

1973/5

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Approved 1/2/73 for  
Submission to "Nature"  
for Publication

COMMONWEALTH OF AUSTRALIA

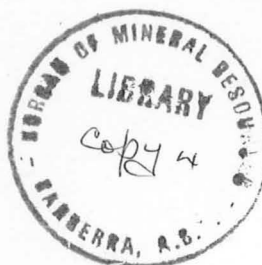
DEPARTMENT OF  
NATIONAL DEVELOPMENT

BUREAU OF MINERAL  
RESOURCES, GEOLOGY  
AND GEOPHYSICS



Record No. 1973/5

012189



RELATIONSHIP BETWEEN PRISTANE TO PHYTANE RATIO,  
CRUDE OIL COMPOSITION, AND GEOLOGICAL ENVIRONMENT  
IN AUSTRALIA\*

by

T.G. Powell and D.M. McKirdy

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RELATIONSHIP BETWEEN PRISTANE TO PHYTANE RATIO,  
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Acyclic isoprenoid hydrocarbons have been widely identified in sediments<sup>1-4</sup>, coal<sup>5</sup>, and petroleum<sup>6-11</sup>. Although isoprenoid hydrocarbons up to C<sub>25</sub> have been recognised<sup>11</sup>, pristane (C<sub>19</sub>) and phytane (C<sub>20</sub>) are usually the most important in terms of concentration. Both are considered to be mainly products of the diagenesis of the phytol side chain of chlorophyll<sup>5</sup>, although other sources are possible<sup>12-14</sup>. In coals<sup>5</sup>, pristane is formed by decarboxylation of phytanic acid, and phytane by dehydration and hydrogenation of phytol. It has been suggested that differences in the pristane to phytane ratio may reflect variations in the degree of oxidation during the early stages of chlorophyll degradation<sup>5</sup>. Thus the formation of phytanic acid, the precursor of pristane, should occur to a greater extent on land during the initial, aerobic stages of plant decay than in an aquatic environment where totally anaerobic decomposition is more likely. High pristane to phytane ratios, which are found in bituminous coals<sup>5</sup>, may reflect source material of terrestrial origin. Some evidence to support this hypothesis is to be found in a recent study of the organic constituents of Dead Sea sediments<sup>14</sup>. The concentrations of bound and free phytanic acid, dihydrophytol and phytol were measured in two reducing and two oxidising sediments. The ratios of phytanic acid to phytol (plus dihydrophytol) were 4.7 and 5.5 in the oxidising environments and 1.1 and 3.4 in the reducing environments. The parent organic matter is essentially of the same type. It is clear that the formation of phytanic acid is favoured in an oxidising environment. It must be noted, however, that reduction of the double bond, as well as oxidation of the alcohol moiety, is necessary to form phytanic acid from phytol. Thus the precise

reaction sequence and conditions for the generation of phytanic acid in the natural environment are not fully understood.

Certain Australian crude oils are known to have higher pristane to phytane ratios than many oils from other countries<sup>5</sup>. During the course of a geochemical survey of commercial and non-commercial crude oils from Australia, considerable variation was observed in their pristane to phytane ratios (Table 1). If the hypothesis for explaining high pristane to phytane ratios is correct, then those oils with such values should be derived from predominantly terrestrial source materials, i.e. the waxes and leaf, pollen and spore cuticles of higher plants<sup>5</sup>. Hedberg<sup>15</sup> has suggested that a high wax content is also indicative of a terrigenous source and, on this basis, many Australian oils with high pristane to phytane ratios are of terrestrial origin (Table 1). However, a number of these high wax oils have low pristane to phytane ratios. This discrepancy is illustrated in Fig 1A, where the pristane to phytane ratios of Australian oils and condensates with a high wax content and from an unequivocal non-marine source are plotted against the average US Bureau of Mines Correlation Index<sup>16</sup> of distillation fractions boiling between 250 and 300°C. Low correlation indices (below 30) indicate a paraffinic base whereas higher values reflect a naphthenic to aromatic oil<sup>16</sup>. Paraffinic oils with low pristane to phytane ratios occur in the northern Perth and Galilee Basins. They are associated with non-marine sediments and must have been derived from the cuticles and spore exines of higher plants. The

Perth Basin oils show evidence of immaturity, viz. poor gasoline yield and a relative lack of naphthenic components. Spores in the associated sediments display little evidence of thermal alteration (G. Demaison, personal communication). A possible explanation for the low pristane to phytane ratios is that the oils are derived from terrestrial organic matter which has undergone little thermal alteration during burial diagenesis. Brown and sub-bituminous coals have low pristane to phytane ratios (1-3) in contrast to high volatile bituminous coals which have higher values (7-10)<sup>5</sup>. Clearly the generation of pristane from phytanic acid is incomplete at the brown coal stage. Thus non-marine oils which move out of the source sediments at an early stage of diagenesis can be expected to have low pristane to phytane ratios.

In Fig. 1B the pristane to phytane ratio is plotted against the correlation index for those high wax oils and associated condensates which originate in clastic sediments of near-shore environments. The high wax content indicates that cuticles of land plants formed at least part of the source material. As a group, these oils are more naphthenic and have lower pristane to phytane ratios than the high wax oils from non-marine sediments. The differences reflect that marine affinity of the host sediments and the possible contribution of debris derived from micro-organisms to the source material. Studies by the authors of the probable source sediments for hydrocarbons in the Triassic and Jurassic reservoirs of the Carnarvon Basin have shown that the organic matter is of mixed terrestrial and marine origin.

Only six crude oils from Australia have a low wax content and an unequivocal marine source (Table 1 and Fig. 1C). They are all characterised by low pristane to phytane ratios and four are of naphthenic to aromatic composition. The remaining oil (Mereenie, Amadeus Basin) is paraffinic but its occurrence in an Ordovician marine sequence precludes any significant contribution of continental land vegetation to its source material.

In Table 2 pristane to phytane ratios are given for 29 non-Australian oils. All those derived from a marine environment have pristane to phytane ratios less than 2.5. Of the eleven instances where US Bureau of Mines analyses are available, seven have high correlation indices indicating a naphthenic to aromatic base (Fig. 1C). The remaining four are paraffinic-naphthenic oils from Lower Palaeozoic rocks in North Africa<sup>10</sup>. A high wax oil from the Uinta Basin, U.S.A.<sup>7</sup>, has a non-marine origin and yet has a low pristane to phytane ratio. Analysis of the n-alkane distribution of this oil has revealed a pronounced odd predominance in the wax range ( $C_{25} - C_{35}$ )<sup>7</sup>, which is indicative of a derivation from immature terrestrial plant material. The Kapuni oil from New Zealand<sup>8</sup> is the only oil to show a pristane to phytane ratio comparable to those from Australia. This oil is thought to originate in a sedimentary sequence in which coals are common, and may well be derived from higher plants<sup>17</sup>.

Several conclusions can be drawn from these results. After Devonian time terrestrial plant material became available as a source for petroleum. Cuticles and spore exines of higher plants gave rise to high wax oils or paraffinic or paraffinic-naphthenic composition. The pristane to phytane

ratios of these oils reflect the degree of thermal alteration during burial diagenesis of the parent organic matter. Thus oils derived from immature terrestrial organic debris have low pristane to phytane ratios, whereas those from similar source material which has undergone appreciable thermal alteration have higher values. In Australia, where high wax oils are the rule rather than the exception (cf. Hedberg<sup>15</sup>) the leaf, pollen and spore cuticles of terrestrial plants appear to have contributed significantly to the source material of crude oil. With the exception of those oils derived from immature terrestrial organic matter, a decrease in paraffin content is accompanied by a decrease in pristane to phytane ratio. This reflects a change in geological environment from non-marine (or deltaic) to marine clastic sediments and an increased contribution to the parent organic matter by the debris of aquatic micro-organisms, which has not been exposed to oxygenated conditions during decay.

The occurrence of paraffinic crudes in Lower Palaeozoic sediments, which were deposited before the advent of land plants, demonstrates that the type of source material is not the sole determinant of crude oil composition. Apart from the changes that can occur in the reservoir<sup>18</sup>, the well known association of paraffinic oils with clastic sediments, and of aromatic oils with carbonate and evaporite sediments<sup>18,19</sup>, suggests that the physico-chemical conditions and biological activity in the depositional environment must exert some control. In clastic sediments deposited after Devonian time it is difficult to distinguish the effect of environment from that of source material since such sediments inevitably contain some terrestrial plant material.

We wish to thank the following companies who generously supplied samples: B.O.C. of Australia Ltd, West Australian Petroleum Pty Ltd, Delhi International Oil Corp., Australasian Petroleum Co. and Broken Hill Pty Ltd. We are also indebted to Messrs Z. Hovarth and R. Moon for technical assistance.

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- 1 Cummins, J.J., and Robinson, W.E., J. Chem. Eng. Data, 9, 304 (1964).
- 2 Eglinton, G., Scott, P.M., Belsky, T., Burlingame, A.L., Richter, W., and Calvin, M. Advances in Organic Geochemistry (edit. Hobson, G., and Louis, M.), 41 (Pergamon Press, Oxford, 1966).
- 3 Meinschein, W.G., Barghoorn, E.S., and Schopf, J.W., Science, 145, 262 (1964).
- 4 Oro, J., and Nooner, J.W., Nature, 213, 1082 (1967).
- 5 Brooks, J.D., Gould, K., and Smith, J., Nature, 222, 257 (1969).
- 6 Bendoraitis, J.G., Brown, B.L., and Hepner, L.S., Proc. Sixth World Petrol. Cong., section 5, 13 (1963).
- 7 Martin, R.L., Winters, J.C., and Williams, J.A., Proc. Sixth World Petrol. Cong., section 5, 252 (1963).
- 8 Dean, R.A., and Whitehead, E.V., Proc. Sixth World Petrol. Cong., section 5, 261 (1963).
- 9 Welte, D., Erdöl u. Kohle, 20, 65 (1967).
- 10 Byramjee, R., and Vasse, L., Advances in Organic Geochemistry 1968 (edit. Schenck, P.A. and Havenaar, I.), 319 (Pergamon Press, Oxford 1969).
- 11 Han, J., and Calvin, M., Geochim. Cosmochim. Acta, 33, 733 (1969).
- 12 Blumer, M., Mullin, M.M., and Thomas, D.W., Science, 140, 974 (1963).
- 13 Blumer, M., and Thomas, D.W., Science, 148, 370 (1965).
- 14 Nissenbaum, A., Baedeker, M.J., and Kaplan, I.R., Geochim. Cosmochim. Acta, 36, 709 (1972).
- 15 Hedberg, H.D., Amer. Assoc. Petrol. Geol. Bull., 52, 736 (1968).

- 16 Smith, N.A.C., Smith, H.M., Blade, O.C., and Garton, E.L., US Bureau Mines Bull., 490, 82p (1951).
- 17 Hazzard, J.C., and Morris A.L., Oil Gas J., 70(13), 172 (1972).
- 18 Evans, C.R., Rogers, M.A., and Bailey, N.J.L., Chem. Geol., 8, 147 (1971).
- 19 Hunt, J.M., Amer. Assoc. Petrol. Geol. Bull., 37, 1837 (1953).
- 20 Mckinney, C.M., and Blade, O.C., US Bureau Mines Rep. Inv. 4289, 154p, (1948).
- 21 Smith, H.M., US Bureau Mines Bull, 642, 136p (1968).
- 22 Blade, O.C., Garton, E.L., and McKinney, C.M., US Bureau of Mines Rep. Inv. 4657, 45p (1950).
- 23 Smith, H.M., US Bureau Mines Rep. Inv. 6542, 89p (1964).

TABLE 1. SOME CHARACTERISTICS OF AUSTRALIAN OILS

Basin - State or Territory	Wells or Fields sampled	Reservoir Ages	Wax +	<u>Pristane</u> <u>Phytane</u>	Correlation Index 250-300°C	Source Environment
Amadeus - N. Territory	1	Ordovician	L	1.5	23	marine
Bowen & Surat - Queensland	9	Devonian to Jurassic	H	5.6-8.6	20-35	non-marine or near-shore marir
	1	Jurassic	L	2.0	47	non-marine or near-shore marir
Carnarvon - W. Australia	5	Triassic & Cretaceous	L	1.7-3.1	55-65	marine
	7	Triassic to Jurassic	H	3.3-4.3	30-42	near-shore marir
Cooper - S. Australia	6	Permian	H	4.0-10.0	15-30	non-marine
Galilee - Queensland	1	Permian	H	2.0	15	non-marine
Gippsland - Victoria	5	U. Cret. to Eocene	H	7.3-12.0	14-32	non-marine
Otway - S. Australia, Victoria	2	Cretaceous	H	7.0 - 7.5	18-21	non-marine
Papuan - Papua New Guinea	2	Miocene	H	3.0-3.3	30-34	near-shore marir
	1	Miocene	L	2.8	56	marine

TABLE 1 (Cont'd)

Basin - State or Territory	Wells or Fields sampled	Reservoir Ages	Wax +	<u>Pristane</u> Phytane	Correlation Index 250-300°C	Source Environment
Perth - W.	6	Permian to Jurassic	H	1.0-1.2	16-21	non-marine
Australia	2	Jurassic	H	3.1-4.2	36-39	near-shore marine
	2	Permian & Cretaceous	H	5.0-5.3	27-43	non-marine

+ High wax oil has a pour point of 50°F; or if pour point is below 50°F, but above 30°F it has a cloud point of USBM fraction 11 above 25°F or a cloud point of fraction 15 above 95°F<sup>15</sup>

H - high; L - low.

TABLE 2. PRISTANE TO PHYTANE RATIOS OF NON-AUSTRALIAN CRUDE OILS CALCULATED FROM PUBLISHED DATA

Field	Country	Reservoir Age	Pristane to Phytane Ratio	CI of USBM Fractions 11-15	Presumed Source	Reference
Alida	Canada	Mississippian	1.0	-	marine	7
Beaver Lodge	USA	Mississippian	1.3	38	marine	7,21
Burgan	Kuwait	-	0.7	40	marine	6,23
Darius	Iran	Cretaceous	0.6	-	marine	7
Djeffra	Libya	L. Dev.-Sil.	1.3	30	marine	10
East Texas	USA	Cretaceous	2.5	37	-	6,20
Eola	USA	Ordovician	1.1	-	marine	7
Gifhorn Trough (5 samples)	W. Germany	Jurassic	0.7-0.9	-	marine	9
Hamada	Libya	L. Dev.-Sil.	1.4	32	marine	10
Hendricks	USA	Permian	1.0	55	marine	7,20
Kapuni	New Zealand	Tertiary	7.2	-	non-marine	8,17
Kawkawlin	USA	Devonian	1.0	38	marine	7,21
Kloster	Yugoslavia	-	1.2	-	-	8
Lee Harrison	USA	Permian	0.5	58	marine	7,21
North Sahara I	Algeria	U. Palaeozoic	1.5	-	marine	10
North Sahara II	Algeria	U. Palaeozoic	1.2	-	marine	10

TABLE 2 (Cont'd)

Field	Country	Reservoir Age	Pristane to Phytane Ratio	CI of USBM Fractions 11-15	Presumed Source	Reference
North Smyer	USA	Pennsylvanian	1.1	-	marine	7
Pembina	Canada	Cretaceous	2.0	-	marine	7
Ponca City	USA	Ordovician	2.0	-	marine	7
Puri	Papua	Miocene	2.5	-	marine	8
Redwater	Canada	Devonian	1.4	40	marine	7,22
Tia Juana	Venezuela	-	0.7	44	marine	8,23
Swanson River	USA	Tertiary	2.0	-	marine	7
Teas	USA	Ordovician	1.3	-	marine	7
Unnamed field, Uinta Basin	USA	Eocene	1.1	-	non-marine	7
Wafra	Kuwait	Eocene	0.6	-	marine	7
Wilmington	USA	Miocene	1.2	54	marine	7,20
Zelten	Libya	-	1.6	-	-	8

Fig. 1      Relationship between pristane to phytane ratio and crude oil composition. A. High wax oils and associated condensates occurring in non-marine sediments. B. High wax oils and associated condensates occurring in near-shore marine clastic sediments. C. Low wax oils occurring in marine sediments.

U.S. BUREAU OF MINES CORRELATION INDEX 250°-300°C FRACTION

