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TASMANITE OIL SHALE

- A PRE-PROPOSAL CONSIDERATION OF A RESEARCH TOPIC

M. SHIBAKA AND G.H. TAYLOR

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CSIRO FUEL GEOSCIENCE UNIT  
PO BOX 136, NORTH RYDE  
NSW, AUSTRALIA, 2113

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## 1. INTRODUCTION

Early in May 1978, Endeavour Resources Limited wrote to CSIRO concerning a possible research project on tasmanite oil shale. The Company subsequently sent about 1 kg (4 lump samples) of shale to CSIRO. These samples have now been examined (supplementing earlier studies by CSIRO on this material) and a brief review has been made of some of the relevant literature. It is emphasized that this report is no more than a preliminary consideration of the problems on which research is required.

## 2. PETROLOGY OF SHALE

Macroscopically the rock is a soft, grey-brown, fissile shale. Microscopically the texture is that of a fine-grained, well-bedded shale in which are set the disc-shaped *Tasmanites* bodies. The organic matter in the rock is principally tasmanite, that is the material of which the *Tasmanites* bodies are constituted. The tasmanite is not randomly distributed but appears to be concentrated in certain beds of the shale, between which the shale is comparatively poor in organic matter.

### 2.1 Inorganic material

Most of the fine-grained mineral matter appears to be clay and quartz in grains up to at least 200  $\mu$  across, with pyrite framboids of micron to ten-micron size. In the samples examined some of the framboids are partly or wholly altered to iron oxides. Carbonate, probably calcite, was observed in crushed granular material but not in situ.

### 2.2 Organic matter

Three distinct types of organic matter are present. Tasmanite is easily the most abundant of these, typically in disc-shaped bodies about 300 to 400  $\mu$  across and 30 to 50  $\mu$  thick. The other materials, present in quite

small amounts, are the coal macerals vitrinite and inertinite. The vitrinite has a low reflectance indicating that, in coal terms, the "rank" would be that of a brown or sub-bituminous coal.

The *Tasmanites* bodies were formerly globular, now compressed to double-walled discs, each wall being of the order of 20  $\mu$  thick. There is no evidence of any organic matter derived from the internal parts of the bodies. There seems no reason to doubt the widely accepted view that the bodies were of algal character.

Tasmanite is yellow to orange, translucent and optically anisotropic - all properties common to exinite in coals of equivalent rank. Similarly, the tasmanite shows very bright yellow-green fluorescence with blue light excitation, confirming the low "rank" of the shale, and indicating that the tasmanite was not significantly oxidized before burial.

### 3. CONCENTRATION OF ORGANIC MATTER BY PHYSICAL METHODS

Part of the recently acquired sample was crushed to -60 mesh and treated in an "Agitair" froth flotation cell, using a standard frother and collector. An orange coloured concentrate very rich in tasmanite was readily collected. This result is encouraging since the samples had been exposed to oxidizing conditions, on the evidence of the oxidized pyrite. Exinite, and presumably tasmanite, is not readily wet by water and also not much affected by mild oxidizing conditions, except in an alkaline environment. It was mentioned by Mr R. Jessop (of the Company) that normal crushing tended to force quartz grains into the comparatively soft organic matter. Other means of liberating the organic matter, such as the use of mild acid conditions with ultrasonic agitation, have been considered but not attempted.

Means of separating the comminuted shale, other than froth flotation, have been discussed and tried elsewhere (e.g. by Cane (1968)). The separation of the organic matter by screening and by methods depending on density contrast appears feasible. Whether one of these techniques, or froth flotation, or some combination is most suitable could be decided only after systematic testing, with analysis of the products. The separation methods used would be influenced by the processes to which the organic matter would be subsequently subjected.

Possible approaches to processing could be based on the preparation of two or more concentrate grades rather than a single one.

#### 4. CHEMISTRY OF ORGANIC MATTER

No new chemical work has been carried out on the recently acquired samples. However, earlier work in CSIRO and by other workers provides some useful information.

The very small amount of organic matter not attributable to tasmanite could be expected to have similar chemical constitution to brown coal and is not further considered here.

According to Cane (1974) in his bibliography of tasmanite, it is generally agreed "that tasmanin is essentially a complex carboxylic lipid derived polymer". A variety of chemical species, alkanes, cyclic and aromatic compounds have been recognized. The probable predominance of alkanes is consistent with the remarkably high hydrogen content quoted by Cane (1968) for the composition of pure entire "spores":

	%
C	78.10
H	10.21
N	0.61
S	5.14
O (diff.)	5.94

The sulphur figure in this analysis is also remarkably high. This figure would certainly need checking since so much sulphur must influence the range of processes to which the organic matter could be subjected, and the properties of the resulting products. Microscopic observation shows the presence of some fine pyrite within tasmanite but further work would be needed to discover whether this could account for any significant part of the alleged "organic" sulphur.

Like all such kerogen and coaly material the tasmanite is a complex mixture of organic compounds (Brooks (1971); Combaz (1971)). Some of these can be extracted with organic solvents and are therefore present more or less in the free state; most of the substance is not extractable under mild conditions.

When the organic matter is heated in the absence of air to 500°C a wide range of pyrolysis products is formed in the resulting "tasmanite oil" for which Cane (1968) gives some properties and analytical data. No work seems to have been done on solvent refining or hydrogenation of tasmanite.

## 5. DISCUSSION

There seems little doubt that concentration of tasmanite by physical means would be feasible and effective. Probably froth flotation with screening would enable a reasonably low-ash concentrate, with possibly a "middlings" fraction, to be obtained. The possibility of concentration therefore seems well worth considering, especially if it is intended to produce bitumen-like material. It is desirable to avoid or minimize the later separation of mineral matter from viscous tar or bitumen.

Rather more information on the chemistry of the tasmanite is needed. Saxby (1976), in this laboratory, has given the most up-to-date and comprehensive account of methods of chemical separation and characterization of organic matter from oil shale. Almost regardless of the chemical constitution of tasmanite, its high hydrogen and low oxygen contents combine to make it a potentially valuable resource. The limited probable size of the deposit (at least 26 million tons, according to Mr Jessop) discourages consideration of the shale as a major resource for the production of liquid fuels. The suggestion of making bitumen for road use seems well worth exploring. For this purpose the high sulphur content of tasmanite may be little or no disadvantage.

The simplest treatment which could be envisaged is that of retorting the shale and recovering one or a series of pyrolysis fractions, some of which could be suited to the production of useful products such as bitumen. Since some of the organic matter would also remain behind as residue the actual yield of useful products may not be very high. Such a residue may be useful as fuel, however.

An alternative approach worth considering is to treat the organic matter in a manner analogous to that used in the solvent-refined coal process. It has been shown in various small-scale plants around the world that most coals, from brown to bituminous, can be processed in this way. The concentrated

organic matter would be treated under pressure at temperatures of, or approaching 400°C with recycle oil, which could probably be obtained from the shale itself. No added hydrogen or catalyst is used. The resulting product is a pitch-like material, solid at room temperature, which softens and melts at 150° to 200°C. A somewhat related process, solvolysis, uses petroleum pitch as the solvent and the reaction is carried out at atmospheric, rather than elevated, pressure. No testing of this kind is known to have been conducted on tasmanite but it seems reasonable to expect that it would behave like low rank coal during this treatment. It is also probable that the properties of the solvent-refined product could be controlled within limits by using different solvents and different conditions of temperature and pressure. Possibly oil derived from the pyrolysis of low grade shale could be used as a solvent. As in the case of solvent-refined coal from high-vitrinite, low-mineral coal prepared for use as an additive in making metallurgical coke, there may be no need for any filtration or separation of a residue after processing. It may also not be necessary to recover the solvent.

Other approaches can be envisaged. For example, the tasmanite shale could conceivably be used to prepare a liquid product for use elsewhere in the solvent treatment of coal. Another area of interest is that of pipe-coating enamels which in the past have been produced from coal tars. Some of our colleagues (notably Mr J.W. Smith) have carried out research in this area, and also on the properties of road tars and binders.

## 6. RECOMMENDATIONS

Unless studies have been made of which the writers are unaware, the following work is necessary before any informed decision can be taken on the future use of tasmanite shale:

1. The deposit needs to be thoroughly characterized using fresh core material from representative sampling sites, using a ply-by-ply examination for at least some cores. Studies would need to be
  - (a) Microscopic (including electron and fluorescence microscopy), supplemented by X-ray diffraction where necessary to assess the mineral content.
  - (b) Chemical, both to assess the organic content and composition of various samples and to understand better

the nature of tasmanite through the use of separation and characterization procedures.

2. The best means of concentrating the tasmanite from the shale needs to be established. Froth flotation, density separation and screening need to be tested alone and in combination to determine the simplest and most effective means of providing concentrates.
3. Small-scale pyrolysis tests need to be carried out to determine the nature, composition and properties of various pyrolysis fractions. (In these and other tests the products should be characterized with possible uses, such as road bitumen, in mind.
4. Small-scale solvent-treatment tests need to be carried out at elevated temperatures and at various pressures.
5. Small-scale hydrogenation tests need to be carried out at elevated temperatures and pressures.
6. In the light of results from 1 to 5 above, it may be necessary to carry out batch or continuous tests as needed to proceed towards large-scale treatment.

((1) to (5) of these recommendations lie within the scope of the Fuel Geoscience Unit but (6) does not. However, it is most probable that arrangements for larger scale testing could be arranged in collaboration with the Unit if necessary.)

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