

Hydrocarbon composition and origins of coastal bitumens from the Northern Territory, Australia

Roger E. Summons¹, John Bradshaw¹, Deirdre M. Brooks², Angus K. Goody², Andrew P. Murray¹ and Clinton B. Foster¹

1. Onshore Sedimentary and Petroleum Geology Program, Australian Geological Survey Organisation, GPO Box 378, Canberra, Australia, 2601
2. BHP Petroleum Pty Ltd, 120 Collins St, Melbourne, Vic., Australia, 3000

Keywords: coastal bitumen, Australia, Northern Territory, biomarkers, diagnostic hydrocarbons, natural oil seeps, oil pollution

Twenty-two coastal bitumens from the Northern Territory were analysed for diagnostic biomarker hydrocarbons. The bitumens fall into three distinct types or families. Within two of these families only minor compositional differences were found and these are attributed to varying degrees of degradation and weathering. The third family was represented by a single sample.

The majority of samples are waxy bitumens derived from a lacustrine source rock and are very similar in composition to the Tertiary lacustrine oils of central Sumatra as exemplified by the Minas oil. These samples appear to be the same as the commonest bitumen occurring along the southern coast of Western Australia and the coastlines of South Australia, western Victoria, northern Tasmania, western Tasmania, and the islands of Bass Strait. A sample collected from the Cobourg Peninsula in 1972 was of a similar lacustrine type pointing to a history of strandings for oils from a common source type. A fossil pollen entrained in a sample of one bitumen specimen was identified as belonging to the genus *Proteaceae*, Sub-family *Grevilleoideae*, Tribe *Grevilleae* and is no older than Late Cretaceous (Maastrichtian) age. This finding indicates that the bitumen has been in contact with Late Cretaceous or Tertiary carrier and/or reservoir beds and is consistent with the biomarker evidence for a Late Cretaceous or Tertiary age source rock.

The second family were oils of predominantly marine origin and likely sourced from a Mesozoic or Cainozoic carbonate sediment. One outlier sample was a marine oil from a probable mixed clastic and carbonate source rock. It was the only sample with significant concentrations of lower molecular weight *n*-alkanes and was distinctive in having an overt signature of C₁₈-C₃₃ monomethyl alkanes.

The size and compositions of the bitumen samples showed a strong geographic bias. Lacustrine waxy samples were mainly found in the east of the survey area from Elcho Island to Croker Island. These were often found as large sheets and were predominantly on west-facing rock platforms. Marine carbonate-derived bitumens, including all the specimens from Bathurst and Melville Islands, were predominant in the west, and these were generally smaller samples from cryptic habitats.

Introduction

The recorded occurrence of bitumen on beaches and rocky headlands in northern Australia dates back to at least 1922 when Reverend Jennison reported a deposit on a beach near Elcho Island Mission (Wade 1924). This was described as 'flat cakes filling lenticular cavities in the flaggy beds'. In the early 1920s several shallow bore holes were drilled in response to these occurrences, and as recently as 1984 other visitors to the area described the bitumen as being sourced *in situ* from the surrounding Palaeozoic and perhaps even Proterozoic sediments. This conclusion was reasonable given the petroleum potential of the Palaeozoic Arafura Basin, especially in the immediate offshore regions (Bradshaw et al. 1990). Here, oil-mature Middle Cambrian sediments with total organic carbon (TOC) contents of over 8% were encountered and over 400 m of continuous oil shows occurred in Ordovician and Devonian sediments in the Arafura-1 well. In contrast, McKirdy and Horvath (1976) analysed a stranded bitumen from 300 km to the west of Elcho Island and suggested it was sourced from a Cretaceous or younger sequence. Because of the weathering patterns and the fact that the Mesozoic sediments in the immediate region are immature, a long distance sub-surface migration from the west to the east was proposed by these authors.

The geochemical analysis of oils, and thus coastal

bitumen, is a proven means of determining the nature of petroleum source rocks. McKirdy and Horvath (1976) and McKirdy et al. (1986) appear to have been the first in Australia to attempt a prediction of the palaeoenvironmental setting, geological age and likely geographic locality of an oil's source beds solely from clues contained in its hydrocarbon composition. They also appear to have been the first to use the predictive power of hydrocarbon signatures as an aid to exploration in identifying Early Cretaceous sediments of the Otway Basin as the possible source rocks for the Otway Basin-type coastal bitumens.

In the years since these pioneering studies there has been a major advance in our understanding of the origins of specific hydrocarbon biomarkers and their use as markers for source rock age, lithology and depositional environment. The state of the art in this field was summarised recently by Peters and Moldowan (1993). Application of the new knowledge and improved analytical techniques to the bitumens found along the southern continental margin (Volkman et al. 1992; McKirdy et al. 1993) and those found along the southeast and southern coastlines of Western Australia (Currie et al. 1992) has led to a radical revision of ideas concerning their geographic origins. The identification of biomarkers for angiosperms, including some normally associated with tropical hardwoods of the family *Dipterocarpaceae*, in the waxy lacustrine bitumens

appears to preclude a local origin for most of the bitumens (Currie et al. 1992). This, and the close similarity of these bitumens to some oils of Southeast Asia led Currie et al. (1992) to propose long distance transport on ocean currents as a mechanism to explain their occurrence along the southern Australian margin.

Volkman et al. (1992) studied bitumens found on the Tasmanian coastline between 1880 and 1915, and archived in local museums. They reported a second distinct family of asphaltic bitumens that most likely originated from marine source rocks. Padley et al. (1991) and McKirdy et al. (1993) have reported results of a systematic evaluation of present-day South Australian and western Victorian occurrences and found that Families 1 to 3, originally described by McKirdy et al. (1986) are, in fact, variants of the waxy lacustrine type. Family 4 is distinctly different and its representatives are dense asphaltic bitumens of marine origin, identical to the Tasmanian museum samples. Thus, it seems that present-day bitumen strandings on the

southern margin consist of material transported from Southeast Asia as well as a distinctive asphaltite of marine, and possibly local, origin.

The present study was conducted as a joint Australian Geological Survey Organisation-BHP Petroleum project to determine the characteristics of bitumens occurring along Australia's northern coastline and to examine whether or not any samples could have originated in the Arafura Sea, Timor Sea or Southeast Asian sedimentary systems.

Experimental section

Helicopter traverses of beaches and headlands between Elcho and Bathurst Islands resulted in the collection of 22 samples from the localities shown in Figure 1.

Sub-samples of the bitumens were separated into saturated, aromatic and polar fractions by chromatography on activated silica gel. Approximately 100 mg of each dissolved in a minimum of dichloromethane was placed on

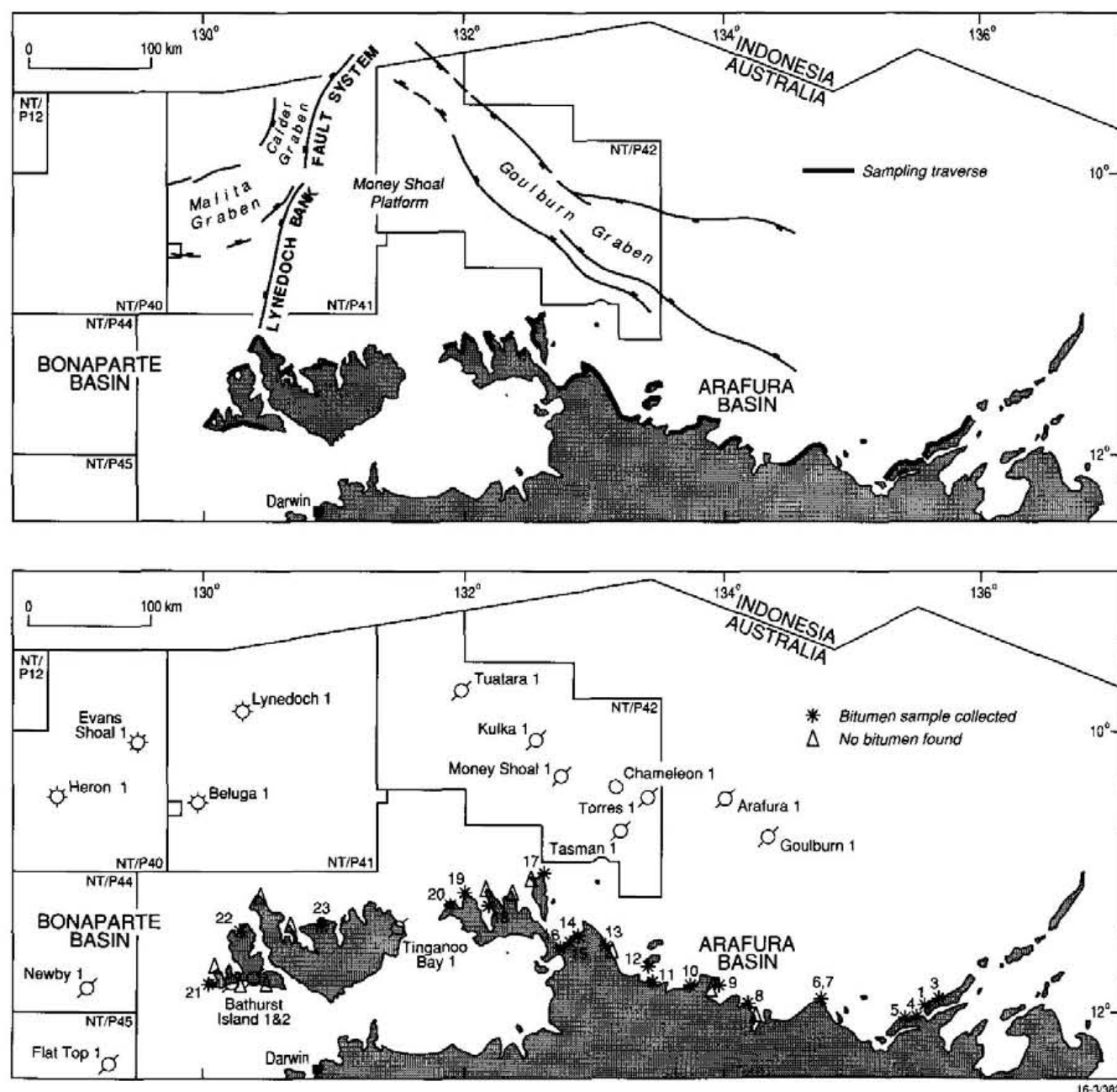


Figure 1 — The course of helicopter traverses for bitumen sampling and the sites where bitumen was found.

a 12 g silica gel column (pre-washed with petroleum spirit) and three fractions were collected (in a 100 ml round bottom flask) by eluting the column with:

- | | |
|--|-----------|
| (a) 40 ml petroleum spirit | Saturates |
| (b) 50 ml petroleum spirit/dichloromethane (1:1) | Aromatics |
| (c) 40 ml chloroform/methanol (1:1) | Polars |

Following reconcentration, the weight percentages of non-volatile saturated, aromatic and polar fractions were determined by gravimetry and the saturated fractions were analysed by gas chromatography (GC) and gas chromatography-mass spectrometry (GCMS).

GC analysis was carried out on the saturated hydrocarbon fractions using a Hewlett Packard (HP) 5890 GC equipped with a HP automatic on-column injector and a fused silica capillary column (25 m × 0.2 mm) coated with cross-linked methylsilicone (HP Ultra-1). The samples, in hexane, were injected on-column at 50°C and the oven programmed to 300°C at 4°C/min with a hold period of 30 minutes. The carrier gas was hydrogen at a linear flow rate of 30 cm/sec. An internal standard (3-methylheneicosane; 10 ng/mg of saturated hydrocarbons) was added prior to analysis.

GCMS analysis was carried out using a VG 70E instrument fitted with a HP 5790 GC and controlled by a VG 11-250 data system. The GC was equipped with an HP Ultra-1 capillary column (50 m × 0.2 mm) and a retention gap of uncoated fused silica (0.2 m × 0.53 mm). The samples, in hexane, were injected on-column at 50°C and the oven programmed to 150°C at 10°C/min then to 300°C at 3°C/min with a hold period of 30 minutes. The carrier gas was hydrogen at a linear flow of 30 cm/sec. The mass spectrometer was operated with a source temperature of 240°C, ionisation energy of 70 eV and interface line and re-entrant at 310°C. In the full scan mode the mass spectrometer was scanned from m/z 650 to m/z 50 at 1.8 sec/decade and interscan delay of 0.2 sec. In the multiple reaction monitoring (MRM) mode, the magnet current and ESA voltage were switched to sequentially sample for 26 selected parent-daughter pairs including one pair (m/z 389 → 234) for the trideuterated methyl sterane internal standard (100 ng/mg saturated hydrocarbons). The sampling time was 40 ms per reaction with 5 ms delay giving a total cycle time of 1.3 sec. Some samples were analysed using a 30 m × 0.33 mm J&W DB-5 column using helium as a carrier gas at a linear flow of 30 cm/sec.

A sample of bitumen (no. 625) was triturated with CH_2Cl_2 , CH_3OH and insoluble material, including kerogen, isolated by centrifugation. The kerogen was mounted in Eukitt media on glass slides for routine palynological analysis using transmitted light and fluorescence microscopy. At no stage was heat used during the preparation.

Results and discussion

Habitat and appearance of bitumen occurrences

Bitumen was found in a variety of settings and adhering to different substrates including Middle Proterozoic sandstones of South Goulburn Island, Cambrian sandstones and siltstones which form the wave-cut platforms of Elcho Island and Howard Island, Cainozoic to Recent pisolitic and lateritic wave-cut platforms along the Arafura mainland coastline and on Elcho Island, Croker Island and Melville Island. It was also found on beaches and foredunes in sand and adhering to boulders along the beaches. There was a strong tendency for bitumen to occur

on western and northern facing headlands as opposed to those facing south or east. There was also variation in the degree of preservation. Small samples on very exposed surfaces were generally hard and of a dry, weathered appearance while larger ones, particularly several found in protected crevices, were soft and had retained some volatile components. The local people of Goulburn Island described seeing masses of soft bitumen washed ashore with seaweed and reported strandings occurring over generations. The variety of settings and habitats indicates that the bitumens have been ocean transported and are not seeps from outcropping strata.

Most of the samples in the present study had lost their more volatile components with few having *n*-alkanes smaller than *n*-C²². Hence, they were very weathered compared with the majority of South Australian specimens analysed in our laboratory (see McKirdy et al. 1993). This could be due to a number of factors such as an origin from a reservoir of moderately biodegraded oil, accelerated weathering in warm tropical waters or prolonged exposure to the tropical climate after stranding. It would not be easy to distinguish between these factors or to identify them in combination. For an unbiodegraded light oil, the result of exposure to seawater at tropical temperatures is predicted to be rapid disintegration and evaporation (Kagi et al. 1988). A waxy oil capable of forming solidified tar balls could be expected to weather more slowly as only the surface layer of hydrocarbons can be directly abraded or biodegraded. Given that larger pieces of bitumen are known to survive in the ocean for periods of a year or more (Blumer et al. 1973; Butler et al. 1976; Lee 1980) and apparently survive oceanic weathering during transport from Southeast Asia to southern Australia (McKirdy et al. 1993), it appears likely that the advanced state of weathering and desiccation of the northern Australia samples is due to prolonged exposure to the tropical environment after stranding on a solid substrate.

Geochemical characteristics of the bitumens

The marked variation in proportion of saturated, aromatic and polar components within the sample suite (Table 1) is mainly attributed to the effects of weathering, the low molecular weight (MW) saturated and aromatic hydrocarbons being most prone to evaporation and biodegradation. Low MW aromatics are also easily lost through their preferential solubility in water compared to aliphatic hydrocarbons. Hence paraffin content or aromaticity cannot be used to directly classify these bitumens. However, gravimetric analysis shows that some samples have up to 80% saturated hydrocarbons and combined with the information regarding their relatedness from the GC profiles we can determine that the parent oil would have been highly paraffinic. A majority of the bitumens contained only high molecular weight *n*-alkanes and these showed a slight odd carbon number preference. Most of the bitumens also contained the rare hydrocarbon, botryococcane (Moldowan & Seifert 1980; e.g. nos 615, 619, Fig. 2). The hydrocarbon distribution pattern for these samples closely resembled that of a Northern Territory sample (no. 422, Fig. 3) which had been collected at Cobourg Peninsula 20 years previously (Hughes & Senior 1973), a sample (no. 378) representative of the Otway Basin bitumens, and samples (nos 436, 437) of lacustrine oil from Sumatra. The Pr/Ph ratio could be measured in one sample only (no. 626) and this was 2.2. This value is close to the Sumatra Minas oil (2.5) but higher than the Cobourg Peninsula and most Otway coastline bitumens which had

Hydrocarbons and coastal bitumens, Northern Territory

Sample location	AGSO No.	% Sats.	% Arom.	% Pols.	nC25 /nC33	Pristane /Phytane	Pristane /nC17	Phytane /nC18	Botryococcane /g/mg of sats.
Northern Territory									
Elcho Island	615	39.8	2.7	57.5	1.4	nd	nd	nd	9.4
Elcho Island (northeast)	616	81.6	4.8	13.6	9.1	nd	nd	nd	3.1
Howard Island (Wormi Pt)	617	68.1	10.2	21.7	1.3	nd	nd	nd	12.4
Howard Island (Malga Pt)	618	44.2	1.3	54.4	2.9	nd	nd	nd	7.2
False Point 1	619	57.2	4.3	38.5	nd	nd	nd	nd	19.1
False Point 2	620	34.4	7.9	57.7	1.4	nd	nd	nd	8.4
Hawkesbury Point	621	17.6	2.6	79.9	2.6	nd	nd	nd	5.8
Braithwaite Point	622	36.1	3.9	60.0	2.5	nd	nd	nd	3.9
Cuthbert Point (west)	623	50.0	5.3	44.7	3.8	nd	nd	nd	6.9
Barclay Point	624	34.7	20.3	44.9	0.1	nd	nd	nd	nd
Anymytali Point (south Goulbourn Is.)	625	24.4	6.2	69.4	0.2	nd	nd	nd	7.3
Brogden Point (northwest)	626	28.5	24.3	47.2	1.4	2.2	1.5	0.5	0.8
Malay Bay	627	37.7	10.4	52.0	nd	nd	nd	nd	15.6
Coombe Point	628	53.2	16.8	30.0	nd	nd	nd	nd	10.2
Mountnorris Bay	629	64.9	10.3	24.8	1.9	nd	nd	nd	6.6
Cape Crocker	630	33.6	2.2	64.2	0.1	nd	nd	nd	13.3
Turtle Point	631	28.4	17.4	54.2	nd	nd	nd	nd	23.7
Vashon Head	632	27.2	19.8	53.0	nd	nd	nd	nd	nd
Lingi Point	633	32.2	30.6	37.2	nd	nd	nd	nd	nd
Melville Island (Radford Pt)	675	7.0	33.2	59.8	nd	nd	nd	nd	nd
Melville Island	676	8.1	22.7	69.2	nd	nd	nd	nd	nd
Bathurst Island	677	33.4	32.0	34.5	nd	nd	nd	nd	nd
Reference									
Ardjuna Basin, northwest Java (coal source)	372	50.6	22.8	26.6	3.1	6.6	1.48	0.22	nd
Minas Oil, Sumatra (shale source)	436	73.0	16.0	11.1	3.6	2.5	0.3	0.1	8.4
Cobourg Peninsula (1972)	443	78.2	12.2	9.7	4.2	1.3	1.0	0.3	10.3
Palau Sasuk Daun Seribu	610	68.3	18.3	13.4	3.1	2.8	0.5	0.2	nd
Southeast Hedinia	645	73.1	23.4	3.5	12	3.0	0.2	0.1	nd

Table 1 — Data showing the composition of the oils after liquid chromatographic separation of the different polarity fractions.

Sample location	AGSO No.	1 C ₃₁ H /C ₃₀ H	2 C ₂₉ H /C ₃₀ H	3 C ₃₀ Dia /C ₃₀ H	4 C ₂₉ Neo /C ₂₉ H	5 Ts /Tm	6 Olean /C ₃₀ H	7 Bicad T /C ₃₀ H	8 C ₂₇ St /C ₂₉ St	9 C ₃₀ St /C ₂₉ St	10 C ₂₉ MS /C ₂₉ St	11 C ₂₉ Dia /(S+R)	12 C ₂₉ St S
Northern Territory													
Elcho Island	615	0.40	0.52	0.02	0.59	2.84	0.07	0.43	1.31	0.27	3.63	0.51	0.40
Elcho Island (northeast)	616	0.52	0.53	0.06	1.11	6.01	0.08	0.50	1.31	nd	3.76	0.34	0.61
Howard Island (Wormi Pt)	617	0.41	0.31	0.02	1.07	3.29	nd	0.35	1.32	0.41	8.01	0.45	0.49
Howard Island (Malga Pt)	618	0.38	0.41	0.06	0.40	3.39	nd	0.29	1.64	0.26	5.83	0.46	0.42
False Point 1	619	0.54	0.67	0.20	0.65	4.41	0.09	0.20	0.47	0.31	7.50	0.71	0.51
False Point 2	620	0.50	0.47	0.06	0.60	3.82	0.01	0.27	1.53	0.32	5.88	0.42	0.56
Hawkesbury Point	621	0.36	0.50	0.06	0.29	3.93	0.04	0.38	2.32	nd	7.96	0.57	0.50
Braithwaite Point	622	0.32	0.56	0.03	0.69	6.44	0.08	0.20	1.07	0.28	4.43	0.54	0.34
Cuthbert Point (west)	623	0.45	0.64	0.16	0.69	4.12	0.10	0.09	0.65	0.14	2.28	0.49	0.38
Barclay Point	624	1.03	1.62	nd	nd	0.59	nd	nd	1.10	0.09	0.64	0.16	0.65
Anymytali Point (south Goulbourn Is.)	625	0.60	0.82	0.06	0.23	1.93	nd	0.37	1.17	0.21	2.37	0.32	0.59
Brogden Point (northwest)	626	0.35	0.45	0.09	0.64	1.03	0.27	4.21	1.26	nd	0.46	0.44	0.32
Malay Bay	627	0.43	0.74	0.14	0.68	2.09	0.23	1.33	1.18	0.18	5.00	0.48	0.62
Coombe Point	628	0.56	0.74	0.08	0.77	2.70	0.01	0.47	1.42	0.37	4.62	0.46	0.61
Mountnorris Bay	629	0.55	0.63	0.08	0.59	2.74	0.02	0.32	1.56	0.50	5.72	0.45	0.54
Cape Crocker	630	0.49	0.77	0.16	0.62	3.09	0.04	0.34	1.39	0.34	7.46	0.45	0.73
Turtle Point	631	0.57	0.69	0.17	0.76	1.57	0.04	0.34	0.39	0.10	1.67	0.28	0.57
Vashon Head	632	1.25	0.98	nd	0.20	0.96	0.10	nd	0.91	0.18	0.46	0.26	0.55
Lingi Point	633	1.04	1.54	nd	nd	0.91	0.01	nd	0.71	0.10	0.24	0.23	0.51
Melville Island (Radford Pt)	675	0.90	1.35	nd	nd	0.56	nd	nd	0.33	0.05	0.04	0.09	0.54
Melville Island	676	1.26	2.27	nd	nd	0.54	nd	nd	0.75	0.10	0.40	0.23	0.48
Bathurst Island	677	1.15	1.39	nd	0.50	2.78	nd	nd	0.91	0.12	0.56	0.47	0.54
Reference													
Ardjuna Basin, northwest Java	372	0.59	0.54	0.29	0.28	0.85	0.44	10.14	nd	nd	nd	0.93	0.44
Minas Oil, Sumatra (shale source)	436	0.43	0.45	0.14	0.84	3.29	0.01	0.04	nd	nd	nd	nd	nd
Cobourg Peninsula (1972)	443	0.52	0.52	0.10	0.51	2.91	0.01	0.19	1.34	0.19	7.07	0.43	0.63
Palau Sasuk Daun Seribu	610	0.49	0.75	0.01	0.65	2.93	0.04	0.07	1.03	0.17	3.21	0.27	0.57
Southeast Hedinia	645	0.56	0.57	0.28	0.56	3.39	0.02	nd	0.30	0.02	0.26	0.48	0.54

Table 2 — Data for source and maturity parameters derived from the GCMS (MRM) analysis of steranes and triterpanes. 1 C₃₁ αβ-hopane (22S + 22R)/C₃₀ αβ-hopane; 2 C₂₉ αβ-hopane/C₃₀ αβ-hopane; 3 C₃₀ αβ-diahopane/C₃₀ αβ-hopane; 4 C₂₉ neohopane (C₂₉ Ts)/C₂₉ αβ-hopane; 5 18α-22,29,30-trisnorhopane/17α-22,29,30-trisnorhopane; 6 18α- +18β-oleanane/C₃₀ αβ-hopane; 7 trans-trans-trans-bicadinane/C₃₀ αβ-hopane; 8 5α,14α,17α(H)-cholestane (20R)/5α,14α,17α(H)-24-ethylcholestane (20R); 9 5α,14α,17α(H)-24-n-propylcholestane (20R)/5α,14α,17α(H)-24-ethylcholestane (20R); 10 4α(Me)-5α,14α,17α(H)-24-ethylcholestane (20R)/5α,14α,17α(H)-24-ethylcholestane (20R); 11 13α,17β-24-ethylcholestane (20S + 20R)/5α,14β,17α(H)-24-ethylcholestane (20S + 20R) + 5α,14β,17β(H)-24-ethylcholestane (20S + 20R); 12 5α,14α,17α(H)-24-ethylcholestane (20S)/5α,14α,17α(H)-24-ethylcholestane (20S + 20R).

Pr/Ph values of about 1.2. Some samples showed different saturated hydrocarbon distributions, particularly those not containing botryococcane. Representatives of these, such as nos 624 and 677, are shown in Figure 2.

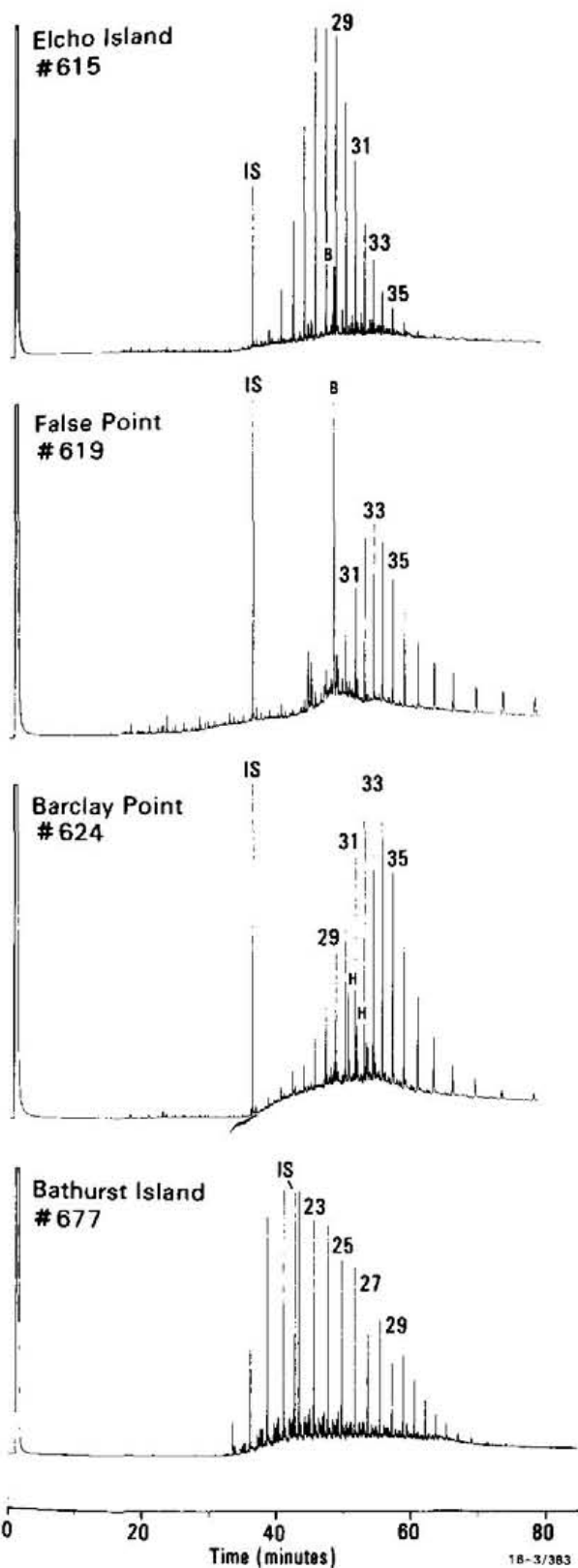


Figure 2 — Gas chromatograms of saturated hydrocarbons from representative samples of bitumens found in this survey. The peaks for individual compounds are annotated as follows: *n*-alkanes with the carbon number alone, internal standard (IS) is iso C₂₂, botryococcane (B), and hopanes (H as in H₃₀ for the C₃₀ member of the series).

High MW triterpane and sterane biomarkers are more resistant to the effects of weathering than are the low MW *n*-alkanes, and the GCMS analysis of these compounds provides the most reliable means of comparing and contrasting samples. Multiple reaction monitoring (MRM) is a particularly diagnostic GCMS technique which allows biomarkers to be identified according to their carbon number and type of ring system. Selected MRM chromatograms for coastal bitumens and a number of comparison samples are shown in Figures 4 to 10. The complete data (not shown) were used to determine the biomarker ratio parameters given in Table 2. Interpretation of the chromatographic data and biomarker ratios is according to the concepts outlined in Peters and Moldowan (1993) and references therein.

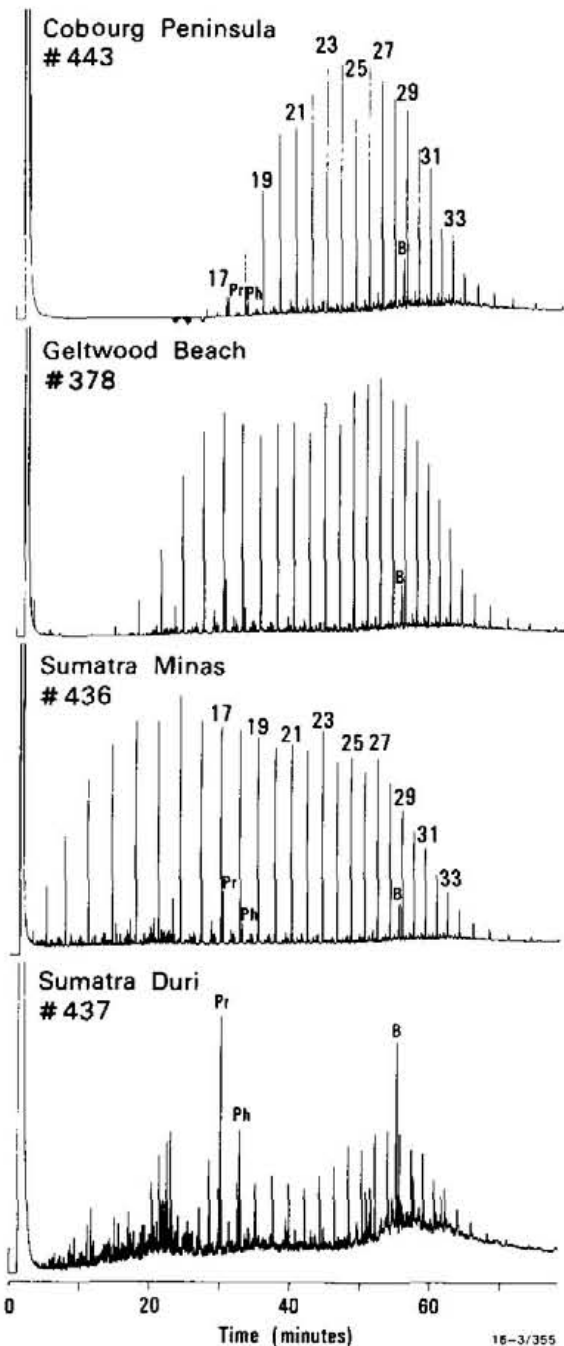


Figure 3 — Gas chromatograms of saturated hydrocarbons for comparative samples of coastal bitumen and possible precursor oils. The peaks for individual compounds are annotated as follows: *n*-alkanes with the carbon number alone, botryococcane (B), pristane (Pr) and phytane (Ph).

Those bitumens which contained botryococcane, nos 615 to 631 excepting no. 624, showed further similarities. In particular, they had sterane distributions strongly dominated by isomers of 24-ethyl-4 α -methylcholestane, a pattern which appears to be diagnostic for lacustrine source environments in the Mesozoic and Tertiary (Summons et al. 1987, 1992; Goodwin et al. 1988). The same samples had triterpanes dominated by C₃₀ $\alpha\beta$ -hopane and low amounts of the diagnostic markers oleanane (Riva et al. 1988) and bicadinanes (van Aarssen et al. 1992). These features are exemplified in Figure 4 (sample no. 615) and Figure 5 (sample no. 443) and indicate that the original carbon source comprised a mixture of terrigenous, algal and bacterial organic matter. These features conform to the general pattern seen in most Otway Basin and Western Australian coastal bitumens and some oils from Southeast

Asian lacustrine source rocks such as the oils of central Sumatra.

Some samples show traces of 24-*n*-propylcholestane, a compound considered to be a reliable indicator of marine organic matter (Moldowan et al. 1985, 1990). This suggests that some bitumens originated from oils which were co-sourced from marine sediments or from non-marine sediments subject to episodes of marine incursion. A similar observation was made in respect of the bitumens stranded on the Otway Basin coastline (McKirdy et al. 1993). This information may prove useful in understanding and identifying the tectonic regime operating during the deposition of the source rocks of the parent oils or the migration pathway of the oils to their reservoirs. For example, it is known that the predominantly lacustrine Pematang Brown Shale Formation source rocks of central

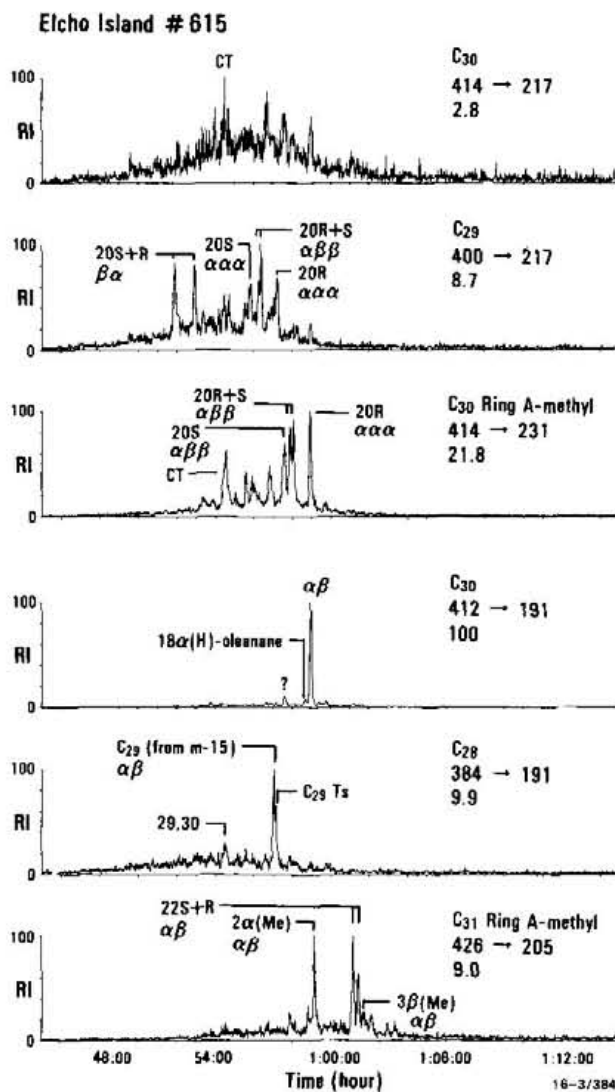


Figure 4 — GCMS (MRM) traces showing biomarker steranes and triterpanes in a lacustrine type (no. 615) coastal bitumen of the present survey. Steranes and methyl steranes are shown in M⁺ → 217 and M⁺ → 231 reaction traces while hopanes and methyl hopanes are shown in M⁺ → 191 and M⁺ → 205 traces respectively. Each trace is identified with the carbon number, the reaction being monitored and a normalised intensity for the largest peak in each trace. The stereochemical assignments are standard abbreviations and are fully elaborated in Peters and Moldowan (1993).

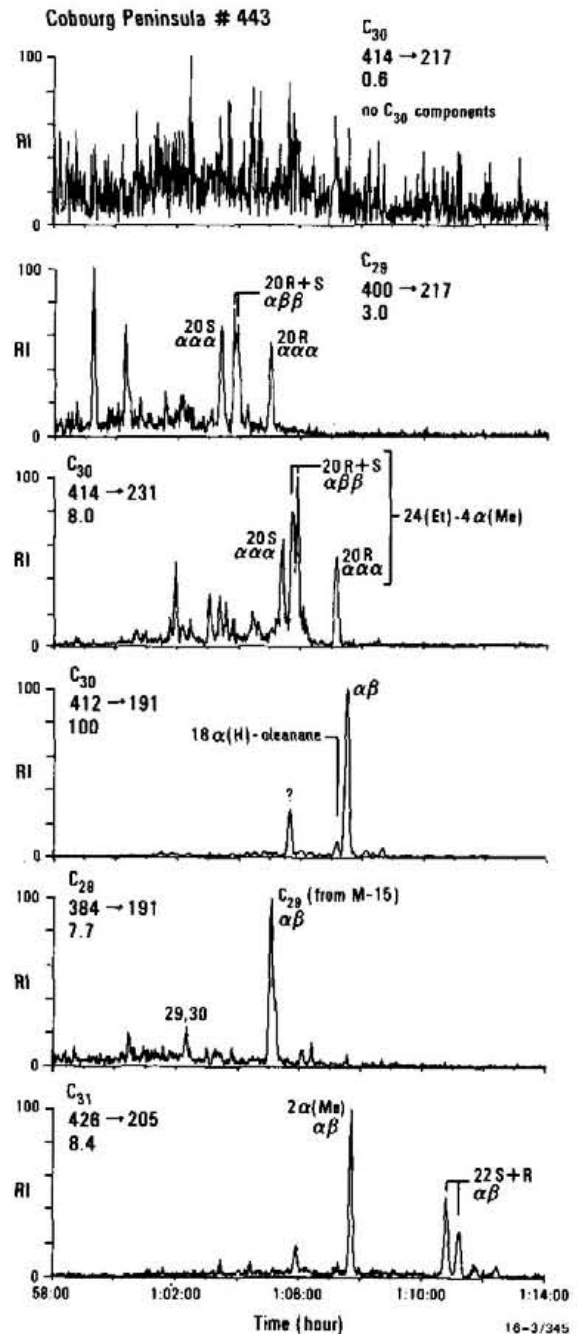


Figure 5 — GCMS (MRM) traces showing biomarker steranes and triterpanes in a lacustrine type (no. 443) coastal bitumen collected from the survey area in 1973.

Sumatra are overlain in parts by marine sediments of the Telisa Formation (Robinson & Kamal 1988; Katz & Mertani 1989). Superposition of traces of marine biomarkers on a predominantly lacustrine signature would be expected in oils co-sourced from these or similar rocks or where a mature marine sediment acted as a conduit for migrating oil.

The biomarker pattern of the lacustrine bitumens is distinctly different from the coal or carbonaceous shale-derived oils of Southeast Asia such as one from the Ardjuna Basin of northwest Java (no. 372, Fig. 7) and an Indonesian bitumen stranding (no. 610). These latter oils have a major resin component in the source material and typically have low concentrations of steranes and methyl steranes, high concentrations of oleananes and other plant-derived triterpanes and abundant bicadinanes.

Five of the bitumens appear to have been derived from predominantly marine sediments and exhibit variations of the pattern typified by sample no. 624 (Fig. 8). Here the steranes are dominated by cholestanes and 24-ethylcholestane together with smaller concentrations of 24-n-propylcholestanes and 4-methyl steranes including dinosterane. The combination of these features is typical of marine oils of Mesozoic or Cainozoic age (Summons et al. 1987, 1992).

Isomer distributions of the steranes give clues about the

source rock lithology. In particular, a low abundance of $\beta\alpha$ -diasteranes compared to $\alpha\alpha\alpha$ and $\alpha\beta\beta$ steranes is normally observed in extracts and oils from carbonate sediments. In the present sample suite, the ratio of 24-ethyl diacholestanes to the regular sterane isomers (Table 1, column 11) varied from 0.09 to 0.26 compared to the lacustrine oils 0.32 to 0.71. The wide ranges for this and other parameters are significant and suggest that even within the two main families of lacustrine oils and marine carbonate oils there is considerable heterogeneity.

Another feature normally associated with carbonate-derived oils is the relative abundance of 2 α -methyl hopanes (MH) and 30-norhopanes (NH) compared to $\alpha\beta$ -hopanes. The parameter H_{29}/H_{30} (Subroto et al. 1991) shows the relative proportion of 30-norhopanes in the sample suite and varies from 0.98 to 2.3 for the carbonate-derived oils as compared with values of about 0.8 or lower for the lacustrine samples. The ratios of MH_{31}/H_{30} , showing the relative amount of 2 α -methylhopane (Summons & Jahnke 1990), also show significant variation but they are generally less than 0.1 in the lacustrine samples versus values near 0.15 for the carbonate-derived bitumens.

One bitumen (no. 677) had a hydrocarbon distribution which did not conform to the pattern for lacustrine or marine carbonate sourced oils. This sample was

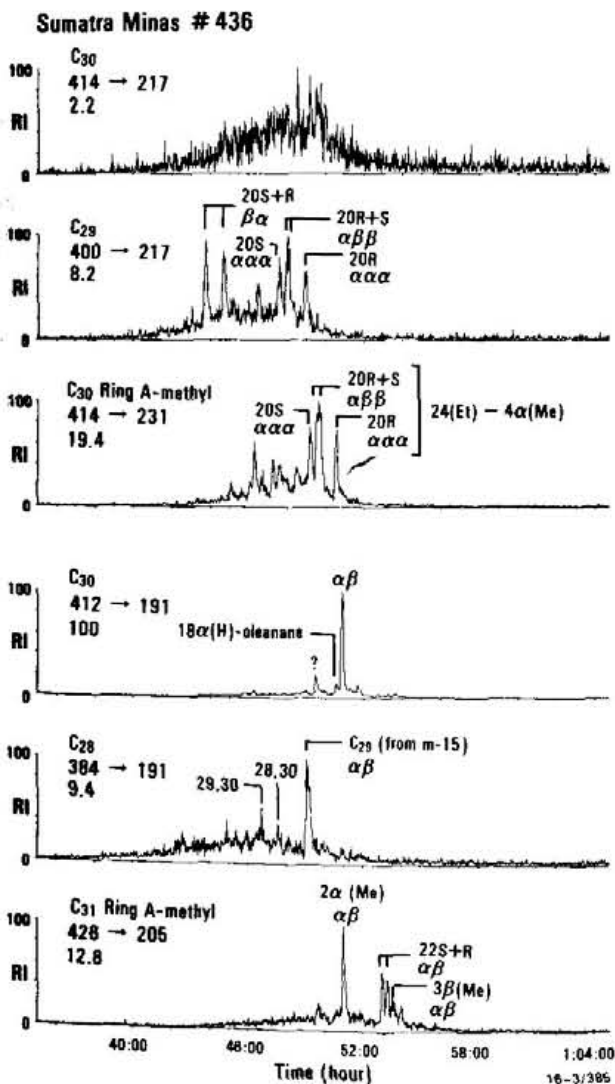


Figure 6 — GCMS (MRM) traces showing biomarker steranes and triterpanes in a lacustrine type oil (no. 436) from the Minas Field of central Sumatra.

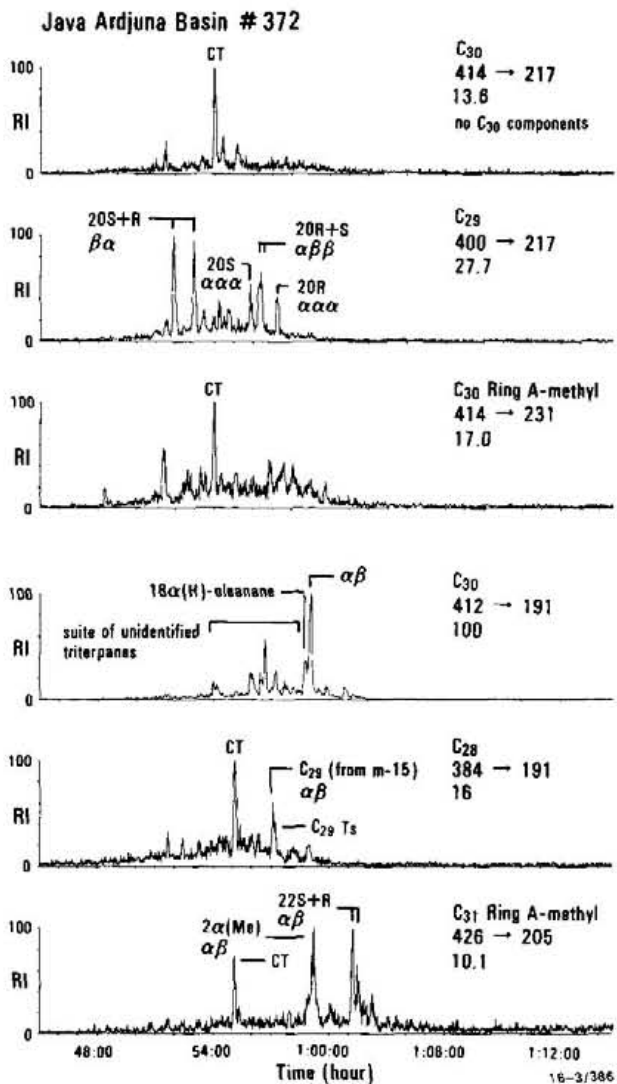


Figure 7 — GCMS (MRM) traces showing biomarker steranes and triterpanes in a terrestrial oil from the Ardjuna Basin of northwest Java.

distinguished by a high abundance of monomethyl alkanes (Fig. 2) and patterns of steranes and triterpanes characteristic of marine oil sourced by a sediment of mixed clastic and carbonate lithology (Fig. 9).

Knowledge of bicadinane distributions is assuming increased importance in oil-source correlations of Cainozoic oils and is particularly useful for distinguishing marine from non-marine bitumens (Fig. 11). Bicadinanes are maturation products of the cadinene biopolymer constituent of some Angiosperm resins (van Aarssen et al. 1992). Such resins are produced in copious amounts by the dipterocarp trees of Southeast Asia (van Aarssen et al. 1990, 1992) and, as a result, high bicadinane concentrations are characteristic of the Tertiary-age terrestrial oils from many Southeast Asian fields (e.g. Grantham et al. 1983; Alam & Pearson 1990; van Aarssen et al. 1992; Murray et al. 1992). Naming of the bicadinanes with trivial labels W, T and R is done here in accordance with the precedent set by Grantham et al. (1983) and continued by Alam and Pearson (1990) and using the elution order in an m/z 191 chromatogram. Because of the ability of MRM analysis to separate C_{30} and C_{31} compounds, we use the 412 \rightarrow 369 and 426 \rightarrow 383 reaction chromatograms and the pattern of an oil from the Ardjuna Basin (no. 372) as a template in order to identify the bicadinanes. The label R' (Alam &

Pearson 1990) referred to a mixture of C_{30} and C_{31} bicadinanes. We refer to R as the C_{30} component of the composite peak and MeT as the C_{31} component. We have used the additional trivial name T1 to denote the C_{30} compound which elutes just after T and has a similar mass spectrum. In formal nomenclature W has been assigned as the major *cis-cis-trans* isomer (Cox et al. 1986) and T as the major *trans-trans-trans*-bicadinane isomer (van Aarssen et al. 1992).

In examining possible sources for the marine oils the authors consider it unlikely that these are related to the Jurassic oils of the Timor Sea. The latter, like most oils of the Westralian petroleum system (Bradshaw 1993), show a number of very characteristic features including abundant dihopanes and 28-, 30-bisnorhopane-compounds not abundant in any samples of the present set. Since the lacustrine samples are likely to originate in Southeast Asia, it is reasonable to suspect that marine oils could also be transported long distances to the Northern Territory coastline. Marine oil is produced in the Bula Basin of Seram (e.g. Price et al. 1983); although its biomarker pattern has some features in common with oils in the bitumen suite, our sample of Seram oil (no. 324, Fig. 10) differs in the respect that rearranged steranes ($\beta\alpha$ -diasteranes) are virtually absent. This makes it an unlikely candidate for the

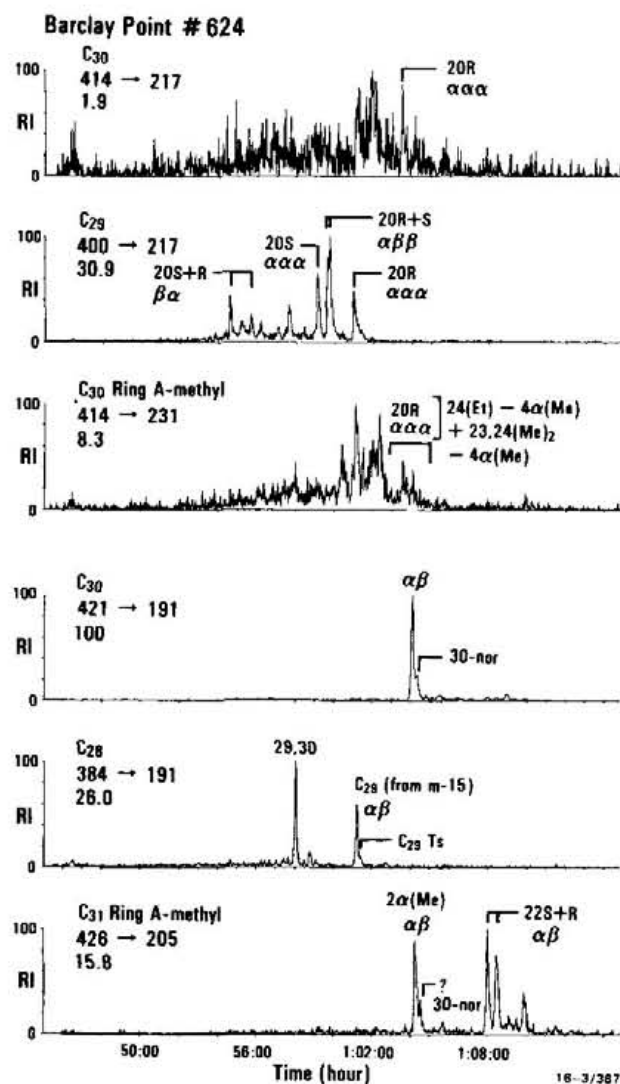


Figure 8 — GCMS (MRM) traces showing biomarker steranes and triterpanes in a marine carbonate type (no. 624) coastal bitumen of the present survey.

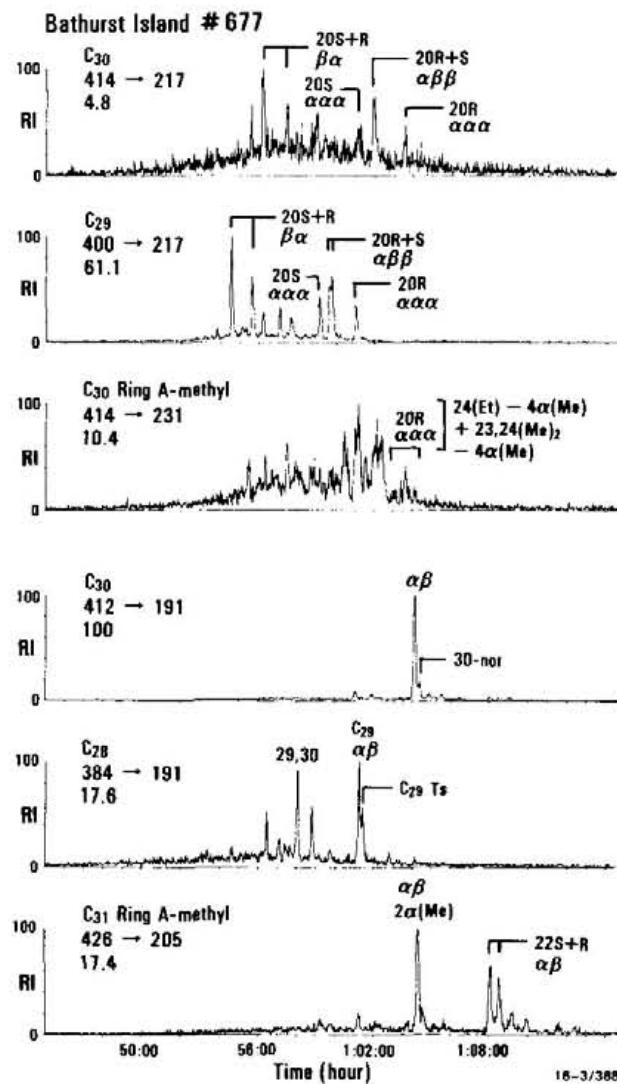


Figure 9 — GCMS (MRM) traces showing biomarker steranes and triterpanes of the outlier (no. 677) coastal bitumen of the present survey.

source of the coastal bitumens since these contain significant amounts of diasteranes. Mesozoic and Cainozoic carbonate sediments which are likely to produce low diasterane oils do occur in basins adjacent to the study area but these are thought to be too immature for oil generation.

It is not possible, on geochemical grounds alone, to distinguish between pollution and natural seepage as possible sources of the marine oils. While we do not discount the possibility of a local source, it is noteworthy that the biomarker profiles of the main marine oil family are in many respects similar to those of oils sourced by the Cretaceous marine carbonate source rocks of the Middle East. Given the vast amounts of such oils which are produced and transported around the globe it would perhaps be surprising if they were not found along a coastline adjacent to a major tanker route. Furthermore, oils of Middle Eastern origin have historically been the primary feedstock for lubricating oils made in Australia and their geochemical signature is well known both from forensic studies of oil spills and from more general environmental studies in Australia (Gilbert 1987; Carpenter et al. 1991; Phillips et al. 1992 and references therein). Pollution cannot be invoked as a source for the waxy bitumens since these are much more consistently distributed in both time and space, having been found

around the coast from the Northern Territory to Victoria and from as early as 1973 (Currie et al. 1992; McKirdy et al. 1993; McKirdy & Horvath 1976). Moreover, there is a history of oil strandings along the Northern Territory coastline dating from before the development of the Middle East oil fields (Wade 1924).

Palynological analysis of sample no. 625

The analysis of oils and bitumens for entrapped palynomorphs has been widely applied, particularly in Russia and China, to assist studies of migration pathways and possible provenance of hydrocarbons (e.g. Chepikov & Medvedeva 1971; Wang et al. 1985). Solvents are used to dissolve soluble organic matter and, if heating is avoided as in this case, palynomorph colour and fluorescence response may be used to derive information about thermal maturity.

Sample no. 625 yielded abundant insoluble debris much of which consisted of unstructured material, woody tissues and modern marine contaminants such as diatoms, dinoflagellates, foraminifera and filamentous cyanobacteria. Among the pollen was a single, dark-walled (thermally matured) grain with no evidence of intexinal (cell) contents as would be expected were it a modern contaminant. This fossil has morphological characteristics consistent for the genus *Proteaceae*, Sub-family *Grevilleoideae*, Tribe *Grevilleae* (M.E. Dettmann pers. comm.). According to studies of Spect et al. (1992) pollen of this morphology first appeared in southern Australian sediments of Late Cretaceous (Maastrichtian, 73 Ma) age and become more persistent from the Middle Tertiary (Eocene, 45 Ma) through to the Holocene. From this evidence, the pollen is no older than Maastrichtian and this suggests that the bitumen (or the rocks along its migration pathway) is also no older than this.

Prospects for a source for Northern Territory coastline bitumens within the Arafura Sea

As discussed above, oils produced commercially from basins near to the study area are thought to be derived from Late Jurassic shales. One local possibility for the source of the bitumens from the western areas of Cobourg Peninsula and Bathurst and Melville Islands is that they are sourced from local Cretaceous and Cainozoic sediments from the Calder Graben of the eastern Bonaparte Basin. This could include the Albian to Aptian age Darwin Formation, thin limestone interbeds from the Santonian part of the Wangarlu Formation and the Tertiary Woodbine Group. In the region of the Arafura Sea, the post-Jurassic sediments are generally considered to be immature. However, the paucity of drilling in the area suggests that care should be exercised before local possibilities could be considered viable or discounted. With this in mind, we examined maturation, generation, expulsion and migration potential in the nearby wells Lynedoch-1 and Tuatara-1. Lynedoch-1 encountered gas in limestone in the Darwin Formation.

In Lynedoch-1, TOC values within the Wangarlu Formation are generally low (0.6 to 1.4%) and average around 0.85 to 0.95%. One very low TOC measurement (0.37%) was recorded within the Darwin Formation in Lynedoch-1. Low average values of HI (c. 50) and S1 + S2 (0.64 mg/g) in both the Wangarlu and Darwin Formations suggest generally poor source quality and negligible potential for oil. Macerals from the Wangarlu Formation viewed under reflected light, show moderate oil-prone source potential, with nine samples averaging 30 to 40%

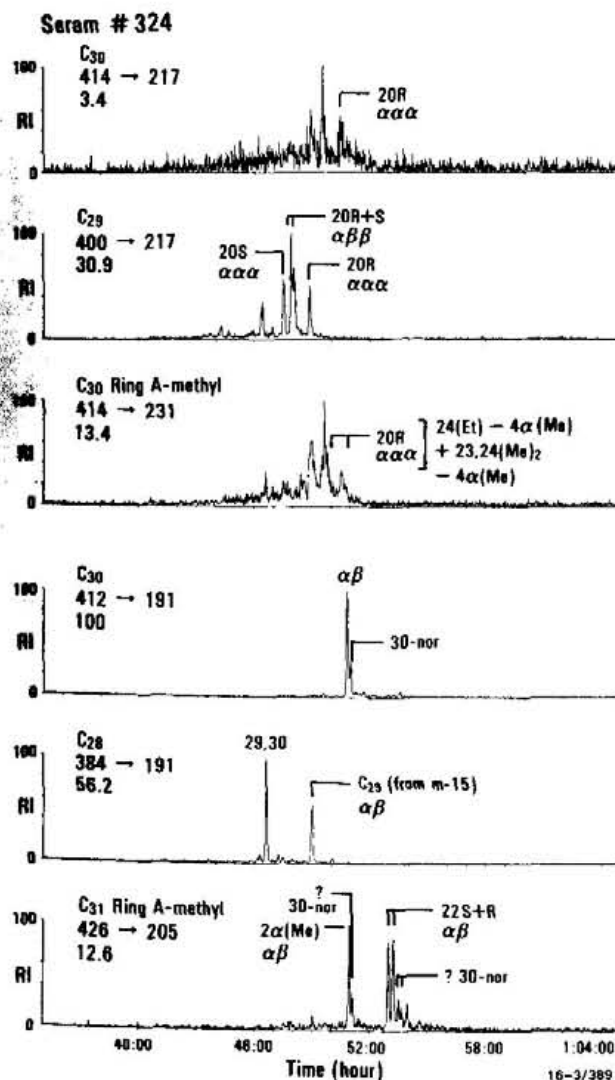


Figure 10 — GCMS (MRM) traces showing biomarker steranes and triterpanes of a marine oil (no. 324) from the Bula Basin of Seram.

exinite, and two containing 13% and 19% alginite. In Tuatara-1, the average TOC in the Wangarlu Formation is also low (0.33% to a maximum 0.64%) and no samples have been analysed using Rock-Eval. The identity of the described macerals, however, indicated a potentially oil-prone source, with exinite averaging 60% of macerals.

Sample descriptions, together with seismic interpretation, imply the Darwin and Wangarlu Formations in Tuatara-1 were deposited in settings more proximal than those at the Lynedoch-1 location. Based on this observation, and on the increasing thickness of both formations into the study area (as seen on seismic), these formations are likely to have been deposited in a more distal environment in the study area compared to Lynedoch-1. If this was the case, the TOC content of the units would be expected to be greater in the

study area than in Lynedoch-1. The maturation and source rock data from this assessment were used to calibrate one-dimensional hydrocarbon maturation modelling using the MATOIL program. Various points within the study area were modelled, together with the two nearby wells. The burial and thermal history model from Lynedoch-1 was used as the control for points within the study area.

The vitrinite reflectance versus depth trend from Lynedoch-1 (Fig. 12) shows a large offset across the Base Albian Unconformity, from 0.68% above to 1.09% below. Such an offset may imply a large amount of uplift and subsequent erosion in the order of 2 to 3 km. There is no evidence from seismic nor palynological data that this amount of section is missing, the maximum being 300 m. The vitrinite reflectance data beneath the Unconformity

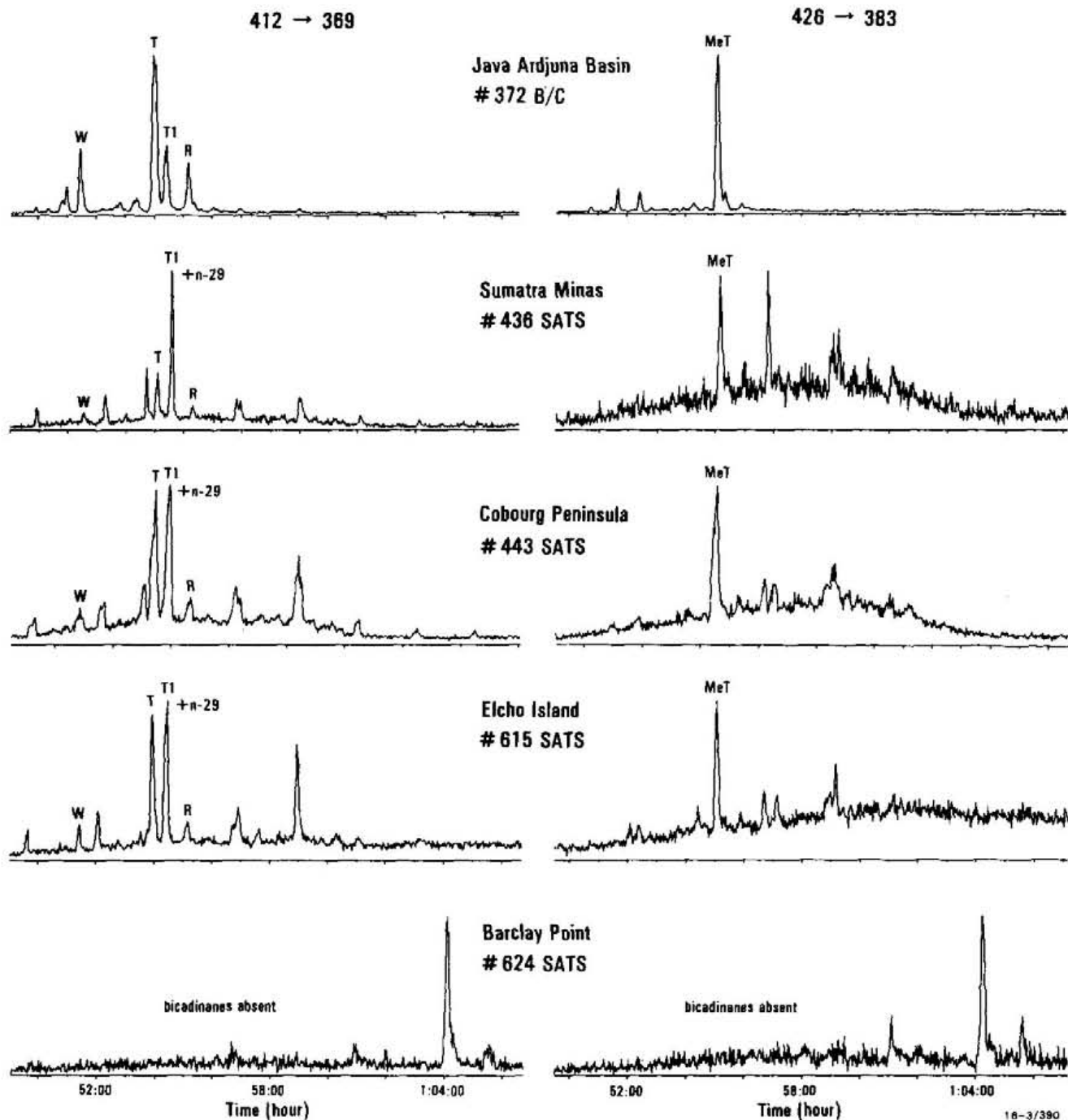


Figure 11 — GCMS (MRM) traces showing bicadinane distributions of coastal bitumens of the present survey compared to the oil (no. 372) from the Ardjuna Basin of northwest Java, a typical distribution for terrestrial oils of Southeast Asia. Peak assignments are discussed in the text.

appears to be reliable. A plausible explanation for the offset is that reflectance data from above the Unconformity is suppressed, as observed in other marine claystones in the Timor Sea region (G. Woodhouse pers. comm.).

Based on the above assumptions, the heat flow model needed to match the measured vitrinite trend with the modelled trend predicts a heating event during the Middle to Late Jurassic, gradually decaying until the Miocene when a second heating episode began, increasing to the present day (Fig. 12). The Jurassic thermal event corresponds with the known timing for rifting of the northwest margin of Australia while the Miocene thermal event corresponds to the collision of the Australian Plate with the Eurasian Plate. The study area was modelled using the above heat flow scenario and assumed Type II kerogen. The results suggest that the lower half of the Wangarlu Formation is currently at peak oil-generative levels of thermal maturation, and that the oil-generative threshold lies just below the top of the Wangarlu Formation. However, the Darwin Formation appears to have been overmature for oil generation since the beginning of the Tertiary. Although the low TOC, HI, and S1+S2 values obtained from samples from both formations in Lynedoch-1 lead to a prediction of zero expulsion of oil, there may be other regions in the study area where source potential is enhanced.

Conclusions

Hydrocarbon signatures show that most bitumens found in a survey of the Northern Territory coastline closely resemble coastal bitumens from Western Australia and the southern continental margin. These are derived from predominantly lacustrine source rocks and closely resemble oils from central Sumatra. They probably originate from a basin or basins in Southeast Asia although it is not possible to be more specific at the present time.

Two 'families' of marine-origin bitumens found in the west of the survey area and on Bathurst and Melville Islands do not resemble any known locally sourced oils, particularly those of New Guinea, the Timor Sea or Seram. While they could possibly represent oils of local origin, it should also be borne in mind that the hydrocarbon compositions resemble those of Cretaceous, carbonate-derived oils produced from the giant fields of the Middle East and transported by tanker around the globe.

Present knowledge indicates that the families of stranded bitumen derived from marine source rocks are probably not originating from the Calder Graben Cretaceous formations. Although these sediments are probably mature in Lynedoch-1 and Tuatara-1, the lean organic content of the Darwin and Wangarlu Formation in these wells are not conducive to oil expulsion. These findings, however, do not exclude the possibility for oil in unexplored parts of the Timor Sea region.

Acknowledgements

The authors wish to thank the Tiwi Lands Council and the Northern Lands Council for access to the survey sites and information which assisted this project. We are also grateful to Philip Fletcher, Janet Hope and Zoltan Horvath for assistance with analytical work, and members of the AGSO Cartographic Services Unit for figure preparation. Financial support for this project was provided by the joint venture participants of NT/P41 and 42 — BHP Petroleum, BP Developments Australia Ltd, Japan Australia LNG (MiMi) P/L and AGSO, and is gratefully acknowledged. Trevor Powell, Tom Loutit, John Volkman, Mary Dettmann and Bob Alexander provided valuable comments on the manuscript. The authors from AGSO received permission to publish from the Executive Director, Australian Geological Survey Organisation.

References

Alam, M. & Pearson, M.J. (1990), Bicinanes in oils from the Surma Basin, Bangladesh. *Organic Geochemistry*, vol. 15, pp. 461-4.

Bradshaw, M. (1993), Australian petroleum systems. *PESA Journal*, vol. 21, pp. 43-53.

Bradshaw, J., Nicoll, R.S. & Bradshaw, M.T. (1990), The Cambrian to Permo-Triassic Arafura Basin, Northern Territory. *The APEA Journal*, vol. 30, part 1, pp. 107-27.

Blumer, M., Erhardt, M. & Jones, J.H. (1973), The environmental fate of stranded crude oil. *Deep-Sea Research*, pp. 239-59.

Butler, J.N., Morris, B.F. & Sleeter, T.D. (1976), The fate of petroleum in the open ocean. In: *Sources, effects and sinks of hydrocarbons in the aquatic environment*. American Institute of Biological Sciences, Washington DC, pp. 287-97.

Carpenter, P.D., Butler, E.C.V., Higgins, H.W., Mackey, D.J. & Nichols, P.D. (1991), Chemistry of trace elements, humic substances and sedimentary organic matter in Macquarie Harbour, Tasmania. *Australian Journal of Marine and Freshwater Research*, vol. 42, pp. 625-54.

Chepikov, K.P. & Medvedeva, A.M. (1971), Spores and pollen in oils and gases as migration indices. *Journal of Palynology*, vol. 7, pp. 56-9.

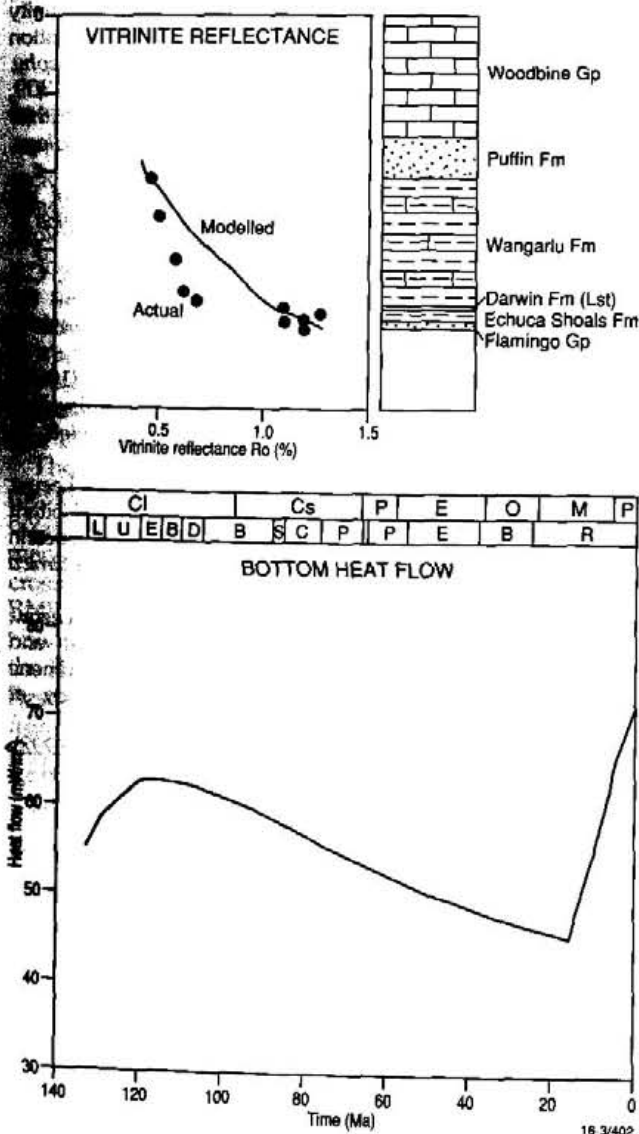


Figure 12 — Maturation profile and heat flow history for the Lynedoch-1 well.

appears to be reliable. A plausible explanation for the offset is that reflectance data from above the Unconformity is suppressed, as observed in other marine claystones in the Timor Sea region (G. Woodhouse pers. comm.).

Based on the above assumptions, the heat flow model needed to match the measured vitrinite trend with the modelled trend predicts a heating event during the Middle to Late Jurassic, gradually decaying until the Miocene when a second heating episode began, increasing to the present day (Fig. 12). The Jurassic thermal event corresponds with the known timing for rifting of the northwest margin of Australia while the Miocene thermal event corresponds to the collision of the Australian Plate with the Eurasian Plate. The study area was modelled using the above heat flow scenario and assumed Type II kerogen. The results suggest that the lower half of the Wangarlu Formation is currently at peak oil-generative levels of thermal maturation, and that the oil-generative threshold lies just below the top of the Wangarlu Formation. However, the Darwin Formation appears to have been overmature for oil generation since the beginning of the Tertiary. Although the low TOC, HI, and S1+S2 values obtained from samples from both formations in Lynedoch-1 lead to a prediction of zero expulsion of oil, there may be other regions in the study area where source potential is enhanced.

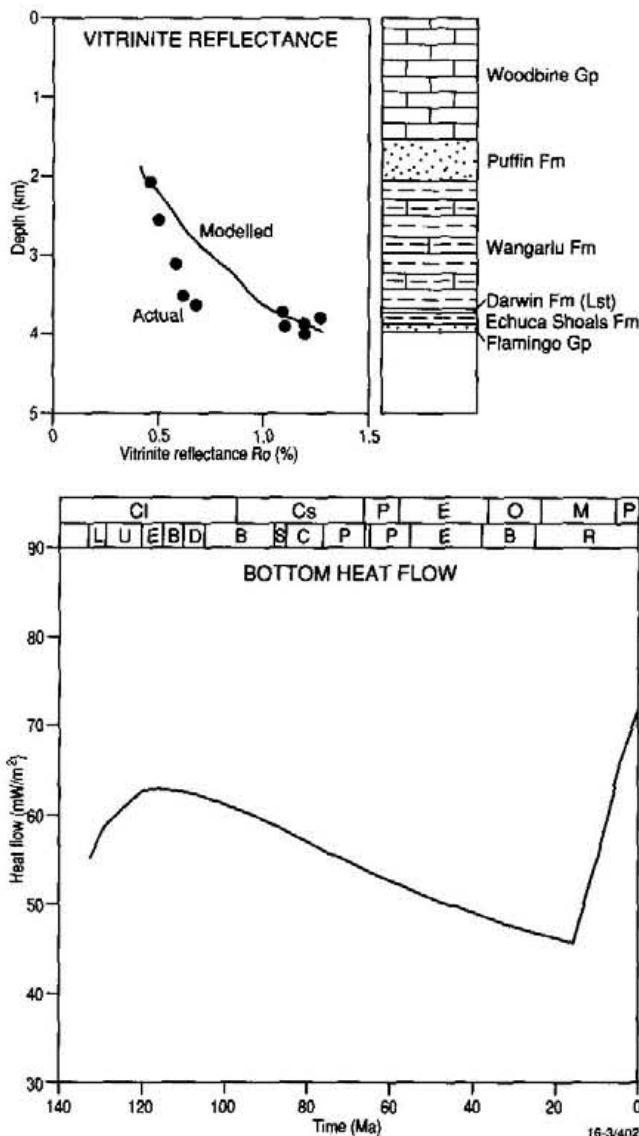


Figure 12 — Maturation profile and heat flow history for the Lynedoch-1 well.

Conclusions

Hydrocarbon signatures show that most bitumens found in a survey of the Northern Territory coastline closely resemble coastal bitumens from Western Australia and the southern continental margin. These are derived from predominantly lacustrine source rocks and closely resemble oils from central Sumatra. They probably originate from a basin or basins in Southeast Asia although it is not possible to be more specific at the present time.

Two 'families' of marine-origin bitumens found in the west of the survey area and on Bathurst and Melville Islands do not resemble any known locally sourced oils, particularly those of New Guinea, the Timor Sea or Seram. While they could possibly represent oils of local origin, it should also be borne in mind that the hydrocarbon compositions resemble those of Cretaceous, carbonate-derived oils produced from the giant fields of the Middle East and transported by tanker around the globe.

Present knowledge indicates that the families of stranded bitumen derived from marine source rocks are probably not originating from the Calder Graben Cretaceous formations. Although these sediments are probably mature in Lynedoch-1 and Tuatara-1, the lean organic content of the Darwin and Wangarlu Formation in these wells are not conducive to oil expulsion. These findings, however, do not exclude the possibility for oil in unexplored parts of the Timor Sea region.

Acknowledgements

The authors wish to thank the Tiwi Lands Council and the Northern Lands Council for access to the survey sites and information which assisted this project. We are also grateful to Philip Fletcher, Janet Hope and Zoltan Horvath for assistance with analytical work, and members of the AGSO Cartographic Services Unit for figure preparation. Financial support for this project was provided by the joint venture participants of NT/P41 and 42 — BHP Petroleum, BP Developments Australia Ltd, Japan Australia LNG (MiMi) P/L and AGSO, and is gratefully acknowledged. Trevor Powell, Tom Loutit, John Volkman, Mary Dettmann and Bob Alexander provided valuable comments on the manuscript. The authors from AGSO received permission to publish from the Executive Director, Australian Geological Survey Organisation.

References

- Alam, M. & Pearson, M.J. (1990), Bicinanes in oils from the Surma Basin, Bangladesh. *Organic Geochemistry*, vol. 15, pp. 461-4.
- Bradshaw, M. (1993), Australian petroleum systems. *PESA Journal*, vol. 21, pp. 43-53.
- Bradshaw, J., Nicoll, R.S. & Bradshaw, M.T. (1990), The Cambrian to Permo-Triassic Arafura Basin, Northern Territory. *The APEA Journal*, vol. 30, part 1, pp. 107-27.
- Blumer, M., Erhardt, M. & Jones, J.H. (1973), The environmental fate of stranded crude oil. *Deep-Sea Research*, pp. 239-59.
- Butler, J.N., Morris, B.F. & Sleeter, T.D. (1976), The fate of petroleum in the open ocean. In: *Sources, effects and sinks of hydrocarbons in the aquatic environment*. American Institute of Biological Sciences, Washington DC, pp. 287-97.
- Carpenter, P.D., Butler, E.C.V., Higgins, H.W., Mackey, D.J. & Nichols, P.D. (1991), Chemistry of trace elements, humic substances and sedimentary organic matter in Macquarie Harbour, Tasmania. *Australian Journal of Marine and Freshwater Research*, vol. 42, pp. 625-54.
- Chepikov, K.P. & Medvedeva, A.M. (1971), Spores and pollen in oils and gases as migration indices. *Journal of Palynology*, vol. 7, pp. 56-9.

- Cox, H.C., de Leeuw, J.W., Schenck, P.A., van Koningsveld, H., Jansen, J.C., van der Graff, B., van Geerestein, B., Kanters, J.A., Kruk, C. & Jans, A.W.H. (1986), Bacadinane, a C₃₀ pentacyclic isoprenoid hydrocarbon found in crude oil. *Nature*, vol. 319, pp. 316-18.
- Currie, T.J., Alexander, R. & Kagi, R.I. (1992), Coastal bitumens from Western Australia — long distance transport by ocean currents. *Organic Geochemistry*, vol. 18, pp. 595-601.
- Gilbert, T.D. (1987), GC-MS profiling of molecular fossils — its use in the identification of environmental pollution by petroleum, coal and oil shale conversion. In: *Proceedings of the Ninth Australian Symposium on Analytical Chemistry*. Royal Australian Chemical Institute, Sydney, pp. 17-20.
- Goodwin, N. S., Mann, A. L. & Patience, R. L. (1988), Structure and significance of C₃₀ 4-methylsteranes in lacustrine shales and oils. *Organic Geochemistry*, vol. 12, pp. 495-506.
- Grantham, P.J., Postuma, J. & Baak, A. (1983), Triterpanes in a number of Far-Eastern crude oils. In: Bjørøy M. et al. (eds), *Advances in Organic Geochemistry 1981*. Wiley, New York, pp. 675-83.
- Grantham, P.J., Postuma, J. & de Groot, K. (1980), Variation and significance of the C₂₇ and C₂₈ triterpane content of a North Sea core and various North Sea crude oils. In: Maxwell, J. R. & Douglas, A. G. (eds), *Advances in Organic Geochemistry 1979*. Pergamon Press, Oxford, pp. 29-38.
- Hughes, R.J. & Senior, B.R. (1973), Progress report on the geology of the Bathurst Island, Melville Island, Cobourg Peninsula and Fog Bay 1:250 000 Sheet areas, Northern Territory. *Bureau of Mineral Resources Record 1973/52*.
- Kagi, R.I., Fisher, S.J. & Alexander, R. (1988), Behaviour of petroleum in northern Australian waters. In: Purcell, P.G. & R.R. (eds), *The North West Shelf, Australia*. Proceedings of Petroleum Exploration Society of Australia Symposium, Perth, pp. 633-42.
- Katz, B. & Mertani, B. (1989), Central Sumatra — a geochemical paradox. *Proceedings of the Indonesian Petroleum Association 18th Annual Convention 1989*, pp. 403-25.
- Lee, R.F. (1980), Processes affecting the fate of oil in the sea. In: Geyer, R.A. (ed.), *Marine Environmental Pollution vol. 1: Hydrocarbons*. Elsevier, Amsterdam, pp. 337-51.
- McKirdy, D.M., Cox, R.E., Volkman, J.K. & Howell, V.J. (1986), Botryococcane in a new class of Australian non-marine crude oils. *Nature*, vol. 320, pp. 57-9.
- McKirdy, D.M. & Horvath, Z. (1976), Geochemistry and significance of coastal bitumen from southern and northern Australia. *The APEA Journal*, vol. 16, part 1, pp. 123-36.
- McKirdy, D.M., Summons, R.E., Padley, D., Serafini, K.M., Boreham, C.J. & Struckmeyer, H.I.M. (1993), Molecular fossils in coastal bitumens from southern Australia: signatures of precursor biota and source rock environments. *Organic Geochemistry*, in press.
- Moldowan, J.M. & Seifert, W.K. (1980), First discovery of botryococcane in petroleum. *Journal of the Chemical Society, Chemical Communications*, pp. 912-14.
- Moldowan, J. M., Fago, F. J., Lee, C. Y., Jacobson, S. R., Watt, D. S., Slougui, N.-E., Jegathanan, A. & Young, D. C. (1990), Sedimentary 24-n-propylcholestanes, molecular fossils diagnostic of marine algae. *Science*, vol. 247, pp. 309-12.
- Moldowan, J.M., Seifert, W.K. & Gallegos, E.J. (1985), Relationship between petroleum composition and depositional environment of petroleum source rocks. *American Association of Petroleum Geologists Bulletin*, vol. 69, pp. 1225-68.
- Murray, A.P., Summons, R.E., Boreham, C.J., Fletcher, P. & Brooks, L.J. (1992), Organic geochemistry of sediments and seep oils from the Visayan Basin, the Philippines. Report for a co-operative research project between Australian Worldwide Exploration and the Bureau of Mineral Resources, Geology and Geophysics. Canberra, June 1992.
- Noble, R.A., Alexander, R. & Kagi, R.I. (1985), The occurrence of bisnorhopane, trisnorhopane and 25-norhopanes as free hydrocarbons in some Australian shales. *Organic Geochemistry*, vol. 8, pp. 171-6.
- Padley, D., McKirdy, D.M., Tewksbury, P.S. & Bye, J.A.T. (1991), Coastal bitumen types and stranding patterns in South Australia and western Victoria. Australian Organic Geochemistry Conference, 11-12 April 1991, University of Melbourne, Australia (Abstract).
- Peters, K.E. & Moldowan, J.M. (1993), *The Biomarker Guide — Interpreting molecular fossils in petroleum and ancient sediments*. Prentice-Hall, New Jersey.
- Phillips, D.J.H., Richardson, B.J., Murray, A.P. & Fabris, J.G. (1992), Trace metals, organochlorines and hydrocarbons in Port Phillip Bay, Victoria: a historical review. *Marine Pollution Bulletin*, vol. 25, pp. 200-17.
- Price, P.L., O'Sullivan, T. & Alexander, R. (1987), The nature and occurrence of oil in Seram, Indonesia. *Proceedings of the Indonesian Petroleum Association 16th Annual Convention 1987*, pp. 141-73.
- Riva, A., Caccialanza, P.G. & Quagliaroli, F. (1988), Recognition of 18β (H)-oleanane in several crudes and Tertiary-Upper Cretaceous sediments. Definition of a new maturity parameter. *Organic Geochemistry*, vol. 13, pp. 671-5.
- Robinson, K.M. & Kamal, A. (1988), Hydrocarbon generation, migration and entrapment in the Kampar Block, Central Sumatra. *Proceedings of the Indonesian Petroleum Association 16th Annual Convention 1987*, pp. 211-56.
- Spect, R.L., Dettmann, M.E. & Jarzen, D.M. (1992), Community associations and structure in the late cretaceous vegetation of southeast Australasia and Antarctica. *Palaeogeography, Palaeoclimatology and Palaeoecology*, vol. 94, pp. 283-309.
- Subroto, E., Alexander, R. & Kagi, R. (1991), 30-norhopanes: their occurrence in sediments and crude oils. *Chemical Geology*, vol. 93, pp. 179-92.
- Summons, R.E. & Jahnke, L.L. (1990), Identification of the methyhopanes in sediments and petroleum. *Geochimica et Cosmochimica Acta*, vol. 54, pp. 247-51.
- Summons, R.E., Thomas, J., Maxwell, J.R. & Boreham, C.J. (1992), Secular and environmental constraints on the occurrence of dinosterane in sediments. *Geochimica et Cosmochimica Acta*, vol. 56, pp. 2437-44.
- Summons, R.E., Volkman, J.K. & Boreham, C.J. (1987), Dinosterane and other steroidal hydrocarbons of dinoflagellate origin in sediments and petroleum. *Geochimica et Cosmochimica Acta*, vol. 51, pp. 3075-82.
- Van Aarssen, B.G.K., Cox, H.C., Hoogendoorn, P. & de Leeuw, J.W. (1990), A cadinene biopolymer present in fossil and extant dammar resins as a source of cadinanes and bicadinanes in crude oils from South East Asia. *Geochimica et Cosmochimica Acta*, vol. 54, pp. 3021-31.
- Van Aarssen B.G.K., Hessels J.K.C., Abbink, O.A. & de Leeuw, J.W. (1992), The occurrence of polycyclic sesqui-, tri- and oligoterpenoids derived from a resinous polymeric cadinene in crude oils from South East Asia. *Geochimica et Cosmochimica Acta*, vol. 56, pp. 1231-46.
- Volkman, J.K., O'Leary, T., Summons, R.E. & Bendall, M.R. (1992), Biomarker composition of some asphaltic coastal bitumens from Tasmania, Australia. *Organic Geochemistry*, vol. 18, pp. 669-82.
- Wade, A. (1924), Petroleum prospects. Kimberley district of Western Australia, and Northern Territory. The Parliament of the Commonwealth of Australia.
- Wang, K.F., Zhang, Y.L. & Jiang, H. (1985), Palynological assemblages of the crude oil from the buried hills of China and the research of the oil source. *Pollen et Spores*, vol. 27, pp. 471-89.