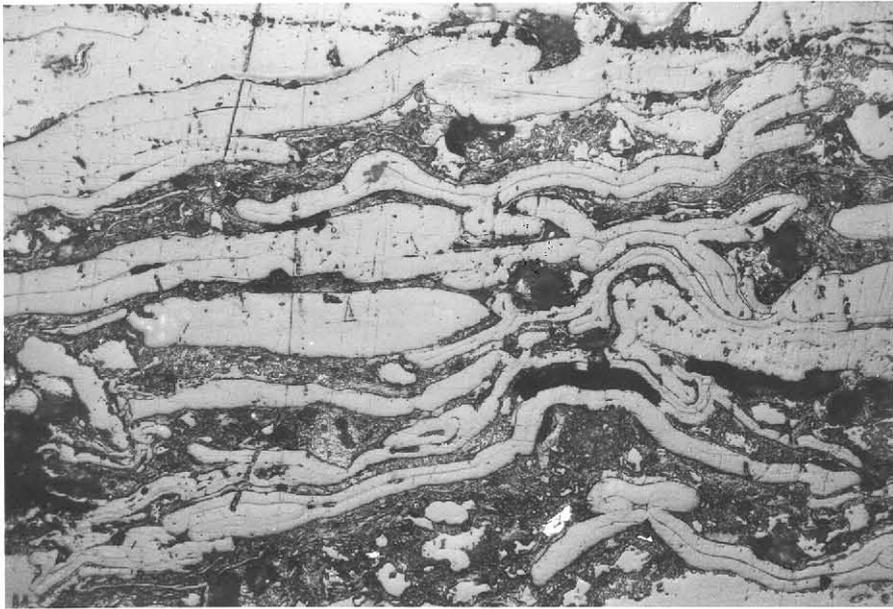


FIGURE 7.

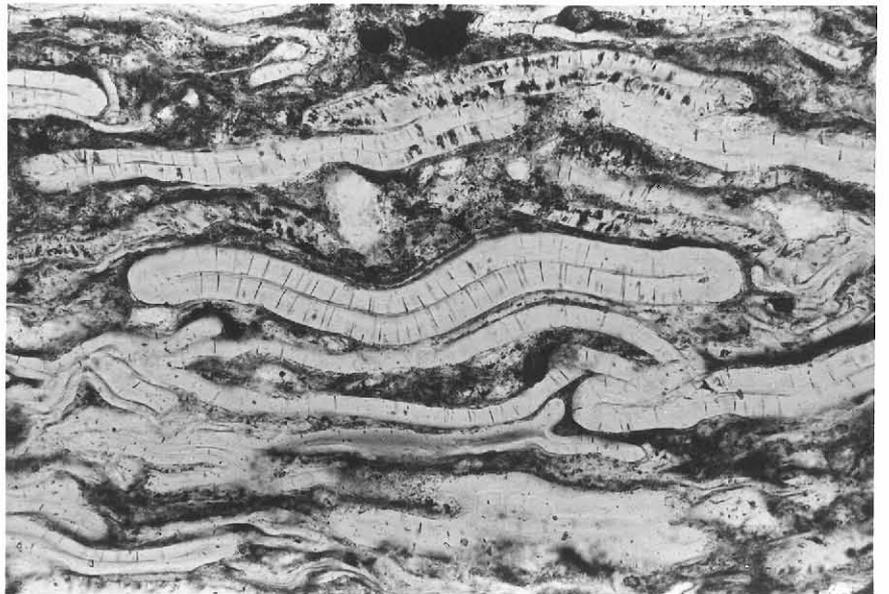


FIGURE 8.

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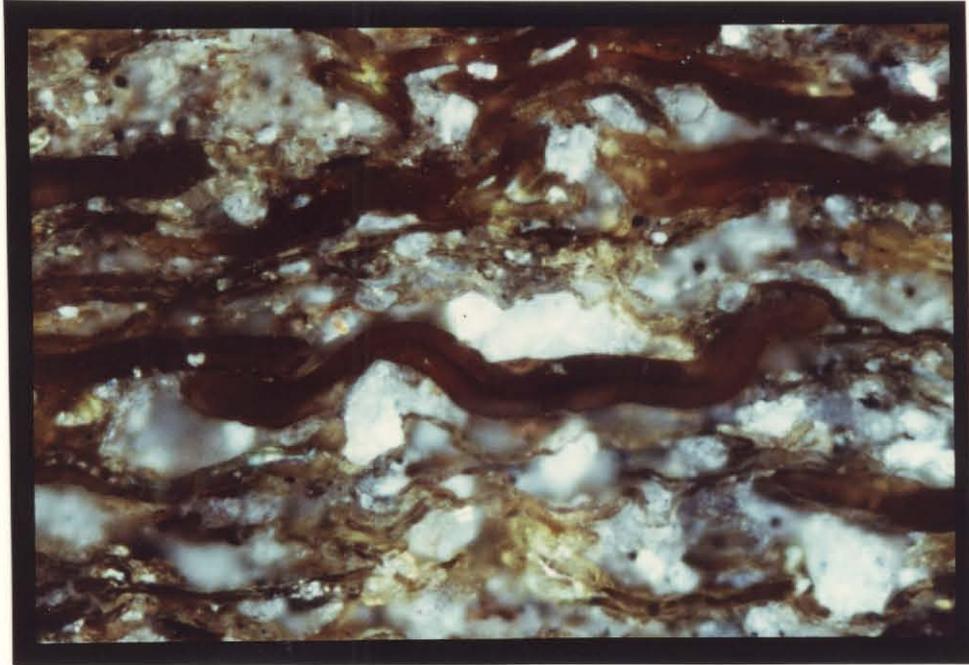


FIGURE 9.



FIGURE 10.

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FIGURE 11.