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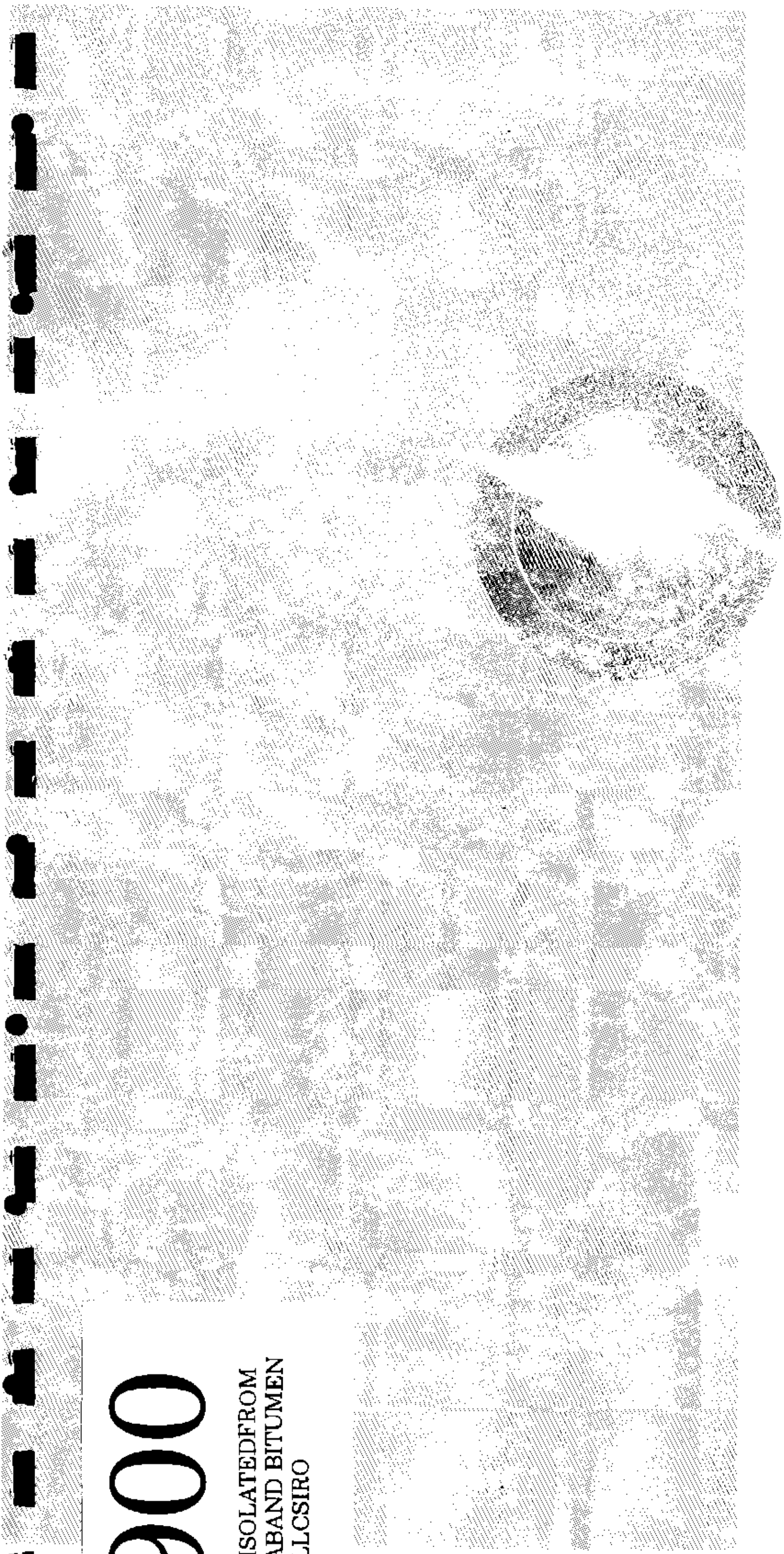

Hydrocarbons Isolated from Lanna Vale Seep Swab and Bitumen Samples.

A. T. Revill

Client:
Carol Bacon, Tasmanian
Development and Resources:
Industry Safety and Mines

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1 Introduction

1.1 Background

Reports of a possible hydrocarbon seep in a recently used quarry at Lanna Vale, south west of Hobart, led Tasmanian Development and Resources (TDR) to contract CSIRO Division of Oceanography to analyse two samples of possible hydrocarbons.

The quarry is based on a Jurassic dolerite deposit which has a possible contact with Permian mudstone (see Appendix 1), which are exposed in a nearby older quarry and are known in other areas of Tasmania to contain the tasmanite oil shale. Thus there is significant interest in assessing if the seep is in fact hydrocarbons and if so whether they are related to the tasmanite oil shale.

2 Methods

2.1 Samples

Two samples were collected from the quarry. One was a swab, using pre-extracted defatted cotton wool, to sample what appeared to be hydrocarbon staining. The second sample was a bitumen from within a fracture in the dolerite. The bitumen was solid but still pliable.

2.2 Analysis

The samples were placed in a small amount of hexane and the extract was then transferred to a silica gel chromatographic column. Aliphatic hydrocarbons were eluted with hexane and the aromatic hydrocarbons with 20% dichloromethane in hexane. The eluates were reduced under vacuum and transferred to vials. The aliphatic fractions were then analysed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) using a non-polar capillary column (HP-1, 50m x 0.32 mm 0.17 µm phase thickness and cool on-column injection. GC conditions were an initial temperature of 40 °C held for 1 minute and then increased at 30 °C/minute to 120 °C and then at 4 °C to 310 °C and held isothermally for 15 minutes with hydrogen as the carrier gas. Typical GC-MS conditions were as above except helium was the carrier gas. The MS was operated in either full scan or selected ion monitoring (SIM) mode, using electron impact (EI) ionisation at 70 eV.

3 Results

3.1 GC Analysis

Figure 3.1 shows the GC chromatograms of both samples. The swab sample exhibits a n-alkane profile from n-C$_{14}$ to n-C$_{32}$ maximising at n-C$_{18}$, which is similar to that of a light oil or refined fraction such as diesel. In contrast, the bitumen chromatogram is dominated by resolved compounds which are not n-alkanes.

3.2 GC-MS Analysis

Examination of the m/z 191 mass chromatogram to highlight cyclic triterpenoids for the samples (Figure 3.2) shows them both to exhibit the same profiles.

Both chromatograms are dominated by a pattern characteristic of tricyclic compounds and not the more usual hopanes. The m/z 217 mass chromatogram (Figure 3.3) shows that steranes are present in the samples, though at relatively low levels. Molecular data from these analyses are summarised along with data from previously analysed tasmanite samples in Table 3.1.

Table 3.1: Molecular data for Lanna Vale seep samples and previous tasmanite samples.

	Parameter			
Sample	1	2	3	4
	Pr/Ph	Pr/n-C$_{17}$	20S/S+R	αββ/αββ+ααα
Lanna Vale Seep				
"Swab"	0.48	0.16	0.57	0.62
Bitumen	n.d.	n.d.	0.61	0.70
Latrobe	0.45	0.62	0.11	n.d.
Oonah				
Upper Seam				
Total	1.6	0.69	0.30	0.15
Fossil Concentrate	1.5	0.60	0.35	0.15
Lower Seam				
Total	1.4	0.48	0.31	n.m.
Siltstone	3.1	0.91	n.m.	n.m.
Douglas River	0.7	0.45	0.54	0.5

n.d. = not detected; n.m. = not measured

parameters:

1. Pristane/Phytane
2. Pristane/n-C$_{17}$
3. C$_{29}$ ααα sterane 20S/(20S + 20R)
4. C$_{29}$ αββ 20R sterane/C$_{29}$ 20R (ααα + αββ) steranes

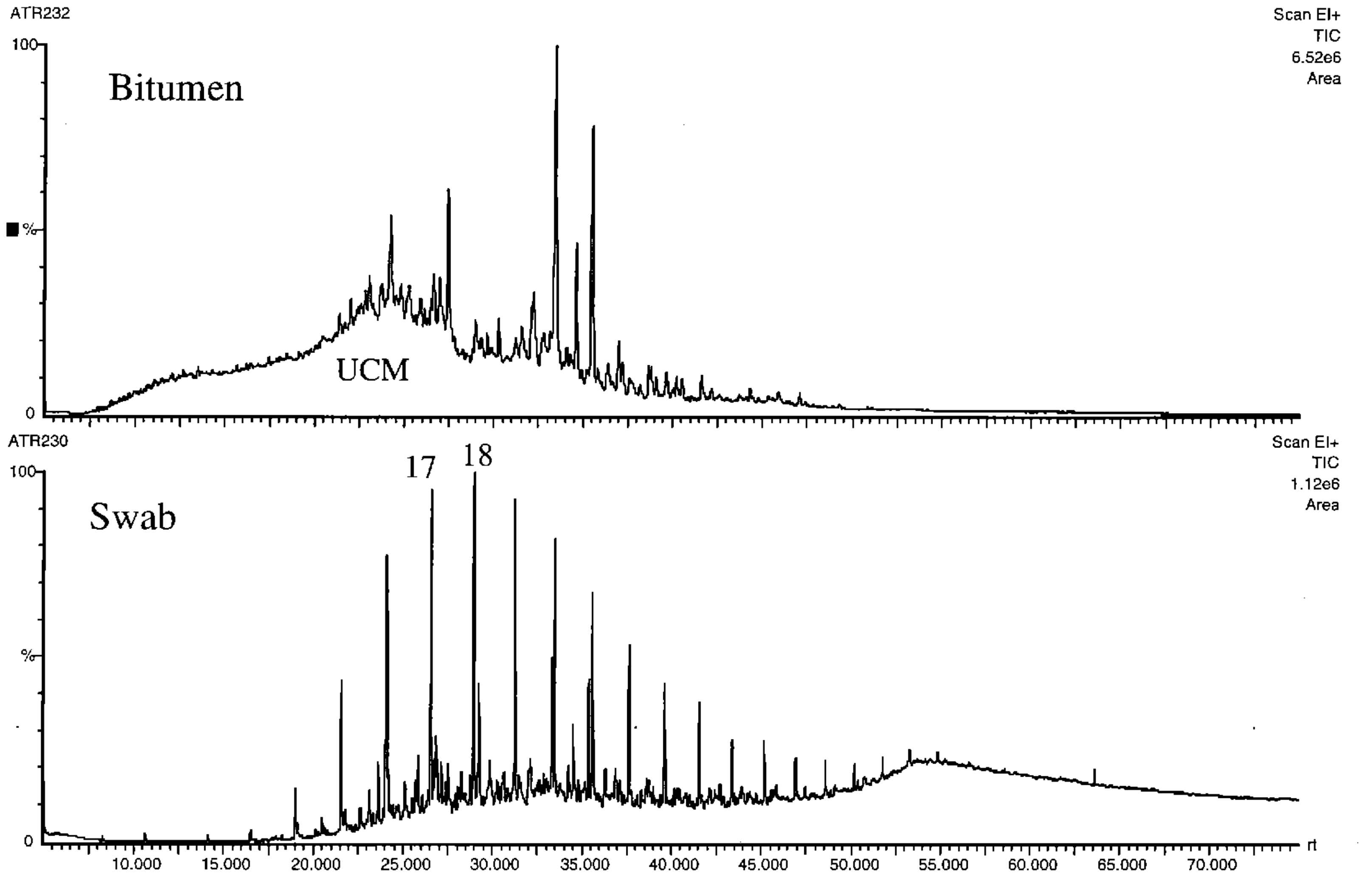

Figure 3.1: Chromatogram of the Lanna Vale Seep Aliphatic Fractions (numbers refer to carbon number; UCM = Unresolved Complex Mixture).

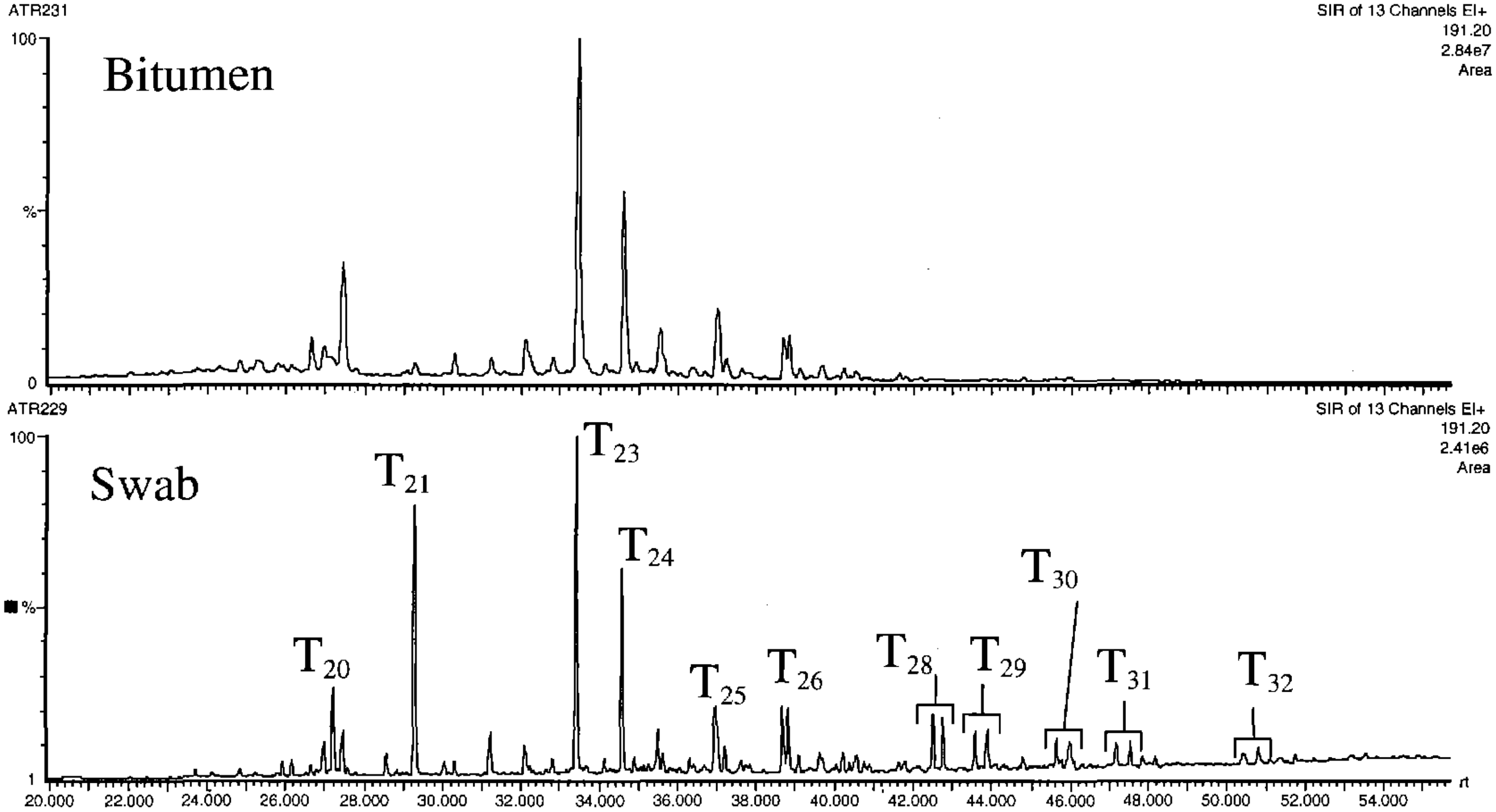

Figure 3.2: *m/z* 191 mass chromatogram showing the distribution of cyclic triterpanes in the Lanna Vale samples. (Note T_n = Tricyclic compounds where n = carbon number)

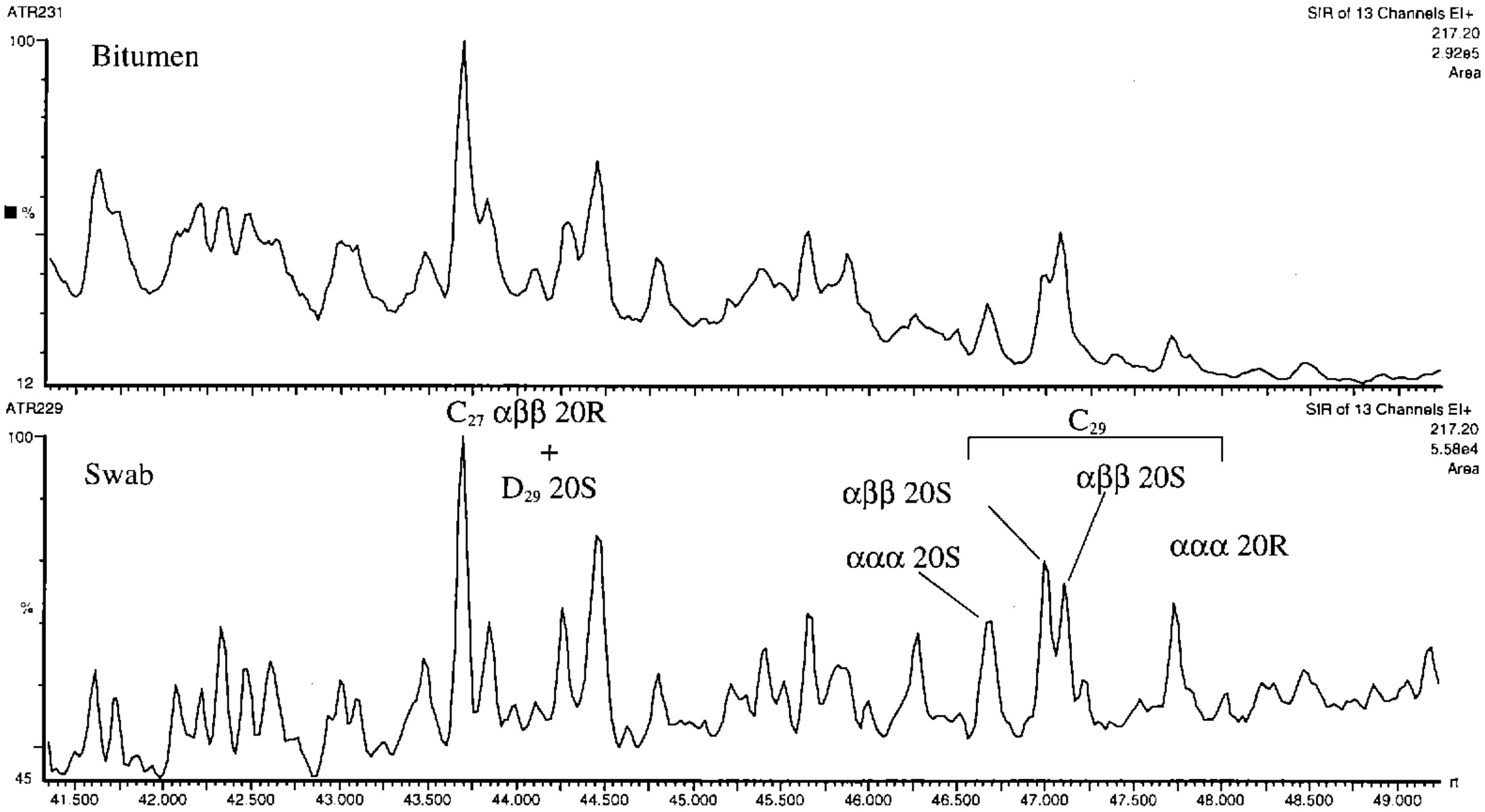

Figure 3.3: *m/z* 217 mass chromatogram showing the distribution of steranes in the Lanna Vale samples. (Note numbers refer to carbon number; D = diasterane; 20S and 20R refer to stereochemistry at carbon 20; α and β refer to stereochemistry at carbons 5, 14 and 17)

4 Discussion

4.1 Aliphatics

The aliphatic fractions of the two samples exhibit some marked differences, most noticeably the presence of a *n*-alkane envelope in the swab sample which is absent in the bitumen. The *n*-alkane profile isolated from the swab sample (Figure 3.1) is characteristic of a light oil or petroleum fraction such as diesel. This is also in keeping with the visual observation made at the time of collection, that this sample was a "stain" and had a more liquid character than the bitumen. This *n*-alkane profile is similar to that expected for hydrocarbons generated from tasmanite. For example in a study of tasmanite samples of increasing maturity (Revill *et al.*, (1994), it is noticeable that there is an increase in these low molecular weight *n*-alkanes. The potential for this to be due to contamination of this sample is unlikely as there is a co-occurrence of abundant tricyclic alkanes (Figure 3.2). This type of profile is characteristic of tasmanite and any diesel contamination would be expected to be accompanied by at least a trace of regular hopanes. The lack of such a n-alkane profile in the bitumen sample could be due either to severe weathering/biodegradation or a different source material.

Interestingly, in none of the samples of tasmanite analysed to date has there been such a well developed *n*-alkane profile, suggesting that this may be the most thermally mature sample of tasmanite derived hydrocarbons analysed so far.

4.2 Maturity Parameters

The suggestion that these samples are thermally mature is further supported when comparing the molecular data for the swab sample with the previous tasmanite samples analysed (Table 3.1). Parameters 3 and 4, which are indicators of thermal maturity, clearly show a trend from the least mature sample (Latrobe 0.11 and n.d. respectively) through to the most mature (previously) from Douglas River (0.54 and 0.5) and this trend appears to be extended by the swab sample (0.57 and 0.62) and the Bitumen (0.61 and 0.70). Indeed, it would appear from this data that the bitumen may be an "over mature" sample and may have been generated at temperatures corresponding to the late oil window.

4.3 Tricyclic Hydrocarbons

The tricyclic profiles (Figure 3.2) again show significant differences between the two samples. The swab sample exhibits a distribution extending from C_{20} up to C_{32} compounds which is very similar to that seen previously in samples of tasmanite (Revill *et al.*, 1994). In contrast, however, the bitumen sample shows a much more restricted distribution, extending only to C_{26} compounds and with an apparent lack of C_{20} and C_{21} compounds. It is unclear as to why this may be the case, except that the loss may again be due to extra heating of the bitumen compared with the swab sample, which may have led to side chain cracking. Literature reports suggest that maturation may lead to enhanced generation of the lower tricyclic homologues (Peters *et al.*, 1990) but there is no indication that this is due to cracking of the higher homologues. In addition, these compounds have been reported to be extremely resistant to biodegradation (Palacas *et al.*, 1986).

4.4 Source of the Hydrocarbons

From the analyses performed, it is clear that while the bitumen and swab sample may have been derived from similar source material, there is evidence that they may have undergone different heating events or some other alteration leading to the bitumen appearing to be thermally more mature, namely:

- A lack of *n*-alkanes in the aliphatic fraction (not necessarily maturity derived)
- A higher calculated thermal maturity from sterane data
- A restricted tricyclic profile.

It is unclear as to how this difference may have come about, but there are clearly at least three possibilities:

1. The source material, assumed at this point to be the Permian mudstone, was buried to a depth which caused some oil generation. There was then a period of time when burial was insufficient to mature the organic matter followed by a second burial, possibly deeper which led to further generation from previously unmatured material and the over-maturation of the hydrocarbons previously generated.
2. Hydrocarbons have been generated by a heating event and then have migrated into the dolerite. The rate of migration has been such that hydrocarbons which initially migrated have been severely biodegraded due to exposure to the atmosphere which in extreme cases can lead to an artificially high maturity assessment. Subsequent to this "fresh" hydrocarbons have migrated into the dolerite and so the two co-exist.
3. The intrusion of the dolerite into the Permian mudstone caused localised heating of the source material which is analogous to natural thermal maturation and therefore causes hydrocarbon generation. It is well known that where intrusions such as this have occurred, the organic matter closest to the contact will become more thermally mature than the material further away. The extent and degree of maturation will depend on the temperature of the intrusion and the distance away from the contact that the heat permeates.

The likelihood of point 1 can really only be assessed by an investigation of the local geology, but given what is know so far, this option appears unlikely. Options 2 and 3 are more difficult to assess. Indicators of severe biodegradation such as changes to hopane and sterane distributions, are present in only low concentrations in hydrocarbons generated from tasmanite. There is also little or no literature on the effects of over maturation or biodegradation on the tricyclic distribution, which makes it difficult to assess the likely effects of a dolerite intrusion or prolonged exposure to the atmosphere.

5 Conclusions

Analysis of the two samples from the Lanna Vale seep has shown the following:

- The hydrocarbons in both samples share a similar source
- The source is likely to be Permian mudstone containing tasmanite
- There appears to be maturity differences between the two samples. The reasons for this are unclear at present.

6 References

Palacas, J. G., Monopolis, D., Nicolaou, C. A., and Anders, D. E. (1986) Geochemical correlation of surface and subsurface oils, western Greece. *Org. Geochem.* **10,** 417-423.

Peters, K. E., Moldowan, J. M., and Sundararaman, P. (1990) Effects of hydrous pyrolysis on biomarker thermal maturity parameters: Monterey phosphatic and siliceous members. *Org. Geochem.* **15,** 249-265.

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Appendix 1

Geological setting of the Lanna Vale seep

(Prepared by TDR)

THE LONNAVALE OIL SEEP

This area was visited briefly late in 1996, following reports by bushwalkers of an unidentified mineral occurrence.

The location (~ 482700mE 5247800mN) is a recently-used quarry, presumably used by the Forestry Commission to supply road metal to recent logging roads in the area. It is on the Russell Road, about 6km NW of Lonnavale.

The quarry is located in fine grained Jurassic dolerite, close to a contact with fossiliferous Permian mudstones, which are well exposed in a small, older, quarry about 300m to the south east. The contact is probably faulted, and the Lonna Creek, striking NE, on the NW side of the quarry may be related to this fault.

The dolerite exhibits two generations of fractures and breccia veins, probably fault related: the earliest are approximately vertical, striking about NE, and the later veins dip ~45° and strike about NW. The earlier veins contain laumontite, calcite and (?)pumpellyite. The later veins are more complex and vuggy, containing coarsely crystalline calcite (to 10cm), with finer grained, partly crystallised pyrite, heulandite, laumontite, chabazite, and stilbite with montmorillonite and fine grained serpentine, prehnite and pumpellyite(?).

Bitumen also occurs in the later vein set, and is abundant in some samples. It is dark brown to black, vitreous, soft and sticky when fresh, but hardens and darkens to dull black on exposure to air. It leaves oil stains on paper readily, indicating a moderate content of moderate molecular-weight hydrocarbons. The bitumen exhibits an irregular to globular habit in some samples, up to 2cm in size, and is partly intergrown and partly veined and overgrown by calcite and zeolites, indicating contemporaneous formation and a natural origin.

Ralph Bottrill