BIOMARKER GEOCHEMISTRY OF THE EARLY CAMBRIAN OIL SHOW IN WILKATANA-1: IMPLICATIONS FOR OIL GENERATION IN THE STANSBURY BASIN

Report for Canyon (Australia) Pty Limited

by

DAVID M. McKIRDY

Organic Geochemistry in Basin Analysis Group
Department of Geology and Geophysics
University of Adelaide

May 1994

Introduction

The search for Cambrian petroleum in South Australia began in 1956 with the drilling by Santos Limited of twenty wells at Wilkatana in the southwest Arrowie Basin (Fig. 1: Gravestock and Hibburt, 1991; Hibburt, 1993). Several of these wells encountered oil shows, comprising small amounts of 26° API gravity paraffinic oil and associated semi-solid wax, in marine dolomitic limestones of the Early Cambrian Wilkawillina Limestone. These hydrocarbons are located in vuggy porosity just below a major unconformity and sequence boundary that separates the lower Wilkawillina Formation (sequence C1.1) from the overlying Parara Limestone* (sequence C1.2) (Fig. 2). According to Wopfner (1970), the hydrocarbons represent the inspissated and water-washed remains of a deroofed Cambrian oil pool.

The first detailed account of the geochemistry of the Wilkatana oil was provided by McKirdy *et al.* (1983). This study outlined the sterane, triterpane and acyclic isoprenoid alkane distributions of a sample of waxy reservoir bitumen from Wilkatana-1. It concluded that the oil was 1) relatively immature, 2) of marine algal affinity, and 3) probably derived from an argillaceous (rather than pure carbonate) source rock.

The present report critically reassesses the biomarker geochemistry of the Wilkatana crude, using new analytical data; compares its molecular composition with that of other Australian Cambrian oils; and discusses the implications of this historic oil discovery in the Arrowie Basin for the prospectivity of the Early Cambrian sedimentary rocks of the adjacent Stansbury Basin.

Sample and Analytical Procedures

The reservoir bitumen from Wilkatana-1 examined in this study was recovered from vughs in core of dolomitic limestone from the Wilkawillina Limestone. The sample was obtained from Dr J. Armstrong (Santos) and is the same material analysed by McKirdy *et al.* (1983).

Prior to GC-MS analysis, the saturated hydrocarbons were fractionated further into paraffins (*n*- and *iso*-alkanes) and naphthenes (branched/cyclic alkanes) by urea adduction. Repeat GC analysis of the saturates and GC-MS analysis of the naphthenes were carried out at AMDEL Limited - Petroleum Services using the procedures described by McKirdy and Chivas (1992).

---

* In order to distinguish it from the formation of the same name in the Stansbury Basin, the Parara Limestone in the Arrowie Basin has recently been renamed the Mernmerna Formation, thereby adopting the original nomenclature of Dalgarno and Johnson (1962)

Results

Analytical data are summarised and presented herein as follows:

	Table	Figure
Liquid chromatography and urea adduction	1	3
GC of saturated hydrocarbons	2	4
GC-MS of naphthenes	3	5-8

The chemical structures of the main classes of biomarker alkanes identified in the Wilkatana-1 crude may be found in Appendix 1. The theoretical basis of the following interpretation of the oil's biomarker (or molecular fossil) assemblage is elaborated in Peters and Moldowan (1993).

Discussion

Bulk Composition

The Wilkatana-1 (Wilkawillina) reservoir bitumen has a *paraffinic-naphthenic* composition (Table 1; Fig. 3), not paraffinic as previously reported (see Wopner, 1970; McKirdy *et al.*, 1983). Accordingly, its saturates chromatogram (Fig. 4) displays a prominent naphthene hump (i.e. an unresolved complex mixture of branched/cyclic alkanes); and a *n*-alkane distribution dominated by the waxy C_{23+} homologues (range = C_{13}–C_{36+}; maximum at C_{24}).

This high wax, paraffinic-naphthenic crude differs in character from Cambrian oil shows in the Officer and Georgina Basins. The latter oils clearly are more aromatic in composition (Fig. 3) and, in some cases, have undergone partial biodegradation. The Wilkatana-1 oil has obviously lost its light ends, possibly as a result of evaporation and water washing (as suggested by Wopfner, 1970). Whether it has also been altered by *in situ* biodegradation is by no means certain. The moderately high values of its pristane/*n*-heptadecane and phytane/*n*-octadecane ratios (Table 2; Fig.4) could reflect *slight* biodegradation, but are also about what would be expected if the parent marine crude oil was of relatively low thermal maturity (see below).

Source Affinity

The distributions of specific classes of biomarker alkanes in the Wilkatana-1 crude (Tables 2 and 3) document its marine source affinity. The pristane/phytane ratio (pr/ph = 1.1) and ethylcholestane/cholestane ratio [C_{29} / C_{27} $5\alpha(H),14\alpha(H),17\alpha(H)$ (20R)-sterane = 1.3] of the oil are both low and together indicate its derivation from *marine algal remains deposited in a sub-oxic* *setting*. Its C_{27}–C_{29} sterane distribution (Fig. 5) is similar to those of two Cambrian marine-sourced crude oils found in the Georgina Basin, Northern Territory (Fig. 8).

Diasteranes (C_{27}–C_{29}) are present in the Wilkatana-1 oil, but in low to moderate abundance relative to the regular (unrearranged) steranes. The diasterane/sterane ratio of a crude oil is controlled, in the first instance, by the clay content of its source rock. The value of this parameter in the Wilkatana oil (C_{29} dia/ster = 0.47) is consistent with *a moderately argillaceous source lithofacies, e.g. calcareous shale or argillaceous limestone.*

The primary (?)planktonic algal source material was *extensively reworked by bacteria during early diagenesis* and this accounts for the oil's high hopane/sterane ratio (C_{30} hop / C_{29} ster = 6.1). The C_{27}–C_{35} triterpanes (hopanes and moretanes: Fig. 6) are derived from the cell-wall lipids of prokaryotic microorganisms (bacteria and cyanobacteria). Notable characteristics of this particular hopane distribution are the marked dominance of norhopane (C_{29}) and hopane (C_{30}) over the homohopanes (C_{31}–C_{35}); a medium norhopane/hopane ratio (C_{29}/C_{30} hop = 0.68); a low $17\alpha(H)/18\alpha(H)$ 22,29,30-trisnorhopane ratio (Tm/Ts = 0.90); and a low C_{35} homohopane index (C_{35} / C_{31}–C_{35} hop = 0.05). Collectively, such features suggest that *the source rock of the Wilkatana-1 oil was a calcareous shale deposited beneath a sub-oxic water column.*

The C_{20}–C_{26+} tricyclic terpanes (Fig. 7) are molecular fossils of another group of bacterial lipids. Details of their adundance relative to each other (e.g. C_{23} / C_{20}–C_{24} = 0.27), and to the hopanes (e.g. C_{23} tricyclic / C_{30} hopane = 0.035) and tetracyclic terpanes (e.g. C_{23} tricyclic / C_{24} tetracyclic = 0.45), are source-related and therefore potentially useful in future oil-oil and oil-source correlations. The C_{24} tetracyclic terpane is the most common member of the 17,21-secohopane series. These compounds are thought to be derived by the microbial or thermal degradation of hopanes (or the precursor hopanoids). Their abundance in Early Palaeozoic Australian oils appears to be particularly sensitive to the salinity of the source rock depositional environment. Thus high C_{24} tetracyclic / C_{30} hopane ratios (≥ 0.2) are common in oils expelled from hypersaline source rocks. The value of this parameter in the Wilkatana-1 crude (0.08) seems to indicate that *normal marine salinities prevailed during deposition of its source rock.*

The most likely candidates for the potential source beds of the Wilkatana-1 oil are the Mernmerna Formation (formerly Parara Limestone) and Oraparinna Shale in the transgressive and highstand tracts of Early Cambrian sequence C1.3 (Gravestock and Hibburt, 1991). These deep-water calcareous shale lithofacies are the most organic-rich sediments documented in the Arrowie Basin (TOC = 0.79–1.43%). Where intersected by the BRD-2 drillhole in the central Flinders Ranges (Fig. 1), the Mernmerna Formation is still within the oil generation window (vitrinite reflectance calculated from methylphenanthrene index = 0.96%: McKirdy *et al.*, 1991).

Thermal Maturity

Several maturation-dependent biomarker parameters are listed in Table 3. Among these the C_{29} sterane and C_{32} hopane epimer ratios [viz. $5\alpha(H),14\alpha(H),17\alpha(H)$-ethylcholestane 20S/20R = 0.57; $5\alpha(H),17\alpha(H),21\beta(H)$-bishomohopane 22S/22R = 1.38] concur in suggesting that *the Wilkatana-1 oil is relatively immature*. The maturity of its source rock at the time of primary migration, expressed as equivalent vitrinite reflectance, is estimated to have been ~0.6–0.7%.

Comparison with Other Australian Cambrian Oils

Biomarker data are available on oil shows from Cambrian sequences in the Officer, Georgina and Amadeus Basins (McKirdy *et al.*, 1983, 1984, 1986, 1987; Gravestock *et al.*, 1987; Weste *et al.*, 1984). C_{27}–C_{29} sterane distributions are very useful in demonstrating genetic relationships (or the lack thereof) between different oils. The sterane signature of the Wilkatana-1 crude, so far the only oil recovered from the Arrowie Basin, is quite distinct from those of Early Cambrian marine and non-marine oils in the Officer Basin (Fig. 8). Two marine oils from the Georgina Basin are similar to the Wilkatana oil in having C_{29}-dominant sterane signatures, but differ from it in other respects. For example, their high concentration of tetracyclic terpanes (C_{24} tetracyclic / C_{30} hopane = 0.2) is indicative of a hypersaline source affinity.

Relevance to Hydrocarbon Generation in the Stansbury Basin

Although there is evidence of staining by migrated hydrocarbons in the Parara and Kulpara Limestones on Yorke Peninsula (McKirdy *et al.*, 1991), no *bona fide* oil shows have yet been recorded in the Cambrian sediments of the Stansbury Basin. Bearing in mind that the Arrowie and Stansbury Basins were contiguous depocentres in the same Early Cambrian seaway, the Wilkatana-1 oil discovery takes on wider significance. In particular, the correlatives of the Oraparinna Shale and Mernmerna Formation in the Stansbury Basin (viz. the Heatherdale Shale and Parara Limestone: Hibburt, 1993) are likely to have been *organic-rich, oil-prone source rocks capable of generating Wilkatana-type crude oil*. It is therefore not surprising that the carbon isotopic composition of the Wilkatana-1 oil ($\delta^{13}C_{PDB}$ = -27.4 ‰: Table 1) should be intermediate between that of kerogens from the Parara Limestone in Stansbury West-1 ($\delta^{13}C_{PDB}$ = -28.7 ‰, atomic H/C = 0.50) and the Heatherdale Shale from Sellick Beach ($\delta^{13}C_{PDB}$ = -25.4 ‰, atomic H/C = 0.19) (McKirdy and Powell, 1974). In fact, on the basis of these two kerogen analyses, *the Heatherdale Shale is the more likely source of oil with an isotopic composition like that of the Wilkatana crude*. The available TOC data confirm enhanced preservation of kerogen in parts of the Heatherdale Shale (TOC up to 2.43%: McKirdy, 1993) and, to a lesser extent, in the Parara Limestone (TOC up to 0.91%: McKirdy *et al.*, 1991).

Conclusions

1. Waxy, paraffinic-naphthenic reservoir bitumen from the Early Cambrian Wilkawillina Limestone in Wilkatana-1 contains a diverse assemblage of biomarker hydrocarbons, including acyclic isoprenoid alkanes, steranes, tricyclic and tetracyclic terpanes, and triterpanes.

2. These molecular fossils indicate that the Arrowie Basin's only oil show was derived from marine organic matter, comprising the remains of primitive eukaryotic algae and prokaryotic microorganisms (bacteria, cyanobacteria). This organic matter accumulated under suboxic conditions; and the resulting source rock lithofacies was a calcareous shale.

3. The residual, (?) water-washed Wilkatana-1 crude is relatively immature, having been expelled from its source rock (probably in the Oraparinna Shale or Mernmerna Formation) at an estimated vitrinite reflectance of ~0.6–0.7%.

4. Black shales within the stratigraphic equivalents of these formations in the Stansbury Basin (viz. Heatherdale Shale and Parara Limestone) are likely to have generated and expelled Wilkatana-type oil. The timing of this oil migration event currently is being investigated in the Department of Geology and Geophysics, University of Adelaide, as part of Matthew Carson's Honours research project.

References

DALGARNO, R. and JOHNSON, J.E., 1962. Cambrian sequence of the Western Flinders Ranges. *Geological Survey of South Australia, Quarterly Geological Notes* **4**: 2-3.

GRAVESTOCK, D. I. and HIBBURT, J. E., 1991. Sequence stratigraphy of the eastern Officer and Arrowie Basins: a framework for Cambrian oil search. *APEA Journal*, **31(1)**: 177-190.

GRAVESTOCK, D. I., HIBBURT, J. E., McKIRDY, D. M. and KUANG, K. S., 1987. The Cambrian setting for oil and gas in South Australia. *APEA Conference, Surfers Paradise, Poster Display and Extended Abstract.*

HIBBURT, J. E. (compiler), 1993. Petroleum exploration and development in South Australia. *South Australian Department of Mines and Energy, Report Book* **93/9**.

McKIRDY, D. M., 1993. Cambrian source rock geochemistry, Stansbury Basin. Part 2. Reconnaissance sampling of Karinya Shale and Heatherdale Shale for total organic carbon analysis. *Report for Canyon (Australia) Pty Limited* (unpublished).

McKIRDY, D. M. and POWELL, T.G., 1974. Metamorphic alteration of carbon isotopic composition in ancient sedimentary organic matter: new evidence from Australia and South Africa. *Geology* **2**: 591-595.

McKIRDY, D. M. and CHIVAS, A.R., 1992. Nonbiodegraded aromatic condensate associated with volcanic supercritical carbon dioxide, Otway Basin: implications for primary migration from terrestrial organic matter. *Organic Geochemistry* **18**: 611-627.

McKIRDY, D. M., ALDRIDGE, A. K. and YPMA, P. J. M., 1983. A geochemical comparison of some crude oils from pre-Ordovician carbonate rocks. In: *Advances in Organic Geochemistry 1981* (eds., M. Bjoroy *et al.*), Wiley, Chichester, pp. 99-107.

McKIRDY, D. M. , KANTSLER, A. J., EMMETT, J. K. and ALDRIDGE, A. K., 1984. Hydrocarbon genesis and organic facies in Cambrian carbonates of the eastern Officer Basin, South Australia. In: Palacas, J. G. (ed.) *Petroleum Geochemistry and Source Rock Potential of Carbonate Rocks.* AAPG Studies in Geology **18**: 13-31.

McKIRDY, D. M., COX, R. E., MORRIS, D. G. and GATEHOUSE, C. G., 1986. Cambrian oils and source rocks in the Georgina and Officer Basins: a comparative study. *Australian Organic Geochemistry Conference, Australian National University, Canberra, Program and Abstracts.*

McKIRDY, D. M., COX, R. E., FOSTER, C. B., GORTER, J. D. and MORRIS, D. G., 1987. Biomarker geochemistry of some Early Palaeozoic crude oils: influence of precursor microbiota and source rock environment. *8th International Symposium on Environmental Biogeochemistry, Nancy, France, Abstracts*, p. 53.

McKIRDY, D. M., GRAVESTOCK, D. I. and GATEHOUSE, C. G., 1991. Cambrian petroleum and source rock geochemistry of South Australia. *Australian Society of Exploration Geophysicists & Geological Society of Australia Conference, Sydney, Abstracts*, **30**: 63-64.

MELLO, M.R., GAGLIANONE, P.C., BRASSELL, S.C. and MAXWELL, J.R., 1988. Geochemical and biological marker assessment of depositional environments using Brazilian offshore oils. *Marine and Petroleum Geology*, **5**: 205-223.

PETERS, K.E. and MOLDOWAN, J.M., 1993. *The Biomarker Guide: Interpreting Molecular Fossils in Petroleum and Ancient Sediments*. Prentice Hall, Englewood Cliffs, 363 p.

WESTE, G., SUMMONS, R. E., McKIRDY, D. M., SOUTHGATE, P. N., HENRY, R. L. and BREWER, A. M., 1984. Cambrian palaeoenvironments and source rocks of the eastern Officer Basin. *Geological Society of Australia, Abstracts*, **12**: 542-544.

WOPFNER, H., 1970. Early Cambrian paleogeography, Frome Embayment, South Australia. Bulletin of the American Association of Petroleum Geologists **54**: 2395-2409.

Table 1 : Bulk chemical and isotopic composition of reservoir bitumen from Wilkatana-1

Chemical composition of C_{12+} fraction :

Paraffins (normal and iso alkanes)	33.9%
Naphthenes (branched and cyclic alkanes)	20.8%
Aromatic hydrocarbons	1.1%
Resins (ONS compounds)	38.3%
Asphaltenes	5.9%

Carbon isotopic composition :

$\delta^{13}C_{PDB}$	-27.4‰
Oil type :	paraffinic-naphthenic
Reservoir :	Wilkawillina Limestone
Age / Sequence :	Early Cambrian (C1.1)

Table 2 : Alkane parameters of total saturates fraction of Wilkatana-1 reservoir bitumen

n-Alkanes :	
range	C_{13} – C_{36+}
maximum	C_{24}
odd / even predominance	none
Isoprenoid alkanes :	
pristane / phytane	1.13
pristane / *n*-heptadecane	0.78
phytane / *n*-octadecane	0.59

Table 3 : Biomarker parameters of naphthenes fraction of Wilkatana-1 reservoir bitumen

		m / z	*Specificity*
Steranes :			
C_{27} : C_{28} : C_{29} $\alpha\beta\beta$ sterane	31 : 30 : 39	218	source
C_{29} / C_{27} $\alpha\beta\beta$ sterane	1.28	218	source
C_{29} / C_{27} diasterane	0.84	217 , 259	source
C_{29} diasterane / sterane	0.47	217 , 259	source , maturity
C_{29} $\alpha\alpha\alpha$ sterane 20S / 20R	0.57	217	maturity
C_{29} $\alpha\beta\beta$ / $\alpha\alpha\alpha$ 20R sterane	0.82	217	maturity , migration
Triterpanes (Hopanes, Moretanes) :			
C_{27} Tm / Ts	0.90	191	maturity , source
C_{29} / C_{30} hopane	0.68	191	source
C_{35} / C_{31} – C_{35} homohopane	0.053	191	source , maturity
C_{32} 22S / 22R bishomohopane	1.38	191	maturity
C_{30} moretane / hopane	0.17	191	maturity
Hopane / Sterane :			
C_{30} hopane / C_{29} sterane	6.09	191 , 217	source
Tricyclic and Tetracyclic Terpanes :			
C_{23} tricyclic / C_{24} tetracyclic	0.45	191	source
C_{23} / C_{20} – C_{24} tricyclic	0.28	191	source
C_{24} tetracyclic / C_{30} hopane	0.076	191	source

Figure 1

Arrowie Basin structure, outcrops and well locations (after Gravestock and Hibburt, 1991). Note location of Wilkatana-1 in southwest corner of the basin.

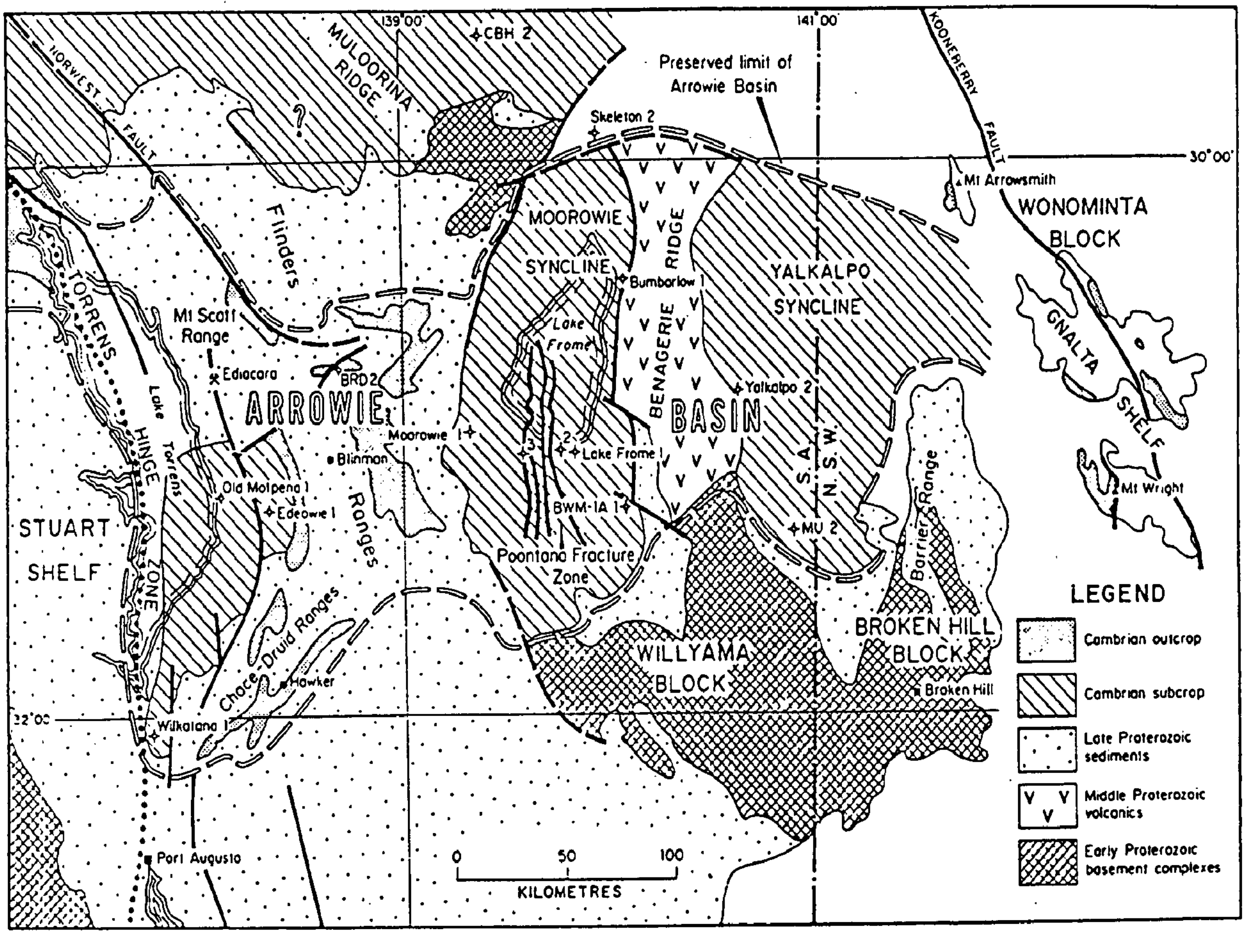
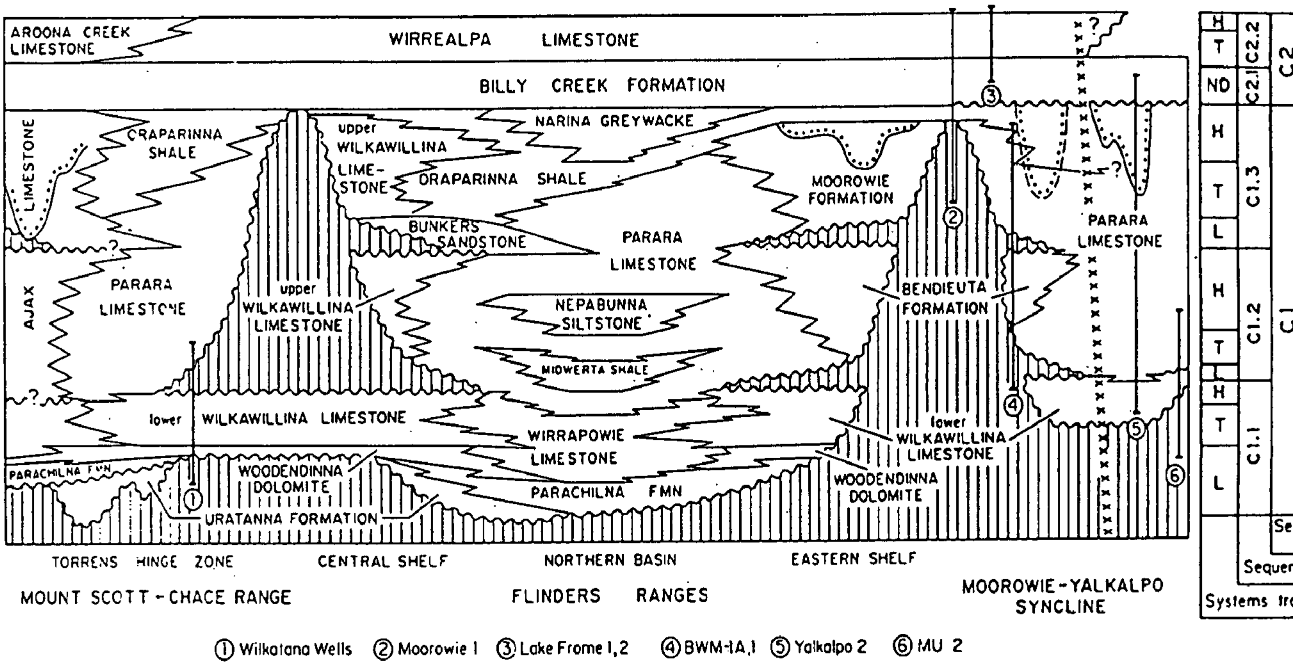


Figure 2

Lower Cambrian formations and sequence stratigraphic framework of the Arrowie Basin (after Gravestock and Hibburt, 1991)



COMPOSITION OF CAMBRIAN OILS

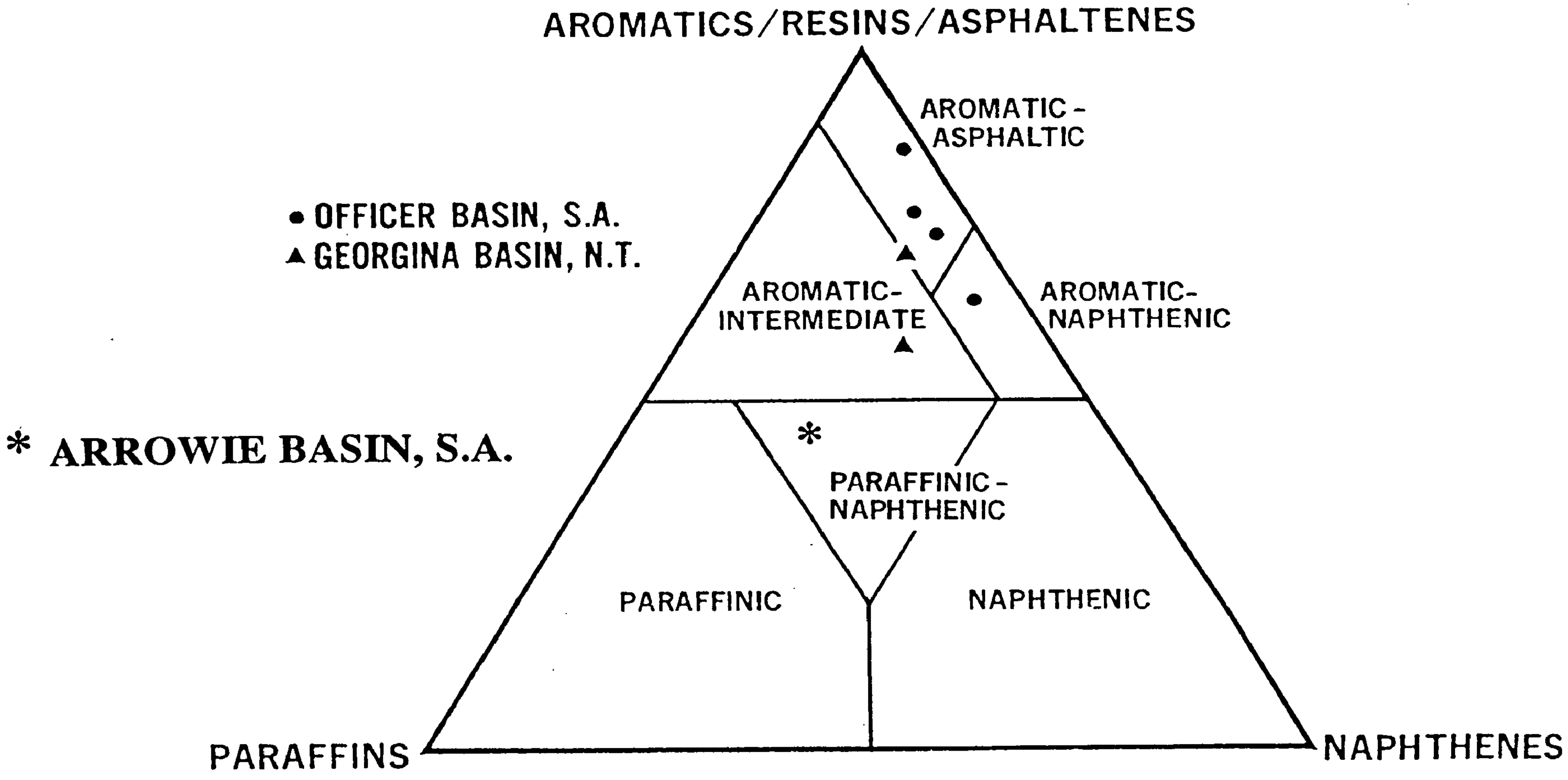


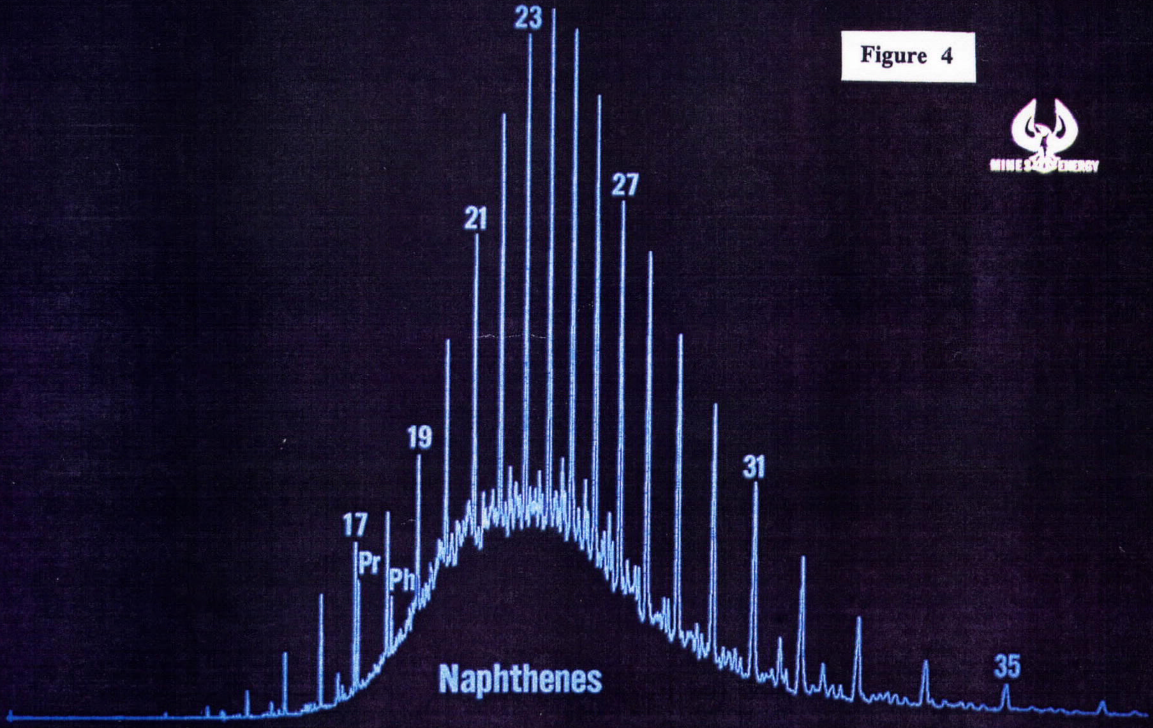
Figure 3

CAMBRIAN OIL

WILKATANA-1

WILKAWILLINA LIMESTONE

Figure 4



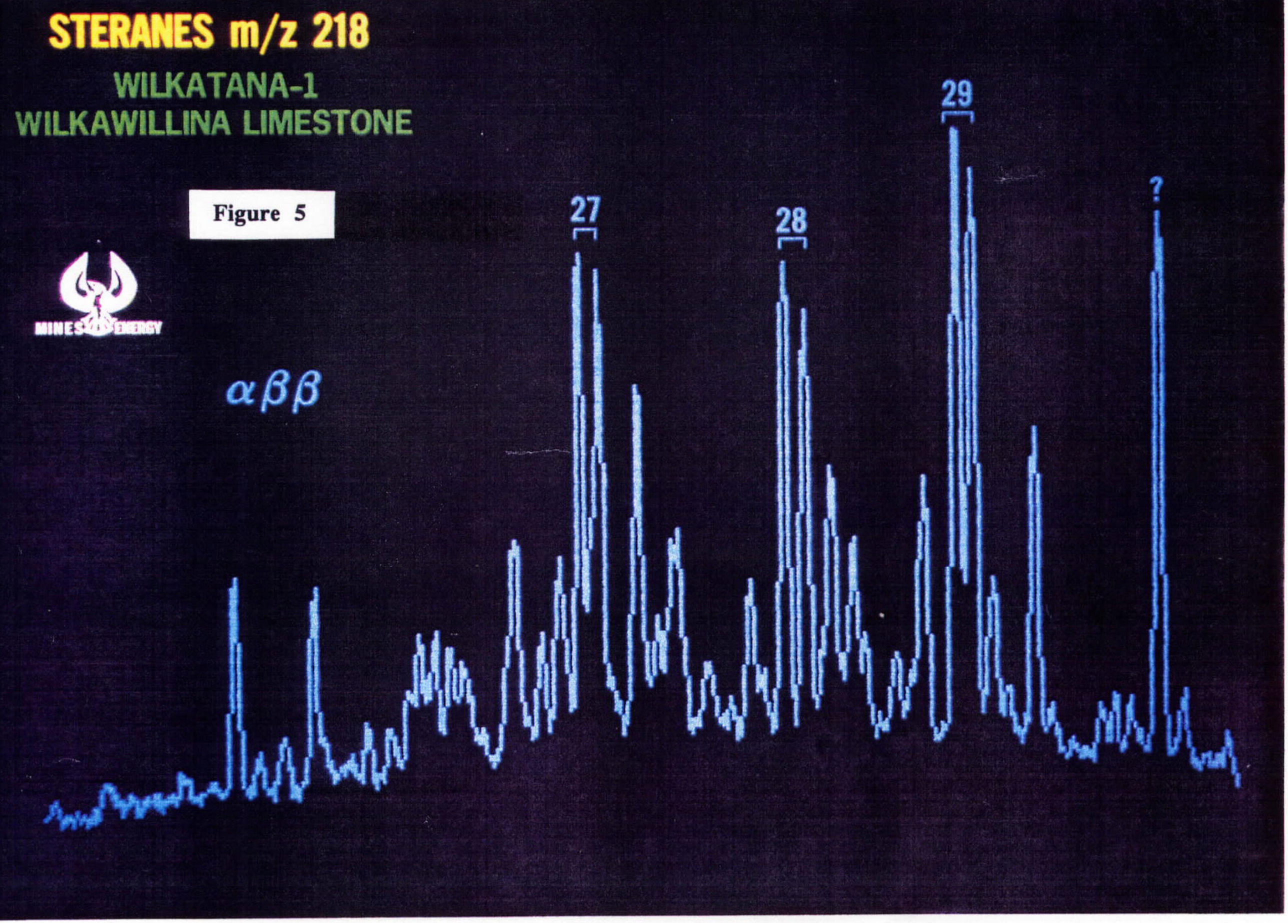


Figure 5

STERANES m/z 218
WILKATANA-1
WILKAWILLINA LIMESTONE
MINES ENERGY
$\alpha\beta\beta$
27
28
29
?

Figure 6

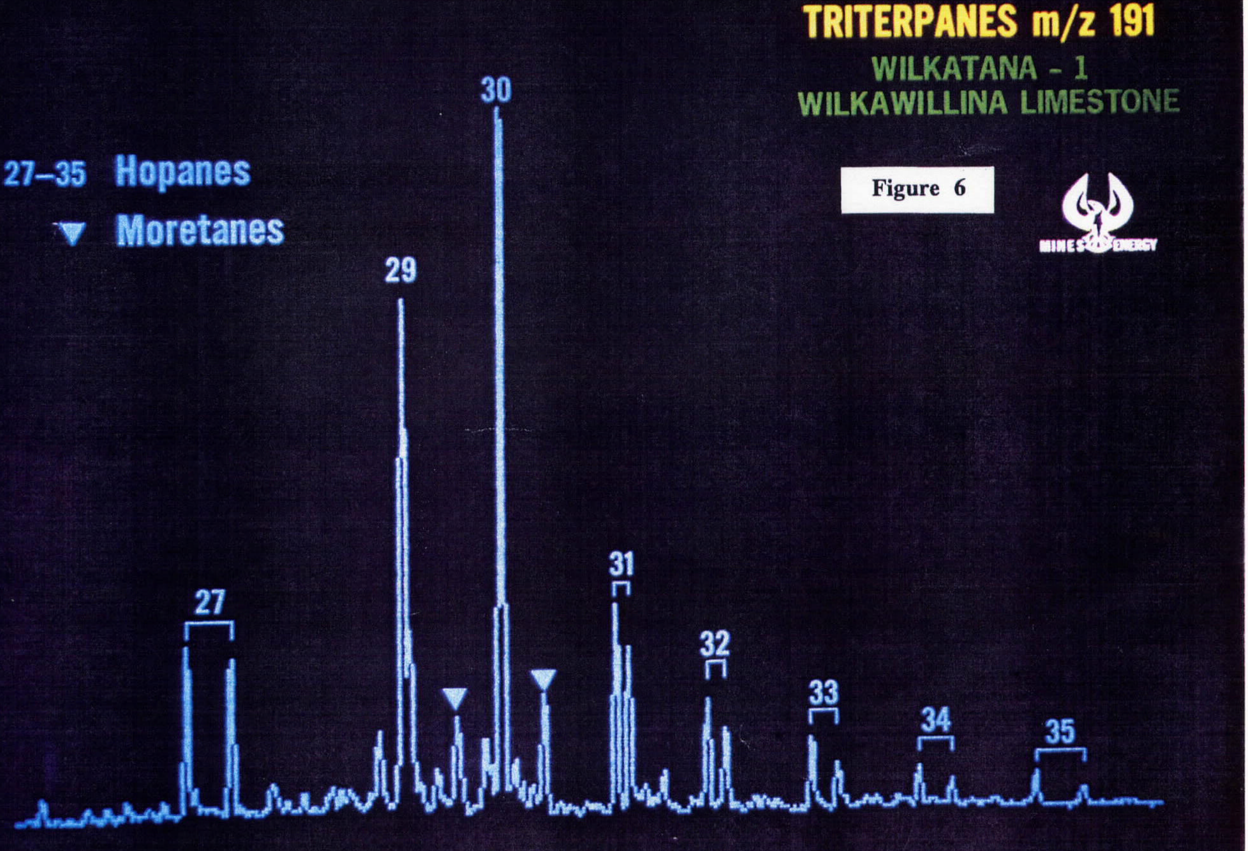
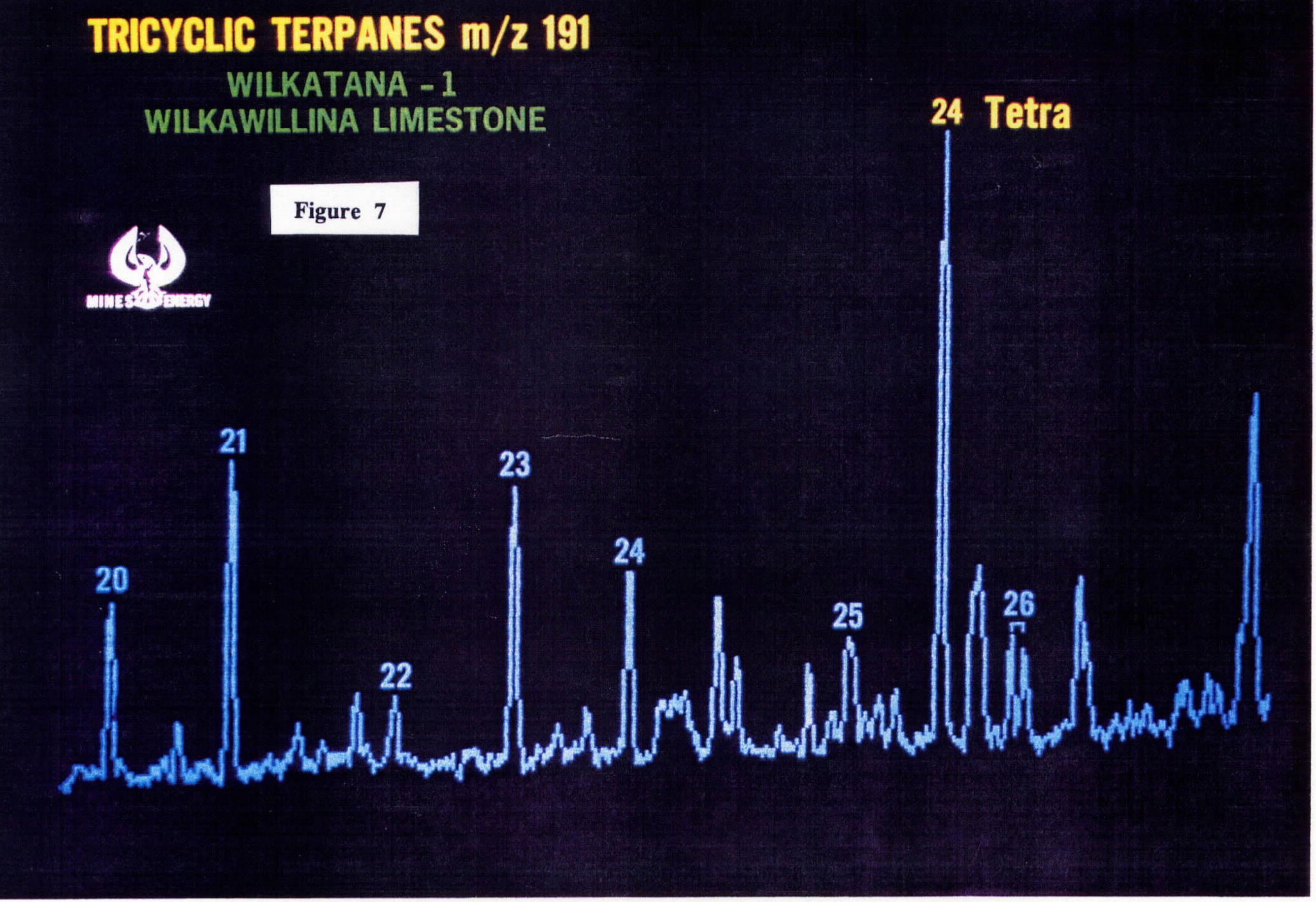

TRITERPANES m/z 191
WILKATANA - 1
WILKAWILLINA LIMESTONE
27–35 Hopanes
▼ Moretanes
MINES ENERGY
27
29
30
31
32
33
34
35

Figure 7



TRICYCLIC TERPANES m/z 191

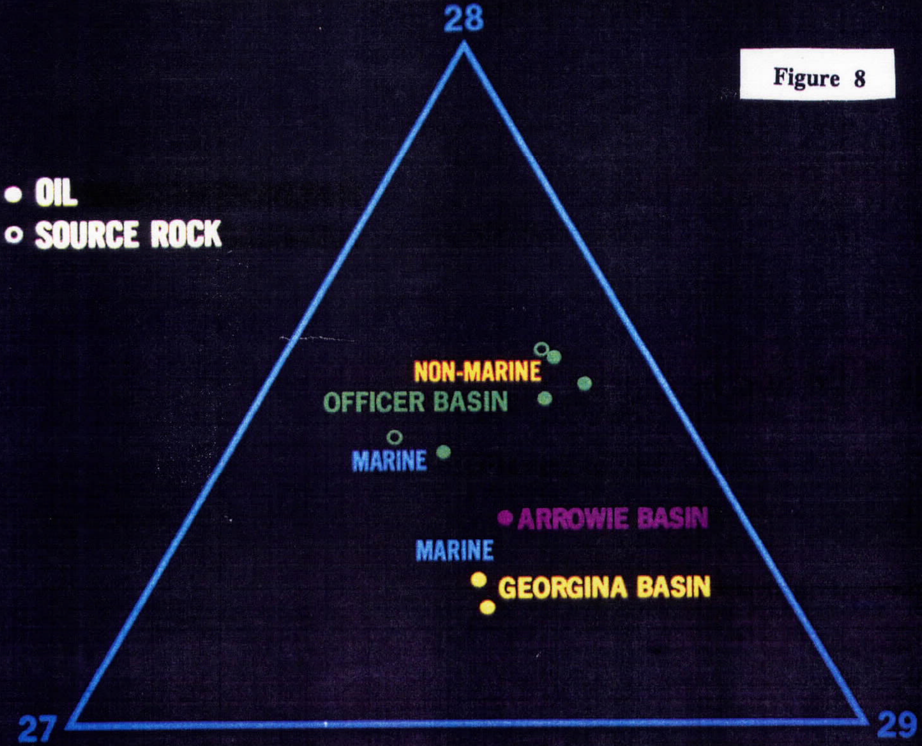
WILKATANA - 1

WILKAWILLINA LIMESTONE

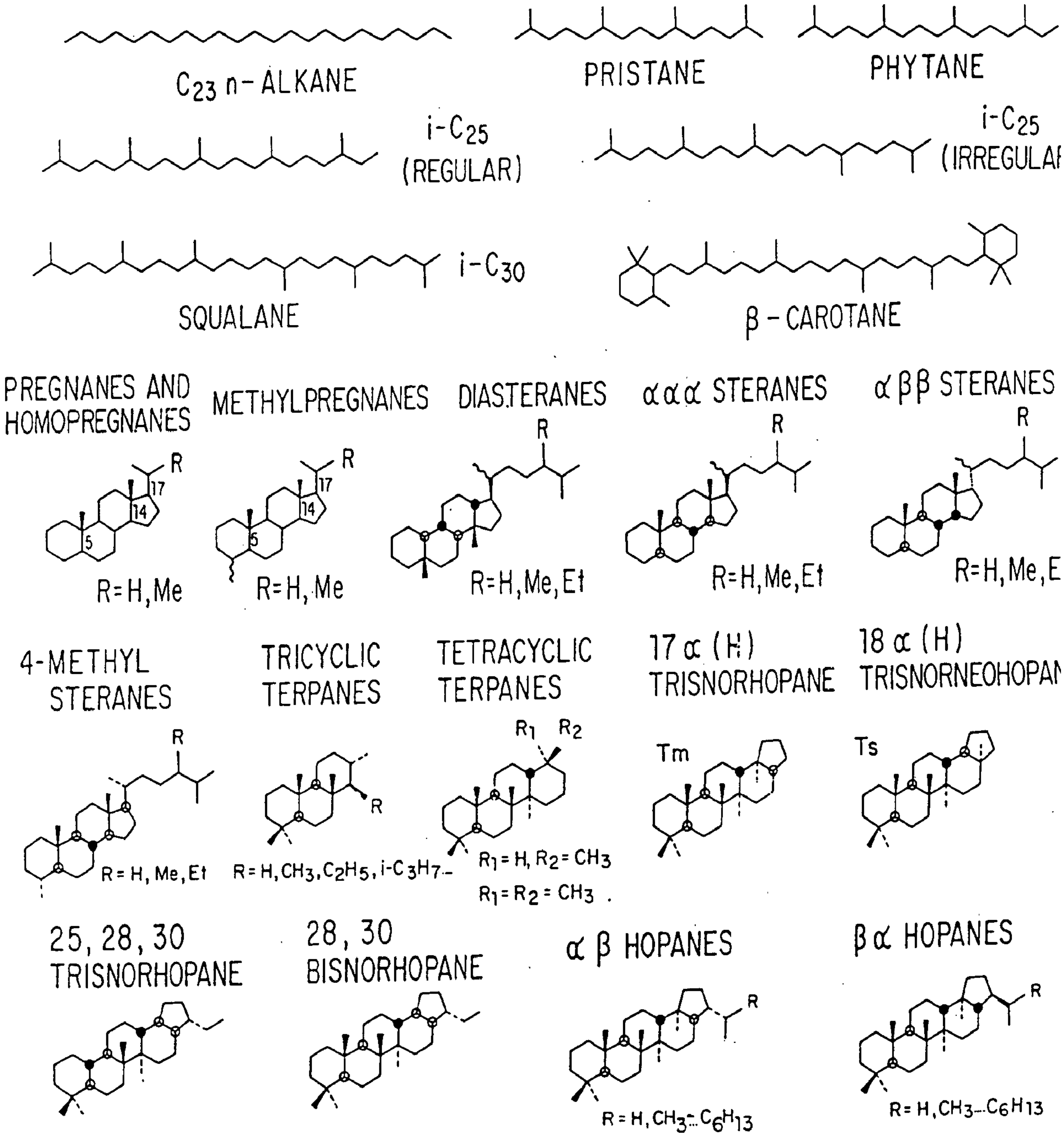
C_{27}—C_{29} STERANES IN CAMBRIAN OILS AND SOURCE ROCKS

MINES ENERGY

Figure 8



APPENDIX



Mello et al. (1988)