



Molecular fossils in coastal bitumens from southern Australia: signatures of precursor biota and source rock environments*

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Abstract—Weathered waxy crude oil and black asphaltite (tar) are regularly washed ashore along the coastlines of South Australia and western Victoria. These bitumens generally strand on medium to high-energy, sandy beaches in west or southwest facing bays. Some very weathered bitumens have been discovered in Holocene dune deposits up to 200 m from the present-day coastline. Differences in the sulphur content and carbon, hydrogen and sulphur isotopic compositions of the coastal bitumens suggest that they belong to at least four oil families, one of which may be emanating from submarine seeps along Australia's highly faulted southern continental margin. The remainder appear to be flotsam carried south from S.E. Asia, possibly Sumatra.

The waxy bitumens (Families 1–3) range from paraffinic to aromatic-intermediate in bulk composition and contain up to 2.6% S. Their density (13–38° API) dictates that they are near-surface drifters. They have low pristane/phytane ratios (pr/ph ≤ 2), abundant 4 α -methyl steranes (C₃₀ with 24-ethyl substitution) and, in most cases, high concentrations of botryococcane. This biomarker assemblage indicates accumulation of freshwater algal source material (including the remains of *Botryococcus* sp. and dinoflagellates) under anoxic to suboxic conditions. The additional presence of 28,30-bisnorhopane, dinosterane and 24-*n*-propylcholestane among the molecular fossils in Family 3 bitumens suggests derivation from a lacustrine organic facies subject to marine incursions; or, alternatively, mixing in the reservoir of two end-member (lacustrine and marine) oil types. Trace amounts of oleanane, and isomeric bicadinanes in the waxy bitumens constrain the age of their source rocks (Late Cretaceous or younger) and also preclude their local derivation; an Indonesian origin is considered likely, implying long-distance transport by surface ocean currents.

The Family 4 bitumens (~5° API) are bottom drifters. These sulphur-rich (3–6% S), aromatic-asphaltic crudes have molecular signatures that include: pr/ph ~1; C₂₇ > C₂₉ > C₂₈ > C₃₀ desmethyl steranes; dinosterane dominant over 4 α -methyl-24-ethylcholestane; an enhanced concentration of 28,30-bisnorhopane relative to hopane; and the absence of 2- or 3-methylhopanes. A distal, anoxic marine facies of the Late Cretaceous Belfast Mudstone in the eastern Otway Basin, or its lithostratigraphic equivalent in the Duntroon Basin, are possible local sources of the asphaltic bitumens.

Key words—coastal bitumen, asphaltite, oil seeps, source rocks, kerogen, Otway Basin, Duntroon Basin, Australia, Indonesia, stable isotopes of carbon and sulphur, aliphatic biomarkers, botryococcane, 4 α -methyl steranes, oleanane, bicadinanes, diterpanes, GC-MS, oil exploration

INTRODUCTION

The stranding of bitumen along the southern coastline of Australia was first reported in the early 19th Century. Later, on the premise that it represented weathered crude oil and tar from adjacent submarine seeps, coastal bitumen provided the impetus for the first petroleum exploration in South Australia and Tasmania (Sprigg and Woolley, 1963; Sprigg, 1986). Lumps of variously weathered waxy crude oil and

black asphaltite (tar) are regularly washed ashore along the coastlines of South Australia and western Victoria; rarer strandings are recorded from the south coast of Western Australia and the west and south coasts of Tasmania (McKirdy and Horvath, 1976; Bendall *et al.*, 1991; Currie *et al.*, 1992; Volkman *et al.*, 1992).

Since late 1989 the stranding of bitumen on selected beaches between Kangaroo Island and Cape Otway (Fig. 1) has been systematically monitored (Padley *et al.*, 1991). Our preliminary findings suggest that coastal bitumens generally strand in west or southwest facing bays which are not protected by offshore reefs or subtidal seagrass. They are commonly found at the high water mark on medium to high-energy, sandy beaches with a gentle to moderate slope. They also occur within blowouts in Holocene dune deposits at the back of the beach. Some very

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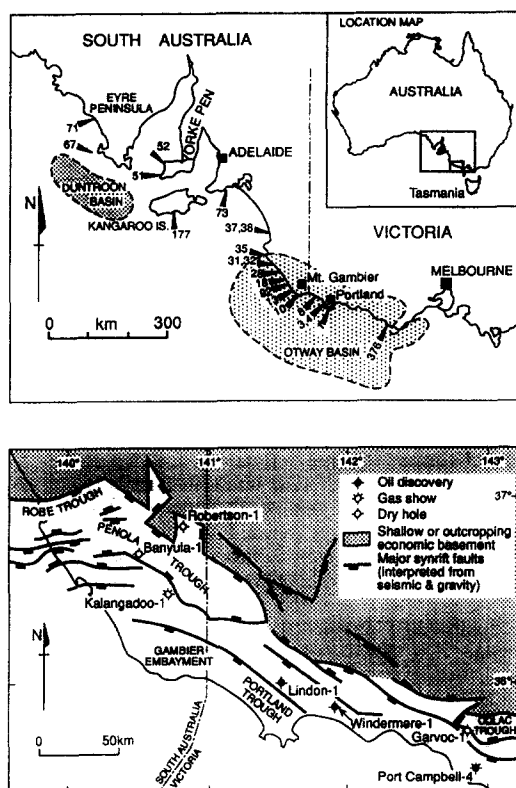


Fig. 1. Southern Australian continental margin showing the location of the Otway and Duntroon Basins, major structural elements, coastal bitumen stranding sites, and the petroleum exploration wells sampled in this study.

weathered bitumens have been discovered in fossil blowouts up to 200 m from the present-day coastline. In one such case, the bitumen is closely associated with a layer of pumice and other seaborne debris (e.g. cuttlefish). Dating of the latter materials is currently being attempted.

Previous geochemical studies of these coastal bitumens have documented differences in their sulphur content and carbon, hydrogen and sulphur isotopic compositions which indicate that they belong to at least four separate oil families (McKirdy, 1984a, b, 1985a, b; McKirdy *et al.*, 1986, 1988). Moreover, the presence in some waxy bitumens of abundant botryococcane, the saturated derivative of botryococcene, a C_{34} acyclic isoprenoid alkene synthesised only by *Botryococcus braunii*, and of 4-methyl-24-ethylsteranes probably derived from freshwater dinoflagellates (McKirdy *et al.*, 1986; Summons *et al.*, 1987, 1992), signifies that their parent oils were generated from lacustrine source rocks. Accordingly, it was proposed by McKirdy *et al.* (1986) that source beds rich in lacustrine algal organic matter (Type I kerogen) may occur in Late Jurassic–Early Cretaceous rift-valley sediments preserved at depth in the Voluta Trough of the offshore Otway Basin, and possibly also in the Duntroon Basin (Fig. 1).

The part of the Australian Plate comprising the Otway and Duntroon Basins has long been con-

sidered a favourable site for submarine oil and gas seepage. Historically, the coastal bitumens have been linked to offshore oil seeps on the basis of (1) oceanographic studies which establish the direction of surface currents; (2) the weathering characteristics of the bitumens; (3) the highly faulted nature of the southern continental margin; and (4) claims that the quantity of stranded bitumen temporarily increases following local earthquake activity (Sprigg and Woolley, 1963; McKirdy and Horvath, 1976; Sprigg, 1986). Recent work in the Otway Basin (McKirdy and Heggie, 1987; Heggie *et al.*, 1988; O'Brien and Heggie, 1989) has established the widespread occurrence of anomalously high concentrations of C_1 – C_4 hydrocarbons in seafloor sediments at water depths of 450–2500 m. These gas anomalies lie above major faults which appear to be acting as conduits for thermogenic hydrocarbons migrating upwards from mature to overmature Cretaceous source rocks, or discrete petroleum accumulations.

Notwithstanding the aforementioned circumstantial evidence for a local origin of the bitumens, no *bona fide* submarine seepage of oil has yet been located in either the Otway Basin or the Duntroon Basin. In addition, recent studies of coastal bitumens in Western Australia (Currie *et al.*, 1992) and the Northern Territory (Summons and Boreham, unpublished data) raise the possibility of long-distance marine transport of waxy crude oil from Indonesian waters. Hence, in order to develop tenable models (geological and oceanographic) for the source, entrapment, subsurface migration, seaborne transportation and weathering of the southern Australian bitumens, it becomes essential to document their physical properties and chemical composition. Fortunately, these bitumens have rather unusual biomarker geochemistries which provide specific clues to the nature of their precursor organic matter, and constrain both the age and palaeoenvironment of their source rocks.

In this paper we report the results of a geochemical survey of a representative suite of 23 bitumens collected from South Australian and Victorian beaches (Fig. 1). For the purpose of testing possible correlations with local (Otway Basin) and Indonesian sources, we also examined 12 organic-rich sediments of Mesozoic age and five conventionally-produced crude oils.

GEOLOGICAL SETTING

The Otway Basin is one of several extensional sedimentary basins located along the southeastern margin of Australia which formed in response to the rifting and eventual breakup of eastern Gondwana. In this case, Late Jurassic to Early Cretaceous sediments deposited during the rift phase of basin development are of particular interest because they host (1) lacustrine potential source beds, and (2) the most

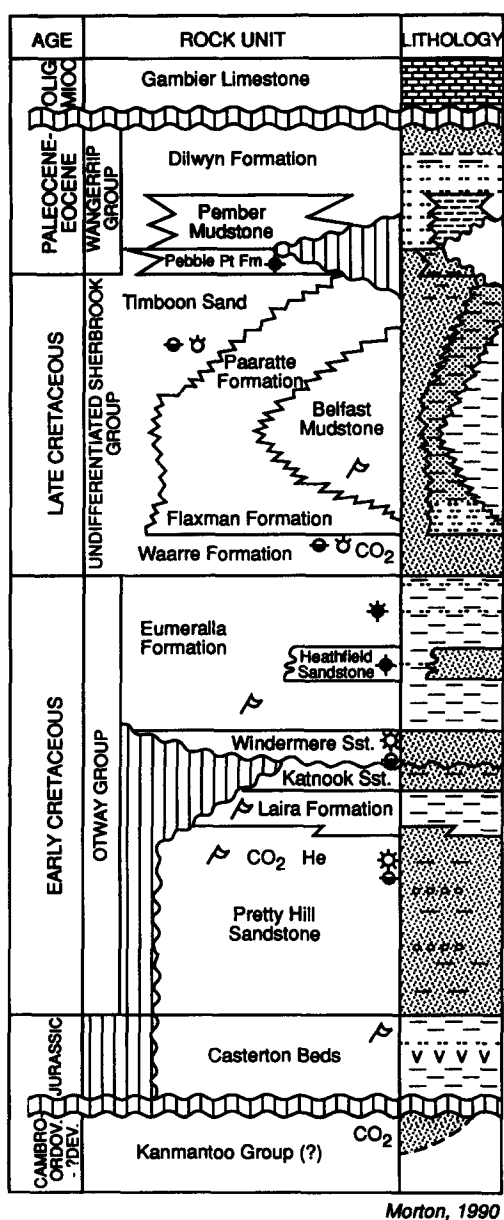


Fig. 2. Stratigraphic distribution of petroleum source rocks (flag symbol) and reservoir rocks in the Otway Basin.

recent oil and gas discoveries in the area (Kopsen and Scholefield, 1990) (Fig. 2).

Filling of fault-bounded grabens and half-grabens commenced in the western part of the basin (Robe and Penola Troughs) in mostly lacustrine environments with deposition of the Casterton Beds, a sequence of carbonaceous shale, minor feldspathic sandstone and siltstone, and interbedded olivine basalt and volcanoclastics (Gravestock *et al.*, 1986). This early rift succession is overlain by the more extensive sediments of the Otway Group, comprising in turn the Pretty Hill Sandstone (braided fluvial sands with carbonaceous siltstone and mudstone); the Laira Formation (lacustrine shale, in part very carbonaceous, with siltstone and minor sandstone); the

Katnook Sandstone (meandering to distal braided fluvial sandstone and interbedded carbonaceous siltstone); and the Eumeralla Formation (lacustrine and paludal silty claystone with interbedded, fine-grained sandstone and thin coal seams) (Morton, 1990). Sandstones within the Eumeralla Formation (Windermere and Heathfield Members: Fig. 2) are important reservoir units in the late rift-fill sequence.

The Otway Basin was located at high palaeolatitudes (70–80°S), well within the Antarctic Circle, during the Early Cretaceous (Indurum, 1985; Barron, 1987). Oxygen isotope data on diagenetic calcite in the Otway Group suggest mean annual temperatures of less than 5°C (Rich *et al.*, 1988). Nevertheless, a diverse assemblage of fossil plants, invertebrates and vertebrates (including turtles and hyslopodontid and theropod dinosaurs) has been recorded in these sediments. Their biota as a whole is consistent with a cool-temperate, humid climate subject to seasonal extremes (Rich *et al.*, 1988, 1989). The polar forests of the Australo-Antarctic rift valley and adjacent uplands comprised both deciduous and evergreen trees, notably ginkgos and araucarian and podocarp conifers, with an understorey of seed ferns, equisetaleans and bryophytes (Douglas and Williams, 1982; Drinnan and Chambers, 1986; Rich *et al.*, 1988). Algae were abundant in aquatic (swamp and lacustrine) environments (Dettmann, 1986).

Rift-associated subsidence decreased in the late Albian, and Otway Group sedimentation was terminated by a mid-Cretaceous episode of differential uplift, tilting and erosion which represents the onset of continental breakup of Australia and Antarctica between 100 and 90 Ma ago (Veevers, 1986). Uplift of the northern margin of the basin resulted in the deposition of a southward and westward thickening wedge of deltaic sediments (Sherbrook Group), including the moderately carbonaceous and pyritic Belfast Mudstone. The palaeolatitude of the basin at this time was about 60°S. Seafloor spreading rates were low (Cande and Mutter, 1982), and variations in the balance between rates of subsidence and deposition were probably critical in determining the extent and duration of marine incursions (Gravestock *et al.*, 1986). The Tertiary sequence consists of a second deltaic complex (Wangerrip Group) unconformably overlain by marine shelf carbonates (Gambier Limestone) (Fig. 2).

The total Mesozoic and Cainozoic sequence of the Otway Basin locally attains thicknesses up to 10 km. Organic-rich lithofacies (mudstone, siltstone, shale and coal) range in age from Late Jurassic to Eocene. However, vitrinite reflectance data (Cook, 1980; McKirdy, 1984a; Struckmeyer, 1988) and thermal modelling studies (Middleton and Falvey, 1983; Williamson *et al.*, 1987; O'Brien and Heggie, 1989) indicate that, throughout most of the basin, Tertiary sediments lack adequate thermal maturity to have been effective sources of petroleum hydrocarbons. Organic petrological studies (Struckmeyer, 1988;

Table 1. Composition of coastal bitumens from southern Australia and selected crude oils from the onshore Otway Basin

Sample (BMR No.)	Specific gravity °API	Sulphur content wt %	C ₁₂₊ Fraction					Pr/Ph	Bot/n-C ₂₉	Oil type*
			n + Iso (%)	Naph (%)	Arom (%)	Res (%)	Asph (%)			
Bitumen Family 1										
CB-1	27	0.30	38.0	15.2	8.3	43.8	3.7	2.2	0.27	PN
CB-38 (378)	25	0.30	45.6	17.7	8.6	23.9	4.2	2.0	0.45	P
CB-51	ND	0.22	22.3	24.3	2.3	43.6	7.5	[0.7]	0.50	[AI]
CB-67	ND	0.14	25.1	21.3	6.0	42.6	4.9	[0.7]	0.65	[AI]
CB-71	ND	0.15	30.8	26.3	4.1	34.8	4.0	[0.2]	0.35	[PN]
CB-77	38	0.13	35.2	21.9	3.0	34.7	5.2	[0.6]	0.28	[PN]
CB-84	35	0.17	29.5	28.4	0.5	36.1	5.4	[1.2]	0.30	[PN]
Bitumen Family 2										
CB-37 (604)	ND	0.60	37.9	20.3	6.8	26.3	8.7	1.0	0.61	PN
CB-31 (379)	21	0.90	62.7	11.1	7.2	14.9	4.1	0.5	0.02	P
CB-52	ND	1.4	24.0	20.2	6.0	40.2	9.7	1.0	0.28	[AI]
Bitumen Family 3										
CB-3	26	2.1	23.8	20.8	14.4	33.9	7.1	1.0	0.08	AI
CB-4	15	1.6	42.5	12.4	13.8	24.2	7.1	1.1	0.06	P
CB-8 (380)	16	2.4	28.9	23.1	14.5	28.0	5.5	0.9	0.05	PN
CB-10	24	1.8	52.0	14.0	12.9	18.2	2.9	1.0	0.08	P
CB-13	18	1.4	28.9	4.2	13.3	47.4	6.2	[0.9]	0.05	[AI]
CB-18	20	2.6	44.8	16.3	10.0	23.0	5.9	1.0	0.05	P
CB-28 (605)	17	1.3	25.9	7.7	11.1	29.7	25.7	1.2	0.24	AI
CB-35 (607)	17	2.3	40.5	11.2	14.8	25.8	5.5	1.0	0.07	PN
CB-73	ND	2.6	15.5	19.7	4.4	18.8	41.5	1.5	0.46	AI
CB-92 (606)	?20	2.0	27.9	21.7	12.2	25.1	13.1	0.7	0.19	AI
CB-376	13	2.1	11.9	23.9	18.7	37.6	7.8	0.8	0.27	AI
Bitumen Family 4										
CB-32 (381)	5	3.3	12.0	6.7	6.7	29.9	44.7	1.1	0.00	AI
CB-177	ND	ND	6.6	7.2	18.3	17.8	50.1	1.2	0.00	AA
Crude oils										
Pt Campbell-4 (45)	45	0.10	77.4		14.4	7.2	1.0	5.6	0.00	P
Lindon-1	28	0.08	30.1	27.3	8.5	30.1	4.0	3.4	0.00	PN
Windermere-1	41	0.04	54.1	29.2	8.4	7.6	0.7	6.1	0.00	P

*P = paraffinic, PN = paraffinic-naphthenic, AI = aromatic-intermediate, AA = aromatic-asphaltic.

[] = significantly modified by biodegradation.

ND = not determined.

Serafini, 1989; Padley, 1990a, b), supplemented by Rock-Eval pyrolysis, have highlighted the existence of three major source rock intervals in the western Otway Basin: Casterton Beds, Laira Formation

and lower Eumeralla Formation (Fig. 2). Selected organic-rich samples of all three fluvio-lacustrine to lacustrine units were included in the present study.

Table 2. Elemental and isotopic composition of selected coastal bitumens from southern Australia

Sample (BMR No.)	Whole bitumen						Hydrocarbons			
	C (%)	H (%)	N (%)	S (%)	Ash (%)	H/C (atomic)	$\delta^{34}\text{S}$ (‰)	δD (‰)	$\delta^{13}\text{C}_{\text{sat}}$ (‰)	$\delta^{13}\text{C}_{\text{arom}}$ (‰)
Bitumen Family 1										
CB-1	85.18	13.07	1.20	0.3	0.5	1.83	-2.2	-136	-25.1	-24.3
CB-38 (378)	85.67	12.94	0.82	0.3	<0.2	1.80	-2.5	-139	-25.2	-24.2
CB-51									-25.1	-24.4
CB-67									-25.4	-24.6
CB-71									-25.5	-24.5
CB-77									-25.6	
CB-84									-25.4	
Bitumen Family 2										
CB-37 (604)									-26.0	-25.2
CB-31 (379)									-26.1	-25.3
CB-52									-25.7	-25.5
Bitumen Family 3										
CB-3	81.36	11.71	0.81	2.1	0.5	1.71	-0.2	-97	-26.5	-25.9
CB-4	84.20	12.21	1.04	1.6	0.3	1.73	-4.9	-100	-26.4	-26.0
CB-8 (380)	84.60	12.26	1.33	2.4	0.8	1.73	-4.6	-98	-26.1	-26.0
CB-10	84.52	12.29	1.45	1.8	0.2	1.73	-5.4	-98	-26.4	-26.0
CB-13	84.16	12.14	0.65	1.4	0.2	1.72	-4.9	-99	-26.2	-25.9
CB-18	85.14	12.25	0.81	2.6	0.3	1.71	-5.6	-100	-26.5	-26.0
CB-73									-26.6	-25.7
CB-376	84.41	11.66	0.25	2.1	0.4	1.65	-2.5	-97	-26.7	-26.4
Bitumen Family 4										
CB-32 (381)	85.05	9.78	0.97	3.3	0.2	1.37	-6.8	-107	-30.0	-29.4
CB-177				?					-30.2	-29.6

Table 3. Maturity of coastal bitumens and selected crude oils from southern Australia

Sample (BMR No.)	C ₂₇ Sterane (% 20S)	C ₂₉ Hopane (% 22S)	Moretane Hopane	Ts Tm	MPI-1	VR _{calc} %
<i>Bitumen Family 1</i>						
CB-1	47	56	0.10	2.5		
CB-38 (378)	43	56	0.09	2.4	0.41	0.51
CB-51	44	58	0.10	2.3		
CB-67	45	58	0.10	2.3		
CB-71	52	56	0.10	2.3		
<i>Bitumen Family 2</i>						
CB-37 (604)	49*	56*	0.04*	2.3*		
CB-31 (379)	48*	57*	0.04*	1.4*	0.56	0.61
CB-52	45	60	0.09	1.2		
<i>Bitumen Family 3</i>						
CB-3	45	60	0.08	1.0		
CB-4	46	60	0.07	0.9	0.79	0.77
CB-8 (380)	52*	61*	0.08	1.1*		
CB-28 (605)	47*	57*	0.04*	1.3*		
CB-35 (607)	58*	54*	0.04*	1.0*		
CB-73	52	58	0.09	1.8		
CB-92 (606)	46*	58*	0.03*	1.1*		
CB-376	48	61	0.09	0.8		
<i>Bitumen Family 4</i>						
CB-32 (381)	49*	59*	0.05*	0.8*	0.75	0.75
CB-177	54*	57*	0.07*	0.8*		
<i>Crude Oils</i>						
Pt Campbell-4 (45)	57*	59*	0.06*	0.7*		
Lindon-1	50	60	0.15	0.7	1.21	1.07
Windermere-1	45	58	0.17	0.3	0.49	0.57
Parameter	1	2	3	4	5	6

Unless otherwise indicated parameters 1–5 calculated from peak areas in MID mass fragmentograms (* denotes value based on MRM data):

Parameter 1, $100 \times (20S)\text{-}24\text{-ethyl-}5\alpha,14\alpha,17\alpha\text{ (H)-cholestane} / [(20S) + (20R)\text{-}24\text{-ethyl-}5\alpha,14\alpha,17\alpha\text{ (H)-cholestane}]$.

Parameter 2, $100 \times (22S)\text{-}17\alpha,21\beta\text{ (H)-bishomohopane} / [(22S) + (22R)\text{-}17\alpha,21\beta\text{ (H)-bishomohopane}]$.

Parameter 3, $17\beta,21\alpha\text{ (H)-moretane} / 17\alpha,21\beta\text{ (H)-hopane}$.

Parameter 4, $18\alpha\text{-trisorneohopane} / 17\alpha\text{-trisorhopane}$.

Parameter 5, Methylphenanthrene Index of Radke and Welte (1983) measured as described in McKirdy and Chivas (1992).

Parameter 6, Calculated vitrinite reflectance derived using calibration of Boreham *et al.* (1988).

MATERIALS AND METHODS

Samples

The coastal bitumens and Australian oils analysed in this study are listed in Tables 1–3. The bitumens were retrieved from ocean beaches between Cape Otway, Victoria and Sheringa Beach on western Eyre Peninsula, South Australia (Fig. 1). Most of the bitumen samples were collected in 1983 by D. R. Vinall specifically for proprietary studies of the source rock and petroleum geochemistry of the Otway and Duntroon Basins then being undertaken by the senior author (McKirdy, 1984a, b). Sample 92 was recovered from Geltwood Beach by R. C. Sprigg in 1961; sample 376 was collected from Lion Headland by A. J. Hill in 1985; and sample 177 is part of a 7 kg block of asphaltite found at Bales Bay, Kangaroo Island, by one of the authors (DP) in 1991. Oils from Port Campbell-4, Lindon-1 and Windermere-1 are drill-stem test samples, whereas the two Indonesian crudes are from producing oil fields in Sumatra (Minas) and Java. The source rock samples (Tables 3 and 4) are washed cuttings from five onshore wells in the Otway Basin: Banyula-1, Kalangadoo-1, Robertson-1 and Casterton-1 in (or adjacent to) the Penola Trough, and Garvoc-1 on the southeastern flank of the Colac Trough (Fig. 1).

Sample preparation

Freshly collected waxy bitumens are coated (or more rarely mixed) with variable amounts of sand, shell and other debris. To ensure complete removal of such foreign matter, the bitumens were dissolved in excess dichloromethane at ambient temperature using ultrasonication and the solution filtered through a bed of Florosil in a sintered glass funnel. Solvent was removed by evaporation on a steam bath.

Organic petrology

The rock samples were selected for detailed geochemical analysis on account of their high total organic carbon contents (TOC > 1%) and, in particular, high proportions of liptinite in their organic matter and/or high hydrogen indices (HI > 150). Cuttings were crushed to ~2 mm, split to obtain representative portions and mounted in cold setting polyester resin. Upon hardening, the resin-bonded blocks were cut perpendicular to the layering induced by settling of the grains in the mounting medium and then hand-ground in stages on wet carborundum paper (120 to 1200 grit). The final polish was achieved with aqueous slurries of first chromium sesquioxide and then magnesium oxide on SELVYT cloth-covered mechanical laps.

Table 4. Source rock geochemical data, Otway Basin

BMR Sample No.	Well name	Depth (m)	Formation	TOC (%)	T _{max} (°C)	HI (mg S ₂ /g TOC)	EOM (ppm)	HC yield (mg/g TOC)	Sat Arom	Pr/Ph	Pr/n-C ₁₇
3902	Banyula-1	1981-1987	Eumeralla	27.8	429	229	1389	3.6	8.0	3.2	0.8
3903		2002-2005	Laira	32.2	437	196	556	ND	ND	ND	ND
3904		2779-2782	Pretty Hill	40.5	439	298	287	19.8	1.0	2.1	0.9
3905	Garvoc-1	1048	Eumeralla	31.1	417	174	5714	0.3	9.0	1.0	0.7
3906	Kalangadoo-1	1455.6	Eumeralla	16.3	429	450	3131	5.6	1.0	5.5	1.8
3907		1615-1630	Eumeralla	1.1	439	79	225	7.8	1.3	1.2	0.5
3908		1676-1691	Eumeralla	5.4	430	239	1000	10.1	2.0	1.5	0.8
3909	Robertson-1	1750-1762	Pretty Hill	2.6	439	195	109	ND	ND	0.6	0.5
—		1762-1765	Pretty Hill	7.1	432	515	2189	17.3	2.1	1.9	0.6
—		1765-1768	Pretty Hill	2.4	435	305	460	18.9	1.2	2.8	0.9
—	Casterton-1	1759-1762	Pretty Hill	13.8	437	352	4057	13.4	0.7	3.9	0.6
—		2362-2365	Casterton	45.9	441	192	8905				

BMR = Bureau of Mineral Resources; ND = not determined.

HC = extractable hydrocarbons (saturates + aromatics).

*Extracts combined for analysis by liquid chromatography.

The majority of the maceral analyses were performed in the Geology Department, University of Wollongong, using a Leitz Orthoplan microscope fitted with a permanently centred, variable diameter diaphragm, a MPV2 microphotometer and a digital data processing unit. Vitrinite reflectances were measured in monochromatic light at 546 nm using immersion oil (DIN 58884) of refractive index 1.518, and calibrated against synthetic spinel and garnet standards of 0.413, 0.917 and 1.726% reflectance. Procedures were in accordance with Australian Standard AS 2486 (Standards Association of Australia, 1981). Fluorescence-mode observations were made in violet/ultraviolet light excitation using a 100 W mercury lamp and a filter system comprising 3 mm BG3 and 4 mm BG38 excitation filters, a TK400 dichroic beam splitting mirror, and a K490 suppression filter. The maceral nomenclature and classification used is summarized in Table 3. The abundance of each maceral group (as volume %) occurring in coal, shaly coal and dispersed organic matter in clastic lithologies was estimated separately with the aid of visual comparison charts (Struckmeyer, 1988). Following a similar procedure, maceral analysis of samples from Casterton-1 was undertaken by Serafini (1989) in the Department of Geology and Geophysics, University of Adelaide, with a Leitz Ortholux II microscope.

Kerogen isolation and pyrolysis-gas chromatography (Py-GC)

Kerogen concentrates were prepared by serial acid digestion of the extracted rock in HCl and HF, and flotation in chloroform. Pyrolysis-gas chromatograms of the kerogens were obtained using a Pyroprobe Model 120 (Chemical Data Systems) which was interfaced to a Hewlett Packard 5700 gas chromatograph fitted with a SGE inlet splitter and a 25 m × 0.25 mm fused silica capillary column (HP Ultra 1). Details of instrument operation, and compound identification and quantification in the resulting Py-GC traces, are given in Powell *et al.* (1991).

Isolation and fractionation of hydrocarbons

Powdered rock samples were Soxhlet extracted with azeotropic dichloromethane/methanol (97:3) for 48 h. The extractable organic matter (EOM) was fractionated into saturated hydrocarbons, aromatic hydrocarbons and NSO compounds by standard liquid chromatography on activated silica. Asphaltenes were precipitated from the coastal bitumens and crude oils with petroleum ether prior to two-stage liquid chromatography on alumina and silica gel, as described by McKirdy and Chivas (1992). An aliquot of the saturated hydrocarbon fraction was treated with urea to separate the normal and iso-alkanes (adduct) from the cyclic and multibranched alkanes (non-adduct).

Elemental and isotopic analyses

The carbon, hydrogen, nitrogen, sulphur and ash contents of representative coastal bitumens were determined by standard microanalytical methods of the Australian Microanalytical Service, AMDEL (Melbourne, Victoria). D/H and $^{34}\text{S}/^{32}\text{S}$ ratios of selected whole bitumens were measured at Global Geochemistry Corporation (Canoga Park, Calif.). Results are reported as δD and $\delta^{34}\text{S}$ values relative to the SMOW and CDT standards, respectively.

Portions (~4 mg) of the saturated and aromatic hydrocarbon fractions of the coastal bitumens were heated at 900°C for 4 h over CuO and Ag wire in evacuated quartz combustion tubes. Following separation from the co-produced H_2O on a vacuum line, the CO_2 was collected for introduction to the mass spectrometer. $^{13}\text{C}/^{12}\text{C}$ ratios were measured on a VG602 isotope mass spectrometer at the CSIRO Division of Soils (Glen Osmond, South Australia). Appropriate corrections were made for the ^{17}O contribution. Anthracite was used as a working standard and the resulting data are presented as $\delta^{13}\text{C}$ values relative to PDB.

Gas chromatography (GC)

Saturated hydrocarbons isolated from the coastal bitumens and the Robertson-1 (Laira Formation) extract were analysed by flame ionization GC on a Perkin Elmer Sigma 2 instrument fitted with a WCOT fused silica capillary column (25 m \times 0.3 mm i.d., SGE QC3/BP1) and a flame ionisation detector (FID). Samples were injected in splitless mode and the oven was programmed from 80 to 290°C at 5°C min⁻¹. GC-FID of the saturates fractions of the Port Campbell-4 crude oil and other rock extracts was carried out using a Varian 3400 instrument equipped with a 25 m \times 0.2 mm i.d. WCOT fused silica capillary column (HP Ultra-1), on-column injection at 60°C, and a temperature programme rate of 4°C. In both systems the column stationary phase was crosslinked methylsilicone and the carrier gas was hydrogen.

Gas chromatography-mass spectrometry (GC-MS)

The branched/cyclic alkane (urea non-adduct) fractions of the bitumens were analysed in multiple-ion detection (MID) mode at Masspec Analytical (Stroud, Glos). Details of the instrumentation and analytical procedure are given in McKirdy *et al.* (1986).

Selected total alkane fractions and branched/cyclic sub-fractions were analysed in the multiple reaction (metastable peak) monitoring (MRM) mode, as described by Summons (1987) and Summons and Powell (1987), using a VG 7070E double focussing mass spectrometer in tandem with an HP 5790 gas chromatograph and a VG 11-250 data system. The mass spectrometer was operated at 70 eV and a source temperature of 250°C. The gas chromatograph was fitted with a 50 m \times 0.2 mm i.d. HP Ultra-1 capillary

column. Samples in hexane were injected on-column at 60°C. The oven was heated from 60 to 300°C at 4°C min⁻¹. Hydrogen at a linear flow rate of 30 cm s⁻¹ was the carrier gas. Sterane compounds were identified using the following parent-to-daughter transitions: C_{29} desmethyl steranes, $\text{M}^+400 \rightarrow m/z$ 217; C_{30} desmethyl steranes, $\text{M}^+414 \rightarrow m/z$ 217; C_{30} 4-methyl steranes, $\text{M}^+414 \rightarrow m/z$ 231. The C_{27} , C_{28} and C_{30} hopanes were detected by their respective M^+370 , 384 and 412 $\rightarrow m/z$ 191 transitions, and their methyl analogues by $\text{M}^+ \rightarrow m/z$ 205. Bicinanes W, T, R (Grantham *et al.*, 1983) and T1 were detected using the $\text{M}^+412 \rightarrow m/z$ 369 transition. MeT is a ring-methylated derivative of T detected in the $\text{M}^+426 \rightarrow m/z$ 383 transition and it partially co-elutes with R. The composite GC peak for MeT plus R was referred to as R' in earlier work by Alam and Pearson (1990). W has been assigned as *trans-trans*-bicadinane (Cox *et al.*, 1986) and T as *cis-cis-trans*-bicadinane (van Aarssen *et al.*, 1992). T1 and MeT (our nomenclature) refer to an isomer and a ring-methylated derivative of T, respectively.

Branched/cyclic alkanes from the Lindon-1 and Windermere-1 oils, coastal bitumen 10 and the Casterton-1 (Pretty Hill Sandstone and Casterton Beds) extracts were analysed using a Hewlett Packard 5987 GC-MS and data system in the multiple ion detection (MID) mode. GC conditions were as follows: 60 m \times 0.24 mm i.d. WCOT fused silica column (Chromapak) connected directly to the ion source; on-column injection; hydrogen carrier gas; temperature programme 50–274°C at 8°C min⁻¹, 274 to 300°C at 1°C min⁻¹, 300°C for 11 min.

RESULTS AND DISCUSSION

Analytical data on the bulk chemical and isotopic compositions of a suite of coastal bitumens and conventional crude oils from the Otway Basin are

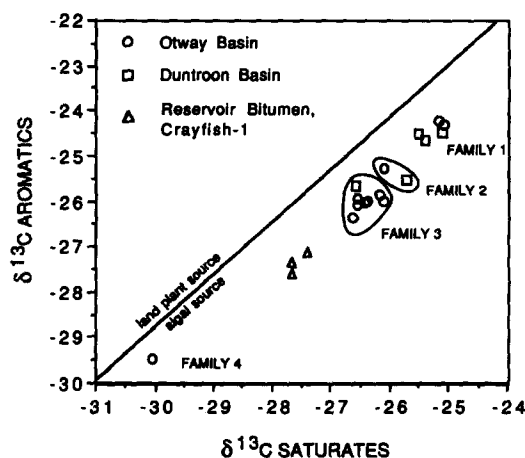


Fig. 3. Carbon isotopic compositions of C_{12+} saturated and aromatic hydrocarbons in coastal bitumens from southern Australia. The oblique line, based on the work of Sofer (1984), separates land-plant-derived oils from those of algal origin.

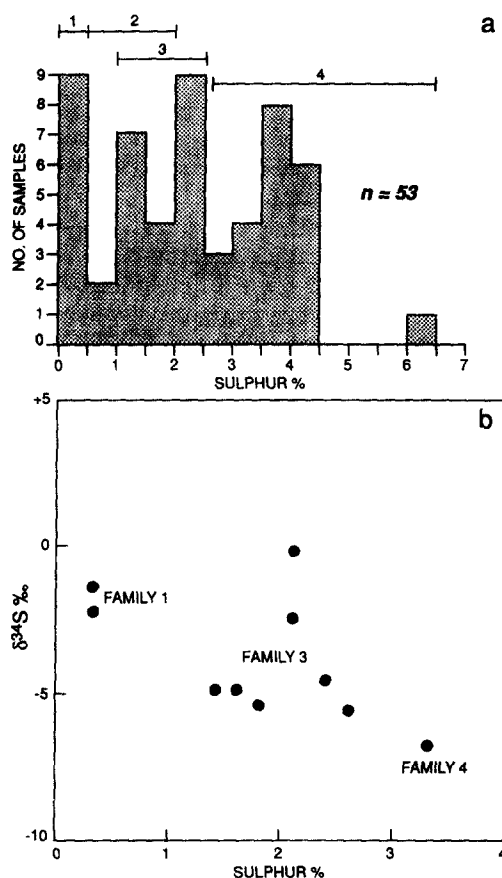


Fig. 4. (a) Sulphur contents and (b) sulphur isotopic compositions of selected coastal bitumens from southern Australia. Range bars refer to sulphur contents of bitumen Families 1-4.

summarized in Tables 1 and 2 and Figs 3 and 4. The thermal maturity of these materials, as indicated by various maturation-sensitive biomarker ratios and, in selected cases, the methylphenanthrene index, is shown in Table 3. Organic petrological and geochemical data on potential source rocks in the Otway Basin are presented in Tables 4 and 5. Representative GC-FID traces of the saturated hydrocarbons in these petroleum and source rocks are shown in Figs 5-7. The contrasting distributions of desmethyl and 4-methyl steranes and pentacyclic triterpanes in a waxy bitumen and an asphaltite are illustrated in Figs 8 and 9, whereas Fig. 10 displays the bicadinane distributions of four coastal bitumens and two Indonesian crude oils. The diterpane distributions of a waxy bitumen, and an indigenous crude oil from the Otway Basin are compared in Fig. 11. Derived source-dependent biomarker ratios and relative abundances in selected bitumens, oils and rock extracts are documented in Tables 6-8. Py-GC traces (Fig. 12) allow molecular typing of the kerogens preserved in the Otway Basin source rocks. The structures of key biomarker alkanes discussed in the text are shown in the Appendix.

Table 5. Source rock organic petrological data, Otway Basin

Sample No. BMR (UW)	Well name	Depth (m)	Formation	R _{max} (%)	Vitrinite	Inertinite (% of OM)	Liptinite	Major liptinite macerals*	Pyrolysis yield (µg/g TOC†)
3902 (21462)	Banyula-1	1981-1987	Eumeralla	0.60	50	19	31	sp, c, ld, sb, r, a, b	16.0
3903 (21463)		2002-2005	Laura	0.58	56	20	24	sp, c, ld, sb, a, r, f	ND
3904 (21472)		2779-2782	Pretty Hill	0.79	30	26	44	ld, sp, ?a, c, r, sb	18.1
3905 (20620)	Garvoc-1	1048	Eumeralla	0.47	33	47	20	sp, c, r, sb, b	11.0
3906 (21479)	Kalangadoo-1	1455.6	Eumeralla	0.39	5	47	48	sp, sb, c, ld, r, f	11.7
3907 (21498)		1615-1630	Eumeralla	0.43	45	24	31	sp, sb, ld, c, r, b, ?a	11.1
3908 (21499)	Robertson-1	1676-1691	Eumeralla	0.46	62	18	20	sp, c, sb, ld, r, f, b, a	ND
3909 (21604)	Casterton-1	1759-1762	Pretty Hill	0.59	10	28	62	a, ld, sp, c	30.0
		1759-1762	Pretty Hill	0.58	75	5	20	c, ld, ex, sp, b, r	ND
		2362-2365	Casterton	0.69	85	4	11	c, ld, ex	ND

BMR = Bureau of Mineral Resources; UW = University of Wollongong.

R_{max} = maximum vitrinite reflectance; ND = not determined.

*Listed in order of decreasing abundance: a = alginite; b = bitumen; c = cutinite; ex = exsudatinitite; f = fluorinitite; ld = liptodetrinite; r = resinite; sb = suberinite; sp = sporinite.

†C₁-C₃₀ n-alkanes + n-alk-1-enes.

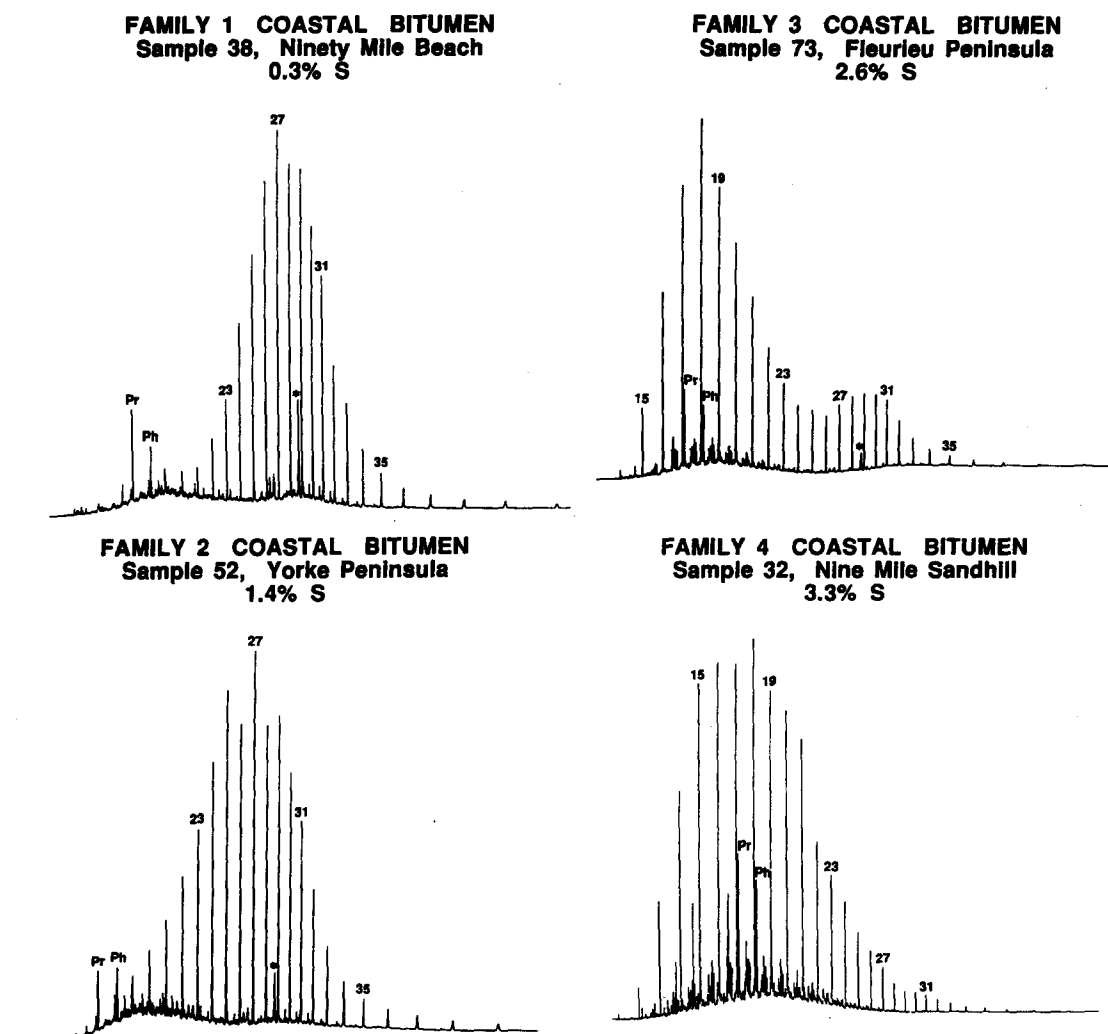


Fig. 5. Saturates chromatograms of representative coastal bitumens. Key: Pr = pristane; Ph = phytane; * = C_{34} botryococcane; numbers refer to carbon chain length of n -alkanes.

Classification of coastal bitumens

As previously demonstrated (McKirdy, 1984a, 1985a, b; McKirdy *et al.*, 1986), coastal bitumens from South Australia and western Victoria can be assigned to four different families, all of predominantly algal origin, on the basis of the carbon isotopic composition of their C_{12+} saturated and aromatic hydrocarbons (Fig. 3). Moreover, the hydrocarbons in Families 1–3 are enriched in ^{13}C by 3–5‰ compared to a Family 4 bitumen. This significant carbon isotopic difference is accompanied by differences in whole-bitumen sulphur content and S isotopic composition (Fig. 4), saturates distribution (Figs 5 and 6) and bulk chemical composition (Table 2).

Waxy bitumens (Families 1, 2 & 3)

Family 1 (<0.5% S) and Family 2 (0.6–2% S) bitumens are high pour point, waxy paraffinic to

paraffinic–naphthenic crudes with intermediate pristane/phytane ratios ($pr/ph = 1$ –2) and (in most cases) exceptionally high concentrations of botryococcane ($C_{34} \text{ botr}/C_{29} \text{ } n\text{-alkane} = 0.3$ –0.7) (Table 1). In some cases, selective depletion of C_{12} – C_{25} n -alkanes is quite marked (Fig. 5) and is the result of partial biodegradation, possibly during weathering at sea. These bitumens are characterized further (Table 7) by high hopane/sterane ratios (C_{27} – C_{34} hop/ C_{27} – C_{29} ster > 2); and variable cholestane/ethylcholestane ratios (C_{27}/C_{29} ster = 0.6–1.3). The 4α -methylsteranes (C_{30} with 24-ethyl substitution: Summons *et al.*, 1987) are abundant relative to desmethyl steranes (C_{30} 4α -Me ster/ C_{29} ster = 2–6). This biomarker assemblage indicates accumulation of lacustrine algal source material, including *Botryococcus* sp. and freshwater dinoflagellates, under suboxic conditions. Sulphate-bearing waters and iron-poor bottom sediments are necessary to account for the elevated sulphur contents of the Family 2 bitumens (McKirdy *et al.*, 1986).

**LAND-PLANT-DERIVED OIL
OTWAY GROUP
Pt. Campbell-4, 1789-1799 m**

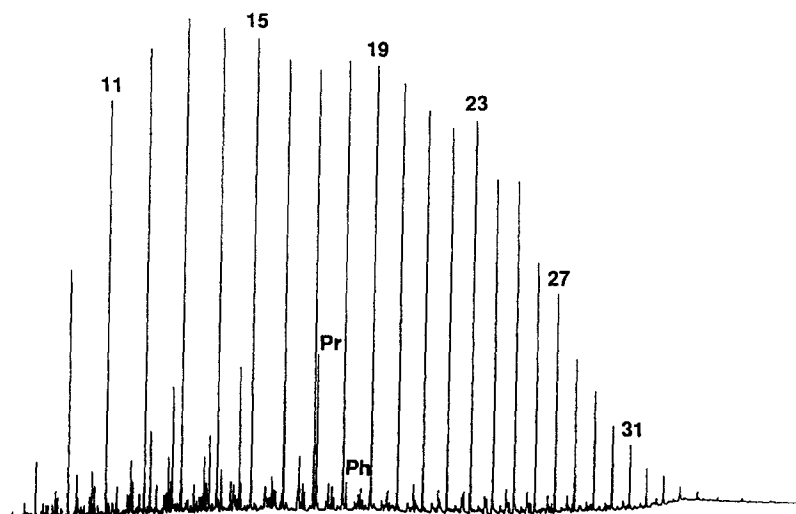


Fig. 6. Saturates chromatogram of a crude oil recovered from the Eumeralla Formation in Port Campbell-4, Otway Basin. Key: as for Fig. 5.

Some 'fine tuning' of the proposed genetic classification is required to accommodate the very low abundance of botryococcane and 4α -methylsteranes in certain waxy bitumens (e.g. sample CB-31: Tables 1 and 7). These bitumens, herein assigned to Family 2', also contain trace amounts of dinosterane and 24-propylcholestane (Table 1) signalling the minor contribution of marine algae (see Summons *et al.*, 1987; Moldowan *et al.*, 1990) to their source material.

Family 3 bitumens likewise contain significant concentrations of C_{23+} *n*-alkanes, botryococcane and 4α -methyl steranes but tend to be richer in sulphur (1–2.6% S), have uniformly low pristane/phytane ratios ($pr/ph \leq 1$), and include samples of aromatic-intermediate bulk composition. The Family 3 bitumen shown in Fig. 5 is actually one of the least waxy of its type. The additional presence of 28,30-bis-norhopane, dinosterane and 24-propylcholestane among their molecular fossils suggests derivation from an anoxic lacustrine organic facies subject to episodic marine incursions or, alternatively, mixing in the reservoir of two end-member (lacustrine and marine) oil types.

A subordinate land plant contribution to the source beds of the Family 1–3 bitumens is evident from the trace amounts of oleanane and isomeric bicadinanes (W, T, T1 and R), ring-methylated bicadinane (MeT) and some diterpanes (notably C_{18} – C_{20} labdanes and phyllocladane) (Table 8; Figs 8, 10 and 11). These terpenoid hydrocarbons collectively constrain both the age and palaeoenvironment of the source rocks which produced the bitumens (or, more precisely, their parent oils).

Oleanane occurs in oils from Late Cretaceous or younger source rocks to which angiosperms have contributed organic matter (Riva *et al.*, 1988), whereas the diterpanes are derived from resin acids produced by both gymnosperms (mainly conifers) and angiosperms (Alexander *et al.*, 1987). Bicadinanes hitherto have been found only in Tertiary-sourced oils from S.E. Asia (Grantham *et al.*, 1983; Cox *et al.*, 1986; van Aarssen *et al.*, 1990a, b, 1992; Alam and Pearson, 1990). However, the present-day biogeography of the Dipterocarpaceae, the tropical hardwood source of dammar resin which is a known precursor of the bicadinanes (Van Aarssen *et al.*, 1990a, b, 1991, 1992), requires a fossil record of ancestral forms extending back at least as far as the mid-Late Cretaceous (Cronquist, 1981). More problematical for sourcing them within the offshore Otway and Duntroon Basins is the lack of recognisable dipterocarp plant fossils anywhere in the Cretaceous and Tertiary of Australia (D.C. Christophel, personal communication, 1991).

Asphaltic bitumens (Family 4)

In marked contrast to the waxy coastal bitumens, the Family 4 bitumens are heavy, sulphur-rich (3–6% S), aromatic-asphaltic crudes best described as asphaltites (Padley *et al.*, 1991). Their saturated hydrocarbon distributions (Fig. 5) are typical of unaltered marine crude oils (e.g. $pr/ph \sim 1$; $pr/n-C_{17} \sim 0.3$; unimodal *n*-alkane profile with maximum below C_{20}). Other molecular signatures that are consistent with their presumed anoxic, marine source affinity are

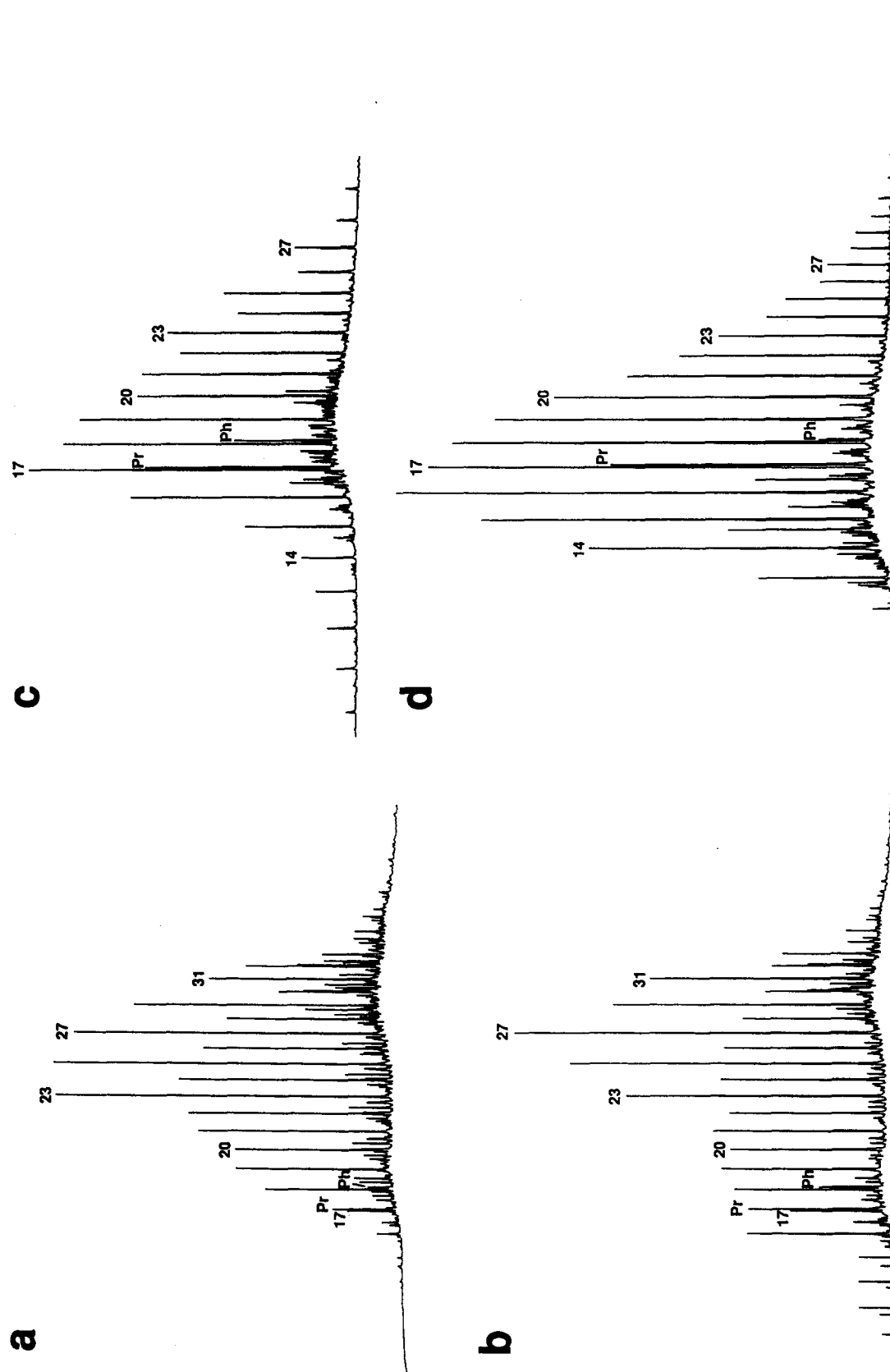


Fig. 7. Saturates chromatograms of selected Cretaceous immature source rocks in the Otway Basin. (a) Eumeralla Formation, Banyula-1 (1981–1987 m); (b) Pretty Hill Sandstone, Banyula-1 (2779–2782 m); (c) Pretty Hill Sandstone, Robertson-1 (1762–1768 m); (d) Casterton Beds, Casterton-1 (2362–2365 m). Key: as for Fig. 5.

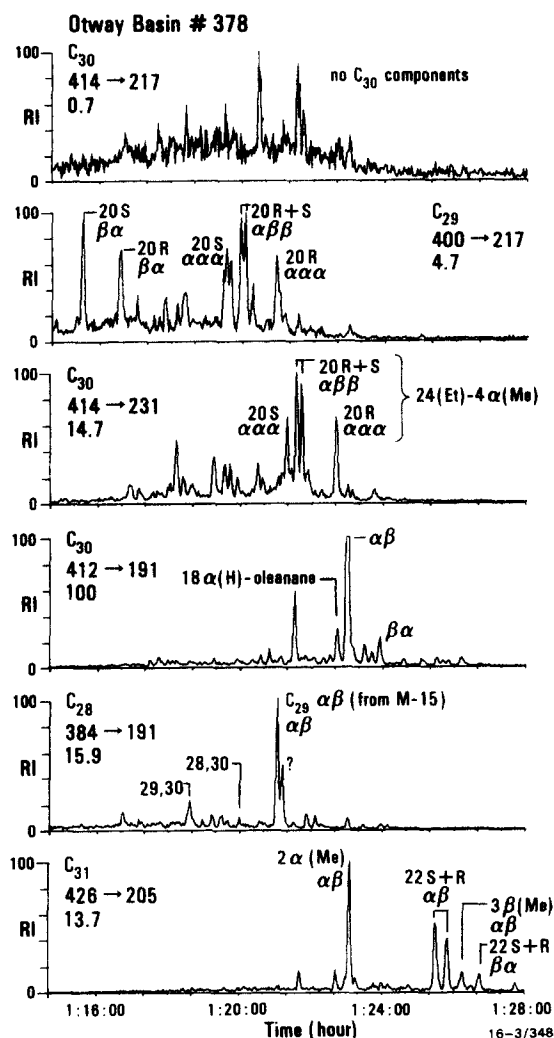


Fig. 8. MRM chromatograms showing the distributions of steranes ($M^+ \rightarrow 217$ and 231) and triterpanes ($M^+ \rightarrow 191$ and 205) in a Family 1 waxy bitumen (CB-38/BMR #378).

desmethyl steranes ($C_{27} > C_{29} > C_{28} > C_{30}$), dinosterane dominant over 4α -methyl-24-ethylcholestane, an enhanced concentration of 28,30-bisnorhopane relative to C_{30} hopane, and the absence of botryococcane, oleanane and the bicadinanes (Tables 1 and 8; Figs 9 and 10). The presence of dinosterane in relatively high concentrations suggests that their source rock is no older than mid-Triassic (Summons *et al.*, 1992). One unusual feature of the asphaltites is their complete lack of methyl hopanes (Fig. 9). This is uncommon in marine oils which usually contain 2α -methyl hopanes and lesser amounts of their 3α -methyl counterparts (Summons and Jahnke, 1990). Both compound types are markers for methanotrophic bacteria. The asphaltites appear to be closely related to tars from the west coast of Tasmania (Bendall *et al.*, 1991; Volkman *et al.*, 1992).

Potential petroleum source rocks in the Otway Basin

The cuttings samples selected for geochemical

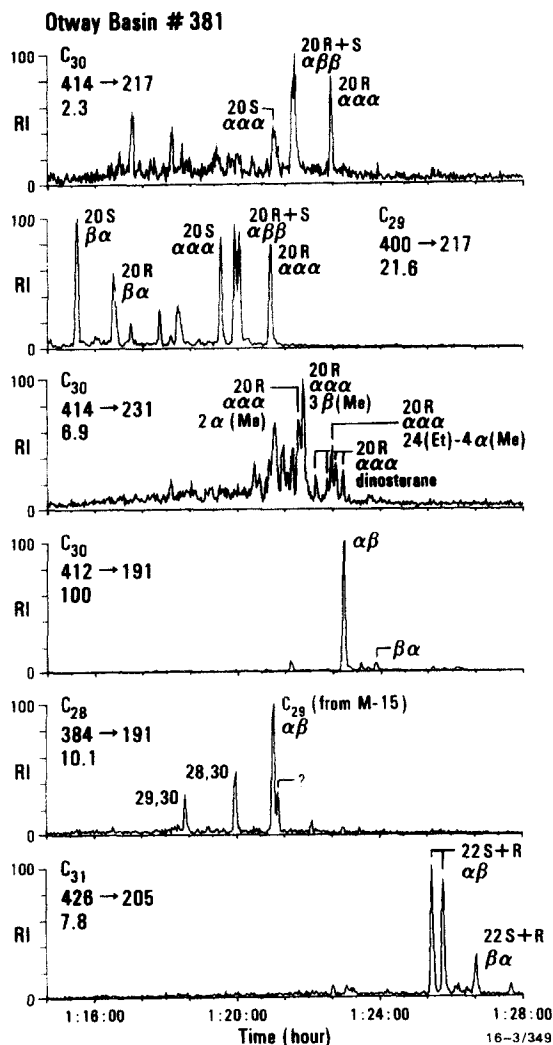


Fig. 9. MRM chromatograms showing the distributions of steranes ($M^+ \rightarrow 217$ and 231) and triterpanes ($M^+ \rightarrow 191$ and 205) in a Family 4 asphaltic bitumen (CB-32/BMR #381). Assignment of $20R$ -dinosteranes was made with reference to Summons *et al.* (1987, 1992).

evaluation of their hydrocarbon source potential contain organic matter which, for the most part, is of low thermal maturity ($T_{max} = 417\text{--}441^\circ\text{C}$; vitrinite R_i , $max = 0.39\text{--}0.60\%$) (Tables 4 and 5). This accounts for the low yields of extractable C_{12+} hydrocarbons (< 20 mg/g TOC); the marked predominance of odd-carbon-numbered homologues in the C_{23+} n -alkanes; and, in some sediments, low ratios of pristane to phytane ($pr/ph \leq 2$) (Table 4; Fig. 7). For samples 3904, 3905, 3907 and 3908 land plants were the major contributors of organic matter (Table 5); and their low pr/ph values may be the result of incomplete conversion of functionalized precursors (e.g. phytanic acid) to the C_{19} isoprenoid alkane. However, the low ratio of pristane to phytane in sample 3909 ($pr/ph = 1.9$) accurately reflects deposition of algal-rich, lacustrine organic matter under suboxic conditions. High ratios of saturated to aromatic hydrocarbons in extracts of the Eumeralla Formation

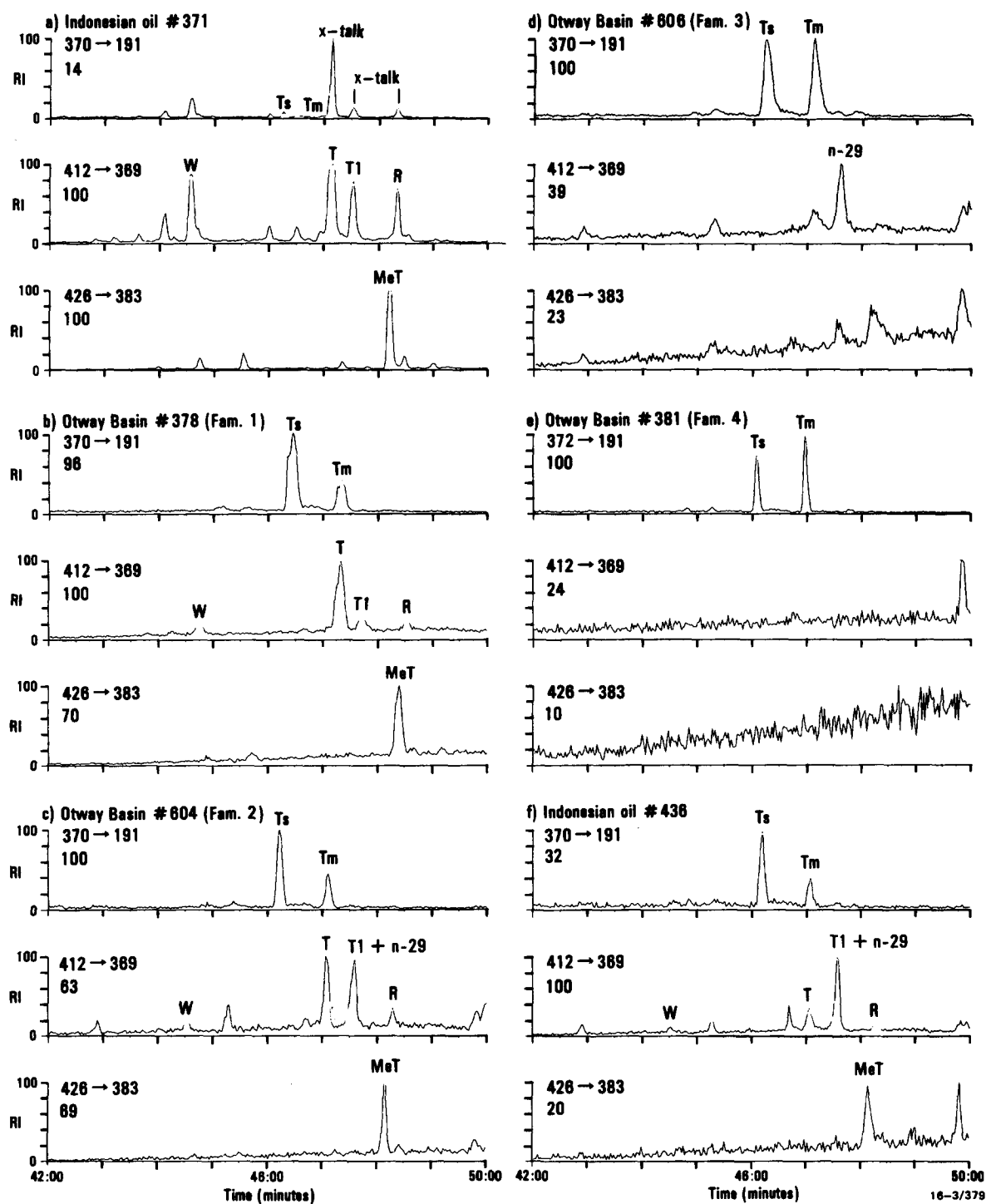


Fig. 10. MRM chromatograms showing the distributions of bicadinanes in Family 1-4 coastal bitumens with the corresponding data for a coal-derived Ardjuna Basin oil (#371) and the lacustrine Minas oil (#436) from the Central Sumatra Basin. Refer to experimental section for assignments. Data for oil #371 were obtained using a branched/cyclic hydrocarbon fraction, and "x-talk" indicates where bicadinane signals are evident in the trisnorhopane channel (370 → 191). The remaining data are for total saturated hydrocarbons, and some interference from *n*-alkanes is evident in the 412 → 369 channel used to detect C_{30} bicadinanes.

from Banyula-1 and Garvoc-1 (sat/arom = 8-9: Table 4) suggest that these two samples may be stained.

There is a poor correlation between the visually

estimated kerogen abundances (6-69% by volume) and the measured TOC contents (1-46%). The richer samples typically include significant amounts of coal and shaly coal, as well as common to abundant

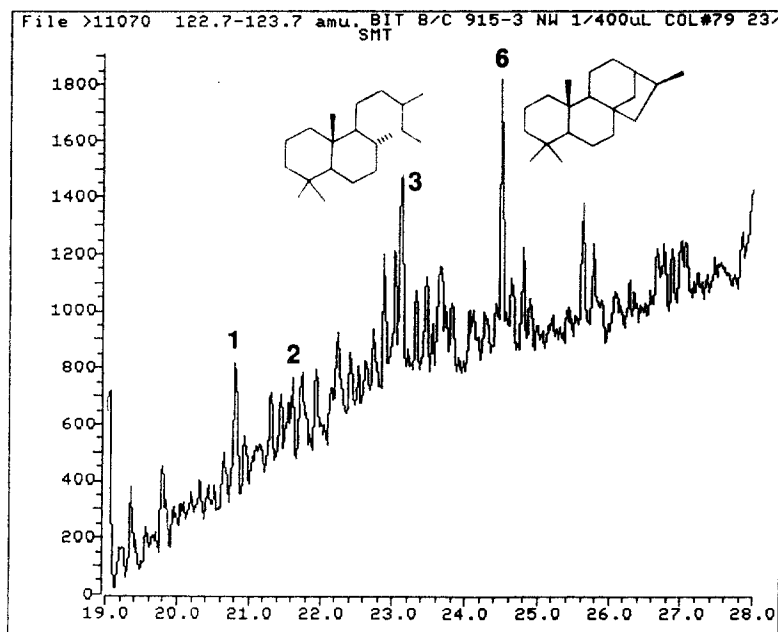
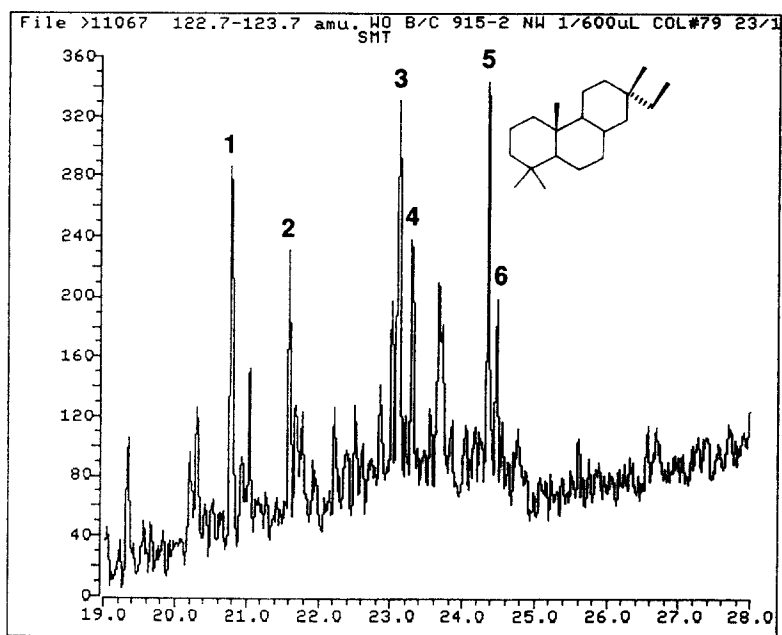
FAMILY 3 BITUMEN**CAPE NORTHUMBERLAND, S.A.****OIL, EUMERALLA FM.****WINDERMERE-1, VIC.**

Fig. 11. GC-MS-MID m/z 123 fragmentograms showing distributions of diterpanes in a Family 3 waxy bitumen (CB-10) and the Windermere-1 (Eumeralla) crude oil. Peak identification: 1-3, C_{18} - C_{20} labdanes; 4, C_{19} norisopimarane; 5, C_{20} isopimarane; 6, C_{20} 16 β (H)-phytylcladane.

dispersed organic matter (DOM). Their hydrogen indices ($HI = 174-450$) and low T_{max} values ($< 440^{\circ}C$) reveal the presence of thermally immature, oil and gas-prone, Type II/III kerogen. In general vitrinite is the dominant component, although the proportion of

liptinite usually equals or exceeds 20%. In several cases, liptinite is the most abundant maceral group. The major individual liptinite maceral is sporinite. For samples containing less than 6% TOC, suppression of kerogen pyrolytic yield by the mineral matrix

Table 6. Sterane distribution and botryococcane index in coastal bitumens, selected crude oils and a rock extract from southern Australia

Sample (BMR No.)	20R $\alpha\alpha\alpha$ Steranes			Botryococcane Index
	C ₂₇	C ₂₈	C ₂₉	
<i>Bitumen Family 1</i>				
CB-1	ND	ND	ND	740
CB-38 (378)	44*	23*	33*	560
CB-51	45	18	37	580
CB-67	43	22	35	870
CB-71	ND	ND	ND	600
<i>Bitumen Family 2</i>				
CB-37 (604)	35*	11*	54*	ND
CB-31 (379)	44*	23*	33*	10
CB-52	41	17	42	460
<i>Bitumen Family 3</i>				
CB-3	39	17	44	170
CB-4	38	18	44	140
CB-8 (380)	41*	25*	34*	140
CB-28 (605)	37*	26*	37*	ND
CB-35 (607)	43*	25*	32*	ND
CB-73	53	14	33	1200
CB-92 (606)	30*	20*	50*	ND
CB-376	43	21	36	130
<i>Bitumen Family 4</i>				
CB-32 (381)	46*	25*	29*	0
CB-177 (5683)	40*	27*	33*	ND
<i>Crude oils</i>				
Pt Campbell-4 (45)	8*	16*	76*	ND
Lindon-1	9	11	80	0
Windermere-1	8	13	79	0
<i>Rock extract</i>				
Robertson-1, 1762–1768 m	54*	27*	19*	0

Unless otherwise indicated ratios calculated from peak areas in MID mass fragmentograms (*denotes value based on MRM data).

Botryococcane Index = C_{34} botryococcane \times 100/[C_{37} – C_{40} head-to-head isoprenoid alkanes] (m/z = 183).

ND = not determined.

effect (Orr, 1983) may have resulted in artificially low HI values (see following discussion).

Molecular evidence confirming the hydrocarbon generative potential of Early Cretaceous shales and shaly coals from the Otway Basin is provided by their kerogen Py–GC traces (Fig. 12). On pyrolysis, humic coals yield largely aromatic and phenolic compounds and relatively few normal hydrocarbons (n -alkanes and n -alkenes). In contrast, oil-prone terrestrial organic matter produces abundant normal hydrocarbons in amounts that are comparable to or greater than those from marine kerogen, although the total pyrolysate from the latter is both greater in amount and richer in cyclic and aromatic hydrocarbons. With increasing maturation, pyrolysate composition shows a systematic increase in aromatics and a concomitant decrease in normal hydrocarbons and phenolic moieties. However, the original molecular 'fingerprint' of the organic matter persists well into the oil window. Pyrolysates of the Otway Basin sediments are moderately rich in normal hydrocarbons (C_7 – C_{30} n -alkanes + n -alk-1-enes = 11–26 mg/g TOC) of which a high percentage have extended chain lengths ($>C_{17}$). Using the classification scheme of Larter and Sentele (1985), the Otway Group kerogens may be assigned to the paraffinic Type II/III category. As such they have the potential to generate wet gas and minor waxy oil.

In a recent comprehensive study, Powell *et al.* (1991) showed that the capability of Australian

terrestrial carbonaceous sediments to generate and expel paraffinic oil broadly conforms with the established trends in petrographic composition (i.e. the relative proportions of liptinite and, in some cases, vitrinite as opposed to inertinite), although there is much variation which cannot be explained at the maceral group level. Among the individual liptinites, suberinite and to a lesser extent cutinite are associated with high pyrolytic yields of waxy normal hydrocarbons, whereas sporinite and liptodetrinite-rich samples generally give lower yields. In this sample set it could be argued that the C_{17+} normal hydrocarbons evident in the kerogen pyrolysates (Fig. 12) are derived from the subordinate cutinite and suberinite components of the liptinite fraction (Table 5). The highest pyrolytic yield of normal hydrocarbons was obtained from the Pretty Hill Sandstone in Robertson-1 (sample 3909), reflecting the unusually high liptinite content of its DOM and the dominance of alginite among its liptinite macerals.

There is little obvious difference between the pyrograms of samples 3906 (TOC = 16.3%, HI = 450) and 3907 (TOC = 1.1%, HI = 79), both from the Eumeralla Formation in Kalangadoo-1. Clearly, the anomalously low hydrogen index of the latter sample is an analytical artefact attributable to the mineral matrix effect.

Organic matter in the basal part of the Pretty Hill Sandstone at Robertson-1 differs markedly from the mostly higher-plant-derived material preserved elsewhere in the Otway Group and in the underlying Casterton Beds. About 10% of the cuttings from 1749–1762 m depth in this well are oil shale in which *Botryococcus*-related alginite (telalginite) and lamellar alginite (lamalginite) are major constituents (Table 5; Struckmeyer, 1988). Transitions between the oil shale and siltstone containing a higher proportion of woody-herbaceous DOM are also present in these cuttings. Detailed screening of this gross interval by Rock-Eval pyrolysis (Table 4) revealed that the oil shale lithofacies (TOC = 7%; genetic potential = 37 kg hydrocarbons/tonne; HI = 515) is quite thin and located between 1762 and 1765 m depth in Robertson-1.

Provenance of waxy and asphaltic bitumens

The onshore oil discoveries at Port Campbell-4, Lindon-1 and Windermere-1 & 2 appear to have originated from land-plant-dominated source rocks. Such carbonaceous shales and coals (TOC = 5–56%; HI = 230–450) are best developed within the lower part of the Early Cretaceous Eumeralla Formation (McKirdy, 1986, 1987; McKirdy and Watson, 1989; Kopsen and Scholefield, 1990; McKirdy and Chivas, 1992). However, extensive studies of the Otway Basin, and to a lesser degree the Duntroon Basin, have so far failed to identify local potential source beds for both the waxy and asphaltic coastal bitumens. Notwithstanding the alginite-rich character and excellent genetic potential of its dispersed organic

Table 7. Source-dependent biomarker ratios in selected coastal bitumens, a crude oil and rock extracts from Southern Australia

Sample (BMR No.)	30NH Hop	29,30BNH Hop	28,30BNH Hop	DiaH Hop	2 α MeH Hop	C ₂₇ Ster C ₂₉ Ster	C ₃₀ Ster C ₂₉ Ster	3 β MeSter C ₂₉ Ster	4 α MeSter C ₂₉ Ster	Σ C ₂₉ Dia Σ C ₂₉ Ster	Σ Hop Σ Ster
<i>Bitumen Family 1</i>											
CB-38 (378)	0.98	0.032	0.005	0.101	0.07	1.33	0.00	0.48	2.1*	0.42	11.7
<i>Bitumen Family 2</i>											
CB-37 (604)	0.52	ND	ND	0.109	0.10	0.64	0.22	ND	5.5†	0.60	9.2
CB-31 (379)	1.08	0.068	0.013	0.035	0.17	1.33	0.00	0.24	0.18†	0.67	2.2
<i>Bitumen Family 3</i>											
CB-8 (380)	1.99	0.073	0.007	0.003	0.08	1.21	0.06	ND	0.28†	0.32	5.6
CB-28 (605)	1.15	0.108	0.024	0.028	0.13	0.98	0.23	ND**	0.61†	0.32	2.3
CB-35 (607)	1.15	0.130	0.000	0.000	0.13	1.32	ND	ND	0.83†	0.32	2.5
CB-92 (606)	1.25	0.008	0.000	0.000	0.14	0.61	0.22	ND	0.88†	0.22	3.0
<i>Bitumen Family 4</i>											
CB-32 (381)	0.79	0.023	0.047	0.060	0.00	1.56	0.08	ND	0.43‡	0.52	1.9
CB-177	0.78	0.044	0.086	0.054	0.00	1.21	0.11	ND	ND	0.69	1.0
<i>Crude oil</i>											
Pt Campbell-4 (45)	0.55	0.015	0.013	ND	0.03	0.10	ND	0.34	ND	0.73	1.5
<i>Rock extracts</i>											
Banyula-1 (3902)	0.85	0.005	ND	ND	0.01	0.06	ND	0.22	ND	0.38	13
Banyula-1 (3904)	0.63	ND	ND	ND	ND	0.06	ND	0.09	ND	0.16	10
Kalangadoo-1 (3906)	0.28	0.003	0.005	ND	ND	0.01	ND	0.21	ND	0.32	10
Kalangadoo-1 (3907)	0.51	0.003	0.007	ND	0.01	0.09	ND	0.09	ND	0.60	9.3
Robertson-1 (3909)	0.96	0.012	0.002	ND	0.06	0.49	ND	0.16	0.07	0.32	8.2
Robertson-1	ND	0.022	0.007	ND	ND	2.88	0.00	ND	ND	0.32	ND
Parameter	1	2	3	4	5	6	7	8	9	10	11

Ratios calculated from peak areas in MRM traces as follows:

- 17 α ,21 β (H)-30-norhopane/17 α ,21 β (H)-hopane.
 - 29,30-bisnorhopane/17 α ,21 β (H)-hopane.
 - 28,30-bisnorhopane/17 α ,21 β (H)-hopane.
 - 17 α -diahopane/17 α ,21 β (H)-hopane.
 - 2 α -methyl-17 α ,21 β (H)-hopane/17 α ,21 β (H)-hopane.
 - (20R)-5 α ,14 α ,17 α (H)-cholestane/(20R)-24-ethyl-5 α ,14 α ,17 α (H)-cholestane.
 - (20R)-24-propyl-5 α ,14 α ,17 α (H)-cholestane/(20R)-24-ethyl-5 α ,14 α ,17 α (H)-cholestane.
 - (20R)-3 β -methyl-24-ethyl-5 α ,14 α ,17 α (H)-cholestane/(20R)-24-ethyl-5 α ,14 α ,17 α (H)-cholestane.
 - [(20R)-4 α -methyl-24-ethyl-5 α ,14 α ,17 α (H)-cholestane + (20R)-4 α -methyl-23,24-dimethyl-5 α ,14 α ,17 α (H)-cholestane]/(20R)-24-ethyl-5 α ,14 α ,17 α (H)-cholestane.
 - Σ C₂₉ diasteranes/ Σ C₂₉ steranes.
 - Σ C₂₇-C₃₄ hopanes/ Σ C₂₇-C₂₉ steranes.
- *24-Ethyl alone.
†24-Ethyl dominant over dinosterane (4 isomers of 23,24-dimethyl).
‡Dinosterane dominant over 24-ethyl.
ND = none detected; ** $\alpha\beta$ isomers of 4 α -methyl-23,24-dimethyl cholestane coelute with 3 β -methyl-24-ethyl cholestanes.

matter at Robertson-1, lacustrine shale in the Early Cretaceous Pretty Hill Sandstone (Fig. 2) of the Robe-St. Clair-Penola Troughs can no longer be considered a suitable source rock for the waxy bitumens (Families 1–3). The mismatch between its biomarker assemblage and those of the bitumens is clearly shown in Tables 6 and 7. Likewise, there are

significant differences between the diterpane distributions of a representative Family 3 bitumen [16 β (H)-phylocladane > C₂₀ labdane > C₁₈ labdane] and an intra-Eumeralla crude oil from Windermere-1 (isopimarane > C₂₀ labdane > C₁₈ labdane) (Fig. 11). Indigenous Otway Basin oils also differ from the waxy bitumens in other important respects, notably

Table 8. Triterpane abundances in selected coastal bitumens and two Indonesian crude oils

Sample (BMR No.)	Oleanane Hopane	Bicad T Hopane	Bicad MeT Hopane	Oleanane Σ Bicad	Major bicadinanes*
<i>Bitumen Family 1</i>					
CB-38 (378)	0.076	0.450	0.295	0.124	W, T, Tl, MeT, R
<i>Bitumen Family 2</i>					
CB-37 (604)	0.063	0.222	0.192	ND	W, T, Tl, MeT, R
<i>Bitumen Family 3</i>					
CB-8 (380)	0.022	ND	ND	ND	W, T, Tl, R
CB-28 (605)	0.049	0.069	0.056	ND	W, T, Tl, MeT, R
CB-35 (607)	ND	0.081	0.050	ND	W, T, Tl, MeT, R
CB-92 (606)	0.049	0.300	0.039	ND	W, T, Tl, MeT, R
<i>Bitumen Family 4</i>					
CB-32 (381)	—	—	—	—	—
CB-177 (5683)	—	—	—	—	—
<i>Crude oils</i>					
Java (371)	0.690	11.5	16.5	0.018	W, T, Tl, MeT, R
Minas (436)	0.053	0.456	0.298	ND	W, T, Tl, MeT, R

*Compound assignments given in Methods section and Fig. 10.

— Oleanane and bicadinanes absent.

ND = not determined.

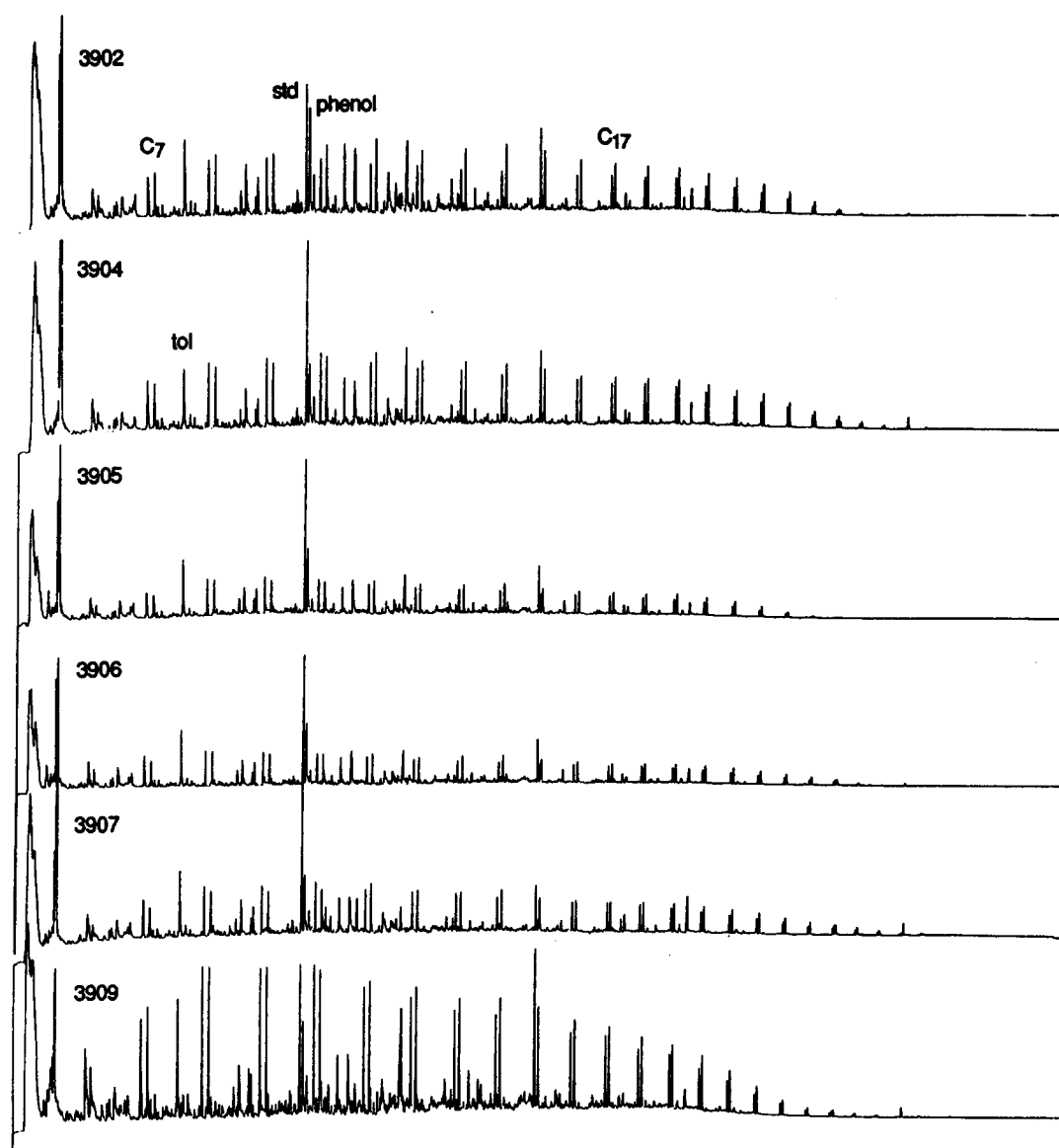


Fig. 12. Py-GC traces of kerogens isolated from immature potential source rocks in the Otway Basin. See Tables 4 and 5 for key to sample identification. Peaks used in quantitation are the C_7 - C_{30} normal alk-1-enes/alkanes. Internal standard is poly- α -methylstyrene.

C_{27} - C_{29} desmethyl sterane distributions dominated by 24-ethyl cholestane and their lack of botryococcane (Table 6).

During the Late Cretaceous, the configuration of the Southern Ocean was restricted enough to allow only limited access (via the Indian Ocean) to the deep oxygenated waters of the World Ocean. Therefore, it is reasonable to infer the existence of anoxic to suboxic organic facies in distal parts of the Late Cretaceous Belfast Mudstone (Fig. 2) within the eastern Otway Basin, or its partial lithostratigraphic equivalent in the Duntroon Basin (middle shale of the Wigunda Formation: R. Morgan, personal communication, 1992). World-wide deposition of marine sapropel is recorded in sediments of the same age

(Turonian-Santonian) from the North and South Atlantic and Western Tethys Oceans (Schlanger and Jenkyns, 1976; Jenkyns, 1980; Zimmerman *et al.*, 1987). Thus, global oceanic stagnation at this time could lead to widespread deposition of marine sediments containing oil-prone Type II kerogen. Any such organic-rich mudstone along Australia's southern continental margin, where penetrated by future petroleum exploration or ODP wells, or sampled by dredging of the seabed, would be an obvious candidate for detailed evaluation as a source for the Family 4 bitumens.

Specific molecular features of the waxy bitumens (viz. presence of oleanane and bicadinanes) attest to their derivation from organic matter to which

tropical vegetation was an important contributor. The Otway and Duntroon Basins are therefore excluded as possible depocentres of their source beds. Throughout their Cretaceous histories both basins were located at high palaeolatitudes. On the other hand, the Family 1–3 bitumens have molecular fossil assemblages (Tables 6–8) that resemble those of deep lacustrine source rocks (Pematang Brown Shale) and associated crude oils from onshore Central Sumatra (Seifert and Moldowan, 1981; Williams *et al.*, 1985; Longley *et al.*, 1990). Isotopically similar crudes sourced by a lacustrine facies of the Talang Akar Formation are produced from the North Seribu Trough, offshore N.W. Java (Pramono *et al.*, 1990), although these oils appear to lack botryococcane. In the adjacent offshore Sunda Basin, another family of lacustrine oils genetically linked to the Banuwati Shale (Robinson, 1987) are isotopically much heavier than those from the North Seribu Trough (Pramono *et al.*, 1990). Like the Family 1 bitumens, the Indonesian lacustrine oils invariably have low sulphur contents, whereas the Family 2 & 3 bitumens are sulphur-rich (0.6–2.6% S). The partly marine source affinity of the waxy Family 3 bitumens (cf. 28,30-bisnorhopane, dinosterane and 24-*n*-propylcholestane) suggests derivation from a lacustrine organic facies subject to marine incursions; or, alternatively, comingling in the reservoir of lacustrine and marine oil types. Marine-sourced oils are not common in Indonesia, although they do occur in the Sulawati Basin, Irian Jaya; the Banggai/Sula Basin, East Sulawesi; and the Bula Basin, Seram (Robinson, 1987; Price *et al.*, 1987).

Marine weathering and transport of bitumen

Individual bitumen pieces vary in both size and morphology reflecting differences in the bulk chemistry and degree of weathering of the parent oils. The most common waxy type (Families 1–3) comprises soft, round, black lumps which become hard and brown as weathering progresses. Weathering results in evaporative loss of light ends; an increased proportion of ONS-compounds and asphaltenes, mainly at the expense of aromatic hydrocarbons which are preferentially oxidized; and a progressive change from bimodal to unimodal *n*-alkane profile (maximum in C₂₃₊ range), due in part to biodegradation. The second type of bitumen (Family 4) is jet black asphaltite which breaks with a conchoidal fracture and may occur in spectacular blocks (up to 67 × 35 × 6 cm in size) that display a characteristic pattern of shrinkage cracks. Other categories of stranded material include fresh crude oils, and rounded fragments of dammar resin. Coastal bitumens *sensu stricto* (those attributable to nearby submarine oil seeps, or to far-travelled 'pelagic tar') are lumps of pure bitumen that contain little or no sand, although they may have a sand coating. When fresh oil (e.g. from tanker spills) washes ashore it almost immediately soaks into the sand forming globules

which, upon weathering, harden into discs of bitumen-cemented sand.

The waxy bitumens (15–38° API gravity) are near-surface drifters. Their molecular fossils point to a distant origin somewhere in the Indonesian Archipelago (e.g. Sumatra). Once discharged naturally or accidentally into the ocean (e.g. by way of rivers or submarine seepage), the parent oil could be rapidly carried southward in the warm surface waters of first the South Equatorial Current (Wilson and Allen, 1987) and then the Leeuwin Current (Cresswell and Golding, 1980; Church *et al.*, 1989) which eventually feeds into the Great Australian Bight. Such a transport mechanism was suggested by Currie *et al.* (1992) to account for similar bitumens along the coastline of Western Australia. The occurrence of dammar resin, a product of the tropical hardwood forests of S.E. Asia (Gianno, 1990), among the flotsam collected from the same South Australian beaches as the waxy bitumens tends to corroborate the proposed oceanic influx of non-indigenous (i.e. Indonesian) crude oil.

The coastal current model of Bye (1983) explains why, once in South Australian waters, the freshest waxy bitumen strands most frequently between Beachport, S.A. and Discovery Bay, Victoria. Fragments of waxy bitumen recovered from beaches on Eyre and Yorke Peninsulas and Kangaroo Island in South Australia, and to the east of Cape Bridgewater in Victoria, tend to be less abundant, smaller in size and more weathered, indicating that they are further travelled.

In contrast, the high specific gravity of the asphaltites (~5° API) ensures that they are bottom drifters. Some asphaltite blocks have been colonized by 'goose' barnacles and serpulid worm tubes, indicating that this type of bitumen may remain on the seabed for prolonged periods. Its stranding pattern is strongly influenced by bottom currents directed across the continental shelf towards southern Kangaroo Island and the Beachport Conservation Park, the observed loci for the occurrence of asphaltic bitumen in South Australia (Padley *et al.*, 1991). A local origin in offshore basins of the southern Australian continental margin seems likely for these asphaltites.

CONCLUSIONS

Sandy ocean beaches along the coasts of South Australia and western Victoria are focal points for the stranding of two varieties of seaborne petroleum: weathered waxy crude oil and black asphaltite (tar). These so-called coastal bitumens may be assigned to four genetic families on the basis of differences in sulphur content, whole-oil D/H and ³⁴S/³²S ratios, and the carbon isotopic compositions of their saturated and aromatic hydrocarbons. Their maturation-sensitive sterane and triterpane ratios and methyl

phenanthrene distributions are characteristic of crude oils expelled from source rocks of low to moderate maturity ($VR_{calc} = 0.5\text{--}0.8\%$ in waxy bitumens; $\sim 0.75\%$ in asphaltites).

Weathering has affected the coastal bitumens to various degrees, depending on their primary bulk composition (waxy vs asphaltic) and the duration of their exposure to the marine environment. Weathered waxy bitumens (Families 1–3) exhibit progressive changes, including loss of volatile components and water-soluble light ends, enhanced proportions of C_{12+} ONS-compounds and asphaltenes, and a unimodal n -alkane profile skewed towards the C_{25+} range. Accordingly, their bulk composition varies from paraffinic to aromatic-intermediate. The asphaltic bitumens (Family 4) are more resistant to physical and chemical weathering, and display little evidence of biodegradation.

The waxy bitumens contain an array of aliphatic biomarkers indicative of a freshwater algal source affinity. Green algae, notably *Botryococcus* sp., and dinoflagellates were major contributors to the parent kerogens. Three distinct lacustrine source facies can be inferred, all subject to minor inputs of terrestrial organic matter from adjacent tropical forests. The presence in the bitumens of bicadinanes, derived from ancient dipterocarp hardwoods, and oleanane, a non-specific angiosperm marker, suggest that their source rocks are of Late Cretaceous or Tertiary age. One group of waxy bitumens (Family 3) also contains molecular fossils attributable to marine algae, signifying either their derivation from a lacustrine source facies subject to marine incursion or mixing in the reservoir of two oil types.

Palaeoclimatic inferences based on the molecular fossil assemblages of the waxy coastal bitumens preclude their origin from within Mesozoic and Tertiary basins of the Australo-Antarctic Rift. However, their biomarker geochemistry resembles that of certain crude oils and source rocks from Tertiary rift basins in Sumatra and Java. Warm surface ocean currents operating along the western and southern continental margins of Australia seem capable of transporting these bitumens and other flotsam (e.g. dammar resin) from the Indonesian Archipelago into South Australian waters.

The asphaltic bitumens appear more uniform in composition than the waxy bitumens, and are of unambiguously marine origin. Their aliphatic hydrocarbon distributions are devoid of freshwater algal and higher plant biomarkers; and are otherwise remarkable only for the complete absence of methyl hopanes. The presence of dinosterane loosely constrains the age of their source rocks (mid-Triassic or younger).

The heavy, asphaltic bitumens may have a local origin within Late Cretaceous marine mudstones of the offshore Otway and/or Duntroon Basins, although definitive oil-source correlations have yet to be established. Given their nature as bottom drifters,

and the direction of bottom currents across the continental shelf of southeastern Australia, such an hypothesis is consistent with the observed stranding pattern of asphaltite in South Australia and western Tasmania.

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APPENDIX

Structures of Key Molecular Fossils

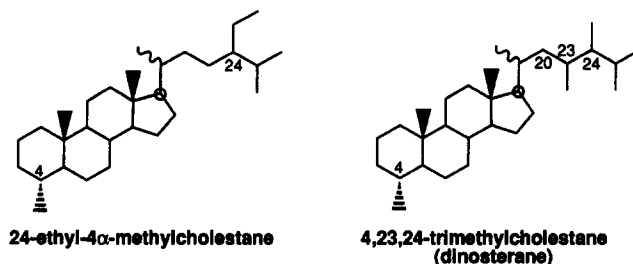
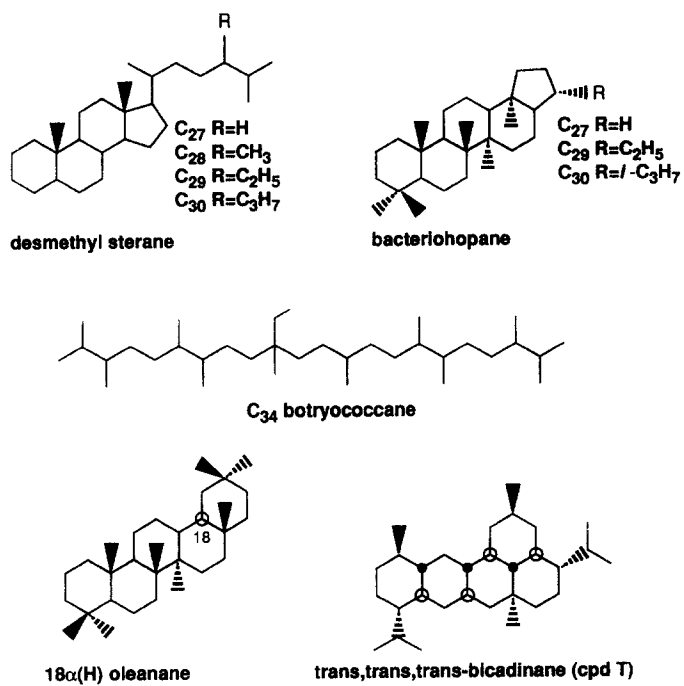


Fig. A1. (Continued overleaf)

Fig. A1 (*continued*)