

JOINT SYMPOSIUM ON OIL SHALE, TAR SANDS, AND RELATED MATERIAL
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THE CONSTITUTION OF TASMANITES

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INTRODUCTION

Thirty years ago, the plenary session of the first Conference on Oil Shale and Cannel Coal (1) adopted a resolution that a standard nomenclature for oil shale was most desirable and that a suitable classification should be secured. No such scheme has ever been adopted. One of the difficulties of any system based on the nature of kerogen itself, has been the virtual absence of recognisable features in the organic matter of the rock, the biological progenitor having been so macerated and metamorphosed that little of the original structure remains. One notable exception is the oil shale called tasmanite, which has characteristics so different from normal that, for over a century, it was believed to be utterly dissimilar from all others. In their early classification, Down and Himus (6) regarded tasmanite as unique and placed it in a separate category.

The purpose of this paper is to record the nature and thermal behaviour of this peculiar oil shale, large deposits of which were, until recently, regarded as endemic to Tasmania. However, in 1966, Tourtelot, Tailleux and Donnell (16) described a particularly rich, although not so distinctive, deposit which has been found in Alaska. This paper deals exclusively with the Tasmanian deposit. The chemistry of the Alaskan material will be the subject of a later contribution.

It is outside the scope of the paper to discuss the geological features of tasmanite as these have been amply covered elsewhere (14). For completeness, however, a summary is given.

RESULTS AND DISCUSSION

Occurrence and Nature

Tasmanite occurs as a single dichotomous seam, or two closely associated seams, about 5 feet thick in the Upper Permian in a relatively restricted area in northwestern Tasmania, fairly close to the coast. It would appear that the boundary of the deposit followed roughly the coast of the Permian sea and was associated with shallow waters of the early coastal islands. Above and below the tasmanite are mudstones associated with pebbly conglomerates. Insignificant patches of tasmanite have also been observed at other isolated places in northern Tasmania as well as on the mainland of Australia. There is no recorded occurrence in southern Tasmania.

The mineral matrix consists largely of fine siliceous marlstone, silica particles and clay, together with small amounts of carbonates and sulphides. The total mineral matter varies between 50% and 90% of the entire rock, with a corresponding specific gravity range of 1.2-1.6.

The composition of the ash does not vary very much with the richness of the seam and adventitious inclusions of quartz, grit and pyrite are to be found throughout the deposit. A range of representative analyses (various authorities) of the ignited mineral matter is shown (% w/w) in Table 1.

The rock itself is grey-brown in colour, soft, fissile and combustible. When examined closely, many samples of tasmanite have a minute speckled appearance made up of innumerable orange spots just visible to the naked eye. These discrete particles are tasmanite "kerogen".

The Organic Matter

The organic matter of tasmanite is different from any other rock type and consists nearly entirely of numberless yellowish clearly differentiated small discs embedded in the mineral matrix. The discrete particles, when viewed under the microscope perpendicular to the bedding plane, appear, when whole, as translucent disc-shaped bodies, roughly 1/2 mm in diameter with a creased and sculptured surface (see Figure 1. A satisfactory vertical section is shown in Ref. 6, Figure 3). In transverse section, innumerable distorted overlapping flattened sausages

are observed and it is not unreasonable to assume that the undistorted entities were nearly spherical in shape and have become flattened and creased under geological pressure. The nature of the surface sculpturing and the spore morphology have been discussed by Singh (15) and Wall (17). Opinion on the exact nature of the "spore cases" has varied widely and, in this paper, the term "spore" will be used to designate the particulate bodies which, in aggregate, make up most of the kerogen of tasmanite. It is not meant to infer that they are true spores in the botanical sense.

TABLE 1
Analysis of Tasmanite Ash

Constituent	Range %
Silica	70 - 77
Alumina	11 - 16
Fe ₂ O ₃	5 - 7
CaO	0.4 - 4
MgO	0.7 - 3
SO ₃	0.4 - 2
K ₂ O	2 - 3
Na ₂ O	0.5 - 2

Descriptions of tasmanite date from 1857 when the first record of the rock appeared in the "Papers and Proceedings of the Royal Society of Van Dieman's Land" - now Tasmania. In the ensuing decade, several references to this "combustible schist" or "white coal" were made in the scientific literature until, in 1864, the name "tasmanite" was given by Church (5). Somewhat later, Newton (13) isolated the spore bodies mentioned above and applied the generic name "Tasmanites" in deference to their origin and specifically "punctatus" because of their punctuation or surface markings.

Initially the spores were believed to be algal in origin, but Newton (13) in 1875 rejected this idea and suggested that they were "allied to Lycopodiaceous macrospores". For a long time, these disc-like microfossils were regarded, not without suspicion, as belonging to a plant possibly allied to the Lepidodendroids or Equisetales. However, in 1941, Kräusel (10) showed that the tasmanite discs were indeed fossil leiospheres derived from an alga probably belonging to the Chlorophyceae and this has remained the consensus, the genus retaining the name "Tasmanites". Somewhat later, Wall (17) reaffirmed the identity of Tasmanites and showed its close affinity to the extant spherical green alga Pachysphaera pelagica (Ostenfeld 1899), both of which he placed in the Leiosphaeridae. The paleobotany of both Tasmanites and Leiosphaerida have been discussed by Eisenack (7). It would appear that the relationship between Pachysphaera and Tasmanites is closely paralleled by Bottryococcus braunii which is sometimes found in vast quantities in the Coorong in South Australia and in certain lakes in Siberia. In the case of Bottryococcus, the Permian alga responsible for the torbanites of Scotland and Australia so closely resembles its present day counterpart that palaeobotanists cannot justify a separate genus and have decided to retain the same name for both. Wall's contention that "Pachysphaera is regarded as a living representative of the fossil genus Tasmanites" would apply equally well to Bottryococcus, which contributes both to the extant Coorongite and to the fossil fuel torbanite.

Isolation of Tasmanite Kerogen

The beneficiation of the organic matter (kerogen) in oil shale by protracted leaching has received extensive study over a long period (4, 12). Usually chemical dissolution and removal of the mineral matter is either weak and ineffectual or is so drastic as to attack the kerogen itself. In the case of tasmanite, however, an initial efficient separation may be achieved by crushing and weak acid leaching followed by systematic screening. As the individual spores are large and of a relatively narrow size range, conventional sieves may be used. Singh (15) gives the extremes as 200-533 μ with a mean diameter of 366 μ .

It is interesting to note that the screen fractions showed the systematic change in properties given in Table 2. The smaller mesh size consists of broken spores, pieces of cuticle, fine silica and clay, whereas the +30 mesh consists essentially in aggregates and adventitious matter.

If gangue be removed as "sink" in an aqueous solution of specific gravity 1.2 and the "float" be screened on a 30, 40, 50, 70, 100 mesh screen system, virtually pure spores may be collected within the -40, +50 mesh size.

TABLE 2

Properties of Tasmanite vs. Particle Size

Screen size	Ash % w/w	Colour of Ash
+30	27	red
-30, +50	41	pink
-50, +70	67	pale pink
-70	88	pinkish grey

Constitution of Tasmanite Kerogen

The organic matter of tasmanite may be divided, from the viewpoint of morphology, into:

1. Entire or nearly entire spores which make up about three quarters of the kerogen.
2. Residual organic matter which, under the microscope, appears as spore fragments, cuticle, vegetal dust and other detritus.

If the spores be removed, the residual organic matter is still oil yielding, although to a lesser degree (about 14 gal/ton), and it is uncertain how much of the non-spore material is made up by contributions from vascular plant remains.

The examination described below was carried out on a sample of "spore case" concentrate which had been prepared, many years previously, by flotation concentration in a ferric chloride solution. The sample, which received no chemical treatment, is referred to hereafter as "the concentrate".

A second quantity of the screened spore concentrate was treated according to the eleven stage purification described by Getzsche, Vicari and Scharer (8). Unfortunately, this prolonged treatment ruptured many spores, but on re-screening a quantity of entire, chemically pure, spores was recovered. Getzsche et al asserted that the purified organic matter was nitrogen and sulphur free and had an elemental analysis corresponding to C = 72.5%, H = 9.2%, O = 18.2%, but one must regard these data of questionable value. Later work by Kurth (11) cast grave doubts on the above analysis and he demonstrated that normal spores had a remarkably uniform composition which is shown in Column IV, Table 3 (even when purified according to Getzsche et al). However, Kurth found that the non-spore organic material was variable in composition and a representative analysis is given in Column III of Table 3.

TABLE 3

Composition of Purified Tasmanite Kerogen (% w/w)

	Range of Spore Material	Non-spore Material	Purified Spore Material	Pure Entire Spores
Carbon	76.9 - 78.8	66.1	78.50	78.10
Hydrogen	9.8 - 10.4	10.2	10.35	10.21
Nitrogen	0.59 - 0.64	1.3	0.64	0.61
Sulphur	4.66 - 5.12	2.0	4.70	5.14
Oxygen (diff)	5.81 - 9.67	20.4	5.81	5.94

Once again one must emphasize that it is imprudent to regard kerogen as a specific substance and, as Cane has pointed out elsewhere (2), it seems extremely improbable that any kerogen has a chemical constitution in the classical sense. Nevertheless, within the accepted definition, these spores, together with much broken material etc., are indeed the kerogen of tasmanite.

Although both the macroscopic and microscopic features of tasmanite might lead one to suspect a chemistry somewhat dissimilar from other shales, this has not been shown to be the case, except for the more important role of sulphur and the nature of the "solubles". Superficial examination of elemental analyses would suggest a "rank" lower than other algal shales, but careful plotting of published data on a Ralston diagram shows no significant trend and, on a S + N free basis, the elemental composition is not abnormal. If, however, one's consideration includes nitrogen and sulphur, it can be seen that the latter element is notably high - organic sulphur exceeds 5% in some samples on a d.a.f. basis. The only other organic rock surpassing this figure is Kimmeridge oil shale [Himms (9)] which, in most aspects, is exceptional.

Tasmanite kerogen which has been concentrated by the flotation/screening technique discussed above is a brown free-flowing powder of specific gravity about 1.09. The ash of the first stage concentrate (flotation/screening) was 24.3%, and, after the prolonged chemical

purification of Getzsche et al (8), this was reduced to 1.1%. The elemental analysis (d. a. f. basis) is shown in Table 3. The concentrate oil yield was 141 gal/ton (U. S.) from which the calculated yield of pure spore material was 186 gal/ton. The oil yield of the spores, purified by the Getzsche method, was 189 gal/ton.

Infra-red examination of the purified de-ashed spores showed absorption maxima corresponding to the normal C-H stretch, C-H bend, carbonyl (ester) and $(CH_2)_n$ rock frequencies characteristic of most kerogens. The benzene/methanol extract spectrum was much the same, except for a strong absorption at 680 cm^{-1} , to which a polysubstituted aromatic structure is tentatively assigned. There were no abnormalities in the spectra of either the kerogen or its pyrolysate except that the latter showed a somewhat more substituted aromatic nature in the $740\text{--}820\text{ cm}^{-1}$ region than other shale oils with which the writer has had experience.

Thermal Behaviour

On heating at the rate of 100°C per hour, the concentrate behaved in a manner similar to other algal shales, although thermal instability occurred at a lower temperature. Noticeable decomposition commenced at $255\text{--}270^\circ$ with evolution of water contaminated with colloidal sulphur and carbon dioxide and, at a somewhat higher temperature, the production of a dank smelling, honey-like viscid material from which crystals deposited on cooling. This early product, which amounted to 3.2% of the concentrate, was unlike true tasmanite oil and it is assumed that it represents portions of the resinous soluble matter mentioned below. It is interesting to note that the concentrate purified by Getzsche's method did not show this varnish-like distillate nor the incipient decomposition at 270°C .

Evolution of tasmanite oil, accompanied by the copious production of hydrogen sulphide, started at about 340°C , reached a maximum at about 430°C and was virtually complete at 480°C . Hydrogen sulphide accounts for nearly half the total sulphur. There was some indication, and this has been noted by previous workers (11), that the initial pyrolysis is dissimilar to that occurring in excess of 340°C , at which temperature oil production starts in earnest.

Although no serious attempt was made to measure the energetics of the pyrolysis, calculation of the kinetics of the oil forming reactions showed a rate constant of $0.21 \times 10^{-4}\text{ sec}^{-1}$ at 350°C , a result strictly comparable with published figures on other shales. The available data did not permit the calculation of activation energies.

When the de-ashed spores were heated to about 350° , there was complete structural collapse and the retort charge was transformed into a bubbling mass of bitumen-like material. This, of course, is the tarry intermediate, characteristic of the penultimate stage (3) of kerogen pyrolysis. Apparently there is sufficient mineral matter in the case of the concentrate to maintain a degree of solidarity, although a coherent mass of coke was obtained.

Tasmanite oil

Table 4 gives the general properties of tasmanite oil which has been produced by gentle pyrolysis of the concentrate, the temperature being maintained below 450° .

* Table 4

Properties of Tasmanite Oil

Specific Gravity @ 15°C	0.854
Refractive Index @ 15°C	1.4684
Tar Acids %	4.5
Tar Bases %	3.2
Sulphur %	2.22
Nitrogen %	0.34
Saturates %	43.9

The oil is a thin brown liquid with a remarkably clinging odour, thought to be connected with the nitrogen bodies rather than sulphur compounds. It is low in wax but high in sulphur, the amount of which, with respect to distillation temperature, goes through a maximum and then decreases. The sulphur bodies are alkyl and aryl thiols, thiophene and more complex substances. As with all materials of this nature, it is difficult to state with certainty how much sulphur in the oil has been formed during pyrolysis from inorganic sulphur and the organic matter, but oils exceeding 2.7% S have been produced from the upper portions of the seam.

The nitrogen compounds (tar bases) are largely alkyl pyridines and quinolines, but another type of nitrogen compound appears present which could possibly be alkaloidal in structure.

This contention is supported by a pronounced physiological reaction when working with the isolated bases. This bio-active material is being examined by another group in this University.

Solubles

The nature of the material extracted by a benzene/methanol mixture is different from that of all other shales so far examined. The extract was a brown resinous varnish-like material (4.1% w/w on the concentrate) unlike the normal waxy or bitumenous extract. An infra-red spectrum showed considerably more aromatic characteristics than usual and it is believed that the extract may consist substantially of portion of the resistant coat discussed by Wall (17). Possibly the extract may, in its present form, be related to abietic acid as early research gave strong indications of retene structures in the dehydrogenated extract.

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Figure 1. Tasmanite Spores