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TABLE 6.8: SUMMARY OF CARBON ISOTOPIC, ELEMENTAL, PYROLYSIS (PHGC) AND REFLECTIVITY DATA ON SELECTED PROTEROZOIC KEROGENS, AMADEUS BASIN. (CONTINUED)

Well or Locality	Core No. and Depth (m)	Formation and Lithology	Type	$\delta^{13}\text{C}_{\text{PDB}}$ ‰	H/C atomic	C/N	V.M. ¹ %	K E R O G E N D A T A			$\bar{R}_o$ max ² %
								benzene n-C ₆	toluene n-C ₇	ethylbenzene n-C ₈	
Alice Springs 3	9	Bitter Springs	IV	-25.0	0.28	117	25.9	2.76	3.45		1.95
	67.6	Gillen Mbr. dolomite									
	42	Bitter Springs	IV		0.46	74	17.0	1.82	1.28	1.65	
	203.0	Gillen Mbr. dolomite & gypsum									
Williams Bore ³		Bitter Springs	II		0.82	57					
		Loves Creek Mbr. dolomitic limestone									
Jay Creek ⁴		Bitter Springs		-28.4							
		Loves Creek Mbr. chert									
Ellery Creek ⁴		"		-27.2							

1. Volatile matter = weight loss (percent, ash-free basis) after pyrolysis at 600°C for 5 min. (see Appendix 1 for details). 2. Mean maximum reflectivity (in oil) of vitrinite-like phytoclasts (>2µm diameter), except where otherwise indicated. All data after A.J. Kantsler (pers. comm., 1976). 3. Stromatolite ST 8, Table 4.24. 4. After Oehler *et al.* (1972). * Characterization uncertain because of incomplete elemental analysis.

ERRATA - VOLUME 1

P. 40, para. 3, line 4 : For '(maximum at n-C₁₇)' read '(maximum generally at n-C₁₅)'.

P. 81, last para. line 2 : For 'and unlike those' read 'are unlike those'.

P. 249, para. 1, line 6 : Should read ' ... in the vicinity of Mount Solitary, '.

P. 275 : Insert following reference

HEDBERG, H.D., 1974. Relation of methane generation to undercompacted shales, shale diapirs, and mud volcanoes. Bull Am. Ass. Pet. Geol., 58, 661-673

THE DIAGENESIS OF MICROBIAL ORGANIC MATTER:
A GEOCHEMICAL CLASSIFICATION AND ITS USE IN
EVALUATING THE HYDROCARBON-GENERATING POTENTIAL
OF PROTEROZOIC AND LOWER PALAEOZOIC SEDIMENTS,
AMADEUS BASIN, CENTRAL AUSTRALIA

by

David Malcolm McKirdy, M.Sc.

A thesis presented to the
Australian National University in
partial fulfilment of the requirements
for the degree of Doctor of Philosophy

Department of Geology

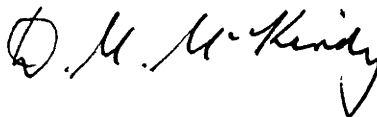
November 1977

*"With each one of our works we bring
to Christ a little fulfilment"*

Teilhard de Chardin : Le Milieu Divin

For
my Father
who dared to think it possible
and
Alison
who endured it

Except where otherwise acknowledged in the text,
all observational, experimental and interpretive
work summarised in this thesis is solely that of
the author.

A handwritten signature in dark ink, appearing to read 'D. M. McKirdy'. The signature is written in a cursive style with a large, stylized 'M' and a long, sweeping tail on the 'y'.

D. M. McKirdy

ABSTRACT

Although organic matter derived from aquatic micro-organisms (algae, bacteria and protozoa) and preserved in fine-grained marine sediments is widely regarded as the main precursor of oil and gas, most methods of source-rock evaluation rely heavily on the measurement of diagenetic changes in allochthonous higher plant residues (or interbedded coals). Such methods are inapplicable to Proterozoic and Lower Palaeozoic sequences which antedate the appearance in the geological record of abundant continental floras. Accordingly, a detailed geochemical study has been made of the diagenesis and incipient metamorphism of microbial organic matter, with particular reference to its ability to generate hydrocarbons. Twelve individual suites of samples with diverse thermal histories, but all containing organic matter of microbial origin, have been investigated. They include extant algae and bacteria; unlithified pelagic calcareous muds; coorongite, oil shales and boghead coals; marine shales, carbonates and phosphorites; stromatolites; and Precambrian carbonaceous shales and cherts.

Analyses of the solvent-extractable organic matter (EOM) and coexistent kerogen in these samples show that microbial detritus is far from uniform in composition. Four principal types can be differentiated and their respective maturation pathways defined in terms of kerogen composition (H/C and O/C atomic ratios) and structure (as determined by infra-red spectroscopy, pyrolysis-hydrogenation-gas chromatography, and X-ray diffraction). For each type of kerogen, the yield (mg/g organic carbon) and composition (percent saturates, percent total hydrocarbons) of the associated EOM varies systematically with

increasing maturation, although low-rank carbonates and phosphorites commonly give anomalously high EOM yields. A preliminary classification (or subdivision) of microbial diagenesis is proposed which combines these organic parameters with certain optical properties of the kerogen (colour of liptinite, reflectivity of vitrinite-like phytoclasts and/or zooclasts). The classification comprises the same four stages of diagenesis recognised by Foscolos et al. (1976), plus the zone of anchimetamorphism, and these are related to patterns of expected petroleum occurrence (viz., biogenic methane, oil, gas condensate, dry gas, and barren).

As a test of the proposed classification, it is applied to the interpretation of organic geochemical data on fine-grained non-reservoir rocks in sixteen well sections of the Proterozoic - Lower Palaeozoic sequence in the Amadeus Basin. Organic-rich intervals are identified and their hydrocarbon generating potential assessed in terms of primary kerogen type and present level of organic maturation. Dark grey to black, pyritic, fossiliferous shales and siltstones of the Ordovician Pacoota Sandstone and Horn Valley Siltstone have been the most prolific source rocks in the basin. Oils are correlated with their source rocks using total alkane chromatograms, n-alkane profiles and $\delta^{13}\text{C}$ values as geochemical 'fingerprints'. Areas of immature, mature (oil-prone) and post-mature (gas-prone and barren) sediments are broadly delineated. In terms of source-rock richness and maturity the most prospective area for further discoveries of liquid hydrocarbons lies to the immediate north and northeast of the Mereenie Anticline in subcrop of the Larapinta Group.

ACKNOWLEDGEMENTS

This research project was carried out under the joint supervision of Dr. C.E.B. Conybeare, Geology Department, ANU, and Dr. D.J. McHugh, Chemistry Department, Faculty of Military Studies, UNSW (Duntroon). I wish to record my appreciation of their guidance and encouragement throughout the study.

I thank Professor D.A. Brown for making available the facilities of the Geology Department, ANU, during my tenure of a two-year Australian Public Service Post-Graduate Scholarship between March 1973 and February 1975. I am also grateful to Dr. K.S.W. Campbell for his much needed administrative support and encouragement during the final throes of the writing.

The project was completed in the Petroleum Technology Laboratory, Bureau of Mineral Resources, Geology and Geophysics, Canberra. I am indebted to Mr. J.A.W. White, Chief Petroleum Technologist, for generously allowing me to devote so much time to the thesis. Special thanks are due to the following BMR personnel: Mr. Z. Horvath, for enthusiastic and skilled technical assistance in the Laboratory; Mr. M.R. Moffat and staff of the Petroleum Exploration Branch Drawing Office, for drafting the figures; Mr. D. Barnes, for XRD analysis of kerogens; Dr. M.R. Walter, for help with microscopic work and photography, identification of acritarchs in the Stairway Sandstone, and comments on Section 4.7; and Dr. D.H. Tucker, Mr. B.A. McKay, and Mr. L.E. Kurylowicz for discussion, general assistance and moral support.

Dr. P.J. Cook, Research School of Earth Sciences, ANU, supplied the DSDP core samples and kindly found time to read and comment on most of the first draft of the thesis. Dr. P.A. Trudinger and Ms. L.A. Chambers, Baas-Becking Geobiological Laboratory, reviewed parts of Chapter 4.

The pyrolysis-hydrogenation-gas chromatography was undertaken in the Chemistry Department, Royal Military College, Duntroon. I am grateful to Professor R.J. Bearman for allowing me access to this equipment, and to Mr. J.W. Tardif for instruction in its use.

The thesis owes much to the advice and painstaking efforts of Mr. A.J. Kantsler, Geology Department, University of Wollongong, to whom the author submitted numerous kerogen and rock samples for petrographic analysis, measurement of reflectivity, and photography. The black and white plates (except Plate 4.10) were prepared by Mrs. R. Varga. The help of Professor A.C. Cook, in allowing this work to be done in his department, is gratefully acknowledged.

Magellan Petroleum Australia Ltd., through Mr. R.M. Hopkins, provided samples of oil, condensate and drill-hole core, and allowed me to consult well completion reports on unsubsidized exploration holes. Dr. D.A. McNaughton kindly sent me a folio of unpublished information on previous investigations of source rocks in the Amadeus Basin. BOCAL gave permission to quote rank and formation temperature data from Ashmore Reef No. 1. The freeze-dried cultures of B. braunii and D. gigas were prepared and made available by Dr. J. Ferguson, BMR, and Dr. G.W. Skyring, Baas-Becking Geobiological Laboratory.

I express my appreciation to Mrs. Heather Drury, Mrs. Shirley Driessen, Mrs. Margaret May and Mrs. Joan Brumby who shared the unenviable task of typing the thesis. And finally, to my wife, Alison, goes my thanks for her constant support and encouragement over the last three years.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	v
ACKNOWLEDGEMENTS	vii
Table of contents - Volume 1	ix
PART I - The problem in perspective	
CHAPTER 1. INTRODUCTION	
1.1 Background of the research	1
1.2 Diagenesis and hydrocarbon generation	2
1.3 Pre-Devonian source rocks	4
1.4 Amadeus Basin	6
1.5 Objectives of the present investigation	7
CHAPTER 2. SCOPE AND PLAN OF THESIS	
2.1 Scope	9
2.2 Analytical techniques	10
2.3 Samples selected for the classification	11
2.4 Amadeus Basin wells studied	13
2.5 Oils and condensates	14
2.6 Sources of unpublished data	15
2.7 Presentation	15
2.8 Summary	16
PART II - Towards an organic geochemical classification of diagenesis for use in evaluating the source-rock potential of Pre-Devonian sediments	
CHAPTER 3. MICROORGANISMS AS SOURCES OF PETROLEUM HYDROCARBONS - A LITERATURE REVIEW	
3.1 Introduction	18
3.2 The oldest crude oils	19

TABLE OF CONTENTS (cont'd)

	<u>Page</u>
 CHAPTER 3 (cont'd)	
3.2.1 North America	20
3.2.2 Russia	21
3.2.3 Africa and the Middle East	22
3.3 Early organic evolution and petroleum genesis	23
3.4 Petroleum precursors in contemporary marine microorganisms	26
3.4.1 Microbial lipids	28
3.4.2 Geochemical signatures of algae, bacteria and zooplankton	33
3.4.3 Recent experimental studies	34
3.5 Characteristics of marine crude oils	36
3.5.1 Original or immature oils	36
3.5.2 Effects of thermal maturation	37
3.5.3 Proterozoic and early Palaeozoic oils	39
3.6 Concluding remarks	42
 CHAPTER 4. STUDIES OF THE COMPOSITION AND MATURATION OF MICROBIAL ORGANIC MATTER	
4.1 Introduction	43
4.2 Extant algae and bacteria	43
4.2.1 Geological significance of organisms	44
4.2.2 Discussion of results	45
4.2.3 Implications for microbial diagenesis	47
4.3 Plio-Pleistocene sediments, Timor Trough	49
4.3.1 Geological setting	50
4.3.2 Previous geochemical investigations	51
4.3.3 Results	52
4.3.4 Discussion	52
4.3.5 Hydrocarbon potential	65
4.3.6 Summary	68

TABLE OF CONTENTS (cont'd)

	<u>Page</u>
CHAPTER 4 (cont'd)	
4.4 Mesozoic and Tertiary carbonates, Ashmore-Sahul Block	69
4.4.1 Geological setting	70
4.4.2 Previous investigations	72
4.4.3 Results	73
4.4.4 Discussion	74
4.4.5 Relevance to petroleum genesis on Northwest Shelf	84
4.4.6 Summary	85
4.5 Coorongite, torbanites and oil shales	86
4.5.1 Geological setting of samples	88
4.5.2 Previous geochemical investigations	88
4.5.3 Results	93
4.5.4 Discussion	94
4.5.5 Summary	101
4.6 Phosphorites	103
4.6.1 Previous geochemical investigations	106
4.6.2 Results	108
4.6.3 Discussion	108
4.6.4 Summary	123
4.7 Stromatolites	124
4.7.1 Results	125
4.7.2 Discussion	125
4.7.3 Summary	133
4.8 Other studies	135
4.8.1 Palaeozoic well sections	135
4.8.2 Precambrian carbonaceous shales and cherts	148
4.9 Concluding remarks	161a

TABLE OF CONTENTS (cont'd)

	<u>Page</u>
CHAPTER 5. A CLASSIFICATION OF THE DIAGENESIS AND ANCHIMETAMORPHISM OF MICROBIAL ORGANIC MATTER	
5.1 Introduction	162
5.1.1 Previous classifications of organic diagenesis	162
5.1.2 The present classification	167
5.2 Eodiagenesis	168
5.2.1 Organic processes and reactions	168
5.2.2 Characteristics of extractable organic matter	170
5.2.3 Kerogen types	171
5.3 Mesodiagenesis	175
5.3.1 Changes in extractable organic matter	175
5.3.2 Kerogen evolution	176
5.4 Telodiagenesis	179
5.5 Anchimetamorphism	180
5.6 Synthesis	180
PART III - Hydrocarbon-generating potential of Proterozoic and Lower Palaeozoic sediments, Amadeus Basin	
CHAPTER 6. PETROLEUM SOURCE ROCK STUDIES, AMADEUS BASIN	
6.1 Introductory review	185
6.1.1 Geological setting	186
6.1.2 Oil and gas occurrences	195
6.1.3 Previous geochemical work	197
6.1.4 Some problems	200
6.2 Proterozoic sediments	202

TABLE OF CONTENTS (cont'd)

	<u>Page</u>
CHAPTER 6 (cont'd)	
6.2.1 Mount Charlotte No. 1	202
6.2.2 Erldunda No. 1	207
6.2.3 Ooraminna No. 1	211
6.2.4 Alice Springs No. 3	205
6.3 Cambrian rocks (Pertaoorrta Group)	219
6.3.1 Mount Charlotte No. 1	219
6.3.2 Highway Anticline No. 1	220
6.3.3 Alice No. 1	222
6.4 Cambro-Ordovician rocks (Larapinta Group)	226
6.4.1 Pacoota Sandstone	227
6.4.2 Horn Valley Siltstone	230
6.4.3 Stairway Sandstone	234
6.5 Correlation of reservoir hydrocarbons with source rocks	238
6.5.1 Gas	238
6.5.2 Oil and condensate	239
6.6 Preliminary regional assessment of hydrocarbon potential	243
6.6.1 Southern area	243
6.6.2 Central folded belt	244
6.6.3 Northern area	246
6.7 Epilogue	249
APPENDIX	252
BIBLIOGRAPHY	259
ENCLOSURES	Back pocket
All Tables, Figures and Plates	Volume 2

"..... the way one states a problem
greatly influences the investigation
of it"

E. G. Baker (1967, p. 300)

PART I - THE PROBLEM IN PERSPECTIVE

CHAPTER 1 INTRODUCTION

1.1 Background of the research

1.2 Diagenesis and hydrocarbon generation

1.3 Pre-Devonian source rocks

1.4 Amadeus Basin

1.5 Objectives of the present investigation

1.1 BACKGROUND OF THE RESEARCH

Until quite recently oil exploration was essentially a matter of delineating promising subsurface structures by means of geological mapping and seismic techniques, and then drilling them to ascertain whether or not hydrocarbons were present. The emphasis was on the trap or 'container' rather than its 'contents' (Welte, 1972). Nevertheless, no matter how large or porous the trap, it will not contain oil or gas unless there is a suitable source rock in the vicinity. Source-rock studies, despite their rather chequered and controversial history (outlined in Dott and Reynolds, 1969), are now generally accepted as having an integral part to play in modern petroleum exploration. Oil source beds are fine-grained sedimentary rocks in which petroleum hydrocarbons have been generated by the action of heat on dispersed organic matter (kerogen and asphaltenes) and from which oil has been subsequently expelled.

Many studies (e.g. Bornhauser, 1950; Hunt, 1953; Jones and Smith, 1965; Barbat, 1967; Hedberg, 1968; Reed and Henderson, 1972) have noted a relationship between the composition (or quality) of a crude oil and the facies or depositional environment of its source rock. More recently other authors (Philippi, 1974; Lijmbach, 1975; Powell, 1975; Powell and McKirdy, 1975; Vandenbroucke et al., 1976) have stressed the importance of the relative proportion of marine (largely microbial) and non-marine (higher plant) organic detritus deposited with a sediment in determining the kind of petroleum it may ultimately produce. For example, oils generated from source beds rich in the allochthonous debris of higher plants (spores, pollen and leaf cuticles) characteristically have a paraffinic base, low sulphur and high wax contents, a straight-chain paraffin (normal alkane) distribution dominated by the C_{23+} homologues, a high ratio of pristane to phytane, and an excess of pentacyclic over tetracyclic naphthenes. In contrast, oils derived principally from the

remains of marine organisms (phyto- and zooplankton) are usually of the naphthenic-aromatic type.

1.2 DIAGENESIS AND HYDROCARBON GENERATION

Although some hydrocarbons in petroleum are inherited directly from the lipid fraction of dead and decaying organisms (plant and animal) deposited with the original sediment (Hunt, 1974), the genesis of crude oil is essentially a diagenetic (i.e. post-depositional) process. Provided the type of organic matter is appropriate, it occurs only if the thermal history of the buried sediment is sufficiently intense and prolonged (Philippi, 1965; Landes, 1967; Vassoyevich et al., 1970; Connan, 1974; Cornelius, 1975).

Hydrocarbons heavier than methane are generated mainly in the temperature interval 75 - 150°C, equivalent in a sedimentary basin to depths in the range 1500 - 4500 m. This is the same interval through which dehydration of clay minerals in shales releases additional fluids for transporting the hydrocarbons (Perry and Hower, 1972). Some hydrocarbons move in solution, either true-aqueous (Price, 1976) or micellar (Baker, 1967; Cordell, 1973), whereas others are squeezed out as the ratio of free water to fixed water between the clay layers decreases (Dickey, 1975; Hunt, 1975).

Central to the considerable advances made during the last 10 - 15 years in our understanding of the origin of petroleum has been the development of techniques for measuring the degree of diagenesis (or level of organic metamorphism, LOM: Hood et al., 1975) of sedimentary organic matter, and hence defining, in the subsurface, zones of oil generation, conservation and degradation. The methods are based on such parameters as

- 1) coal rank and vitrinite reflectivity (Brooks, 1970;

- Hacquebard and Donaldson, 1970; Shibaoka et al., 1973);
- 2) spore and pollen colour (Gutjahr, 1966);
 - 3) colour and structure of plant pollen and leaf cuticle (Staplin, 1969);
 - 4) state of preservation of palynoplanktonic microfossils and amorphous organic matter (Correia, 1971);
 - 5) kerogen colour (Correia, 1971; Burgess, 1974), fluorescence (Correia and Peniguel, 1975), electron spin resonance (ESR: Pusey, 1973) and elemental composition (McIver, 1967; Durand and Espitalie, 1973; Tissot et al., 1974);
 - 6) analysis of cuttings gas ($C_1 - C_4$) and gasoline range ($C_4 - C_7$) hydrocarbons (Evans and Staplin, 1971; Evans et al., 1971; Bailey et al., 1974; Snowdon and Roy, 1975); and finally
 - 7) the composition of heavy (C_{15+}) extractable organic matter (EOM: Bray and Evans, 1961; Philippi, 1965; Tissot et al., 1971).

It is important to remember that some of these methods make use of organic matter (or features of its composition) derived specifically from land plants (e.g. vitrinite, spores and pollen, odd-even predominance, OEP, in $C_{23} - C_{35}$ n-alkanes). All of them fail to allow for inherent differences in the composition of marine and non-marine organic materials and their response to thermal alteration during burial diagenesis. The nature of the starting material influences not only the composition of the resulting petroleum hydrocarbons, but also their rate of formation, and determines the proportion of the parent kerogen that is capable of eventual transformation into hydrocarbons.

Most previous studies of the post-burial thermal alteration of sedimentary organic matter appear to have been made on rocks which contain significant amounts of terrigenous plant debris. As a result, our present

knowledge of the geochemical processes involved in petroleum genesis rests heavily on diagenetic changes observed in organic matter that is a mixture of marine and non-marine plant remains. Thus a somewhat anomalous situation exists whereby sedimentary organic matter of strictly marine origin (algae, bacteria, protozoa) is generally regarded as the principal source of crude oils and yet its behaviour during diagenesis is only poorly documented.

1.3 PRE-DEVONIAN SOURCE ROCKS

The occurrence of terrigenous plant materials in marine sediments is remarkably common, even in those deposited in deep water or far from land (Aizenshtat et al., 1973; Powell and McKirdy, 1973a; Powell et al., 1976), unless of course they were laid down before the proliferation of vascular plants. Because the latter is the case for all pre-Devonian sediments, any proposed source-rock study of an area such as the Amadeus Basin, central Australia, where the major part of the sedimentary succession comprises rocks of late Proterozoic and early Palaeozoic age, is immediately confronted by two obstacles:

1. The most commonly used indicators of organic maturation (i.e. those based on higher plant residues) are not available to provide a measure of the degree of thermal alteration of organic matter in non-reservoir rocks.
2. The literature is notably deficient in detailed organic geochemical studies of fine-grained sediments in pre-Devonian petroleum provinces (e.g. the Russian and Siberian Platforms, North America and North Africa: Keller, 1963; Becker and Patton, 1968; Vassoyevich et al., 1971) on which the collection and interpretation of source-rock data might otherwise have been modelled.

Without the option of recourse to certain of the conventional rank

parameters, or to suitable previous studies of Lower Palaeozoic and Proterozoic source rocks, it becomes necessary to find alternative compositional variables which reflect diagenetic changes in autochthonous marine organic matter free of associated vascular plant remains.

Fortunately the many published investigations of the diagenesis and incipient metamorphism of sedimentary organic matter are not entirely irrelevant to the problem at hand. It would be surprising indeed if, with increasing depth of burial, the same processes that have been reported in younger sediments (and summarized in Fig. 1.1) did not also operate in pre-Devonian rocks and produce similar gross changes in the composition of their indigenous organic matter. On fossil evidence the bulk of the marine biomass at that stage of the earth's history comprised microscopic algal and bacterial life-forms (Schopf, 1970, 1975; Tappan, 1971).

The problem thus becomes one of assembling pertinent geochemical data on a range of sediments known to contain predominantly microbial organic matter. This would permit

- 1) recognition and characterization of the various types of organic detritus that microorganisms are capable of contributing to the marine environment;
- 2) monitoring of the diagenetic evolution of each type throughout its burial, lithification and coalification (i.e. prolonged exposure to elevated temperatures); and finally
- 3) correlation of the principal stages in that evolutionary history with the expected sequence of hydrocarbon generation (biogenic methane, oil, gas condensate, and dry gas).

On the basis of such information, quantitative evaluation of the hydrocarbon potential of Proterozoic-Lower Palaeozoic sequences, such as that in the Amadeus Basin, then becomes feasible.

1.4 AMADEUS BASIN

Geologically the intracratonic Amadeus Basin (Fig. 1.2) is the oldest confirmed petroleum province in Australia. In addition to major hydrocarbon accumulations in the Mereenie oil and gas field and the Palm Valley gas field, both of which contain hydrocarbons in Ordovician formations, exploratory drilling elsewhere in the basin has encountered shows of oil and gas in Proterozoic, Cambrian and Ordovician rocks (Fig. 1.3). In 1963 a drill-stem test of Proterozoic sediments in the Ooramina No. 1 wildcat well yielded a minor flow of dry gas which rates as one of the most significant indications of indigenous Precambrian petroleum outside the USSR (Murray, 1965; Vassoyevich et al., 1971).

The Amadeus Basin has had a complex sedimentary and tectonic history (Wells et al., 1970) which produced a variety of potential hydrocarbon source rocks and traps (anticlinal, fault and stratigraphic) of different ages. For a given structural or stratigraphic 'play', knowledge of the temperature and depth of burial required to initiate generation of oil in the source rock and trigger its release into a carrier bed, unconformity or fracture zone, is essential in determining whether or not the trap was actually in existence at the time migration commenced. In the Larapinta Group the two known reservoir sandstones show a regional pattern of variation in porosity which is difficult to explain simply in terms of depth of burial. In places migrating hydrocarbons may have played a key role in preserving intergranular porosity.

Liquid hydrocarbons, particularly in provinces as old as the Amadeus Basin, are susceptible to further thermal alteration after they have accumulated in the reservoir. Depending on the maximum temperature attained and the 'cooking time', condensate or dry gas may be the end product. The fact that there is oil in the Mereenie structure but only

gas (with minor condensate) at Palm Valley suggests that the latter has had a more severe thermal history.

The ability to distinguish areas of immature, oil-prone and gas-prone sediments in the Amadeus Basin at this point of time in its exploration history would greatly facilitate the selection of targets for future drilling. A situation where mature source beds exist in favourable juxtaposition with porous reservoir beds is likely to be more prospective for liquid hydrocarbons than one in which the organic-rich sediments are either immature or alternatively have undergone incipient metamorphism. Obtaining a regional rank (or coalification) picture necessitates the recognition of variations in the type and degree of diagenetic alteration of organic matter preserved in both reservoir and non-reservoir sediments across the basin.

1.5 OBJECTIVES OF THE PRESENT INVESTIGATION

A preliminary organic geochemical study by Powell and McKirdy (1973a) of Mesozoic and Cainozoic marine carbonates, apparently devoid of land-plant material, indicated that diagenetic changes in the yield and composition of EOM were not as rapid or marked as those displayed by sediments containing terrigenous organic matter. The present study was undertaken in order to

- 1) investigate these changes in more detail and to see if they could be correlated with a progressive alteration of the structure and composition of the insoluble organic fraction (kerogen);
- 2) examine in a similar manner other rock types representing a range of depositional environments and fossil microbial (algal and bacterial) ecosystems; and
- 3) define the principal stages in the genesis of petroleum

hydrocarbons from autochthonous marine (i.e. essentially microbial) organic matter, in terms of quantitative organic parameters.

The ultimate objective of this work was to construct a geochemical classification that related the diagenesis and incipient metamorphism of microbial organic matter to hydrocarbon generation in sedimentary rocks.

Finally, as a test of the classification, it was used in the interpretation of organic geochemical data obtained from drill-hole samples of Proterozoic and Lower Palaeozoic sediments in the Amadeus Basin. The specific aims of this phase of the investigation were threefold:

- 1) to evaluate and compare the hydrocarbon generating potential of Proterozoic, Cambrian (Pertaoorrtta Group) and Cambro-Ordovician (Larapinta Group) sediments,
- 2) to identify the respective source beds of the hydrocarbons in the Palm Valley and Mereenie structures and in other minor shows, and
- 3) to delineate immature, oil-prone (mature), gas-prone, and barren (metamorphosed) areas in the basin as a guide to future exploration.

CHAPTER 2 SCOPE AND PLAN OF THE THESIS

2.1 Scope

2.2 Analytical techniques

2.3 Samples selected for the classification

2.4 Amadeus Basin wells studied

2.5 Oils and condensates

2.6 Sources of unpublished data

2.7 Presentation

2.8 Summary

2.1 SCOPE

In choosing samples for the studies that were to lead to the classification of diagenesis described in Chapter 5, both core and outcrop material had to be used in order to assemble a varied and representative selection of sediments containing microbial organic matter (Table 2.1). Special precautions were taken to remove weathered or contaminated surfaces when preparing the latter samples for analysis (Appendix 1).

The scope of a regional study on the organic geochemistry of an area as large as the Amadeus Basin is potentially very broad, particularly as there is little information on the organic content and maturation state of its sediments. From the outset, several factors served to restrict both the number of suitable rock samples that were available for analysis, and their distribution within the basin.

Organic matter in sedimentary rocks cropping out at the surface is prone to alteration by weathering (Leythaeuser, 1973) and to contamination by recent plant and animal remains. With only two exceptions all the samples examined from the Amadeus Basin were specimens of drill cores. This obviated possible difficulties in obtaining fresh samples in areas of deep Tertiary weathering (Wells et al., 1970) and avoided the necessity of extensive field work for collection purposes. The decision to concentrate on core material meant that the area covered was confined to the eastern half of the basin where all the exploration and stratigraphic drilling had been carried out (Fig. 1.2). Even so, only 16 wells were studied in a total area of about 44,000 km².

The major source of samples was the BMR Core and Cuttings Laboratory, Fyshwick. Access to cores held in this store is, of necessity, governed by strict regulations which limit the quantity of material that may be removed for destructive analysis. In some wells (e.g. Northwest Mereenie No. 1, Palm Valley No. 2) no cores were cut; in others (e.g. Waterhouse No. 1, West Waterhouse No. 1, West Mereenie No. 1, Johnny Creek No. 1) the only

intervals cored were sandstones. Cuttings were not used as experience has shown that they are commonly subject to contamination by mud additives (e.g. diesel fuel) and cavings. They are also susceptible to artificial thermal alteration during drying at the well site and, unless sealed in cans, may subsequently undergo slow evaporative loss of volatiles during storage which, in the case of the early Amadeus Basin wells, has been for periods as long as 12 years (Table 2.2).

The nature of the organic geochemical information sought was determined in the first instance by the range of appropriate analytical facilities and equipment in the BMR, the Geology Department, ANU, and the Chemistry Department, University of New South Wales (Duntroon). By the time a computerized gas chromatograph - mass spectrometer (GC-MS) facility became operational at Duntroon it was too late to embark on the type of detailed oil - source rock correlation attempted by Welte et al. (1975a). Nevertheless, the techniques employed and the data they generated were considered adequate to detect at least broad variations in source-rock quality with lithofacies, depth and regional maturation level in representative well sections of Proterozoic, Cambrian and Ordovician sediments across the basin. Fortunately, funds were available to enable certain other analytical work beyond the scope of the in-house facilities (viz., stable carbon isotope, major element and phosphate analyses) to be contracted out to commercial service laboratories.

2.2 ANALYTICAL TECHNIQUES

The two principal analytical schemes used in this study, one for fine-grained sediments and the other for reservoir hydrocarbons, are outlined in Figures 2.1 and 2.2 respectively. Details of the individual procedures are given in Appendix 1.

The scheme followed in the analysis of the sediments (Fig. 2.1)

was essentially a synthesis of various methods used in earlier studies by McKirdy (1971) and Powell and McKirdy (1973a). It was designed to permit the correlation of diagenetic changes in the soluble (EOM) and insoluble (kerogen) portions of the total organic matter, in a manner similar to that recently described by Powell et al. (1975: Enclosure 1) for phosphorites. In the present study, however, both saturated hydrocarbons and kerogen were characterized in somewhat greater detail after preliminary work on the geochemical model had indicated the potential value of certain additional parameters as indicators of source, environment and rank.

In view of the time-consuming nature of the method, kerogen was isolated only from those rocks which are particularly rich in organic matter. All the kerogens isolated were subjected to major element (C,H,N and S) and ash analysis to establish their type and rank in terms of atomic ratios and elemental percentages on a dry, ash-free basis (d.a.f.). Selected kerogens were analysed further by X-ray diffraction (XRD, which was also used to identify mineral impurities), infrared spectroscopy (IR), pyrolysis-hydrogenation-gas chromatography (PHGC), carbon isotope mass spectrometry, and microscopic examination in reflected and transmitted light, in order to broaden the basis of their classification into different genetic types and document the response of each type to diagenesis and maturation.

Geochemical analysis of oils and condensates from the Mereenie and Palm Valley reservoirs was carried out using the method of Powell and McKirdy (1972, 1975, 1976). This enabled the Amadeus crude oils to be compared with oils and condensates found in geologically younger rocks elsewhere in Australia.

2.3 SAMPLES SELECTED FOR THE CLASSIFICATION

The first phase of the thesis research involved the selection and analysis of a range of sediments thought to contain microbial organic matter

of various types and levels of thermal alteration. The resulting geochemical data were used to erect a preliminary classification of microbial diagenesis. The individual suites of samples are listed in Table 2.1. To be eligible a rock or sediment had to contain organic matter of predominantly algal (or bacterial) origin. For many samples, this was established simply on the basis of their age (pre-Devonian). In the case of the younger sediments, some of which were deposited in non-marine environments, identification of the source of their organic content depended directly on micropalaeontological and petrographic evidence. Inclusion of young, relatively unaltered sediments, such as those from the JOIDES DSDP Hole 262, was necessary to permit investigation of the crucial early stages of diagenesis.

In terms of geological age, depositional environment, lithofacies and thermal history, the samples in Table 2.2 are considered diverse enough to permit recognition of those aspects of the diagenesis of microbial organic matter that determine its ability to generate petroleum hydrocarbons. Relevant published information on algal sediments and extant, geologically significant microorganisms was incorporated into the model.

Ancillary studies were conducted in the following areas to facilitate the interpretation of the basic geochemical data collected for the classification, through identification of the principal controls on the composition of microbial geolipids and kerogen:

1. The petrography, reflectance and composition of dispersed organic matter in various Lower Palaeozoic and Proterozoic sediments (with Mr A.J. Kantsler and Professor A.C. Cook, Geology Department, University of Wollongong).
2. The organic geochemistry of phosphorites (Upper Proterozoic-Recent) (with Dr T.G. Powell¹ and Dr P.J. Cook², BMR).
3. The state of preservation of microfossils and organic matter in

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shales and siltstones of the McMinn Formation (Middle Proterozoic), McArthur Basin adjacent to an intrusive dolerite sill (with Dr M.J. Muir³ and Mr C.J. Peat, Royal School of Mines, London, and Mr K.A. Plumb, BMR).

4. The relationship between the organic and inorganic geochemistry of pelagic calcareous oozes (Pliocene-Recent) in the Timor Trough (with Dr P.J. Cook², BMR).
5. The regional correlation of kerogen structure and composition with illite crystallinity and magnetic response in the Tapley Hill Formation (Upper Proterozoic), Adelaide Geosyncline (with Dr J. Sumartojo⁴ and Dr V. Gostin, Geology Department, University of Adelaide, and Dr D.H. Tucker, BMR).
6. The chemical structure of algal kerogens using PHGC (with Dr D.J. McHugh and Mr J. Tardif, Chemistry Department, University of New South Wales, Duntroon).

Much of the work on the classification was directed towards ascertaining the compositional variability of microbial kerogens, their usefulness as rank indicators, and the extent to which kerogen type influences the yield and composition of the associated EOM.

2.4 AMADEUS BASIN WELLS STUDIED

Table 2.2 lists the wells from which sediment samples were taken for organic geochemical analysis. Most are subsidized exploration wells or BMR stratigraphic holes, cores from which are held in the BMR Core and Cuttings Laboratory. Material from the non-subsidized wells was supplied by Magellan Petroleum Australia Ltd.

Depending on the availability and spacing of cores down the holes,

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samples were taken at intervals of no more than 150 m. The weight of individual samples was 350-450 gm for 100 mm diameter core, and 100-200 gm for 38 mm diameter core. Where scarcity of suitable core at a particular depth necessitated a composite sample, the maximum stratigraphic interval from which material was selected was 1.2 m. The actual method of sampling varied according to the state of preservation of the original core. Plugs (38 mm or 13 mm diameter) or slabs were cut from intact lengths of the core. Alternatively, if the core was badly broken, pieces were selected at random. Sandstones were sampled as well as the finer-grained, non-reservoir sediments to test for the presence of migrated hydrocarbons.

Some wells were sampled in somewhat greater detail than others, in order to

- 1) allow comparison of the organic matter in different rock types at essentially the same depth and (hence) level of organic maturation;
- 2) provide an indication of the range in concentration and composition of the organic matter in key formations; and
- 3) serve as reference sections for use in locating the zone of present maximum hydrocarbon generation, and establishing regional maturation trends.

2.5 OILS AND CONDENSATES

Two oils and one condensate from the Mereenie field, three condensates from the Palm Valley field, and an oil from Alice No. 1 (Table 2.3) were analysed. With the exception of the oils from East Mereenie No. 4 and Alice No. 1, all were supplied by Magellan Petroleum Australia Ltd specifically for this study. The other two samples came from the BMR reference collection of Australian oils. Unfortunately, samples of the residual hydrocarbons reported in East Johnny Creek No. 1 were not available.

Oil saturated sandstones located immediately above and below the Horn Valley Siltstone in BMR AP No. 1 were processed in the same manner as non-reservoir sediments.

2.6 SOURCES OF UNPUBLISHED DATA

To augment the organic geochemical information obtained during this investigation, and to assist in its interpretation, use was made of unpublished data from several sources. Present formation temperatures were calculated from bottom-hole temperature measurements quoted in well completion reports. Analyses of reservoir and cuttings gas samples collected during drilling and subsequent testing of various wells in the Amadeus Basin (Konecki and Blair, 1970) were used to compute values for percentage wet gas, a supplementary index of organic maturation level. Magellan Petroleum Australia Ltd allowed the author to consult confidential analyses of oil and condensate from the two major fields of the Amadeus Basin. Finally, reference to organic geochemical data on various Cambrian and Proterozoic sediments examined by McKirdy (1971) helped in the construction of the classification.

2.7 PRESENTATION

The thesis is organised into three parts. Part I comprises Chapters 1 and 2 which describe, respectively, the background of the problem chosen for investigation and the organization of the thesis. The results and interpretation of the organic geochemical analyses performed for the thesis are contained in Parts II and III. Part II opens with a review of the literature on microbial organic matter as a source of petroleum hydrocarbons, and the world occurrence of oil and gas in pre-Devonian rocks (Chapter 3). It then goes on to discuss the work that

led to a classification of microbial diagenesis suitable for use in petroleum source-rock studies of Lower Palaeozoic and Proterozoic sediments (Chapter 4). This classification is outlined in Chapter 5. In Part III, following a brief resumé of the petroleum geology of the Amadeus Basin, the classification is used to assess the hydrocarbon-generating potential of the Proterozoic, Cambrian and Cambro-Ordovician sedimentary sequences, respectively, of the Amadeus Basin.

Parts of the research were written up and published before completion of the thesis. The resulting papers, most of which describe work that contributed to the development of the classification, are included as enclosures in the back pocket of Volume 1 of the thesis. Volume 1 comprises the text, appendix, bibliography and enclosures. To facilitate access to the large number of tables and figures, these are bound separately in Volume 2.

2.8 SUMMARY

The scope of the thesis was determined by two factors: the availability of samples, and the nature of the analytical facilities to which the author had access. In view of the limited sophistication of the techniques employed, it was decided to concentrate on obtaining a general picture of the variation in composition displayed by sedimentary organic matter of presumed algal and bacterial origin, and of the geological factors that affect it. The resulting classification of diagenesis, although preliminary, nevertheless defines the main stages in the genesis of petroleum from microbial precursors.

As originally conceived, the present study required that the pre-Devonian sediments of the Amadeus Basin be analysed in sufficient detail to reveal differences or similarities in their organic content attributable (on the basis of the model) to lithofacies, depositional environment, biota, maturation pathway, or thermal history. This proved difficult to achieve in

the time available. Sampling of additional wells (e.g. James Range A No. 1 and East Johnny Creek No. 1) is necessary to fill the gaps that remain in the regional and stratigraphic coverage of the basin. Also further geochemical work (possibly involving GC-MS and other analytical techniques) is required to confirm the provisional identifications made herein of the major source beds in the basin, and to detect more subtle but potentially important diagenetic changes in their organic matter.

Some specific areas in which further research would make an important contribution to our knowledge of the origin and evolution of petroleum in the Amadeus Basin are

- 1) petrographic examination of the dispersed organic matter (kerogen) in non-reservoir sediments, including fluorescence microscopy of the liptinite fraction;
- 2) $\delta^{13}\text{C}$ measurements on kerogen - EOM pairs;
- 3) GC-MS identification of C_{25+} cyclics in the alkane fraction of the Mereenie oil and its suspected source beds; and
- 4) more detailed analysis of the oils and condensates (involving, for example, comparison of their gasoline fraction with the spectrum of C_4 to C_7 hydrocarbons in adjacent fine-grained sediments) to test the hypothesis, developed later in the thesis, that they are products of the progressive in situ thermal alteration of oil in the reservoir.

As a prelude to the discussion of a series of studies on the diagenesis of microbial organic matter, the next chapter of the thesis reviews the geological significance of microbial organic matter as a source of petroleum.

"In my opinion we really don't know
what source beds are"

A.A. Meyerhoff (1974, p. 415)

PART II - TOWARDS AN ORGANIC GEOCHEMICAL CLASSIFICATION
OF DIAGENESIS FOR USE IN EVALUATING THE
SOURCE-ROCK POTENTIAL OF PRE-DEVONIAN SEDIMENTS

CHAPTER 3 MICROORGANISMS AS SOURCES OF PETROLEUM
HYDROCARBONS - A LITERATURE REVIEW

3.1 Introduction

3.2 The oldest crude oils

3.3 Early organic evolution and petroleum genesis

3.4 Petroleum precursors in contemporary marine
microorganisms

3.5 Characteristics of marine crude oils

3.6 Concluding remarks

3.1 INTRODUCTION

Indications of indigenous petroleum (residual bitumen, oil and gas shows, oil seeps) in sedimentary rocks of mid-Proterozoic to early Palaeozoic age occur widely throughout North America, Eurasia, Africa and Australia. Commercial or potentially commercial oil and gas accumulations in reservoirs of this age are known from U.S.S.R., U.S.A., Canada, Algeria, Libya, Oman and Australia. Although a source younger than Silurian has been suggested for the oil and gas in some of these ancient reservoirs, many contain hydrocarbons apparently generated from the remains of aquatic microorganisms preserved in sediments deposited before the appearance of extensive vegetation on land. It was not until the late Silurian or early Devonian that vascular plant residues became a significant source of petroleum hydrocarbons.

Because of their origin from algae and bacteria (and possibly, in part, the lipids of the first marine invertebrates), indigenous Proterozoic and Lower Palaeozoic crude oils constitute a vast untapped store of geochemical data on the nature of the early marine biomass, in the form of biological marker compounds (e.g. singly-branched, isoprenoid and polyterpenoid hydrocarbons). By the same token, these ancient oils also point up the importance of a detailed knowledge of the lipids and other potential hydrocarbon precursors in extant algae (prokaryotic and eukaryotic), bacteria, protozoa and planktonic crustaceans, to an informed understanding of the origin and geochemical characteristics of true marine crude oils of all ages.

This chapter, then, is a survey of the more recent literature - geological, biochemical and organic geochemical - pertaining to the general question of the role of aquatic microorganisms as sources of petroleum hydrocarbons throughout earth history.

3.2 THE OLDEST CRUDE OILS

Arguably the oldest evidence of mobilized organic matter in the geological record is the thucolite, a putative radiolytic polymer of petroleum-type hydrocarbons, associated with the gold and uranium-bearing Witwatersrand sediments (approx. 2700 m.y. old) of the Kapvaal Craton, South Africa (Schidlowski, 1969). Another possible example of originally liquid hydrocarbons in ancient sedimentary rocks is the so-called anthraxolite which occurs as lenses of solid pyrobitumen in the approximately 2000 m.y. old Gunflint Iron Formation, Ontario (Barghoorn et al., 1977). Nearby, on the opposite shore of Lake Superior, is one of the oldest presently known active oil seeps. It is located at the White Pine copper mine, Michigan, and emanates from siltstones and shales of the 1100 m.y. old Nonesuch shale (Barghoorn et al., 1965).

It is now 12 years since Murray (1965), prompted by a significant but non-commercial gas flow from a Proterozoic dolomite in Exoil's wildcat well, Ooraminna No. 1, in the Amadeus Basin (Siller et al., 1963), first canvassed the possibility that Precambrian sediments might contain indigenous petroleum (oil and gas) in commercial quantities. Shortly afterwards, Becker and Patton (1968) published a comprehensive review of the then known occurrences of oil and gas in pre-Silurian rocks, in which they concluded (p. 224): "Marine sedimentary rocks of Precambrian, Cambrian and Ordovician ages constitute a major frontier for petroleum exploration". The reasons for this assertion have been elaborated by Vassoyevich et al. (1971) and Rjabuchin (1976) in papers which discuss the theoretical and geotectonic factors governing oil and gas occurrences in late Precambrian and early Palaeozoic sediments, and describe some of the more significant petroleum provinces comprised of rocks of this age.

According to Rjabuchin (1976), Precambrian (or more specifically, Riphean and Vendian¹), and Cambrian fields accounted for about 3% of world petroleum production at the beginning of 1974, a percentage that is currently increasing. Rjabuchin also points out that more than 100 separate oil and gas deposits, and oil reserves totalling several billion tonnes, are now known in late Precambrian and Cambrian rocks. It is also of interest to note that 11 of the 187 giant oil fields, and 3 of the 79 giant gas fields, cited by Halbouty et al. (1970) include producing reservoirs of Silurian age or older.

3.2.1 North America

The North American continent has 3 main areas of pre-Devonian oil production (Becker and Patton, 1968). The first and most important of these comprises a 320 km wide belt extending from the Central Kansas uplift, southward through Oklahoma and thence southwest across North Texas to the Central Basin platform and Delaware Basin of West Texas and New Mexico. The main productive beds are Cambro-Ordovician carbonates of the Arbuckle and Ellenberger Groups and sandstones of the Ordovician Simpson Group. More than 90% of the oil and gas produced from Cambrian and Ordovician rocks in the U.S.A. has come from this area (L.E. Gatewood, as cited by McCaslin, 1976) which encompasses the giant Sho-Vel-tum (901 million bbl), Greater Seminole (882 million bbl), Oklahoma City (771 million bbl) and Golden Trend (495 million bbl oil, plus 3 Tcf gas) oil fields; and the giant Puckett (6.5 Tcf) and Gomez (4.0 Tcf) gas fields (Halbouty et al., 1970: figures in brackets are the estimated ultimate recoverable

1. Riphean, 1600-680 m.y. B.P. (before present); Vendian, 680-570 m.y. B.P. (Preiss, 1977)

reserves, not all of which, however, are located in pre-Devonian reservoirs). Ordovician rocks (including those of the Arbuckle Group) have been the source for much of the oil in the Oklahoma City field (Webb, 1976). In the Delaware and Val Verde Basins of West Texas, at least some of the gas in early Palaeozoic reservoirs has been traced using isotopic and other organic geochemical techniques to Ordovician and Silurian source beds (Stahl and Carey, 1975).

Elsewhere in the U.S.A., the Ordovician Trenton Limestone of Ohio, Indiana and Michigan had yielded in excess of 500 million bbl of oil and 1 Tcf of gas to the end of 1964 (Becker and Patton, 1968). The Williston Basin of southern Saskatchewan, eastern Montana, western North Dakota and northwestern South Dakota is another important region of Lower Palaeozoic oil production. Here an estimated 600 million bbl of oil has been generated in the Cambrian Winnipeg Formation (Dow, 1974; Williams, 1974). Production is from Ordovician and Silurian carbonates.

3.2.2 Russia

Meyerhoff (1974) highlighted the importance of Precambrian oil and gas in the U.S.S.R. by quoting the example of a single field which contains 35 Tcf of proven Proterozoic reserves. At present two major oil and gas provinces are known in Proterozoic and early Palaeozoic sediments of the Soviet Union (Rjabuchin, 1976). These are

1. the Angara and Tunguska Basins of the Siberian Platform (Vassoyevich et al., 1971; Levchenko, 1975) and
2. the Baltic Basin, part of which lies offshore in the Baltic Sea (Maximov and Muromtseva, 1975).

The former is of particular interest because it includes the famous Markovo field, discovered in 1962 and located in the southern part of the province (Irkutsk amphitheatre, Angara Basin). The Markovo field

produces gas and condensate from late Precambrian (Riphean and Vendian) sandstones and oil (estimated ultimate recoverable reserves 175 million bbl plus: Halbouty et al., 1970) from Vendian sandstones and early Cambrian carbonates (Vassoyevich et al., 1971). Subsequent drilling in the basin has established the presence of at least nine additional oil fields, two of which produce from Vendian clastic sequences and the remainder from Cambrian carbonates (Kontorovich et al., 1974; Drobot and Presnova, 1975). Further north, in the less intensely explored Tunguska Basin, one commercial oil field and three gas-condensate fields have been discovered, all with Cambrian pay zones (Levchenko, 1975).

The Baltic Basin lies on the western margin of the Russian Platform, which itself contains abundant evidence of indigenous Precambrian crude oil as well as thick, organic-rich (up to 30% TOC), black, bituminous shales and carbonates of Vendian age (Vassoyevich et al., 1971). Commercial oil was discovered in the Baltic region in 1969. Sixteen Cambrian oil pools, and at least one Ordovician deposit, are now known. In all cases the oil is believed to be derived from Cambrian source beds (Gurko and Stepina, 1974; Maximov et al., 1974; Maximov and Muromtseva, 1975). Current daily production from the Krasnabor, Ushakov and other smaller fields in the basin varies between 100 and 200 tonnes (Rjabuchin, 1976).

3.2.3 Africa and the Middle East

North Africa is notable for its large oil and gas accumulations in Cambrian and Ordovician sandstones (Becker and Patton, 1968; Halbouty et al., 1970). Among those for which the source rocks have been shown to be wholly or partly of pre-Devonian age are

1. the giant oil fields at Hassi Messaoud (estimated ultimate recoverable reserves 3500 million bbl plus: Halbouty et al., 1970) and Rhourde el Baguel (500

- million bbl) in the Mya Basin of Algeria;
2. the Tin Fouyé - Tabankort oil field, Illizi Basin, Algeria; and
 3. the Hamada and Djefara oil fields of the Hamada Basin, northwest Libya.

The principal source for the Algerian oils appears to be Silurian graptolitic black shales rich in the sapropelic remains of the marine alga Tasmanites (Tissot et al., 1974; Tissot, Espitalie et al., 1974; Welte et al., 1975a). The two Libyan oils mentioned have the same paraffinic to naphthenic composition as that from Hassi Messaoud (Byramjee and Vasse, 1969) and are therefore likely to have a similar source.

Finally, oil has recently been discovered in the Precambrian of Oman (M.R. Walter, pers. comm., 1977). An indigenous source is envisaged for the oil which is geochemically distinct from the younger Permo-Carboniferous and Cretaceous oils of the Arabian Platform.

3.3 EARLY ORGANIC EVOLUTION AND PETROLEUM GENESIS

On the basis of micropalaeontological and related geochemical evidence from Precambrian sedimentary rocks (Cloud, 1972, 1976; McKirdy, 1974; Schopf, 1975; Muir and Grant, 1976; Fig. 3.1), it appears likely that oxygen-releasing photosynthetic microorganisms (primitive, autotrophic, anaerobic and microaerophilic prokaryotes) existed well before 3400 m.y. ago. However, it was not until about 2000 m.y. B.P. that

1. all available oxygen sinks (e.g. Fe^{2+}) became filled;
2. effective oxygen-mediating enzymes had developed;
3. free oxygen began to accumulate in the atmosphere, accompanied by the segregation of a chemically equivalent mass of reduced carbon in bottom sediments;
4. an atmospheric ozone layer became established and screened

- out lethal UV radiation, opening the way for surface-living phytoplankton to colonize the oceans; and
5. epicratonic stable shelf and platform environments formed, permitting the deposition of the first extensive marine carbonates.

Data presented by Ronov and Migdisov (1971) for sediments from the Russian Platform (summarized in McKirdy, 1974, table II) shows that Late Proterozoic (1400-600 m.y.) carbonates contain on average six times more organic carbon than their Early and Middle Proterozoic (2700-1400 m.y.) equivalents.

As envisaged by Cloud (1972, 1976), an increased volume of dispersed organic matter preserved in late Precambrian sediments is both an inevitable consequence and a necessary condition of the gradual accession of oxygen to the atmosphere. This sequestration of organic matter into marine sediments is also inextricably linked to the nature and evolutionary development of the late Proterozoic global ecosystem. It was the conjunction of geotectonic, sedimentological, biological and ecological circumstances mentioned above that led to the production of the organic matter which was destined to become the source of the first crude oils. Vassoyevich et al. (1971, p. 409) describe the situation as follows: "During this time warm, shallow intracontinental seas with a flourishing photosynthesizing bios that was transforming the earth's atmosphere and hydrosphere were more extensive than at any time before. Thus an enormous quantity of organic matter was generated and buried in the course of almost a billion years, and some of this must have become the source of the oldest oils on earth".

According to Tappan (1971), the original marine ecosystem was relatively simple and comprised principally blue-green algae, capable of producing large quantities of organic matter, and bacterial decomposers, neither requiring many preformed nutrients. She continues (p. 1083): "Gradually the system became more complex by the addition within the Precambrian of other algal producers - at least some red algae, in addition to

the green Prasinophyceae (Leiosphaeridia) and Botryococcus, and possibly others - and fungal reducers, and the insertion of the consumer trophic level in latest Precambrian or earliest Cambrian". At this early stage in the ecological succession the bulk of the marine biomass comprised protists (unicellular plants and animals). Food chains were short but food (sinking phytoplanktonic cells and other particulate organic matter) was plentiful. Among the grazing organisms, relatively inefficient filter-feeders were predominant. Zooplankton (e.g. radiolaria, graptozoans) were also important, but detritus-feeders and specialized predators were probably rare or absent. The ratio of producers (algae) to consumers (invertebrates) was high. Gross production in relation to both biomass and community respiration was also high, leading to the accumulation of the excess organic matter in carbonaceous sediments and, ultimately, to the formation of petroleum deposits.

The early Palaeozoic geologic record is characterized by sediments deposited in relatively warm, shallow (< 30 m) epicontinental seas (Tappan, 1971). Thermal stratification ensured that much organic detritus reached the seafloor. It was in such environments of restricted circulation and possible eutrophication (lagoons, epeiric seas fringed by low islands, etc.) that prodigious monospecific blooms of acritarchs and related algae commonly grew (Cramer and Diez, 1974). In their report Cramer and Diez presented data which indicate the existence of world-wide palaeogeographic zones of Lower Palaeozoic source rock deposition. These zones were interpreted as corresponding to temperature-controlled latitudinal provinces in which cosmopolitan phytoplanktonic forms such as Gloecapsomorpha, Leiosphaeridia and Tasmanites were at their zenith following widespread marine transgressions during the early and middle Ordovician and the early Silurian (see also Tappan and Loeblich, 1972; Combaz, 1974).

Primary marine algal productivity was exceptionally high early in the Palaeozoic, as indicated by the abundance of fossil acritarchs, which reach a maximum in Lower to Middle Ordovician sediments (Tappan, 1968, 1971).

Through the Silurian and into the Devonian both phytoplankton and invertebrates were diverse and abundant (i.e. high total biomass), although net community production was low because marine organic detritus was more effectively utilized, largely as a result of the advent of deposit feeders (pelecypods, holothurians). Hence, less algal organic matter survived sedimentation to become buried in marine sediments. By the end of the Devonian acritarchs had declined in abundance and diversity and many of the early Palaeozoic algal taxa had become extinct (Tappan, 1968).

The subsequent history of the marine phytoplankton has been summarized by Tappan (1968, pp. 193-194). It is marked by major fluctuations in diversity and abundance, with peaks in the Late Cretaceous and Paleocene-Eocene. As noted by Combaz (1974), the periods of maximum marine transgression and phytoplankton abundance appear to correspond to the presence of major accumulations of petroleum in rocks of early Palaeozoic, Cretaceous and early Tertiary age. A corollary of this observation is that oils reservoired in other Phanerozoic rocks are likely to be derived, partly or wholly, from the remains of non-marine vascular plants.

3.4 PETROLEUM PRECURSORS IN CONTEMPORARY MARINE MICROORGANISMS

In the present oceans, approximately 95% of the net photosynthetic production (i.e. primary algal organic matter not used in algal respiration) is consumed by grazing zooplankton, other filter-feeders and aerobic saprophytic bacteria in the upper 200 m of the water column (Tappan, 1968). Of the remaining 5%, most goes into solution, some persists as viable, reproducing organisms, some sinks into the aphotic zone where it is consumed by deeper dwelling animals or degraded by heterotrophic bacteria, and only a small fraction (perhaps 0.01% of the total organic carbon: Sackett, 1964) eventually reaches the seafloor. Tappan (op. cit., p. 194) however, points out that although such a small proportion of the original organic production is

buried and preserved "this is compensated for by the astronomical numbers of phytoplankton, as is well evidenced by coccolith chalks, diatomites and petroleum". The amount of organic matter finally incorporated into the bottom sediment may be greater where there is abnormally high photosynthetic activity in the surface waters (e.g. estuaries, sites of marine upwelling: Brongersma - Sanders, 1966) or where circulation is restricted, leading to the development of an anoxic zone in the lower part of the water column.

Parsons (1963) has shown that the total organic matter in the euphotic zone (0-100 m) is distributed approximately as follows: soluble organics, 100; particulate detritus, 10; phytoplankton, 2; zooplankton, 0.2; fish, 0.002 (expressed on a relative scale with the major component as 100). Bacteria act as a bridge between phytoplankton and filter-feeders in the marine food chain. Work by Seki (1970, p. 961) suggests that viable bacteria (and allied microorganisms) comprise "a few percent of the total organic matter in the sea". Once it enters the anoxic zone (which may be above or below the sediment-water interface: Fig. 3.2), particulate organic matter derived from plankton is attacked by anaerobic bacteria and "converted into a biomass consisting of bacterial bodies (the 'reworkers') mixed with microbially resistant part of the planktonic bodies" (Lijmbach, 1975, p. 359). Clearly, organic-rich sediments (3-20% TOC) will form wherever an appropriate imbalance is maintained between primary organic production and settling rates on the one hand, and the rates of organic decomposition and inorganic sedimentation on the other (cf. Richards, 1970).

From the foregoing we may conclude that the major progenitors of microbial organic matter in marine sediments are (in probable order of importance) phytoplankton, bacteria and zooplankton. The question then arises: what part (or parts) of this organic matter constitute the most likely precursors of petroleum hydrocarbons?

It is now generally accepted that the lipids of organisms living in or adjacent to aquatic environments have been a major source of petroleum

throughout geological history. This conclusion is based on

1. the close correspondence between the carbon isotopic composition of crude oils and biolipids (Silverman, 1964; Degens, 1969); and
2. the unmistakable similarity between the molecular structure of certain hydrocarbons and other compounds (e.g. porphyrins) in petroleum, and the characteristic carbon skeletons (Enclosure 2, fig. 1) of biosynthetic hydrocarbons, fatty acids, alcohols, ketones and pigments (Hills et al., 1970).

However, recent laboratory experiments carried out by Lijmbach (1975) and Philp and Calvin (1976) indicate that the "non-lipid" part of algal and bacterial cells may also contribute significantly to the formation of petroleum (see Section 3.4.3)

3.4.1 Microbial lipids

The lipid fraction of microscopic algae, bacteria and zooplankton includes hydrocarbons, fatty acids (present as triglycerides, wax esters and phospholipids), fatty and polyhydroxy alcohols (as, respectively, wax esters and glycosides), pigments and sterols (Kates, 1964; Lee et al., 1971; Nichols, 1973). Lipids may comprise as much as 85% (but generally 3-30%: Abelson, 1967; Lee and Loeblich, 1971; Lee et al., 1971) of the organisms' cellular dry weight. Zooplankton, particularly the deeper living (i.e. meso and bathypelagic) forms, tend to be richer in lipids (3-61%, mean 28%: Lee et al., 1971) than do the phytoplankton. Of the microbial lipids, all of which are potential precursors of petroleum hydrocarbons, the hydrocarbons are the least labile and hence the most likely to survive sedimentation and early burial with their carbon skeletons essentially intact. Extensive studies by Blumer (see e.g. Blumer et al., 1971, and references cited therein) have shown that "hydrocarbons, even

highly unsaturated ones, are remarkably stable in the marine food chain". Oxygenated and unsaturated lipids tend to be less stable in the marine environment. For example, the fatty acids of phytoplankton and zooplankton are susceptible to degradation and resynthesis by anaerobic bacteria (Boon et al., 1975) and, in the case of unsaturated acids, to auto-oxidation (Morris and Calvert, in press).

Hydrocarbons

Aliphatic hydrocarbons constitute 0.006-0.12% (dry cell weight) of blue-green algae (Oró et al., 1967; Han et al., 1968a; Winters et al., 1969; Lee and Loeblich, 1971). In the freshwater to paralic green alga, Botryococcus braunii, the corresponding figure is a high 20%, which increases to more than 70% under conditions unfavourable for active growth (Knights et al., 1970). Of the marine algae studied by Lee and Loeblich (1971), diatoms (bacillariophyta) contained 0.02-1.4% (mean 0.6%, dry cell weight) hydrocarbons, which is (on average) about half the amount in dinoflagellates (pyrrophyta: 0.06-5.8%, mean 1.2%). The ubiquitous anaerobic sulphate-reducing bacterium Desulfovibrio desulfuricans contains 5-9% lipid of which 25% is hydrocarbons (Davis, 1968). The hydrocarbon content of four marine copepods (zooplankton) examined by Lee et al. (1971) was 0.3-2.6% (dry cell weight).

Blumer et al. (1971) analysed representatives of the principal classes of marine phytoplankton for their C_{12} - C_{25} hydrocarbons. For comparison, the composition of the hydrocarbons present in various extant benthonic blue-green and green algae is summarized in Enclosure 2, table III. The C_{15} or C_{17} n-alkane (and/or a corresponding alkene) is almost invariably prominent in the blue-green (cyanophyta), green (chlorophyta) and red (rhodophyta) algae. In diatoms, dinoflagellates and some other algae, however, the major hydrocarbon is commonly the n- $C_{21:6}$ polyunsaturated

alkene (Lee and Loeblich, 1971). Longer chain hydrocarbons ($n\text{-C}_{23}$ to $n\text{-C}_{35}$ alkanes and/or alkenes) are present (and, in some cases, predominant) in certain species of blue-green, green and red algae (Clark and Blumer, 1967; Gelpi et al., 1970; Jones and Young, 1970) and in fungi (Weete, 1972). The singly-branched alkanes, 7-methyl and 8-methylheptadecane (Enclosure 2, fig. 1), occur only in blue-green algae (Gelpi et al., 1970; Han and Calvin, 1970). Dembicki et al. (1976) have recently suggested that, during sedimentation and early burial, algal n -alkanes may be consumed and replaced by bacterial hydrocarbons. Similar bacterial modification of land-plant-derived C_{23+} n -alkanes was postulated by Rogers and Koons (1971) and Johnson and Calder (1973).

The C_{15} - C_{35} normal alkanes have been identified in photosynthetic and nonphotosynthetic bacteria (Albro and Huston, 1964; Davis, 1968; Han and Calvin, 1969; Jones and Young, 1970). A predominance of even over odd-carbon-numbered homologues in the range C_{20} - C_{29} characterizes the n -alkanes of certain anaerobic bacteria (Han and Calvin, 1969; Dembicki et al., 1976). Monounsaturated C_{22} - C_{30} iso and anteiso branched alkenes (Enclosure 2, fig. 1) appear to be more important than normal alkanes in the nonphotosynthetic Micrococcaceae, Sarcina spp. and Micrococcus spp. (Tornabene et al., 1967, 1970; Albro and Dittmer, 1970). Similarly, Han and Calvin (1969) found that unidentified high-molecular-weight branched and cyclic compounds made up 92-95% of the total aliphatic hydrocarbon fraction in two species of photosynthetic bacteria; whereas Gelpi et al. (1970) reported the occurrence of a C_{30} pentacyclic triterpenoid hydrocarbon (comprising 10-38% of the total aliphatic hydrocarbons) in three geochemically important blue-green algae (Lyngbya aestuarii, Nostoc sp. and Chroococcus turgidus). Subsequent work by Bird et al. (1971a), De Rosa et al. (1973) and Forster et al. (1973) now indicates that C_{30} , C_{31} and C_{35} pentacyclic triterpenoid hydrocarbons (alkanes and alkenes) of the hopane type (Enclosure 2, fig. 1) are significant, and possibly character-

istic, constituents of prokaryotic microorganisms (bacteria, blue-green algae). Hydrocarbons of the hopane series ($C_{27} - C_{35}$) have recently been reported from sediments, oil shales and crude oils (Ensminger et al., 1974; Kimble et al., 1974).

The isoprenoid (multiple branched: Enclosure 2, fig. 1) alkanes, pristane (C_{19}) and phytane (C_{20}) occur widely in sediments and crude oils where they are usually considered to be products of the diagenesis of the phytol (C_{20}) alcohol side-chain of chlorophyll. However, pristane and, less commonly, phytane may also occur (pr > ph) as discrete hydrocarbons in certain algae (Clark and Blumer, 1967; Oró et al., 1967; Han et al., 1968b) and bacteria (both photosynthetic and nonphotosynthetic: Han et al., 1968b; Han and Calvin, 1969).

The hydrocarbons of zooplankton include n-alkanes but are characterized by a complex assemblage of C_{19} and C_{20} isoprenoid alkanes and alkenes (Blumer and Thomas, 1965a, b; Blumer et al., 1969).

Fatty acids

Contemporary algae contain fatty acids in appreciably higher concentration than aliphatic hydrocarbons (Schneider et al., 1970). However, algal fatty acids possess shorter chain lengths (C_{10} to C_{22}) than do the hydrocarbons (C_{15} to C_{33}), and exhibit a higher degree of unsaturation. The C_{14} , C_{16} and C_{18} acids occur most frequently, whereas acids with an odd number of carbon atoms in their chains are rare. The unsaturated C_{20} and C_{22} acids present in the eukaryotic algae (Ackman et al., 1968), particularly dinoflagellates (Lee and Loeblich, 1971), appear to be absent from the blue-green algae (Nichols, 1973). The major lipid fatty acids of zooplankton are $C_{16:0}$, $C_{16:1}$, $C_{18:1}$, $C_{20:5}$ and $C_{22:6}$ (Lee et al., 1971), although the C_{16} , C_{19} and C_{20} isoprenoid acids may also be important (Blumer, 1970). The phospholipid - bound $C_{22:6}$ unsaturated fatty acid

is by far the major fatty acid in the structural (as distinct from energy reserve) lipids of zooplankton (Lee et al., 1971).

The degree of unsaturation in biosynthetic fatty acids appears to be partly a function of the temperature at which the organism grew. The tendency to produce a higher proportion of saturated acids is a feature of organisms growing in warm environments (Abelson, 1967).

The exact fate of plankton-derived fatty acids in the marine environment is unclear. Evidence is mounting (e.g. Rhead et al., 1971; Boon et al., 1975; Morris and Calvert, in press) that such acids are rapidly resynthesized by anaerobic bacteria at or near the sediment-water interface (Fig. 3.2) into saturated and monounsaturated, straight and branched (iso, anteiso) chain fatty acids. The C_{15} and C_{17} anteiso acids are the major bacterial acids (Kaneda, 1967; Boon et al., 1977) and, when found in marine sediments (e.g. Cooper and Blumer, 1968; Boon et al., 1975; Morris and Calvert, in press), have been taken as indicators of bacterial activity. Thus, in reducing sedimentary environments, unsaturated algal (and zooplanktonic) fatty acids tend to be converted into saturated fatty acids, but whether this is by microbiological hydrogenation (Rhead et al., 1971), geochemical hydrogenation, bacterial resynthesis or some combination of all three processes has still to be determined. In more oxidizing environments, unsaturated fatty acids may be destroyed by auto-oxidation or, alternatively, incorporated into the protokerogen fraction of the sediment by way of oxidative cross-linking reactions (Abelson, 1967; Boon et al., 1975).

Ultimately, the saturated fatty acids that become buried in sediments undergo decarboxylation reactions which convert them into hydrocarbons with one less carbon atom (Kvenvolden, 1970). Under conditions of persistently low Eh and high pH, such as exist in poorly drained algal mats in sabkha environments, it is conceivable that hydrogenolysis of the fatty acids may occur resulting in alkanes with the same number of carbon atoms as the original acids (Welte and Waples, 1973).

Alcohols

Wax esters are the major class of lipids in many pelagic marine crustaceans (zooplankton) (Lee et al., 1971). They also occur in marine bacteria but have not been reported in phytoplankton. Usually the $C_{16:0}$ saturated fatty alcohol is the principal component alcohol, although the $C_{20:1}$ and $C_{22:1}$ monounsaturated compounds are the major alcohols in zooplankton living in deep waters or near-surface cold waters (Sargent, 1977; Morris and Calvert, in press). Long-chain (C_{26} and C_{28}) polyhydroxy alcohols are present as glycosides in the heterocysts of blue-green algae (Nichols, 1973). The biogeochemical requirements that must be met before these alcohols can become precursors of sedimentary and petroleum hydrocarbons are much the same as for fatty acids. They must first survive auto-oxidation (in the case of unsaturated alcohols) and bacterial degradation, and then undergo hydrogenolysis to remove hydroxyl groups. Some indication of the ability of wax esters to persist in the marine environment is provided by the relatively common occurrence of oil slicks (e.g. Bute Inlet wax) consisting almost entirely of wax esters containing the $C_{20:1}$ and $C_{22:1}$ fatty alcohols characteristic of zooplankton (Sargent, 1977). Such wax esters may be a significant source of petroleum hydrocarbons in sediments deposited in areas of marine upwelling and consequent high zooplankton productivity (Brongersma-Sanders, 1966).

Steroid alcohols (sterols), which readily revert to steranes (Enclosure 2, fig. 1) during early diagenesis, are usually considered to be indicative of eukaryotic algae (e.g. diatoms, dinoflagellates), zooplankton and fungi (although see e.g. Reitz and Hamilton, 1968; Bird et al., 1971a, b, for reports of their occurrences in prokaryotic algae and bacteria).

3.4.2 Geochemical signatures of algae, bacteria and zooplankton

By virtue of their unique carbon skeleton or their unusually

high concentration in living organisms, some aliphatic hydrocarbons and lipids (fatty acids, alcohols etc.) that are potential hydrocarbon precursors appear to be characteristic of particular groups of extant microorganisms (see preceding section). They are termed chemotaxonomic markers. Such hydrocarbons (or, in the case of fatty acids and alcohols, the corresponding hydrocarbon derivative) afford a means of recognizing the contribution of specific micro-biotas to the source material of hydrocarbons in sediments and crude oils. Examples of hydrocarbons which have potential as geochemical signatures of algae, bacteria and zooplankton are given in Table 3.1.

3.4.3 Recent experimental studies

On heating the chloroform-insoluble residues of bacterial cultures, and a Recent algal mat, with water in a stainless steel tube (at temperatures in the range 100 - 330°C for periods up to 168 hours), Lijmbach (1975) found that both the bacteria and the algal mat were converted into crude-oil-like material. The degree of conversion was much lower in the case of the algal mat. This work is particularly interesting because it provides some valuable clues to the type of alkane distributions that might be expected in sediment extracts and crude oils derived from algae and/or bacteria (cf. Section 3.5). They are as follows:

1. The bacteria yielded saturated hydrocarbons that comprised mostly high-molecular-weight cycloalkanes (up to C₆₀) and only about 10% normal alkanes.
2. The proportion of n-alkanes in the saturated hydrocarbons produced by heating the algal mat residue was more than twice that obtained from the bacteria under similar experimental conditions.
3. The C₁₅₊ normal alkane distribution generated by heating a mixed bacterial culture at 330°C for 168 hours (Fig. 3.3a)

is characterized by

- 1) a maximum at C_{17} and a range extending up to C_{35} ,
 - 2) a strong predominance of C_{15} and C_{17} over the adjacent even-carbon-numbered alkanes,
 - 3) a slight predominance of even-carbon-numbered alkanes in the range C_{20} to C_{26} , and
 - 4) a low proportion of C_{23+} homologues.
4. By comparison, the corresponding n-alkane profile for the algal mat (Fig. 3.3b) has
- 1) a maximum at C_{16} and extends up to only C_{30} ,
 - 2) no odd/even predominance in the $<C_{20}$ range,
 - 3) a strong even/odd predominance between C_{20} and C_{26} , and
 - 4) a higher proportion of C_{23+} alkanes.

The one common feature of the respective bacterial and algal mat n-alkane patterns is the predominance of the C_{20} - C_{26} even-carbon-numbered alkanes. It is this very feature that Dembicki et al. (1976, p. 203) interpreted as being diagnostic of organic matter "produced in highly saline, carbonate environments where aerobic and anaerobic bacteria have subsisted on the remains of blue-green algae". Although the biota comprising the algal mat used by Lijmbach were not identified, they almost certainly included blue-green algae and bacteria. Moreover, because the mat came from Qatar in the Persian Gulf, it probably grew in a sabkha (i.e. evaporite and carbonate-depositing) environment (cf. Kendall and Skipwith, 1968).

A study of the oxidative degradation of algal and bacterial cell wall materials by Philp and Calvin (1976) confirmed the presence of C_6 - C_{19} normal and C_{18} isoprenoid alkyl structures which, upon burial and thermal maturation, could be expected to give rise to hydrocarbons.

3.5 CHARACTERISTICS OF MARINE CRUDE OILS

3.5.1 Original or immature oils

Taking the Miocene oils of the Monterey Formation in the Santa Maria Basin, California, as examples of 'immature' marine crude oils, Milner et al. (1977) postulated that the following features were original characteristics of a marine-source oil

1. low API gravity
2. relatively high sulphur content (2-5%)
3. normal alkanes well developed, with a slight predominance of even-carbon-numbered homologues in the range C_{18} to C_{30}
4. high C_{15+} content (up to 80% of crude) and low gasoline content ($C_4 - C_7$ as little as 2% of crude)
5. bimodal naphthene distribution, with the dominant mode at about C_{17} , and a lesser one (containing mostly tetracyclic hydrocarbons) at C_{26}
6. phytane/pristane >1
7. benzothiophenes more abundant than dibenzothiophenes.

To this list may be added

8. pristane/ n - $C_{17} \approx 1$
9. phytane/ n - $C_{18} > 1$
10. C_{15+} saturates/ C_{15+} aromatics ≈ 0.5 ,

features not specifically mentioned by Milner and co-workers, but nevertheless clearly evident from their Table IV and Figure 14.

Among the essential prerequisites for the formation of a marine crude oil are an organic-rich source rock that was deposited in a highly reducing environment rich in sulphur (as mercaptans, H_2S and/or free S), and contains sapropelic (i.e. amorphous) organic matter derived from prolific algae and other planktonic marine organisms in the overlying waters. The

resulting oil will be naphthenic to aromatic in composition (Vandenbroucke et al., 1976), although a paraffinic composition appears to be typical of immature indigenous early Palaeozoic marine crudes (Martin et al., 1963; Williams, 1974: see also Section 3.5.3). Whether the oil is high or low in sulphur will depend on the mineralogy of the source rock.

The diagenetic incorporation of sulphur into dispersed organic matter (protokerogen and/or asphaltenes) requires the host sediments to be relatively free of iron and other metal cations such as Cu^{2+} and Zn^{2+} (Lijmbach, 1975). That this condition is more readily satisfied in calcareous sediments (limestones, dolomites, marls) than in clay-rich clastic sediments (pelites, lutites) may, as pointed out by Hunt (1967, p. 230), "also be a factor in the high sulphur content of many oils associated with carbonates". Thus, marine oils generated in calcareous rock sequences are commonly asphaltic and sulphur-rich (several percent S), in contrast to low-sulphur (<1% S) oils from argillaceous sediments (Krejci-Graf, 1963). Oils in the latter category tend to be less aromatic (i.e. naphthenic to paraffinic) in character.

This contrast between the composition of carbonate/evaporite and shale/sandstone-derived marine oils has been attributed to differences in certain key aspects (redox potential, nature and level of in situ bacterial activity etc.) of the depositional environment of their source rocks (Barbat, 1967; Powell and McKirdy, 1975; Enclosure 1).

3.5.2 Effects of thermal maturation

The chemical evolution of an 'immature' or original crude oil that occurs as a result of prolonged exposure to heat in the reservoir, or in response to deeper burial of the reservoir, produces oils with

- a higher API gravity (McNab et al., 1952; Evans et al., 1971)
- a lower content of sulphur (Ho et al., 1974) and nitrogen

(Milner et al., 1977)

- a more paraffinic C_{15+} ($>270^{\circ}C$ boiling range) fraction
(Evans et al., 1971).

The dominant maturation mechanism for pooled oils is thermal cracking. This is a disproportionation process whereby larger hydrocarbon and non-hydrocarbon molecules fragment into smaller "hydrogen-enriched, saturated structures and increasingly condensed, hydrogen-depleted, aromatic (unsaturated) structures" (Milner et al., 1977, p. 108; see also Silvermann, 1964, 1971). Among the other changes sustained by original marine crude oils during thermal maturation are:

1. a gradual elimination of any odd (Martin et al., 1963)
or even (Albaiges and Torradas, 1974; Milner et al., 1977)
carbon-number preference in the n-alkanes;
2. a progressive decrease in the concentration of tetracyclic
naphthenes (e.g. steranes) and pentacyclic naphthenes
(e.g. hopanes) and concomitant loss of optical activity
(Milner et al., 1977); and
3. a small (up to $2^{\circ}/\text{oo}$) increase in the $\delta^{13}C$ value of the
oil (or reservoir bitumen) during the latter stages of
maturation when the residual, highly condensed, aromatic
compounds (asphaltenes) become so depleted in long alkyl
side-chains that fragmentation proceeds primarily by loss
of $^{12}CH_4$ (Rogers et al., 1974).

For a recent discussion of the effects of biodegradation, water-washing and other transformation processes on crude oil composition, the reader is referred to Milner et al. (1977).

The carbon isotopic composition of marine crude oils generally falls in the range $\delta^{13}C_{PDB} = -29.5$ to $-20^{\circ}/\text{oo}$ (cf. non-marine oils, -32.5 to $-30^{\circ}/\text{oo}$: Silvermann, 1964).

3.5.3 Proterozoic and early Palaeozoic oils

Indigenous Lower Palaeozoic marine crude oils tend to be either paraffinic or paraffinic-naphthenic in composition and have a low sulphur content ($<0.1\%$ S) (Martin et al., 1963; Barbat, 1967; Byramjee and Vasse, 1969; Bestougeff et al., 1969; Williams, 1974). The writer could find no reference in the literature to naphthenic or aromatic pre-Devonian oils. In terms of their carbon isotopic composition ($\delta^{13}\text{C}_{\text{PDB}} = -35$ to $-24^{\circ}/\text{oo}$, median value = $-29.5^{\circ}/\text{oo}$: Degens, 1969), pre-Devonian oils are somewhat lighter (i.e. more depleted in ^{13}C) than younger marine oils.

Those oils of early Palaeozoic age for which there is evidence of a high degree of thermal maturation have a paraffinic-naphthenic base. Good examples are the Silurian-source oils of Algeria (viz. Hassi Messaoud, Mya Basin and Tin Fouyé-Tabankort, Illizi Basin: Balducchi and Pommier, 1970; Tissot et al., 1974) and N.W. Libya (Hamada and Djeffara, Hamada Basin: Byramjee and Vasse, 1969).

Less mature oils are mostly of paraffinic composition and may be as heavy as 24°API . Four such oils, all from Ordovician reservoirs in the U.S.A., were analysed by Martin et al. (1963). Crude oils of this type appear to be particularly common in the Williston Basin, U.S.A., where Ordovician shales of the Winnipeg Formation are their source beds (Williams, 1974). A feature of all these oils is a marked predominance of odd-carbon-numbered n-alkanes in the $<\text{C}_{20}$ range.

The characteristic $\text{C}_{15} - \text{C}_{20}$ n-alkane profile, and the carbon isotopic composition ($\delta^{13}\text{C}_{\text{PDB}} = -28.4$ to $-26.6^{\circ}/\text{oo}$), of the Williston Basin oils not only closely matched the corresponding parameters in extracts of the Winnipeg shale, but also differed from those of two other oil - source rock systems in the basin. Thus Williams (1974) was able to demonstrate, by geochemical means, the existence of three separate families (or genetic

types) of Palaeozoic oil in the Williston Basin.

The odd-carbon-number predominance evident in the $C_{10} - C_{20}$ n-alkanes of ancient paraffinic crude oils is considered by Martin et al. (1963) to reflect their direct derivation (via decarboxylation) from saturated (as distinct from unsaturated) fatty acids. In sedimentary environments unsaturated fatty acids tend to polymerize and become part of the proto-kerogen complex (Abelson, 1967). Subsequent random cracking produces n-alkanes with a smooth carbon-number distribution. According to Martin and his co-authors, the uniformly warm palaeoclimatic conditions believed to have prevailed during much of the early Palaeozoic would have favoured the biosynthesis of a higher proportion of saturated fatty acids by the extant marine biota.

Normal alkane profiles displaying a similar odd/even predominance between C_{15} and C_{20} have been reported by Kontorovich et al. (1974) for oils in Cambrian carbonates (maximum at n- C_{17}) and Vendian (late Proterozoic) sandstones (maximum at n- C_{17}) of the Siberian Platform. Normal alkanes comprise 10-17% of the oils in carbonate reservoirs and 23-26% of the oils in sandstones. The total sulphur content of the Vendian oils is 0.07-0.18%, which (not unexpectedly) is considerably lower than that of the Cambrian oils (0.11-1.5% S) (Drobot and Presnova, 1975).

Isoprenoid hydrocarbons ($C_{11} - C_{21}$) have been identified by Gurko and Stepina (1974) in three Cambro-Ordovician oils from the Baltic Basin. The total isoprenoid content of the oils decreases systematically from 4.1% in the Bernat field (present formation temperature = 40°C) to 1.5% at Ladushkin (present formation temperature = 85°C), apparently reflecting an increase in degree of thermal alteration due to deeper burial of the reservoir. The ratio of pristane (C_{19}) to phytane (C_{20}) is low in all three oils (1.04-1.81).

Source-rock studies of Lower-Middle Cambrian sediments in the Baltic Basin have been carried out by Maximov et al. (1974). This work included determination of C_{20+} n-alkane distributions (maximum at $C_{25} - C_{27}$),

C_{15} - C_{20} isoprenoid profiles ($pr/ph = 1.09-2.57$), and naphthene ring-number distributions in chloroform extracts of the sediments.

Possibly the oldest oil to have been the subject of detailed geochemical analysis is that of a seep emanating from the 1000-1100 m.y. old Nonesuch shale at the White Pine copper mine, Michigan (Barghoorn et al., 1965; Eglinton et al., 1966). The most recent investigation of this oil (Hoering, 1976) showed that the following hydrocarbon types were present in appreciable concentrations:

- normal alkanes (C_{11} - C_{32} ; essentially smooth carbon-number distribution)
- isoprenoid alkanes (C_{14} - C_{20} ; $pr/ph \approx 2$)
- 2-methyl and 3-methyl alkanes (C_{19} - C_{28}).

Surprisingly, no steranes or triterpanes were detected (if present, they constitute <50 ppm of the oil). Hoering (op. cit., p. 813) concluded:

"The presence of an abundant amount of normal hydrocarbons indicates that lipid synthesis was prevalent a billion years ago and had many of the same properties it has had subsequently. Isoprenoid hydrocarbons with less than 20 carbon atoms point clearly to the widespread use of chlorophyll as a photosynthetic pigment. The preponderance of 2-methyl and 3-methyl substituted hydrocarbons over all of the other possible positional isomers suggests, but does not prove, a large contribution of bacterial lipids.

The lower concentration of sterane hydrocarbons is puzzling. Such compounds are fairly common in rocks of more recent geological age, and they have probably been derived from sterols known to exist in unicellular organisms. The chemical stability of steranes over long periods of time under geological conditions is not well established. Possibly they have been dehydrogenated into aromatic hydrocarbons, and a search through this fraction of the petroleum seep may give a clue".

3.6 CONCLUDING REMARKS

This review has attempted to explore the nature and consequences of the pivotal relationship between the evolutionary development of marine life and the origin of petroleum. The first crude oils were apparently generated from shallow-water marine shales and carbonates during mid-Proterozoic time (approx. 2000-1400 m.y. B.P.). There is no a priori reason why basins containing thick sequences of unmetamorphosed Proterozoic and Lower Palaeozoic marine sediments should not be regarded as prospective for petroleum hydrocarbons.

In Australia, several basins display ample evidence of hydrocarbon generation in rocks of late Proterozoic and/or early Palaeozoic age. Probably the best example is the Amadeus Basin (see Chapter 6). Other areas with significant Cambrian or Ordovician potential are the Canning Basin (Horstman et al., 1976), Georgina Basin (Smith, 1976) and Arrowie Basin (Devine, 1975) (see also Section 4.8.1).

Finally, although the geochemical characteristics of marine crude oils are reasonably well documented in the literature, little attention has been paid to the organic geochemistry of their supposed source rocks. It is this problem which provides the theme for the next chapter.

CHAPTER 4 STUDIES OF THE COMPOSITION AND MATURATION OF MICROBIAL ORGANIC MATTER

4.1 Introduction

4.2 Extant algae and bacteria

4.3 Plio-Pleistocene sediments, Timor Trough

4.4 Mesozoic and Tertiary carbonates, Ashmore-Sahul Block

4.5 Coorongite, torbanites and oil shales

4.6 Phosphorites

4.7 Stromatolites

4.8 Other studies

4.8.1 Palaeozoic well sections

4.8.2 Precambrian carbonaceous shales and cherts

4.9 Concluding remarks

4.1 INTRODUCTION

In this chapter the results of organic geochemical investigations of 12 individual suites of samples are presented and discussed. The first suite is a selection of extant algae and bacteria. The second comprises unlithified Plio-Pleistocene calcareous sediments from a deep ocean trough. The rest consist of sedimentary rocks differing in lithology, depositional environment, age and thermal history, but all containing organic matter that is largely (and in many cases, solely) of microbial origin.

As a group the samples represent a wide variety of sedimentary deposits that accumulated under conditions ranging from lacustrine, through paralic and neritic, to deep-sea marine. In age (early Archaean to Recent) they span the entire history of life on earth. Rock types sampled include: calcilutite, massive limestone and dolomite, stromatolitic carbonate, chert, phosphorite, shale, siltstone, oil shale and coal. In terms of rank or degree of thermal alteration, they cover the range from very early diagenesis (i.e. exposed to little more than surface temperatures) to greenschist facies metamorphism.

The choice of such a diverse array of samples was necessary in order to establish the nature and compositional limits of sedimentary organic matter derived specifically from algae and bacteria; and to permit examination of its response to progressive thermal alteration (maturation) during diagenesis and incipient metamorphism, with particular reference to its ability to generate petroleum hydrocarbons.

4.2 EXTANT ALGAE AND BACTERIA

In considering the types of sedimentary organic matter that can be derived from microorganisms it is important to know the bulk composition of the precursor algae and bacteria. Accordingly, the major element

compositions of freeze-dried cultures of the colonial green alga, Botryococcus braunii, and the saprophytic sulphate-reducing bacterium, Desulfovibrio gigas, were determined and compared with published analyses for eight other algae and bacteria and an algal mat (Table 4.1). It should be noted that some of the published analyses are of exhaustively extracted residues, free of readily soluble pigments and intracellular lipids. To facilitate recognition of the relative contribution of lipids, proteins, carbohydrates etc. to their overall composition, H/C and O/C values for the microorganisms are plotted on a van Krevelen diagram (Fig. 4.1) which shows the compositional fields for various natural products.

4.2.1 Geological significance of organisms

B. braunii is an unusual oil-secreting planktonic alga that occurs widely in temperate to tropical freshwater environments, although occasionally it is found in brackish habitats (Stach, 1975). At least two physiologically distinct growth forms are known: the green active state containing 20% (dry weight) hydrocarbons; and the orange (or brown) resting stage (70% hydrocarbons) (Brown et al., 1969; Knights et al., 1970). Botryococcus has been identified as the progenitor of coorongite and balkhashite (discussed in Section 4.5), rubbery deposits that form on the shores of lakes and lagoons and are believed to represent the peat stage of boghead coals (Cane and Albion, 1971, 1973). In these algal coals (e.g. torbanite) and related oil shales Botryococcus is preserved mainly as the maceral, alginite (Fig. 4.1). According to Combaz (1974) fossil occurrences of this alga and related forms date back to the Proterozoic. They are thought to be a major source of aliphatic, hydrogen-rich Type I kerogens (Marchand et al., 1969; Tissot et al., 1974).

D. gigas is representative of the type of bacteria that inhabit the anoxic zone of aquatic sedimentary environments (Fig. 3.1) and participate in the final anaerobic stage of the decomposition (or reworking)

of organic debris raining down from the overlying photic zone. Such bacteria, described as "reworkers" by Lijmbach (1975), are of considerable geochemical importance because they are the last organisms to contribute to, and leave their biochemical imprint upon, the residual organic matter in a sediment. As discussed in the previous chapter, the remains of bacterial bodies in organic-rich sediments are considered by Lijmbach (1975) to be major precursors of petroleum hydrocarbons. The two other bacteria in Table 4.1, R. spheroides and Chlorobium sp., populate the overlying photosynthetic and intermediate zones, respectively, of the depositional environment (see Fig. 3.1). Upon death and settling through the water column, each is in turn subject to bacterial reworking under increasingly anoxic conditions.

The blue-green and other green algae listed in Table 4.1 include extant representatives of genera (e.g. Nostoc, Anacystis, Lyngbya and Chlorella) that have been recognized in ancient carbonaceous sediments, including the Bitter Springs Formation of the Amadeus Basin (see McKirdy, 1976, Table III: Enclosure 2). In favourable present-day environments planktonic forms of both algal classes are capable of producing blooms from which algal oozes result that are modern analogues of the organic content of the Green River and similar oil shale deposits. This is particularly true of blue-green algae, benthonic (and mat-building?) forms of which display an enhanced resistance to bacterial decay (Bradley, 1970).

4.2.2 Discussion of results

Inspection of Table 4.1 reveals that the microorganisms and their insoluble residues are remarkably uniform in bulk composition (dry ash-free basis), with the possible exception of nitrogen. The range of compositions is summarized below:

	<u>Whole organism</u>	<u>Insoluble residue</u>
% C	49.4 - 51.0	47.9 - 51.5
% H	5.4 - 8.1	6.4 - 7.9
% N	6.0 - 9.2	3.7 - 14.8
% O	28.0 - 36.3	27.8 - 34.9
% S	0.5 - 1.3	0.5 - 2.6

The high sulphur value for the algal mat is in part due to unremoved pyritic sulphur. Compared with humic acids and kerogens in Recent marine sediments (see section 4.3), their algal and bacterial precursors are notably richer in oxygen (high O/C value) and nitrogen (low C/N value), but depleted in sulphur (high C/S value).

The gross chemical composition (dry weight basis) of blue-green algal cells in terms of their component biochemical fractions is similar to that of green and other eukaryotic algae (Holm-Hansen, 1968), viz. carbohydrates, 30-55%; proteins, 20-45%; lipids, 15%; nucleic acids, 2-3%; and pigments, 1.5%. The high carbohydrate and protein contents of the algae explains why in Figure 4.1 the samples plot between the compositional fields for these two components. Extracellular sheath mucilage, a suggested major progenitor of algal kerogen (Shearman and Skipwith, 1965), consists of mucopolysaccharide and can account for as much as 44% of the dry weight of certain blue-green algal cultures (Wolk, 1973).

The exhaustively extracted algal and bacterial residues, comprising mostly insoluble cell-wall materials, probably resemble partially degraded microbial cells. Loss of all (or most) of their intracellular lipids and pigments is reflected in their generally lower H/C values (Table 4.1) and a composition displaced towards the evolution path for more humic Type III organic matter (analogous to the vitrinite coalification track in Fig. 4.1). Analysis of the cell walls of A. nidulans (24% carbohydrate, 28% protein, 36% lipid: Drews and Gollwitzer, 1965) suggests, however, that such artificially degraded algae still contain an appreciable amount of lipid

and presumably therefore retain a significant capacity to generate petroleum hydrocarbons. This view is supported by the nature of the products obtained by Philp and Calvin (1976) from the permanganate oxidation of the insoluble cellular residues listed in Table 4.1. It is also consistent with the findings of Oehler (1976) who reported, as a result of experimental studies of the simulated fossilization of the filamentous blue-green alga, Lyngbya majuscula, in synthetic chert (involving heating under pressure at 100 and 165°C for periods of 1-31 weeks), that sheaths and cell walls are more readily preserved than cellular contents.

Of all the microorganisms examined, B. braunii (green active-growth form) is the richest in hydrogen (8.1% H d.a.f.; atomic H/C = 1.95), an indication of its high hydrocarbon content (20% dry cell weight, mostly C₂₇, C₂₉ and C₃₁ n-alkadienes: Knights et al., 1970). Presumably the orange-brown resting state of the alga, in which hydrocarbons (consisting almost entirely of two isomeric highly-branched and unsaturated C₃₄H₅₈ alkenes, botryococcene and isobotryococcene: Maxwell et al., 1968) make up 70% of the dry cellular weight, would plot closer to the compositional field for fats in Figure 4.1. Nevertheless, it is the green form of the alga that gives rise to coorongite and balkhashite (Cane and Albion, 1973), classic examples of H-rich sapropelic 'protokerogens', both of which plot as expected adjacent to the alginite coalification track (see Section 4.5).

4.2.3 Implications for microbial diagenesis

It is apparent that aquatic microorganisms, although lacking the lignin found in higher plants and commonly assumed to be the source of humic (H-poor) organic matter in ancient sediments, do not inevitably give rise to sapropelic kerogens. The conversion of algal and bacterial remains into true sapropel requires relatively shallow water depths and rapid sedimentation to minimize exposure to oxygenated water and attack by aerobic saprophytes. Anoxic conditions allow the preservation of lipids,

proteins and pigments (otherwise easily utilized by aerobic bacteria) in a non-condensed form (Goldhaber and Kaplan, 1975). Degradation by anaerobic bacterial saprophytes is a slower, less efficient process than aerobic decay (Lijmbach, 1975). Coorongite and balkhashite seem to be exceptional sapropelic deposits. They are extremely resistant to oxidation and bacterial degradation and, moreover, they form under aerobic conditions (Cane, 1969; Cane and Albion, 1971).

Rogers et al. (1973) equate sapropelization with "reductive decomposition" and describe it as the process whereby structured detritus (of either higher plant or algal origin) is transformed into amorphous (i.e. sapropelic) organic matter. This transformation increases the H/C atomic ratio of the source organic matter and therefore enhances its capacity to generate liquid hydrocarbons at lower maturation levels. Anaerobic bacteria are almost certainly involved in the process. Hence, it is significant that Lijmbach (1975), on heating bacterial cultures in closed vessels, should find them to be completely converted into chloroform-soluble material containing crude-oil-like hydrocarbons. Algal cultures, under the same experimental conditions, gave much lower yields.

Whereas anoxic conditions favour the formation of aliphatic (Type I) debris, post-mortem decay of photosynthetic microbiota in oxygenated aquatic environments will preferentially generate H-poor, O-rich humic matter. Maillard-type condensations of cellular degradation products, including amino acids, carbohydrates and other simple molecules, give rise to water soluble complexes which then undergo further polymerization to fulvic and humic compounds. This transformation involves decarboxylation, dehydrogenation, ring closure and increased aromaticity (Nissenbaum and Kaplan, 1972).

Thus, depending on the environment of deposition, and to a lesser extent on the nature of the dominant precursor alga (i.e. whether or not of the lipid-rich Botryococcus type), microorganisms can be the source for all three types of sedimentary organic matter recognized by Tissot et al. (1974). The assumption that algal kerogens are necessarily H-rich and possess an

aliphatic structure is clearly incorrect.

4.3 PLIO-PLEISTOCENE SEDIMENTS, TIMOR TROUGH

Two important and interrelated controls of crude oil composition are the depositional environment of the source rock and the relative contributions of marine and higher plant remains to its original organic content (Philippi, 1974; Powell and McKirdy, 1975). Also important, but as yet poorly understood, is the role of microbiological activity during the sedimentation and early diagenesis of the precursor organic matter. Hence it was decided to investigate further the non-thermal phase of early diagenesis and its implications for the origin of petroleum. The basic approach employed was to examine the soluble and insoluble organic matter preserved in a stratigraphic sequence of geologically young (<5 m.y.), thermally unaltered, marine calcareous sediments for which reasonably detailed sedimentological and palaeontological data were available. Organic matter in marine sediments, and particularly that in marine carbonates, is derived mainly from marine plankton (primarily photosynthetic algae), although terrigenous contributions may be locally important (Bordovskiy, 1965; Nissenbaum and Kaplan, 1972; Goldhaber and Kaplan, 1975). Plio-Pleistocene calcareous oozes cored during drilling at Deep Sea Drilling Project (DSDP) Site 262 in the Timor Sea were chosen for this study, for the following reasons:

1. total organic carbon (TOC) values in excess of 1% had been reported for sediments in the upper part of the drill-hole (Bode, 1974);
2. there is evidence for intense microbiological activity in the sediments (Cook, 1974); and
3. the extrapolated bottom-hole temperature was only 15°C (Veevers et al., 1974).

The aim of the study was to identify the principal factors that determine the composition and hydrocarbon-generating potential of the organic matter in the sediments.

4.3.1 Geological setting

DSDP Site 262 is located on the axis of the Timor Trough at a water depth of 2315 m (Fig. 4.2). Compared with most other locations selected for drilling by the DSDP this site is unusual in that it is fairly close to land (75 km from the island of Timor) and well above the carbonate compensation depth (CCD). Moreover, it is situated in what is believed to be a partly anoxic, silled basin. The only similar DSDP site is Site 147 located in 892 m of water in the Cariaco Trench (Edgar et al., 1973), although this hole terminated in the upper Pleistocene at a depth (from sea bottom) of 162 m, less than half the penetration achieved at Site 262. Both sites are within 11° latitude of the equator.

The Timor Trough has a maximum depth of about 3500 m (van Andel and Veevers, 1967). The southern (Australian) side of the trough is generally smooth with an average gradient of 1° or less; the northern (Timor) side in contrast is generally irregular, with numerous pinnacles and scarps, and a gradient averaging about 3° but locally reaching 10° or greater. The CaCO_3 content of the bottom sediments ranges between 25 and 50% and the TOC content between 0.6 and 1.9%. Texturally, the sediments are silty clays. Seismic profiling by the BMR has shown that the sea-floor sediments in the trough are flat-lying. The sediments on the Australian side of the trough are draped over the slope (part of the adjacent Ashmore-Sahul Rise: see Section 4.4) whereas those of the Timor side are strongly folded. Thus, the seismic records indicate that the sediments in the axis of the Timor Trough are likely to be in part derived from mass movement of upper slope material down its northern flank.

Drilling of DSDP Site 262 was carried out in November 1972.

The drill-hole intercepted a total of 442 m of grey calcareous sediments comprising 414 m of Quaternary and upper Pliocene planktonic (predominantly nannofossil) ooze, overlying 13 m of upper Pliocene shallow marine foraminiferal dolomitic mud, and 15 m (to total depth) of Pliocene very shallow marine dolomitic shell calcarenite (Fig. 4.3). This sequence is interpreted by Veevers et al. (1974) as having been deposited under progressively shallowing marine conditions down the drill hole. A water depth of less than 30 m is envisaged for the deposition of the sediments at the base of the sequence.

4.3.2 Previous geochemical investigations

A detailed study of the inorganic geochemistry of the porewaters and sediments in each of the 44 cores recovered was undertaken by Cook (1974). This work revealed a number of significant geochemical trends which are summarized in Figure 4.4. Cook attributed the downward increase in salinity to underlying or nearby evaporite deposits from which highly saline waters are emanating. The overall inverse relationship between alkalinity and sulphate concentration in the porewaters, together with the abnormally high alkalinities above 250 m, were taken to indicate a high level of bacterial activity (possibly including both fermentation and sulphate reduction) below the sediment-water interface.

Bode (1974) found that the TOC content of the sediments decreases markedly down the drill-hole, ranging from greater than 1% in the upper part of the sequence to about 0.1% at the bottom. Analysis of canned core samples from the interval 5-310 m for low-molecular weight hydrocarbons (McIver, 1974) showed them to contain up to 97,000 ppm methane. McIver concluded that the sediments from Site 262 have considerable potential to generate liquid and/or gaseous hydrocarbons should they be subjected to deeper burial and higher temperatures for sufficient time geologically to initiate the thermal

cracking process.

4.3.3 Results

The results of the organic analyses conducted on sediments from DSDP Site 262 are contained in Tables 4.2, 4.3, 4.5 and 4.6. Table 4.2 indicates the depth in the drill-hole from which the samples originated and includes data on the concentrations and isotopic compositions of the TOC; the yield and composition of C_{15+} extractable organic matter (EOM); and the relative concentration of certain alkanes in the C_{15+} aliphatic hydrocarbon fraction. Elemental compositions of kerogens isolated from selected sediment samples are given in Table 4.3. Some kerogens were subjected to additional analysis by IR spectrometry (Table 4.7) and pyrolysis-hydrogenation-gas chromatography (PHGC: Table 4.8).

The organic geochemistry of the 3 major sedimentary units is summarized in Tables 4.5 and 4.6 by way of mean values for each organic variable measured, together with mean values for some relevant inorganic parameters. For comparison, data from the Cariaco Trench and the Red Sea are incorporated in Tables 4.4 and 4.5.

4.3.4 Discussion

Like the inorganic parameters summarized in Figure 4.4, nearly all the organic parameters measured show quite marked (if somewhat less regular) variation with depth. Some of these variations undoubtedly reflect changes in the depositional environment; others are functions of post-depositional (early diagenetic) processes.

Total organic carbon

There is a clear overall increase in percentage TOC up the drill-

hole (Fig. 4.5; see also Table 4.5). The abrupt increase at about 350 m corresponds fairly closely with the Plio-Pleistocene boundary and also with the boundary between Units 2 and 3. It is probably at this point that the major downwarping of the area occurred, leading to the formation of a deep basin, the development of anoxic conditions, an increased rate of sedimentation (estimated at $18.5 \text{ cm}/10^3 \text{ y}$ by Veevers et al., 1974) and the enhanced preservation of detrital organic matter. As a result, the TOC content of the Pleistocene sediments averages approx. 1% which is three times greater than that of the underlying Pliocene sediments (Table 4.5). It is also much greater than the values given by Hunt (1974) for normal oceanic marine sediments which generally average between 0.1 and 0.6% TOC. The only comparable deep sea sediments are from anoxic locations such as the Black Sea (where values range up to 15% TOC) and the Cariaco Trench (up to 5%). However, both these sites are significantly shallower than the Timor Trough, where there is a greater water column for the particulate organic matter to settle through, and more opportunity for oxidation, attack by bacteria and consumption by filter-feeding organisms.

Carbon isotopic composition

An apparent change with time in the balance of marine and terrigenous inputs is indicated by the trend observed in the stable carbon isotopic composition of the TOC (Fig. 4.8). The organic matter in Units 3 and 2 has $\delta^{13}\text{C}$ values in the range -18.8 to -21.8‰ which indicate a marine planktonic source (Sackett, 1964; Degens, 1969). More negative values (-21.8 to -24.3‰) between 175 and 80 m (and above 15 m) suggest a period of enhanced input of terrigenous organic matter to the trough (Nissenbaum and Kaplan, 1972). Most photosynthetic continental plants (those using the Calvin-Bassham cycle) exhibit $\delta^{13}\text{C}$ values of about -26‰ (Smith and Epstein, 1971). The reason that $\delta^{13}\text{C}$ values more negative than

-24.3‰ are not in fact observed in the TOC of Unit 1 is probably because it comprises a mixture of terrigenous and planktonic organic matter, although another contributing factor may be in situ bacterial activity at the time of deposition. Eadie and Jeffrey (1973) and Schultz and Calder (1976) have noted that organic matter in surface sediments of the Gulf of Mexico is usually enriched in ^{13}C by 3-4‰ relative to the particulate organic matter in the overlying water column. They attributed this difference to microbial activity at the sediment-water interface. The latter authors also suggested that higher sedimentation rates could reduce or eliminate this fractionation effect.

The stable carbon isotopic composition of marine phytoplankton is temperature dependent (Degens et al., 1968a). Fluctuations in the temperature of the surface waters may therefore influence the $\delta^{13}\text{C}$ value of organic matter in the bottom sediments (Rogers and Koons, 1969), although this effect is thought to be significant only in polar regions and in the centre of large ocean basins (Sackett and Rankin, 1970; Rogers et al., 1972). In the Timor Trough, so close to an emergent land mass, variation in the amounts of terrigenous and marine-derived organic matter obviously has been the major factor controlling the carbon isotopic composition of organic matter reaching the sea floor. Until oxygen isotope measurements have been made on the carbonate fraction of the sediments to provide reliable palaeotemperatures, the magnitude and direction of a possible secondary temperature effect must remain in doubt.

Extractable organic matter

The bitumen or C_{15+} EOM similarly increases up the drill-hole (Fig. 4.5; Table 4.5), both in absolute concentration (ppm) and as a proportion of the total organic matter (mg/g C). Values of between 1000 and 1600 ppm in the upper part of Unit 1 are comparable with those reported by Simoneit and Burlingame (1974) for the Pleistocene clays of the Cariaco

Trench.

As with organic carbon, the increase in extract yield is somewhat erratic. Nevertheless, allowing for the greater number of points on the organic carbon plot, there is a fairly good correlation between the two parameters. Their sympathetic fluctuation throughout the sequence may reflect variations in the rate of deposition, high organic values coinciding with periods of slower sediment accumulation or, alternatively, higher actual organic productivity in the surface waters. However, the overall trend in both EOM and TOC is one of increase up the hole, apparently a result of the change to increasingly anoxic bottom conditions.

Changes in the source of the organic material may also have profound effects. The ratio of aliphatic to aromatic hydrocarbons remains fairly constant down the drill hole, except for the interval 70-160 m (Fig. 4.5). This interval represents the culmination of what appears to have been a steadily increasing input of land plant material (Plate 4.1) from the nearby island of Timor. The excess of aliphatic hydrocarbons derives from long-chain paraffins present in the waxy coatings of leaves and spores. Higher plant debris is not as readily degraded by bacteria as is plankton-derived organic matter (Goldhaber and Kaplan, 1975). Consequently, one should expect to find indications of diminished bacterial activity at this point in the sequence. Such indications are indeed present, viz. a decrease in porewater alkalinity and a corresponding increase in porewater sulphate concentration between 150 and 100 m (Fig. 4.4), although it should be noted that there are no alkalinity fluctuations associated with sulphate peaks lower down the hole.

Aliphatic hydrocarbon patterns

Confirmation of a progressive change in the relative amounts of marine planktonic and terrigenous plant matter contributed to the Timor Trough since late Pliocene time is provided by gas chromatograms of the

C_{15+} aliphatic hydrocarbons (Fig. 4.6). The numbered peaks are normal alkanes (i.e. straight-chain paraffins) and the numbers refer to their chain length. Peaks labelled pr and ph are the isoprenoid alkanes pristane and phytane, respectively. The unresolved group of peaks before $n-C_{23}$ (loosely termed a 'naphthene hump') consists of branched and cyclic alkanes. The vertical variation in n-alkane distributions is illustrated in Figure 4.7.

The sediments of Unit 3 (exemplified in Figure 4.6 by the samples from 396 m and 345 m depth) have aliphatic hydrocarbon distributions dominated by a complex mixture of naphthenic hydrocarbons with retention times less than $n-C_{23}$. A sample from DSDP Hole 229 in the Red Sea (see Table 4.5) gave a similar alkane pattern (Hunt, 1974). In the overlying sediments (Units 2 and 1) the relative concentration of higher molecular weight (C_{23+}) alkanes, mainly n-alkanes displaying a strong odd-carbon number preference increases to a maximum around 150 m before declining again towards the top of the hole. A high odd/even carbon number ratio ($CP1 > 2$) in the C_{23+} n-alkanes (Table 4.2; Fig. 4.8) is also characteristic of higher plants of terrestrial origin (Mazliak, 1969). Similar n-alkane distributions have been observed in a wide variety of nearshore and deep-sea marine sediments (see Gaskell et al., 1975, and references therein), including those of the Cariaco Trench (Simoneit and Burlingame, 1974), and have been attributed to the allochthonous remains of continental vegetation. Thus, it is apparent from the total alkane chromatograms (Fig. 4.6) and the corresponding n-alkane profiles (Fig. 4.7) that the proportion of terrigenous organic matter contributed to the bottom sediments of the trough reached its peak in sediments at present located about 150 m from the top of the sequence.

Microbial hydrocarbons Studies of hydrocarbons in algae and bacteria (reviewed in Chapter 3) suggest that the $C_{15} - C_{22}$ alkanes found in recent marine sediments originate largely from marine phytoplankton and possibly also photosynthetic bacteria. Depending on the composition of the microbiota

in the water column, the principal hydrocarbon contributed to the underlying sediment is likely to be the C_{15} , C_{17} , C_{19} , or C_{21} n-alkane (or an equivalent alkene). For example, in blue-green and green algae, the most common major alkane (and/or alkene) is n- C_{17} (Han et al., 1968a,b; Winters et al., 1969; Gelpi et al., 1970); whereas in photosynthetic diatoms and dinoflagellates it is the n- $C_{21:6}$ alkene (Lee and Loeblich, 1971; Blumer et al., 1971) which, upon hydrogenation in the sediment (Rhead et al., 1971), would yield the corresponding alkane. In any event, a marked predominance of odd over even-carbon-numbered n-alkanes in the range C_{15} to C_{22} is to be expected in young, thermally unaltered marine sediments. Such a feature characterizes the n-alkane distributions of samples from 396 m and 383 m (Fig. 4.7).

The diminished predominance of odd carbon-numbered homologues in the C_{23+} n-alkanes of samples from 345 m and 247 m (Fig. 4.7) may be due to their post-depositional consumption by non-photosynthetic bacteria which convert them into higher molecular weight hydrocarbons (Han et al., 1968b; Dembicki et al., 1976). The hydrocarbons of non-photosynthetic bacteria consist largely of C_{22+} branched alkanes (Tornabene et al., 1967, 1970; Albro and Dittmer, 1970). In situ bacterial metabolism of algal hydrocarbons may also be partly responsible for the virtual absence of n-alkanes below n- C_{20} in many of the cores analysed from Unit 1 (e.g. sample from 156 m: Figs. 4.6 and 4.7), although dilution by the waxy higher-plant-derived (C_{23+}) n-alkanes would also contribute to their reduced relative concentration in the C_{15+} aliphatic hydrocarbons.

Johnson and Calder (1973) invoked bacterial activity to explain an observed decrease in the odd/even predominance of n-alkanes with depth in sediments from a salt marsh. The marked increase in carbon preference index (CPI) of the C_{24} - C_{32} n-alkanes in Unit 1 (Tables 4.2 and 4.5; Fig. 4.8) may represent the failure of the bacterial 'reworkers' to keep pace with the increased input of land-plant debris to the trough.

The prominence of the $n\text{-C}_{22}$ alkane at 345 m (Fig. 4.7) is interesting, particularly in light of an occasional predominance of this hydrocarbon in ancient sediments (Schenck, 1969), especially phosphorites (see Section 4.6). A highly unsaturated $n\text{-C}_{22:6}$ fatty acid occurs in significant concentration in the lipids of some planktonic algae (notably dinoflagellates: Lee and Loeblich, 1971) and zooplankton (Lee et al., 1971), and under certain conditions could give rise to anomalous concentrations of the $n\text{-C}_{22}$ alkane in marine sediments. Its survival in particulate organic matter during sedimentation, followed by its diagenetic conversion to the corresponding $n\text{-C}_{22}$ alkane (presumably involving reactions of the type proposed by Welte and Waples, 1973), requires minimal exposure to oxidizing conditions in the water column and strongly reducing conditions at the sediment-water interface. In the case of the core sample under discussion these requirements seem to have been met: anoxic bottom conditions had not long been established and hence the environment was probably shallow enough to ensure that organic detritus had a relatively short residence time in the aerobic zone.

Naphthene hump Despite the existence in marine algae of certain monomethylalkanes (Blumer et al., 1971) that may have contributed to the complex mixture of branched and cyclic alkanes below $n\text{-C}_{23}$ in the chromatograms (Fig. 4.6), the origin and significance of the 'naphthene hump' are problematic. Hunt (1974) reported similar 'humps' in the C_{15+} saturates of DSDP cores from the Bengal Basin and the Red Sea and commented that they appeared to be a secondary feature originating through diagenesis or migration. There is also the possibility that these naphthenes may represent contamination by bearing lubricants, pipe-joint grease and plastic core tube caps used in the DSDP drilling operations (Simoneit and Burlingame, 1972; Simoneit et al., 1972). Nevertheless, the following observations suggest that the aliphatic hydrocarbons comprising the naphthene hump are not contamination but an indigenous and characteristic

feature of organic-rich marine calcareous sediments at an early stage of diagenesis.

1. Seen in the context of the total organic geochemistry of the sediments at Site 262 their occurrence is too systematic to be the result of adventitious contamination.
2. In view of the high level of post-depositional microbial activity in the sediments, it is not surprising that substantial modification of the original algal lipids by bacteria should have occurred (cf. Dembicki et al., 1976). Among the early diagenetic changes in fatty acid and hydrocarbon composition that have been attributed to in situ bacterial activity is an increase in the concentration of branched compounds at the expense of straight-chain components (Johnson and Calder, 1973).
3. Similar unresolved 'humps' of naphthenic hydrocarbons are observed in the EOM of older, lithologically equivalent Tertiary limestones from the Ashmore-Sahul Rise (see Section 4.4); their relative concentration decreases with increasing depth of burial as n-alkanes are preferentially generated by thermal cracking reactions from ONS compounds and kerogen.

Pristane and phytane The ratio of pristane to phytane is low (≤ 1) and shows a slight but definite increase up the drill-hole (Fig. 4.8; Tables 4.2 and 4.5). Interpretation of this trend is complicated by the number and complexity of the possible diagenetic reactions leading to the formation of these two isoprenoid alkanes in recent sediments (Aizenshtat et al., 1973; Brooks and Maxwell, 1974; de Leeuw et al., 1974; Ikan et al., 1975). Nevertheless several points can be made concerning the origin of pristane and phytane in these deep sea marine sediments, and to the use of the pristane/phytane ratio as a geochemical indicator of depositional environment (cf. Brooks et al., 1969; Powell and McKirdy, 1973b, 1975; Lijmbach, 1975).

Firstly, it is significant that phytane as well as pristane is present in these sediments in concentrations comparable with, and in many cases exceeding, that of the adjacent n-alkane (n-C₁₈ and n-C₁₇, respectively) in the chromatogram (Table 4.2; Fig. 4.8). Recent sediments typically contain small quantities of pristane and either no phytane (Blumer and Snyder, 1965) or only trace amounts, generally less than pristane (Brown et al., 1972).

In view of the very low temperatures (<15°C) to which these sediments have been exposed it is clear that thermally induced diagenetic reactions (e.g. phytanic acid $\xrightarrow[\Delta]{-\text{CO}_2}$ pristane) cannot account for the presence of either hydrocarbon. Whereas it is conceivable that phytane may form as a result of the microbiologically mediated decomposition of the phytyl side chain of chlorophyll (de Leeuw et al., 1976), all diagenetic routes to pristane involve a decarboxylation step that requires heat. Thus, pristane in these sediments must have been deposited as a discrete hydrocarbon (saturated or unsaturated). Organisms in which pristane or related C_{19:1} alkenes have been identified include marine algae (Blumer et al., 1971), zooplankton (Blumer and Thomas, 1965) and land-plants (Hodgson et al., 1968). All three types of organism have probably contributed pristane to the sediments at Site 262.

The phytane/n-C₁₈ ratio is high in Unit 3 (mean value = 9.4) and decreases up the drill-hole (Unit 2 mean = 4.3; Unit 1 mean = 1.8 : Table 4.5). This ratio, in conjunction with a relatively constant pristane/n-C₁₇ ratio (close to 1.0) for the sequence as a whole (Table 4.2; Fig. 4.8), points to a down-hole increase in the concentration of phytane as the cause of the observed trend in the pristane/phytane ratio. The increase in phytane with depth is probably related to the non-thermal diagenesis of chlorophyll-type pigments (which impart a green colour to the ONS fraction of the EOM). Phytane originally derived from halophilic bacteria (Nissenbaum et al., 1973) may also be entering the sediments

dissolved in saline porewaters emanating from subjacent evaporites.

Lack of information on the identity and relative concentration of other isoprenoid species (e.g. dihydrophytol, phytanic acid) in the sediments makes it impossible to predict whether or not the sediments will retain their present low pristane/phytane ratios (≤ 1) upon deeper burial and maturation. In ancient sediments (and crude oils) such low values are considered indicative of a marine (or aquatic) environment in which is deposited organic matter that has largely escaped exposure to oxidizing conditions (Brooks et al., 1969; Powell and McKirdy, 1973b; Powell et al., 1976).

Kerogen

The elemental composition of the kerogen fraction of the sediments (Tables 4.3 and 4.6) also reflects to a considerable degree changes in the source of their organic matter. Figure 4.9 illustrates the vertical variation in the composition of the kerogen. Broadly speaking, the kerogen becomes depleted in hydrogen and richer in oxygen and nitrogen up the drill-hole. However, its composition is somewhat less variable in the upper half of the section where deep water anoxic conditions prevailed. Of the three heteroelements, oxygen and nitrogen are inherited directly from the parent organic matter whereas sulphur may be introduced during diagenesis. Nissenbaum and Kaplan (1972) have shown that autochthonous marine humic acids usually contain more sulphur than terrigenous humic substances, as a result of their reaction with H_2S or elemental S during early diagenesis. This may explain the lower C/S atomic ratios of the kerogens at the top and bottom of the sequence. The peak in the C/S plot between 100 and 150 m corresponds approximately to the maximum influx of terrestrial plant debris. Such material is less prone to utilization by sulphate-reducing bacteria, leading to a diminished supply of sulphide

and free sulphur. The Timor Trough kerogens as a group are enriched in sulphur (range 2.7 - 6.2%, mean 4.0%) relative to normal marine humic acids (range 0.9 - 5.9%, mean 2.1%: Nissenbaum and Kaplan, 1972) and also kerogens from the Red Sea (range 2.0 - 3.2%, mean 2.4%: Table 4.4).

The preceding discussion has been concerned with the effects of source and depositional environment. Diagenesis is commonly at least as important as either of these two effects. The bottom waters in the Timor Trough have a temperature of 2.7°C and the bottom hole temperature is about 15°C which ensures that the Plio-Pleistocene sediments at Site 262 are thermally immature. The plot of H/C atomic ratio versus O/C atomic ratio (Fig. 4.10) shows that their kerogens lie between the coalification tracks for liptinite (exinite) and vitrinite-like materials. The kerogens in Units 3 and 2 occupy the same compositional field which is, however, separate from that of the kerogens in Unit 1. This separation does not correspond with a maturation trend, unless the kerogens from Units 3 and 2 have undergone some low temperature decarboxylation reactions (cf. Nissenbaum and Kaplan, 1972). It is more likely to be a reflection of variation in source material (cf. the relative disposition of the compositional fields of marine and non-marine humic acids).

The Timor Trough kerogens may be compared with those isolated by Saxby (1972) from near-surface sediments (0 - 3.5 m sediment depth) in the Red Sea (Table 4.4). Although of similar isotopic composition and ostensibly similar origin (derived principally from calcareous pelagic organisms: Saxby, 1972) the kerogens from the Red Sea have been exposed to temperatures in excess of 50°C . The effect of this early thermal maturation on their bulk composition is clearly seen in Figure 4.10 where they plot closer to the origin than those from Site 262. As noted by Saxby (1972) the effects of thermal diagenesis appear to be greater in the kerogens from Atlantis II Deep than in the Discovery Deep samples.

This accords with the higher sediment temperatures (up to 62.3°C) observed at the former location which is adjacent to the zone into which hot brines are discharging (Saxby, 1972). The lower (i.e. more negative) $\delta^{13}\text{C}$ values given for the two Atlantis II kerogens probably reflect the sterile conditions obtaining in the host sediments and hence a lack of the in situ bacterial isotope fractionation effect postulated by Eadie and Jeffrey (1973).

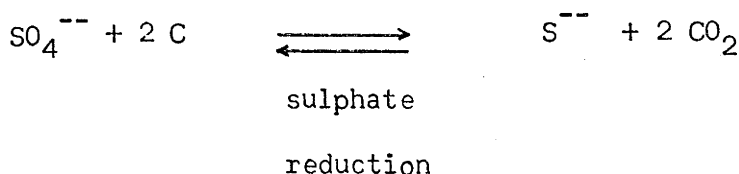
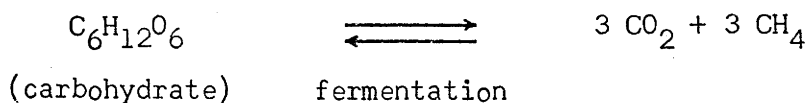
Other evidence of thermal immaturity

In sediments that have undergone little or no thermal alteration, non-hydrocarbon (ONS) compounds usually make up 90% or more of the extractable organic matter (Foscolos et al., 1976), as is the case at Site 262. Heavy C_{15+} hydrocarbons for the most part constitute <5% of the EOM (Table 4.2). Notwithstanding a minor reversal of the trend between 156 m and 107 m (a feature probably attributable to waxy C_{23+} paraffins associated with the influx of terrigenous organic matter), the proportion of C_{15+} hydrocarbons in the EOM decreases upward (Fig. 4.5) from a mean of 3.9% in Unit 3 to 2.0% in Unit 1 (Table 4.5). There is thus an inverse correlation between heavy hydrocarbon content and EOM yield. Rogers et al. (1973) found a similar relationship between lipid extract (i.e. EOM) and hydrocarbon concentration in cores (up to 300 m long) from reducing environments in the Gulf of Mexico. They explained their findings in terms of the generation of hydrocarbons from the lipid fraction during the sapropelization and subsequent early maturation of detrital organic matter. In the case of the Timor Trough there is evidence of sapropelization (Plate 4.1, fig. 2) but early maturation can be discounted. The higher proportion of C_{15+} hydrocarbons in the EOM from Units 3 and 2 is probably related to the nature of the source material.

The marked predominance of odd carbon-numbered homologues in the C_{23+} n-alkanes (CPI range = 1.8 - 5.2; mean = 3.2) is a further indication of the thermal immaturity of the organic matter (Powell and McKirdy, 1973a).

In situ bacterial activity

Whereas the sediments lack any sign of thermal alteration, they display abundant evidence of microbial activity at and below the sediment-water interface. Some of its possible effects on the organic geochemistry of the sediments have been noted already (although these may be due in part to saprophytic bacteria inhabiting the overlying water column). The impact of this bacterial activity on the inorganic geochemistry and mineralogy of the sediments is equally pronounced. The infilling of foraminiferal tests and the replacement of plant fragments by framboidal pyrite (Veevers et al., 1974; Cook, 1974) point to the operation of sulphate reducing-bacteria (as do recent sulphur isotope studies of the pyrite: T.H. Donnelly, L.A. Chambers and P.A. Trudinger, pers. comm., 1976). The alkalinity profile (Fig. 4.4) is an even more graphic indicator of in situ microbial activity. At the pH values found in these sediments (Cook, 1974) the alkalinity of the porewaters may be regarded as a measure of their HCO_3^- content which in turn is determined by the availability of CO_2 . According to Berner (1971), microbiological reactions that commonly occur in sediments include



These reactions result in the removal of sulphate, the development of a high alkalinity and the formation of sulphides, CO_2 and CH_4 . All these

features were noted in the Site 262 sediments (Cook, 1974); together they constitute strong evidence for biological activity involving both methanogenic and sulphate-reducing bacteria. But if the alkalinity profile is taken as an indication of microbiological activity, then the question arises as to when that activity has occurred. There are two main possibilities. The first is that the profile represents present-day bacterial activity, extending 200 - 300 m below the sediment-water interface. Goldhaber and Kaplan (1974) have suggested, on the basis of the porewater sulphate gradient at DSDP Site 38, that bacterial sulphate reduction can continue over periods of several million years and extend to depths of several hundred metres below the sediment-water interface. The second possibility (favoured by the present author) is that the observed alkalinity trend is essentially a fossil profile reflecting a high level of Pleistocene - not modern - bacterial activity. This explanation at first sight appears to be simple and acceptable. However, it does not explain why upward diffusion of porewaters (as indicated by the salinity profile) has not diminished the observed alkalinity levels and displaced the alkalinity peak (or peaks: Fig. 4.4) closer to the present sediment-water interface. The rate of sedimentation may have been more rapid than the rate of upward diffusion but this appears rather unlikely. An alternative is that the high methane content of the sediments between 5 and 310 m (McIver, 1974) is present as solid methane hydrate ($\text{CH}_4 \cdot 6\text{H}_2\text{O}$) which reduces the effective permeability to zero, thus blocking fluid migration in the top 300 m of the section. The temperature and pressure conditions required for the hydrate to form (Katz, 1971) are more than adequately satisfied at Site 262.

4.3.5 Hydrocarbon potential

The question of the hydrocarbon potential of these geologically

young sediments merits consideration. This question is important not so much for the Timor Trough itself but for judging, by inference, the petroleum potential of similar modern oceanic deeps, or ancient analogues which have been subjected to higher temperatures and pressures.

It is apparent (Tables 4.3 and 4.6-4.8; Fig. 4.9) that differences in the organic source material and depositional environment of Units 1, 2 and 3 have led to significant differences in the composition of their respective kerogens. According to Tissot et al. (1974), these basic compositional differences will determine the ability of the sediments to generate petroleum hydrocarbons following burial to greater depth and exposure to higher temperatures.

Because they are richer in hydrogen, the kerogens of Units 3 and 2 display a greater potential for oil generation than those from the overlying sediments. With the possible exception of sample 643 which is unusually rich in oxygen (Table 4.3), they may be classified as immature Type II (tending to Type III) kerogens (after Tissot et al., 1974).

Conversely the kerogens from Unit 1 are more humic in composition, being poorer in hydrogen and generally richer in oxygen than those from Units 2 and 3 (Tables 4.3 and 4.6). This reflects their probable derivation from a mixture of autochthonous marine humic acids (cf. Nissenbaum and Kaplan, 1972) and terrigenous organic matter (including both lignin residues and leaf cuticle). Kerogens from the top (sample 602 and 607) and bottom (sample 627) of the unit appear to contain a higher proportion of in situ marine humic matter. Because they plot close to the beginning of the vitrinite coalification track in Figure 4.10, they may be categorized as Type III kerogens capable of generating abundant CO₂ and methane, but relatively little oil. Kerogens from the middle of Unit 1 have the composition and hydrocarbon generating potential of Type III tending to Type II organic matter.

The results of the analysis of selected kerogens from Units 1 and 3 by IR and PHGC largely confirm this assessment of hydrocarbon potential based on elemental composition, but at the same time show that the differences between them are less pronounced than might be inferred from Figure 4.10 alone and its interpretation strictly according to Tissot et al. (1974).

The IR data (Table 4.7) indicate a basic similarity in the concentration of key functional groups in kerogens from Units 1 and 3. Sample 602 (from near the top of Unit 1) has slightly fewer methyl (CH_3) and methylene (CH_2) groups, consistent with a marginally lower oil generating potential than the other kerogen examined.

The hydrocarbon products obtained from PHGC analysis of kerogen samples 602 (Unit 1, Type III) and 638 (Unit 3, Type II) are remarkably similar in composition and distribution (Table 4.8). For sample 602, 40.1% were n-alkanes, as against 42.3% for sample 638. However, consistent with its higher terrigenous component, the proportion of long-chain (C_{10+}) homologues for sample 602 (52.6% of C_6 - C_{20} n-alkanes) was greater than for sample 638 (42.1%), as was the degree of predominance of odd-carbon numbered C_{10+} n-alkanes (mean OEP = 1.31 and 1.16, respectively) and the proportion of simple aromatics (21.1% and 13.4%, respectively). Finally, sample 602 yielded only slightly less volatile matter (60.9% by weight, ash-free basis) than did sample 638 (64.0%).

It should be noted that the conclusions reached in the foregoing discussion are at odds with the reasoning of Rogers et al. (1973) who consider the present bitumen (i.e. EOM) content of young sediments to be the most reliable measure of their hydrocarbon generating capacity. On this basis, Unit 1 would have the greater source potential for oil.

4.3.6 Summary

1. The Timor Trough is a partly anoxic basin with an enhanced rate of sedimentation and a relatively high rate of accumulation of organic matter.
2. The downwarp of the trough in the late Pliocene-early Pleistocene is reflected in the inorganic and organic composition of the sediments.
3. The organic matter is of mixed marine-continental origin.
4. There is a marked increase in the proportion of land-derived plant material in the upper part of the drill hole.
5. The sediments are thermally immature and there is no evidence of maturation of the organic matter.
6. There is, or has been, a high level of in situ bacterial activity as indicated by high methane concentrations, the removal of sulphate from the pore waters and the high alkalinity values.
7. Possible diagnostic features of bacterially reworked organic matter include: loss of odd-even predominance in the C_{15} - C_{22} n-alkanes, progressive removal of $<C_{20}$ n-alkanes, a high concentration of branched / cyclic alkanes, and a $\delta^{13}C$ value 3-4‰ higher than that of the precursor biota.
8. It is possible but unlikely that present day bacterial activity is continuing as much as 200 - 300 m below the sediment-water interface. Alternatively, solid methane hydrates are effectively filling the pore space, acting as a barrier to the migration of pore fluids and resulting in the retention of a 'fossil' alkalinity high.
9. Although the organic matter is predominantly humic and therefore gas prone, sufficient hydrogen-rich sapropel

(Units 3 and 2) and cuticle (Unit 1) are present to make it likely that the sediments of the Timor Trough will generate oil if subjected to deeper burial and higher temperatures.

10. Contrasting estimates of the ultimate source-rock potential of sediments in the upper and lower parts of the sequence are reached depending on whether bitumen (BOM) content or kerogen composition is taken as the primary measure of their capacity to generate petroleum hydrocarbons.
11. On either basis, the major factors influencing the hydrocarbon-generating potential of the sediments are the source (marine versus terrigenous) of their organic matter and its degree of exposure to aerobic conditions in the water column before entering the anoxic bottom zone.

4.4 MESOZOIC AND TERTIARY CARBONATES, ASHMORE-SAHUL BLOCK

In contrast to the thermally unaltered Plio-Pleistocene calcareous oozes of the Timor Trough, Cretaceous and Tertiary marine carbonates of the adjacent Ashmore-Sahul Block have been more deeply buried and exposed to higher temperatures. For example, present formation temperatures of Miocene - Lower Cretaceous (Albian) limestones in the Ashmore Reef No. 1 well (Fig. 4.2) fall in the range 40-100°C (BOCAL, 1975). Published information on the relationship between formation age and the threshold temperature of intense hydrocarbon generation (Connan, 1974) suggests that these sediments should span the transition from immaturity to oil generation in terms of the diagenetic evolution of their organic matter (i.e. from eodiagenesis to mesodiagenesis : Foscolos et al., 1976).

The depositional environment on the Ashmore Platform during the late Cretaceous and Tertiary was dominated by shallow epicontinental seas (Mollan et al., 1970). A low supply of terrigenous sediment ensured that the organic matter was of predominantly autochthonous marine origin. The

underlying Upper Triassic sediments (interbedded shale, sandstone and detrital limestone) were deposited under near-shore marine to fluvio-deltaic conditions and therefore may be expected to contain mainly terrigenous organic debris. The deeper burial and different origin of their organic matter makes for an interesting comparison with the organic content of the younger carbonates, particularly those at the onset of oil generation. The occurrence of carbonate intervals within what is otherwise a shale-sandstone sequence also illustrates the effect of variations in clay mineral content on hydrocarbon diagenesis.

The aims of the investigation were:

1. to document and correlate the diagenetic changes that occur in the bitumen and kerogen of marine carbonates during the transition from eodiagenesis (immature) to early mesodiagenesis (zone of initial oil generation: Foscolos et al., 1976); and
2. to compare these changes with those already established for the corresponding maturation interval in shales (e.g. Philippi, 1965; Albrecht and Ourisson, 1969; Tissot et al., 1971; Foscolos et al., 1976) and coals (Brooks and Smith, 1967; Brooks et al., 1969; Teichmuller, 1974; Teichmuller and Teichmuller, 1975).

4.4.1 Geological setting

BOCAL's offshore Ashmore Reef No. 1 well was located (Fig. 4.2) on the outer (western) margin of the Ashmore-Sahul Block, a Triassic structural high which flanks the Timor Trough to the north and forms part of the northern boundary of the Browse Basin to the south. It penetrated a sequence of predominantly carbonate sediments to a depth of 3194 m.

The stratigraphy (summarized in Fig. 4.11) and depositional environments of the sediments were described by Mollan et al. (1970). Pertinent aspects of the latter have been mentioned already. The geological

evolution of the area was closely related to the continental breakup of eastern Gondwanaland (Powell, 1976). As this has determined the thermal history of the sediments studied, a brief summary follows.

The Upper Triassic marginal marine sediments in Ashmore Reef No. 1 are graben fill related to the first phase of continental rifting in the Permo-Triassic. A second major phase of the rifting process occurred at the end of the Triassic and was accompanied by uplift and extensive erosion. Following the deposition of volcanic basalt of probable mid-Jurassic age, major tensional movements produced the main period of tectonism which is marked by the regional 'breakup' unconformity. A late Jurassic to early Cretaceous transgression over a highly irregular topographic surface ushered in a period of marine sedimentation (initially restricted) that continued more or less uninterrupted into the Tertiary as open-water marine conditions became widely established. The two principal episodes of erosion prior to the commencement of Cretaceous sedimentation resulted in considerable loss of section at Ashmore Reef (just how much is not known). This means that the burial history of the Upper Triassic sequence has not been one of continuous subsidence. As the thermal maturation of dispersed organic matter is a cumulative and irreversible process, the level of organic metamorphism (LOM: Hood et al., 1975) in these sediments is probably greater than would be expected solely on the basis of their age, depth of burial and present temperature.

The Upper Cretaceous-Tertiary sequence of carbonates and claystones is substantially complete. Minor unconformities within the Upper Cretaceous and at the base and top of the Palaeocene are considered to represent depositional hiatuses rather than periods of uplift and active erosion. Essentially continuous subsidence and open marine sedimentation has occurred since late Cretaceous time so that sediments in the upper 2500 m of the column at Ashmore Reef are presently at (or close to) their maximum depth of burial. Present formation temperatures should therefore represent maximum palaeotemperatures (BOCAL, 1975).

4.4.2 Previous investigations

Powell and McKirdy (1973a) analysed 16 core samples from Ashmore Reef No. 1 for TOC, EOM and saturated hydrocarbons and discussed the results in terms of the effect of source material, rock type and diagenesis on the shape of the n-alkane profiles. Among their findings were:

1. the carbonates contain hydrocarbons derived from the fats of marine microorganisms;
2. the n-alkane distribution (range $C_{16} - C_{25}$) of the carbonates appears to have changed little during the initial stages of diagenesis; any n-alkanes generated from the kerogen must have had chain lengths shorter than C_{25} ;
3. the hydrocarbons in shales below 2800 m are derived from the waxes of higher plants and represent a more advanced state of diagenetic evolution; and
4. the extractable organic matter in the shales, unlike the carbonates, shows obvious signs of progressive alteration with increasing depth of burial, notably a decrease in EOM yield (mg/g C) and in the proportion of saturates, and a shift of the n-alkane maximum to lower carbon number.

In the present work, the data on which these observations were based has been augmented by additional TOC determinations and reinterpreted in the light of 1) analysis of the kerogen from selected cores, and 2) corrections to errors in the published values of EOM yield and percentage saturates for certain key samples (see Section 4.4.3).

Vitrinite reflectance measurements were made by Shell on dispersed organic matter at different levels in the well (BOCAL, 1972). The ranks determined (North American ASTM classification) ranged from sub-bituminous C at 1067 m to medium volatile bituminous at 3627 m. Shell also undertook 'rapid source rock analyses' on 45 ditch cuttings samples which indicated

'moderate to good source rock potential' for the Upper Triassic clastics. Subsequent detailed analyses showed the organic matter to be of the humic type, more likely to generate gas than oil. According to BOCAL (1975), the sediments at the base of the Cretaceous sequence in Ashmore Reef No. 1 have attained an LOM value of 8.7. However, this does not fit the coal rank data given in their earlier report (BOCAL, 1972) which suggest a somewhat higher value (See Table 4.10). In terms of the LOM scale, the generally accepted range for oil generation is 9-11.5 (Hood et al., 1975).

An unpublished investigation by the author of the clay mineralogy of the sediments in Ashmore Reef No. 1 showed that

1. discrete montmorillonite is present only above 700 m;
2. the Cretaceous-Tertiary carbonates between 800 and 2500 m are characterized by a mixed-layer (montmorillonite-illite) + kaolinite + illite assemblage; and
3. the Triassic argillaceous sediments contain predominantly kaolinite and illite with only very minor amounts of mixed-layer clays.

At least two significant changes in the composition of the mixed-layer clays were noted (viz. at approximately 1400 m and 2100 m) but these have not yet been examined in detail. Should they prove to be related to the stepwise removal of interlayer water, then it is possible that they had an important bearing on both the cracking of hydrocarbons from associated organic matter and the expulsion of those hydrocarbons from the sediment (Foscolos et al., 1976).

4.4.3 Results

The organic geochemical data set out in Table 4.9 are based on analyses undertaken by T.G. Powell and published in part as Powell and McKirdy (1973a, fig. 1). Besides being a more complete tabulation of the data, it differs from the published results in several important respects.

1. TOC values have been determined for cores 7 and 15, permitting calculation of their EOM yields (as mg/g C).
2. Core 15 is marl (not calcilutite) and core 27 is argillaceous limestone (not massive limestone).
3. EOM yield for core 21 is 41 mg/g C (not 155 mg/g C).
4. Saturates comprise 37% of the EOM in core 15 (not 13%).

In addition, the alkane parameters are measured from the total alkane chromatograms to obviate possible distortion introduced by evaporative loss of n-alkanes during the molecular sieving of small (<10 mg) total alkane samples (Powell and McKirdy, 1973a).

The elemental composition of kerogen isolated from selected cores is given in Table 4.10, together with independent estimates of their rank derived from vitrinite reflectance measurements on a suite of cuttings samples (after BOCAL, 1972). Supplementary data on the composition and structure of the kerogens were obtained using IR spectrometry (Table 4.11) and PHGC analysis (Table 4.12).

4.4.4 Discussion

Total organic carbon

The organic carbon content of the post-Jurassic carbonates is low but variable (TOC = 0.04 - 0.57%, mean = 0.15%). The variation appears to be related to environment of deposition : the higher values tend to occur in calcilutite, marl and claystone that accumulated in depressions or troughs, whereas the lower values are found in biogenic limestone and calcarenite deposited on rises or shoals (Mollan et al., 1970). Consistent with their argillaceous nature and fluviodeltaic environment, the Triassic sediments are more organic-rich (TOC = 0.44 - 1.11%, mean = 0.90%) than the overlying carbonates.

Extractable organic matter

EOM ranges from 26 to 173 ppm in the upper carbonate sequence; and from 18 to 455 ppm in the Triassic shales, decreasing rapidly with depth. The yield of EOM per gram of organic carbon in the carbonates increases from 49-67 mg above 1000 m to 184 mg below 1800 m before declining sharply to 7 mg in a marl at 2210 m (Fig. 4.11). An otherwise anomalous high of 198 mg at 1230 m probably represents migrated bitumen, as the host rock is a porous calcarenite (Table 4.9). In the Triassic shales the yield of EOM is lower than in the carbonates and decreases with increasing depth. In both the upper (carbonate) and lower (shale) sequences, the yield of total hydrocarbons (mg/g C) varies down the hole in much the same manner as EOM (Fig. 4.11).

Above 2000 m saturates comprise <15% of the EOM and total hydrocarbons $\leq$ 25%. The onset of hydrocarbon generation in the sense of Albrecht and Ourisson (1969) and Connan (1974), occurs between 2000 and 2200 m (Fig. 4.11). In cores 15 and 16 hydrocarbons make up more than 40% of the EOM. The high saturates/aromatics ratio in core 15 is puzzling. It may be in part due to the different lithology (viz. marl). A more likely explanation is that it reflects an error in weighing the aromatic hydrocarbon fraction (only 0.6 mg). Contamination from drilling mud is unlikely in view of the low porosity (8%) of the core and the similarity of the n-alkane distributions in cores 15 and 16. The nature of the saturates and total hydrocarbons plots in Figure 4.11 (which are attenuated by comparison with the classic Albrecht and Ourisson curve) suggests that a zone of hydrocarbon generation is not fully developed in the carbonates at Ashmore Reef because of insufficient section and/or depth of burial.

The Triassic shales sampled below 2900 m document a sharp decline in both saturates and total hydrocarbons (as a proportion of EOM). The extract from core 27 (argillaceous limestone), by contrast, still contains

a relatively high proportion of saturates (22%) and total hydrocarbons (32%).

The temperature at which maximum hydrocarbon generation begins in the carbonates is 90-95°C (Fig. 4.11). This temperature is considerably lower than that for the onset of hydrocarbon generation from Jurassic fine-grained sediments elsewhere on the Northwest Shelf, viz. 115°C (BOCAL, 1975). The corresponding (interpolated) rank of vitrinite-like dispersed organic matter in the carbonates (Table 4.10) suggests that the threshold of hydrocarbon generation occurs at $\bar{R}_o \text{ max} = 0.6 - 0.7\%$, a somewhat higher rank than for shales (0.5 - 0.6% : Teichmuller, 1974; Foscolos et al., 1976), although the lack of precision of the rank data makes it difficult to be sure about this.

Cretaceous and Tertiary carbonates

Saturated hydrocarbon patterns

Figure 4.12 shows the gas chromatograms of the saturated hydrocarbons from selected cores. Core 2 (697 m) is typical of the carbonates above 2000 m in which both the total alkane patterns and the corresponding n-alkane distributions (Fig. 4.13a) show little change with depth. A complex naphthene hump centred on the n-C₂₁ position is reminiscent of a similar feature in the aliphatic hydrocarbons of the calcareous muds at DSDP Site 262 (Figure 4.6), although in the latter it is located at lower carbon number. In core 15 (2210 m), the naphthenes have changed dramatically to a skewed bimodal distribution in which the dominant mode is centred on n-C₂₇. The naphthene distribution in core 16 (2309 m) is also bimodal but one in which the contribution of higher molecular weight hydrocarbons is much less pronounced. The enhanced concentration of naphthenes in the saturated hydrocarbons of the carbonates between 2000 and 2300 m coincides with the onset of hydrocarbon generation noted earlier.

The normal alkane distributions of the carbonates are shown in Figure 4.13a. In general they range from C_{15} to C_{29} with a maximum between C_{17} and C_{19} and include a low proportion (<20%) of C_{23+} homologues. Cores 10, 11, 15 and 16 contain no n-alkanes of chain length greater than C_{26} . The n-alkane patterns of cores 15 and 16 (from the zone of initial hydrocarbon generation) differ hardly at all from those in the overlying carbonates, except perhaps that in profile they are somewhat flatter. Little or no odd-even predominance is evident in the n-alkanes although, as noted by Powell and McKirdy (1973a), the concentration of n- C_{22} is slightly enhanced in some samples (indicated by OEP <1 in Table 4.9). It may also be significant that the major n-alkane in most of the carbonates has an even number of carbon atoms (Table 4.9). Core 7 (a calcareous shale or claystone) is particularly noteworthy in that it displays an even predominance at C_{16} (OEP = 0.63), C_{18} (OEP = 0.94) and C_{22} (OEP = 0.91). Until recently, a predominance of one or more even carbon-numbered n-alkanes in the range C_{18} to C_{32} was thought to be relatively rare in nature. However, this feature is now being reported from an increasing number of geological materials, including sediments extracts (Schenck, 1969; Welte and Ebhardt, 1968; Kvenvolden, 1970; Welte and Waples, 1973; Powell et al., 1975; Dembicki et al., 1976), native bitumen (wurtzilite : Douglas and Grantham, 1974) and crude oil (Albaiges and Torradas, 1974; Milner et al., (1977)). It appears to occur preferentially in organic matter that accumulated in carbonate or evaporite-depositing environments where aerobic and anaerobic bacteria existed on algal remains (Dembicki et al., 1976).

Milner et al. (1977) cited a slight even carbon-number preference in the C_{18} - C_{30} n-alkanes as one of the features they considered to be characteristic of immature (or 'original' - their term) crude oils derived from marine algal organic matter (see Section 3.6). Of the other features ascribed to 'original' marine crudes by Milner and coworkers, the

following can be observed (or inferred) in the EOM isolated from the upper carbonates at Ashmore Reef:

1. pristane/phytane ≤ 1 (Table 4.9),
2. a bimodal naphthene distribution (cores 15 and 16, Fig. 4.12),
3. a relatively high sulphur content (2-5%) (cf. the high S values in kerogens from cores 3-12 and the much lower value in core 15, Table 4.10), and
4. a lack of hydrocarbons in the $< C_{15}$ range.

It should be pointed out that item 4 is a rather debatable inference drawn from Figures 4.12 and 4.13. The analytical techniques employed were not designed to recover light ($< C_{15}$) hydrocarbons. Nevertheless, when significant concentrations of such hydrocarbons are present in a sediment, $C_{12} - C_{15}$ alkanes will usually show up in the chromatogram (e.g. cores 21 and 27, Fig. 4.12).

Kerogen

Of the samples listed in Table 4.10, all those from the upper 2000 m of section contain Type II kerogen (Fig. 4.15), presumably algal sapropel. Kerogen from core 4, being somewhat richer in oxygen, is probably a mixture of humic and sapropelic algal debris. On the basis of their H/C and O/C atomic ratios, the kerogens in these carbonates (with the possible exception of core 4) belong to the liptinite group and, although not yet examined petrographically, are probably best described as bituminites (Teichmuller, 1974, 1975). They are more mature equivalents of kerogens from Units 2 and 3 at DSDP Site 262 (Fig. 4.10).

The nitrogen content of the kerogens is relatively high (1.4 - 3.1%, mean 2.3%), the higher values in the range being comparable with that of the kerogen from the base of Unit 3, DSDP Site 262. The kerogens are also rich in sulphur (2.8 - 5.7%, mean 4.2%), although less so than those

from the Pliocene at DSDP Site 262 (4.6 - 6.2%, mean 5.6%).

Whereas atomic H/C is relatively constant with increasing depth (Fig. 4.14), atomic O/C shows an overall decrease and reflects the loss of carboxyl and hydroxyl functional groups as CO_2 and H_2O during sapropelization (see later in discussion) and early maturation. Atomic ratios C/N and C/S tend to increase with depth suggesting a loss of heterocyclic structures and/or heteroatomic functional groups containing N and S.

Below 2000 m the elemental composition of the kerogen changes dramatically. Kerogen from core 15 plots on the evolution path for micrinite (Fig. 4.15), as would be expected if the generation of hydrocarbons from the kerogen in these carbonates is analogous to the so-called first coalification jump of liptinites (Teichmüller, 1974, 1975; Teichmüller and Teichmüller, 1975). According to Teichmüller, micrinite in bituminous coals is a disproportionation product of the coalification of bituminite (and certain resinites) beyond a rank equivalent to $\bar{R}_0 \text{ max}$ (vitrinite) $\approx 0.65\%$. This transformation is accompanied by the generation of bituminous, petroleum-like substances.

Based on the composition of the kerogen and its associated EOM in core 15, the postulated first coalification jump of liptinite (i.e. bituminite) at Ashmore Reef has involved (Fig. 4.14) a major decrease in H/C atomic ratio, corresponding to the observed generation of predominantly naphthenic hydrocarbons; and a substantial increase in C/S atomic ratio resulting from the release of S-bearing compounds (e.g. H_2S , mercaptans, thiophenes). Accordingly, there has been a net increase in O and N relative to C.

Triassic argillaceous sediments

Saturated hydrocarbons - general features

The total alkane chromatograms (Fig. 4.12) and n-alkane distributions (Fig. 4.13b) of the Triassic shales and argillaceous limestone differ significantly, and at the same time show more variation, than those from the overlying Cretaceous-Tertiary carbonates. The n-alkanes contain a higher proportion of C_{23+} homologues (Table 4.9) which, with the possible exception of those in core 26, lack any significant odd or even carbon-number preference. These are features of terrigenous organic matter at a fairly advanced stage of diagenesis (Powell and McKirdy, 1973a). Note, however, that in cores 21 and 24 the pristane/phytane ratio is much lower than normally would be expected (Brooks et al., 1969) in land-plant-derived organic matter at a rank of $\bar{R}_o \text{ max (vitrinite)} = 1.1 - 1.5\%$ (Table 4.10). Both cracking and migration of hydrocarbons has probably occurred below 3000 m, explaining the decrease in yield of EOM and total hydrocarbons with increasing depth.

Relation between kerogen composition and alkane pattern

Core 21 The position of kerogen from core 21 on the van Krevelen diagram (Fig. 4.15) is suggestive of relatively mature Type II (exinite) organic matter. In view of its fluviodeltaic environment of deposition, it possibly comprises cutinite, sporinite and/or liptodetrinite (although this can only be confirmed by optical methods). Its H/C atomic ratio (0.85) indicates that it has reached the final phase of early mesodiagenesis (after Foscolos et al., 1976). The sediments at this depth therefore should have realized their maximum oil-generating potential. The yields (mg/g C) of EOM and total hydrocarbons from core 21, however, are anomalously low for Type II organic matter of equivalent rank (Foscolos et al., 1976) and reveal the presence of a humic Type III component. The total alkane chromatogram (Fig. 4.12) and n-alkane profile (Fig. 13b) of core 21 are typical of oil-mature terrigenous organic matter.

Core 24 The increase in maturation level between cores 21 and 24 (Table 4.10; Figs 4.14 and 4.15) appears to correspond to the second coalification jump of liptinites (Teichmuller, 1974; Teichmuller and Teichmuller, 1975). Among the effects of this coalification jump on the associated EOM are:

1. a slight decrease in EOM yield (Fig. 4.11);
2. a marked reduction in saturates and total hydrocarbons as a proportion of the EOM (Fig. 4.11);
3. a greatly reduced concentration of long-chain (C_{23+}) n-alkanes (Table 4.9; Fig. 4.13b); and
4. an increase in the concentration of branched/cyclic alkanes within the saturates fraction (compare cores 21 and 24 in Fig. 4.12).

These changes involved catalytic cracking of waxy n-alkanes and other heavy hydrocarbons to lower molecular weight compounds, some of which were lost in the extraction procedure. Catalytic cracking reactions proceed via carbonium ion intermediates which can undergo alkyl isomerization and β -splitting and lead to the formation of branched and cyclic alkanes at the expense of straight-chain hydrocarbons (Eisma and Jurg, 1969).

Core 26 The total alkane chromatogram, n-alkane profile and kerogen composition of core 26 and unlike those in any other sample (Figs 4.12, 4.13b and 4.15, respectively). Earlier in its diagenetic history the kerogen apparently had a Type III (humic) composition equivalent to vitrinite B (i.e. desmocollinite: Teichmuller, 1975). Subsequently, it underwent a coalification jump which altered its gross composition to that of a micrinite (Fig. 4.15). Certain features of the n-alkane distribution support this hypothesis, the first being a relative lack of $<C_{20}$ n-alkanes. Demaison and Shibaoka (1975) noted a similar paucity of $<C_{20}$ n-alkanes in Triassic sediments containing H-poor Type III kerogen of similar rank from the

Barrow Sub-basin. Secondly, the n-alkane profile displays a slight even carbon-number predominance at the C_{20} (OEP = 0.95), C_{22} (OEP = 0.96) and C_{24} (OEP = 0.83) positions. Allan and Douglas (1974) reported such even predominance in the hydrocarbon pyrolysis products of vitrinites but gave no reason for it. If the kerogen of core 26 was originally similar to vitrinite B, then it has been derived in part from lipid materials. Taylor (1966), using electron microscopy, observed intercalations of fatty (lipid) substances in vitrinite B from coal where they are thought to be relics of the anaerobic bacterial decomposition of cellulose (Teichmüller, 1975). A feature of the lipids of certain bacteria is a predominance of even carbon-numbered homologues in their $C_{18} - C_{32}$ n-alkanes (Dembicki et al., 1976). Geochemical 'micrinitization' of this lipid component of the kerogen would thus account for its position near the micrinite evolution pathway in Figure 4.15 and the residual even carbon-number preference in the n-alkanes.

Core 27 The hydrocarbons (Figs 4.12, 4.13b) and kerogen (Fig. 4.15) in the argillaceous limestone of core 27 are probably derived from waxy, land plant precursors similar to those of cores 21 and 24. The lower clay (higher carbonate) content of the sediment has retarded catalytic cracking of its long-chain n-alkanes (Fig. 4.13b). Carbonates have a higher thermal conductivity than shales (Birch and Clark, 1940) and this too may have tended to inhibit the response of its organic content to burial diagenesis. The kerogen probably contains some 'micrinitized' liptinite.

IR and PHGC analysis of kerogen

IR (Table 4.11) and PHGC (Table 4.12) analysis of selected Tertiary and Triassic kerogens provided further insight into the changes that occur in Type II kerogens (bituminite, ?cutinite, ?liptodetrinite) during the passage from eodiagenesis (cores 2-13) to mesodiagenesis (cores 15-27). Comparison of the IR I_{1700}/I_{1600} values of kerogens from Unit 3, DSDP site 262 (Table 4.7)

and core 3, Ashmore Reef No. 1, shows that the initial stage of the thermal alteration of dispersed organic matter (bituminite) in carbonates, corresponding to the temperature range 15-60°C, involves loss of carbonyl groups, probably as CO₂. With increasing burial (cores 3, 7 and 12), all three IR ratios (Table 4.11) increase, suggesting a decrease in the 'aromaticity' of the kerogen. This is supported (Table 4.12) by the lower proportion of simple aromatics in the kerogen PHGC products of core 12 (12.8%, cf. core 3, 17.9%). The apparent increase in 'aliphaticity' with depth (the converse of increasing aromaticity, and the reverse of what occurs during coalification) probably reflects a change in the state of preservation of the original organic detritus. Conditions seem to have been more favourable for sapropelization lower in the carbonate sequence.

PHGC data on the kerogens from cores 3 and 12 (Table 4.12) show that

1. their structure is not greatly different from that of the kerogen in sample 638, DSDP Site 262, a less mature Type II (bituminite) kerogen; and
2. sapropelization results in a slight but real increase in the relative content of longer-chain alkyl structures, as measured by % C₁₀₊ n-alkanes.

The latter feature may arise through the incorporation of anaerobic bacterial lipids into the kerogen complex.

Lack of IR/PHGC information on sample 15 precludes a direct examination of the changes in kerogen structure that characterize the first coalification jump in bituminites. However, IR data (Table 4.11) for the kerogen in cores 21 and 24 shows that the second coalification jump in liptinite (?cutinite and/or liptodetrinite) involves appreciable loss of alkyl and carbonyl groups. In core 27, the loss of alkyl groups from the kerogen has been slower, as indicated by its higher I_{2900}/I_{1600} and I_{1450}/I_{1600} values.

It is interesting to note the relatively fixed content of n-alkanes (viz. 40.5 - 42.3%) among the PHGC products of Type II kerogens from DSDP Hole 262 (Table 4.8) and Ashmore Reef No. 1 (Table 4.11), over the vitrinite reflectance range <0.4 - 1.5% (i.e. eodiagenesis to late mesodiagenesis). The proportion of simple aromatics also appears to remain constant, increasing to >21% only in core 27, Ashmore Reef No. 1. This latter increase, however, is probably not entirely rank-related. That it also represents the contribution of lignin-based residues of land plants is suggested by the almost identical value for percent simple aromatics in sample 602, DSDP site 262 (Table 4.8).

4.4.5 Relevance to petroleum genesis on Northwest Shelf

This study has demonstrated the existence of two stratigraphically separate zones (or intervals) of hydrocarbon generation in the sedimentary sequence penetrated by Ashmore Reef No. 1. The upper zone (marginally oil-mature) is located between 2000 and 2400 m in Lower Cretaceous - Palaeocene marine carbonates. The lower zone (post oil-mature) occurs below 2800 m in Upper Triassic fluvio-deltaic, fine-grained clastics. The two zones are an expression of differences in precursor organic matter, depositional environment, host-rock lithology and thermal history.

The organic geochemistry of the sediments in the two intervals is consistent with the occurrence of two families of oil on the Northwest Shelf (Powell and McKirdy, 1973c; Powell, 1975). A simplified view of the genetic relationship between the oils and their source-rocks is set out in Table 4.13. Although the lower zone of hydrocarbon generation is confined to the Triassic at Ashmore Reef, it is not suggested that these sediments are (or ever have been) a source of significant quantities of C_{15+} hydrocarbons. The Triassic in the Barrow and Dampier Sub-basins generally contains H-poor kerogen unsuitable for oil generation (Powell, 1975;

Demaison and Shibaoka, 1975). The paraffinic family of oils is considered to have originated from Jurassic (to Lower Cretaceous) fine-grained clastics (for the most part missing at Ashmore Reef) which contain abundant H-rich terrigenous organic matter (e.g. cutinite, sporinite).

4.4.6 Summary

1. Marine carbonates of low diagenetic rank typically contain Type II kerogen derived from anaerobic bacterial decay of mainly algal remains and referable to bituminite, a member of the liptinite group of coal macerals.
2. The onset of hydrocarbon generation from bituminite in carbonates occurs at a temperature of 90-95°C.
3. The threshold of intense oil generation from such organic matter may be defined as that depth at which
 - 1) saturates first exceed 15% of the EOM,
 - 2) total hydrocarbons first exceed 25% of the EOM, and
 - 3) algal huminite attains a rank equivalent to $\bar{R}_{\text{O max}} \approx 0.6\%$.
4. During the initial phase of oil generation the kerogen undergoes a dramatic change analogous to Teichmüller's first coalification jump of liptinites. This transformation involves disproportionation reactions that lead to a residual Type III kerogen similar in elemental composition to micrinite, and EOM rich in naphthenic hydrocarbons, as co-products.
5. Crude oils generated from bituminite-like organic matter are likely to exhibit the following characteristics:
 - 1) naphthenic base
 - 2) high sulphur content (2-5%)
 - 3) pristane < phytane

- 4) majority of n-alkanes in range C_{15} to C_{26} .
6. Contrary to current dogma, the presence of Type III organic matter (vitrinite $\bar{R}_o \text{max} = 0.6-1.5\%$) in a fine-grained marine sediment may mean that it has generated oil. It is therefore important to distinguish between such Type III kerogen (equivalent to rank micrinite) and Type III kerogen that has been derived via geochemical coalification (i.e. diagenetic maturation) from algal huminite. The latter is capable of generating gas but not oil and may be recognized by the fact that its associated EOM has an n-alkane distribution with a single maximum between C_{20} and C_{25} .

4.5 COORONGITE, TORBANITES AND OIL SHALES

It is now generally accepted that the major precursors of organic matter in many oil shales (Robinson and Dinneen, 1967; Cane, 1968; Bradley, 1970) and the boghead coals (Moore, 1968; Teichmuller, 1975) were algae. The algae along with other microorganisms, lived in aquatic environments that supported abundant growth and yet favoured the accumulation and preservation of vast quantities of organic debris (algal ooze) in their bottom muds. Such environments included shallow lakes and playas, lagoons associated with coal swamps, and restricted shallow marine basins (Dulhunty, 1944; Robinson and Dinneen, 1967; Swarbrick, 1974).

In many boghead coals, and in some oil shales, the alga responsible for the deposit has been recognised and identified in terms of its modern and fossil equivalents. Two notable examples are the genera Botryococcus (fossil equivalents Pila, (?) Reinschia) and Pachysphaera (fossil equivalent Tasmanites). The former is a colonial alga found in lacustrine or lagoonal environments, whereas the latter is a marine unicellular form. Both are green algae rich in lipids, notably olefinic hydrocarbons in the case of Botryococcus. Botryococcus braunii is relatively widespread in modern

freshwater environments but in only a few does it give rise to a peculiar rubber-like material called coorongite (or balkhashite) which is believed to be an intermediate in the formation of torbanite, a boghead coal (Cane, 1969). Where recognizable remains of these organisms occur in oil shales and sapropelic coal (e.g. Permian torbanite, Sydney Basin) they are preserved as the maceral alginite. In oil shale (e.g. Permian tasmanite shale, northern Tasmania), they are also commonly referred to as 'yellow bodies' (Robinson and Dinneen, 1967). The famous lacustrine Green River Formation (Eocene), U.S.A., and the lesser known (but equally extensive) marine Toolebuc Limestone (Cretaceous) in Queensland contain oil shales for which algal precursors may be inferred, although none has been identified. Despite the difference in their depositional environments these two deposits have another important feature in common. Both contain significant amounts of non-algal organic matter in the form of spores and pollen (Bradley, 1970; Swarbrick, 1974).

Kerogens derived from organisms similar to Botryococcus and Tasmanites are rich in aliphatic structures, have original high H/C and low O/C atomic ratios and when present in fine-grained organic-rich sediments are among the most prolific petroleum source rocks known (e.g. Cretaceous, Arabian Gulf; Silurian, northern Africa). Although organic matter of this kind (classified Type I kerogen by Tissot et al., 1974) has been the subject of numerous investigations (e.g. Marchand et al., 1969; Combaz, 1971, 1974; Correia and Connan, 1974) there is little published information on the yield and composition of its associated EOM. In order to help fill this gap, the present study was undertaken. Its specific aims were to

- 1) analyse and compare the soluble (bitumen) and insoluble (kerogen) fractions of the oil shales, coorongite and boghead coals mentioned in the preceding discussion;
- 2) identify some of the distinguishing features of the EOM

(particularly the alkane fraction) associated with Type I kerogen;

- 3) examine briefly the major compositional changes involved in the alleged biogeochemical sequence

Botryococcus $\longrightarrow$ coorongite $\longrightarrow$ torbanite;

- 4) ascertain the key biological, environmental and diagenetic factors which lead to the formation of Type I, (as opposed to Type II or Type III organic matter) from algal precursors; and
- 5) characterize, geochemically, the onset of hydrocarbon generation in Type I organic matter.

4.5.1 Geological setting of samples

Brief details of the algal deposits examined (including age, basin, locality, sediment type and depositional environment) are given in Table 4.14. Further information on their origin and geological setting may be obtained from the references cited.

4.5.2 Previous geochemical investigations

Coorongite

Because of its enigmatic nature and occurrence coorongite has been the subject of extensive organic geochemical research since its discovery in 1865, and in recent years most notably by R.F. Cane. In a series of papers (Cane, 1967, 1969; Cane and Albion, 1971, 1973), he has considered at length the origin of coorongite from the alga B. braunii, and its significance as an intermediate in the formation of torbanite and oil shale kerogen. Based mainly on the IR and NMR spectra of coorongite,

torbanite, model compounds and polymers, and lipid metabolites of B. braunii, and in the light of present knowledge of the phytochemistry of the alga, Cane and Albion (1971, 1973) finally proposed the scheme shown in Figure 4.16. Cane (1969) reported the results of preliminary analysis of the coorongite using mass spectroscopy, flash pyrolysis and various chemical degradation techniques which demonstrated (among other things) 'a structural backbone of long alkyl chains' containing up to 30 carbon atoms.

Douglas et al. (1969) investigated the hydrocarbon fraction of coorongite and showed it to comprise only 0.53% by weight of the sample (cf. EOM, 50%). It contained alkanes, alkenes (branched and unbranched) and alkylbenzenes. The n-alkanes (range C_{14} - C_{27} ; maximum C_{17}) lacked any odd or even predominance. Although not commented on by the authors, the n-alk-1-enes (range C_{16} - C_{28} ; maximum C_{19}) showed an apparent preference for even-carbon-numbered chain lengths in the range C_{22} to C_{26} . The presence of C_{18} - C_{20} isoprenoid alkanes (norpr/pr = 0.6; pr/ph = 1.1), in conjunction with the nature of the alkane and alk-1-enes, prompted Douglas and coworkers to suggest the involvement of bacteria in the formation of coorongite.

Elemental analyses of coorongite are given by Moore (1968) and Marchand et al. (1969).

Oil shales

The Green River Formation oil shale deposits are without doubt the most intensively studied sediments in the organic geochemical literature. In the present context, exhaustive review of this literature would serve little purpose. Instead only a selection of those investigations that are immediately relevant to the present work will be mentioned. The references cited will guide the reader to further background information.

Analyses of the normal and isoprenoid alkanes have been

undertaken by Cummins and Robinson (1964) and Eglinton et al. (1966).

The bimodal n-alkane profile (range $C_{13} - C_{33}$; maximum C_{17} , C_{29}) indicates a dual origin (algal and higher plant) for the oil shale lipids. A low pr/ph value (0.3) and a marked odd/even preference ($CPI = 3.6$) in the C_{25+} n-alkanes are consistent with a relatively mild history (although a maximum burial temperature of 90-125°C has been suggested by Bradley, 1970).

Robinson et al. (1965) studied changes in EOM yield, n-alkanes and acyclic isoprenoids with depth in a 274 m core from the Sulphur Creek No. 10 well in the Piceance Creek Basin. They found that with increasing depth

- 1) CPI of the long-chain n-alkanes decreased from 3.6 to 1.2, and
- 2) EOM yield showed a somewhat irregular increase, from 64-106

mg/g C in the upper 61 m to 111-144 mg/g C in the lower 152 m.

Closer examination of their data also reveals a parallel increase in pr/ph ratio, from 0.2 to 0.7. These changes probably reflect differences in source material and environment, rather than an increased maturation level, given the narrow depth interval involved. It is also noteworthy that pristane tends to exceed n-heptadecane in concentration ($pr/n-C_{17} = 0.6-2.6$; mean = 1.4).

Recent GC-MS studies of the high-molecular-weight branched and cyclic hydrocarbons in the Green River oil shale illustrate the range and variety of structurally complex biological marker-type alkanes (and alkenes) present in algal sediments (see also Chapter 3), while at the same time indicating, by way of comparison with the less altered Messel oil shale, Germany (Eocene: maximum palaeotemperature approx. 40°C), the type of low temperature reactions microbial lipids may undergo during early diagenesis (Kimble et al., 1974).

The kerogen fraction of the Green River oil shale actually comprises two major fractions, one that yields oil on pyrolysis, and another that does not (Bradley, 1970). The latter (inert) constituent

makes up 30-35% of the total organic matter in the shale. A range of physical and chemical techniques have been employed in various attempts to unravel the structure of the Green River kerogen. The results of this research have been reviewed by Robinson (1969) who concluded that the kerogen is a macromolecular, predominantly naphthenic material in which alkyl chains and aromatic centres form only a minor part of the total structure. About one half of the oxygen is present as ether linkages and the rest in the form of acid or ester groups. Nitrogen and sulphur are likely to occur mainly in heterocyclic ring systems.

There is little published information on the Toolebuc Formation oil shales. Senior and Smart (1973) reported preliminary analyses of samples from two widely separated drill holes (BMR Croydon No. 1, Carpentaria Basin, and Springvale No. 6, Eromanga Basin) which showed a remarkable similarity in their total alkane distributions. Saxby (1976) quoted the elemental composition of kerogen in a sample of the oil shale (15% TOC) from the Julia Creek area and showed that it plotted on a van Krevelen diagram between the coalification tracks for alginite and exinite.

Tasmanite

Burlingame et al. (1969) compared the fatty acid contents of tasmanite shales from Alaska (61.9% TOC) and Tasmania (29.0% TOC). The fatty acids were isolated by a series of extraction procedures, two of which included saponification and oxidation of the kerogen fraction. Surprisingly no isoprenoid acids were found in the extracts or among the oxidation products. Differences in the fatty acid distributions of the samples were attributed to the supposedly more thermally altered state of the Alaskan material. However, this is not supported by the kerogen elemental data quoted (Tasmanian atomic H/C = 1.44; Alaskan atomic H/C = 1.57). In a subsequent paper, Simoneit and Burlingame (1973, p.595) concluded that

the kerogen in the Tasmanian tasmanite comprised "mainly a random, saturated hydrocarbon polymer, probably derived from saturated and olefinic lipids and sterols". The authors also made passing reference to the hydrocarbons which apparently comprise the bulk of the EOM and were "analogous in range and compound type" to those of the Green River oil shale. This cryptic statement, at least insofar as it relates to the straight-chain paraffins is at odds with the C_{23+} n-alkane distribution of Tasmanian tasmanite published by Brooks and Smith (1967) which, unlike that of the Green River shale, has a maximum at n- C_{26} and displays no odd or even predominance.

Cane (1968) discussed the elemental composition, IR spectra and pyrolysis behaviour of various kerogen fractions isolated from Tasmanian tasmanite. He also examined the benzene-methanol extract and noted that it appeared to contain compounds related to abietic acid, a common component of tree resins (Eglinton, 1969). Analogous tricyclic aromatic structures were reported by Burlingame et al. (1969) and Simoneit and Burlingame (1973).

Combaz (1971) used a low temperature (280°C) pyrolysis-gas chromatography technique (similar to that described by Giraud, 1970) to study the thermal degradation of various tasmanite kerogen and spore concentrates (including a Permian sample from the famous Mersey River locality of north-west Tasmania). The hydrocarbons evolved were in the range n- C_7 to n- C_{19} and had a bimodal distribution in which the $C_{11} - C_{19}$ mode was usually dominant.

Torbanites (boghead coals)

A comparative geochemical study by Robinson and Dinneen (1967) of the bitumen (EOM) and kerogen in the twelve oil shales included data (summarized in Table 4.15) on three samples, designated 'algal oil shales' because of the presence of yellow bodies. One of these samples was a Permian torbanite from Coolaway Mountain (53 km NNW of Newnes) in the

Sydney Basin. Although similar in many respects to the South African torbanite (Table 4.15), the Australian sample differed in containing a much lower concentration of acyclic isoprenoid alkanes, a higher H/C atomic ratio and a higher odd carbon-number predominance in the C_{23+} n-alkanes. All three features indicate a lower rank.

Douglas et al. (1969) reported n-alkanes in the range $C_{15} - C_{39}$ (maximum $C_{21} - C_{23}$) and pristane and phytane ($pr/ph = 3.7$) in the EOM of a Carboniferous torbanite from Scotland. The presence of isoprenoid alkanes contrasted with the absence of isoprenoid acids in the sediment.

In a recent comprehensive study of a 3 m section of an Upper Permian oil shale-torbanite sequence from the Sydney Basin (exact locality unfortunately not specified), Correia and Connan (1974) employed both physico-chemical analyses of the isolated EOM and kerogen and microscopic examination of the original shales, to show that

- 1) oil yields from Fischer assay of the sediments were directly proportional to the content of recognizable Botryococcus remains;
- 2) the shales in the lower half of the section were relatively immature (vitrinite $\bar{R}_o \text{ max} = 0.46-0.58$) and at the threshold of oil generation;
- 3) alteration by meteoric waters of shales in the upper two-thirds of the sequence produced anomalously high vitrinite reflectivity values ($\bar{R}_o \text{ max} = 0.95-1.06$); and
- 4) the alkane chromatograms were dominated by n-alkanes which displayed a slight odd/even predominance in the $C_{23} - C_{29}$ range, directly inherited from odd-carbon-numbered $C_{23} - C_{31}$ n-alkenes (mostly alkadienes) in the precursor Botryococcus alga (cf. Gelpi et al., 1968, 1970; Knights et al., 1970).

4.5.3 Results

The results of the various analyses performed on the algal

sediments listed in the Table 4.14 are set out in Table 4.16 (concentration and isotopic composition of TOC, yield and composition of EOM), Table 4.17 (kerogen elemental composition and rank); Table 4.18 (kerogen IR spectrometry) and Table 4.19 (PHGC analysis of selected kerogens). In addition, kerogens from two of the oil shales and two of the torbanites were examined optically in transmitted light (Plates 4.2 and 4.3, respectively). At the author's request, polished sections of all three boghead coals and the tasmanite shale were prepared and studied using both reflected white light (Plates 4.4 and 4.5) and blue light (long wavelength UV) excitation (Plates 4.6 and 4.7) by A.J. Kantsler (University of Wollongong), who also made the vitrinite reflectivity measurements quoted in Table 4.17. The estimated maceral composition of each torbanite is given in Table 4.20.

4.5.4 Discussion

Coorongite

The EOM (yield 38 mg/g C), although comprising almost 22% by weight of the original sample, contains less than 1% hydrocarbons. The total alkane chromatogram (Fig. 4.17a) is dominated by n-alkanes but appears to also contain a second prominent homologous series of compounds (possibly the n-alk-1-enes identified by Douglas et al., 1969). Cyclic alkanes comprise a prominent 'naphthene hump' between n-C₁₄ and n-C₂₃. The isoprenoid alkanes, pristane, phytane and (?) norpristane, are present (pr > norpr > ph). The smooth n-alkane distribution (range C₁₄ - C₂₉, maximum, C₁₆: Fig. 4.18) is practically identical with that obtained by Douglas et al. (1969). The isotopic composition of the TOC (mean $\delta^{13}\text{C}_{\text{PDB}} = -31.0\text{‰}$) is interesting because it falls outside the normal range ($\delta^{13}\text{C}_{\text{PDB}} = -5$ to -30‰) for algal organic matter (Enclosure 2, Fig. 6). This may be a reflection of the unusual lipid-rich nature of the precursor alga (cf. $\delta^{13}\text{C}_{\text{PDB}}$ range for

the lipid fraction of marine plankton = -19 to -39⁰/oo).

In terms of its elemental composition (Table 4.17) coorongite is clearly the most hydrogen-rich material (atomic H/C = 1.79-1.82) in the present suite of algal sediments, and among those most depleted of nitrogen and sulphur. Although richer in oxygen than the other samples, it nevertheless plots adjacent to the alginite coalification track on a van Krevelen diagram (Fig. 4.19), confirming its previously recognized role as an intermediate in the formation of Type I organic matter. Comparison with the elemental composition of B. braunii (green active growth phase: Table 4.1) shows that the first step in the diagenetic sequence $\text{alga} \rightarrow \text{coorongite} \rightarrow \text{torbanite}$ involves major losses of oxygen and nitrogen. Logically this would entail removal of the carbohydrate and protein components of the original alga, for which the IR spectra of the alga and coorongite (Fig. 4.20a) provide some evidence (see below). It may require the intervention of bacteria, which could also explain the lack of correspondence between the aliphatic hydrocarbons in the alga and coorongite, particularly the absence in the latter of strong odd/even predominance among the C_{23+} n-alkanes. Douglas et al. (1969) previously invoked bacterial involvement to account for the presence of isoprenoid alkanes (cf. their absence from the lipid fraction of B. braunii).

The highly aliphatic nature of coorongite is evident from both its IR spectrum (Fig. 4.20a) and its PHGC chromatogram (Fig. 4.21a). By comparison with the IR spectrum of B. braunii (Fig. 4.20a), that of coorongite shows a marked enhancement of the characteristic alkyl absorption bands (C-H 2940, 2850 cm^{-1} ; CH_2 , CH_3 1460 cm^{-1} ; $(\text{CH}_2)_n$ where $n > 4$ 720 cm^{-1}); a reduction of the broad band at 3370 cm^{-1} (O-H, N-H); and the augmentation of the 1050 cm^{-1} band by absorptions at 1090 and 1150 cm^{-1} (C-O). This is consistent with the loss of algal carbohydrates and proteins (mentioned previously) and the development of ether linkages during the oxidative polymerization of long-chain alkadienes (Cane and Albion, 1971, 1973).

The PHGC products of coorongite (Table 4.19; Fig. 4.21a) are predominantly n-alkanes (64.3%), over half of which possess chain lengths $> n-C_{10}$.

Torbanites

Petrographic examination of the torbanites showed them to be extremely rich ($>75\%$) in the algal bodies of the Botryococcus type (Table 4.20; Plates 4.4-4.7), confirming their genetic link with coorongite. Consistent with their more advanced stage of diagenetic evolution, the torbanites contained less EOM (9-17 mg/g C) but more hydrocarbons (4.7 mg/g C) than did coorongite. Moreover, hydrocarbons comprised a much higher proportion of the extract (27-45%).

In two of the three torbanites, the saturated hydrocarbons (Fig. 4.17b) are dominated by n-alkanes. The Newnes sample has a somewhat more complex chromatogram, due to a greater concentration of branched/cyclic alkanes in which there is one (as yet unidentified) homologous series of almost equal prominence with the n-alkanes. The relatively high proportion of peaks in the sterane-triterpane region of the chromatogram (cf. Correia and Connan, 1974, fig. 2) testifies to the exceptionally low rank of the sample (vitritine $\bar{R}_0 \text{ max} = 0.2$: Table 4.17).

The torbanite n-alkane profiles (Fig. 4.18a) are similar (range $C_{15} - C_{31}$; maximum, C_{26} to C_{29} ; C_{23+} , 70-78%), except for an obvious predominance of odd carbon-numbered C_{23+} homologues in sample 0158. The n-alkanes of a South African torbanite figured by Correia and Connan (1974) displayed a similar odd/even predominance which, as mentioned, was explained in terms of a supposed derivation from $C_{23} - C_{33}$ odd-carbon-numbered n-alkenes in the precursor alga. If this is valid, the question then arises as to why no such odd-carbon-number preference is evident in sample 0157 (Newnes). The difference in rank between samples 0157 and

0158 (Table 4.17) is so small that it rules out thermal maturation as the cause, although such may be the reason for the lack of appreciable odd/even predominance in sample 0156 (Joadja). One is left with two possible alternatives:

- 1) sample 0158 contains immature higher plant n-paraffins (cf. Brooks and Smith, 1967), or
- 2) sample 0157 underwent a higher degree of bacterial reworking early in its diagenetic history than did sample 0158 (cf. Johnson and Calder, 1973).

The first explanation is not corroborated by microscopic evidence; as no recognizable exinite (cutinite, sporinite) was found during petrographic examination of the coal (Table 4.20). The second alternative finds some measure of support in the higher $pr/n-C_{17}$ ratio of sample 0157 (see below) and is therefore preferred.

The boghead coals as a group are characterised by $pr/ph \geq 1.5$ and $pr/n-C_{17} \geq 1$ (Table 4.16). Lijmbach (1975) noted these features in crude oils generated from source rocks deposited under peat swamp conditions. In such environments phytol is, Lijmbach claims, slowly converted by anaerobic bacteria to phytanic acid which accumulates and is subsequently decarboxylated to pristane and CO_2 during thermal diagenesis. Accordingly the highest value for each ratio (Table 4.16) is found in the torbanite of highest rank (sample 0156, Joadja: Table 4.17).

As anticipated the kerogens plot along the alginite pathway in Figure 4.19 (in close agreement with kerogens from the boghead coals analysed by Marchand et al., 1969) and may be classified as Type I organic matter.

The IR spectra of the kerogens (Fig. 4.20a) are practically indistinguishable from those of the highly aliphatic alginites isolated from torbanites by Millais and Murchison (1969), except perhaps for a doublet in the $995-1025\text{ cm}^{-1}$ region which appears to increase in intensity

with increasing rank. Compared with coorongite, the torbanites are clearly depleted in carbonyl (1700 cm^{-1}) and ether ($1150, 1090\text{ cm}^{-1}$) functions and this is confirmed by their lower O/C atomic ratios (Table 4.17). The higher values of I_{2900}/I_{1600} and I_{1450}/I_{1600} in the torbanites probably reflect a decrease in aliphatic unsaturation (see footnote, Table 4.18), rather than a real increase in aliphaticity. There is certainly no substantial indication of the latter in the PHGC data (Table 4.19). Within the torbanite suite all three IR band intensity ratios decrease with increasing rank (Table 4.18).

The rather large discrepancy in the $\delta^{13}\text{C}_{\text{PDB}}$ values of coorongite (mean value -31.0‰) and the Joadja torbanite (-23.3‰) was unexpected and is difficult to explain. An apparent metamorphic depletion of algal kerogens in ^{12}C was reported by McKirdy and Powell (1974), but this occurred at much higher rank (H/C atomic ratio ≈ 0.15), corresponding to the third coalification jump of vitrinite (Teichmüller, 1975). Possibly the present case is an example of an isotope effect associated with the first coalification jump of liptinites in highly aliphatic (Type I) organic matter. The intervention of bacteria (cf. Eadie and Jeffrey, 1973) in the transformation of coorongite to torbanite may also have contributed to the enrichment of the latter in ^{13}C .

Finally, the vitrinite reflectivity of the Newnes torbanite (Table 4.17) appears to be somewhat depressed with respect to the regional rank ($\bar{R}_o$ max approx. 0.75%: A.J. Kantsler and A.C. Cook, pers. comm., 1976) for this part of the Sydney Basin. The reason for this is not clear, but may be related to the mineral-matter-free alginite matrix in which the coalification of the vitrinite has taken place. As the vitrinite becomes increasingly interstitial it seems to lose the ability to form a more ordered structure. Thus, the reflectivity of vitrinite in sample 0158 may also be an unreliable indication of its true rank.

Oil shales

The TOC contents of the oil shales (8-29%: Table 4.16) are intermediate between those of boghead coals (>50%) and most petroleum source rocks (0.5-7%). EOM yield is high (45-124 mg/g C) but, with the exception of the tasmanite shale, the proportion of extractable hydrocarbons is low (7-15% EOM). Saturates exceed aromatics by as much as a factor of five.

The total alkane chromatograms of two oil shales are shown in Figure 4.17c. That of the Toolebuc oil shale is notable on two counts:

- 1) it lacks C_{25+} n-alkanes; and
- 2) the isoprenoids pristane and phytane are present in unusually high concentrations ($pr/n-C_{17} = 2.8$, $ph/n-C_{18} = 3.2$).

The first feature is surprising, particularly in a relatively immature sediment (kerogen, H/C atomic = 1.26; vitrinite $\bar{R}_o$ max = 0.39: Table 4.17) which contains recognizable land plant remains. Microscopic examination of the kerogen concentrate (Plate 4.2, figure 2) revealed mainly humic material with 20-30% exinite (spores and cuticle) and little or no alginite (A.C. Cook pers. comm., 1973). The absence of waxy straight-chain paraffins is believed to be an artifact of the non-standard procedure employed to separate asphaltenes from the Toolebuc extracts (see Appendix 1). This 'short-cut' method has been shown to result in the co-precipitation of the waxy n-alkanes and asphaltenes. Had the standard IP method been used, a total alkane yield (Table 4.16) and distribution comparable to that of the Green River oil shale (Eglinton et al., 1966) probably would have been obtained for each of the Toolebuc samples analysed.

High $pr/n-C_{17}$ and $ph/n-C_{18}$ ratios appear to be typical of many oil shales, including those of the Green River and Toolebuc Formations. High $pr/n-C_{17}$ values in the former have already been mentioned (Section 4.5.2). Gibert et al. (1975) reported a predominance of isoprenoids among the

alkanes of the Irati oil shale (Permian, Brazil) and took it to be an indication of intense photosynthetic activity. However, the $n\text{-C}_{17}$ alkane (n-heptadecane) in low rank sediments like the Green River oil shale is generally believed to be a chemical fossil inherited directly from blue-green and other photosynthetic algae. Therefore, unless the algal synthesis of chlorophyll (incorporating phytol as an ester-linked side-chain) and n-heptadecane proceed completely independently of one another, it is difficult to envisage how an excess of isoprenoid could arise simply from a high level of photosynthesis. A more promising explanation is that pristane and phytane are contributed to the sediment by certain anaerobic non-photosynthetic bacteria (Han and Calvin, 1969) which also metabolise $\text{C}_{15} - \text{C}_{20}$ n-alkanes from the algal ooze and convert them into hydrocarbons of higher molecular weight (Han et al., 1968b).

The tasmanite alkane distribution (Fig. 4.17c) is characterized by a complex mixture of branched and cyclic hydrocarbons in the $n\text{-C}_{20}$ to $n\text{-C}_{29}$ region of the chromatogram. The isoprenoids are not prominent although the pr/ph ratio is somewhat higher than in the other oil shales. Its n-alkane profile (Fig. 4.18b) resembles that of the Newnes and Joadja torbanites, except for a slight even-carbon-number predominance in the $\text{C}_{20} - \text{C}_{28}$ range. This resemblance of the tasmanite shale to the torbanites is also evident in the IR spectra of its two kerogen fractions (Table 4.18, Fig. 4.20b).

On the basis of their H/C and O/C atomic ratios the oil shale kerogens fall within Tissot's Type I classification (Table 4.17; Fig. 4.19). In terms of rank (measured by H/C atomic ratio) they are close to the boundary between eodiagenesis and early mesodiagenesis as defined by Foscolos et al. (1976). However, as already mentioned, the Toolebuc kerogen contains little or no optically recognizable alginite, and strictly speaking should be classed as a Type II kerogen. This would explain why, in so many other respects its composition differs from that of the

authentic Type I kerogens (Tables 4.17-4.19). Distinctive features of the Toolebuc kerogen, all indicating a more aromatic composition, include

- 1) the lowest H/C atomic ratio,
- 2) the highest C/N and C/S atomic ratios,
- 3) the lowest values for each of the three IR band ratios, and
- 4) PHGC products containing the lowest proportion of n-alkanes and the highest proportion of simple aromatics.

It is hardly surprising then that the appearance of the Toolebuc kerogen in transmitted light should also be quite different from that of the Green River kerogen (Plate 4.2).

4.5.5 Summary

1. Where sediments occur that are very rich in organic matter (> 5% TOC) derived principally from algae, their kerogen is probably of Type I composition. There are at least two different routes by which organic matter of this kind may arise.
2. The first requires conditions favourable for the growth and preservation of special lipid-rich algae. Such algae are relatively rare in the geological record. Only two major varieties have been recognized, one a freshwater-brackish type and the other marine. They are related, respectively to the modern planktonic green algae Botryococcus (colonial) and Pachysphaera (unicellular). On burial both give rise to characteristic and easily recognisable microfossils ('yellow bodies').
3. A second variety of Type I organic matter (exemplified by the kerogen of the Green River oil shale) is derived from microscopic algae, probably benthonic blue-greens, that grow in bloom proportions in relatively shallow warm lakes where they form a layer of living

incoherent algal ooze. A higher than normal rate of preservation of algal lipids in the bottom muds is ensured by bacterial inhibitors dissolved in the waters of the upper 0.3-0.5 m of the ooze (Bradley, 1970, 1973).

4. Type I organic matter is characterized by a highly aliphatic structure and may be recognized geochemically in terms of
 - 1) its elemental composition ($H/C > 1.0$; $O/C < 0.1$);
 - 2) its IR spectrum ($I_{2900}/I_{1600} \geq 0.75$; $I_{1450}/I_{1600} \geq 0.50$),
and
 - 3) its PHGC products (n-alkanes $> 55\%$, $n-C_{10+} > 30\%$, simple aromatics $< 5\%$).
5. The EOM associated with Type I kerogen is less distinctive, but certain features appear to be characteristic. The n-alkanes contain a high proportion ($> 50\%$) of C_{23+} homologues. Immature n-alkane distributions may display a slight odd (Botryococcus) or even (Tasmanites) carbon-number predominance, depending on the precursor alga. Commonly $pr \geq n-C_{17}$ due to intense bacterial reworking of algal lipids.
6. The reflectivity of vitrinite appears to be inversely related to the proportion of alginite in the kerogen and hence may be an unreliable indicator of rank in alginite-rich sediments.
7. The threshold of intense oil generation from Type I organic matter is tentatively defined as that point at which
 - 1) vitrinite $\bar{R}_o$ max exceeds 0.5% (but see point 6 above),
 - 2) H/C atomic ≈ 1.5 , and
 - 3) saturates comprise at least 10% EOM in shales, or 25% EOM in torbanites.

Although based on a very limited number of samples, these findings nevertheless seem to be consistent with the classification of diagenesis proposed by Foscolos et al. (1976). In addition,

pristane is less abundant than phytane during eodiagenesis, but in early mesodiagenesis pr/ph values increase to 3-4.

8. The evidence for alginite undergoing a coalification jump similar to that of bituminite (as described by Teichmüller, 1974, 1975) is equivocal. In the Joadja torbanite there are no petrographic indications that alginite has been extensively transformed into micrinite. That the chemical and isotopic composition of alginite may undergo a 'coalification' jump is suggested by

- 1) the position of kerogen samples 9 and 10 in Figure 4.10, and
- 2) the discrepancy of 6-7‰ between the $\delta^{13}\text{C}$ values for coorongite and the Joadja torbanite.

9. For Type I organic matter, the composition of the products of PHGC is remarkably uniform over the rank range $\text{H/C} = 1.8-1.3$.

4.6 PHOSPHORITES

Marine pelletal phosphorites commonly contain appreciable amounts of both organic matter and pyrite, an association which suggests that they formed under anaerobic conditions. Moreover, the abundance of marine fossils in many ancient phosphorite-bearing sequences, for example the Beetle Creek Formation, Georgina Basin (Russell and Trueman, 1971), indicates a close relationship between phosphate precipitation and high organic productivity. This is confirmed by studies of such recent environments as the continental shelf and upper slope off S.W. Africa (Romankevich and Baturin, 1972) and Peru (Manheim et al., 1975) where formation of phosphorite continues in organic-rich diatomaceous oozes.

The photic zone of the ocean is particularly fertile in regions where strong divergent upwelling brings deep cold waters rich in dissolved phosphate and other nutrients into contact with warm oxygenated water at shallow depth. High organic productivity may also arise in more land-

locked areas of wind driven estuarine-like circulation where nutrients become trapped (Brongersma-Sanders, 1966; Pevear, 1966). Below such areas of high primary phytoplankton productivity, zones of minimum oxygen and maximum dissolved phosphate develop (in the open ocean, at depths between 100 and 500 m) in response to the sinking, consumption and bacterial decomposition of dead planktonic organisms (Manheim et al., 1975; Wang, 1976).

Oxygen depletion is achieved by intense (aerobic) biological activity (Brongersma-Sanders, 1966), presumably involving grazing and saprophytic decay. The latter also releases phosphate. Where the 'oxygen minimum zone' impinges on the seafloor, conditions are favourable for both the enrichment of phosphate in the interstitial waters of the bottom sediments and the accumulation and preservation of high concentrations of organic matter (2-5% TOC off Peru : Manheim et al., 1975), predominantly phytoplanktonic remains (diatoms, dinoflagellates and zooplanktonic faecal pellets). Benthonic organisms (e.g. foraminifera) may or may not be present. Algal pigments (chlorophyll, phaeophytin) impart a green colour to the sediments (Manheim et al., 1975; Boon et al., 1975).

In other words, as recognised by McKelvey (1959) and Brongersma-Sanders (1966), abnormally high algal productivity in situations of upwelling (or estuarine circulation) may lead to the formation of both marine phosphorites and potential source rocks for marine crude oils. The extensive Phosphoria Formation, for example, is considered to have been the source for major Palaeozoic oil accumulations in central Wyoming (Barbat, 1967; Stone, 1967).

As little appeared to be known about the composition of organic matter in phosphorite-bearing sediments, the author instigated a cooperative study (with T.G. Powell and P.J. Cook) of the organic geochemistry of phosphorites. A suite of 20 samples, from a variety of depositional environments and ranging in age from late Precambrian to Miocene, was assembled for analysis. The results of the investigation were published

as Powell et al. (1975) (Enclosure 1). The author's part in this work was concerned mainly with the isolation and analysis of the insoluble kerogen fraction and its use as an index of diagenetic rank. A summary of the major findings is included in the next section.

Subsequently, further work (involving carbon isotopic analysis, IR spectrometry and microscopic examination¹) was undertaken on selected kerogens from the original suite in order to clarify the origin and diagenetic history of their precursor organic matter. The published EOM analyses were recast (and in some instances, corrected), and additional alkane parameters were measured. This was necessary to facilitate comparison of the organic content of the phosphorites with the algal organic matter described elsewhere in Chapter 4, which was deposited under somewhat different conditions.

In addition, a second sample of pelletal phosphorite from the Middle Cambrian Beetle Creek Formation (Georgina Basin, Queensland) was analysed for EOM and kerogen. The organic geochemical facies of the two Beetle Creek phosphorites were then contrasted with that of two slightly phosphatic siliceous limestones from the same formation.

Finally, as part of the Amadeus Basin study (Part III of the thesis), further sampling and analysis of phosphorites in the Ordovician Stairway Sandstone were carried out to permit assessment of the contribution that the phosphorite lithofacies makes to the overall petroleum source-rock potential of the Larapinta Group. The results of this phase of the phosphorite study, however, are presented in Chapter 6 and details of selected samples only will be mentioned here.

The specific aims of this work were

1. to identify (if possible) characteristic features of marine organic matter (EOM and kerogen) which was derived from algal

1. The petrographic work was carried out at the author's request by A.J. Kantsler, University of Wollongong.

blooms and grazing zooplankton, deposited under euxinic conditions, and modified by intense bacterial reworking prior to lithification; and

2. to examine the response of this organic matter to subsequent burial diagenesis by comparison of the kerogen (and associated EOM) in low and high-rank phosphorites, with a view to
 - 1) defining the onset of oil generation
 - 2) predicting the type of oil generated in phosphatic source beds.

4.6.1 Previous geochemical investigations

The behaviour of organic matter during the lithification of recent phosphate-rich diatomaceous oozes on the continental shelf off S.W. Africa was the subject of an elegant study by Romankevich and Baturin (1972). The conversion of organic phosphorus ('phosphatized diatomaceous ooze' : 4.2 - 4.9% TOC) to dense brown phosphorite concretions (0.76 - 1.0% TOC) was accompanied by a progressive loss of organic matter. The components of the organic matter decomposed at different rates, the 'degree of retention' increasing in the following order: carbohydrates, free lipids, nitrogen-bearing compounds and bound lipids. The more labile components were thought to be consumed by sulphate-reducing bacteria. In a more recent geochemical investigation of the fatty acids in ostensibly similar (although apparently not phosphatic) sediments from the same general area (the inner shelf off Walvis Bay), Boon et al. (1975) came to much the same conclusion. Although rich in the remains of diatoms (notably Coscinodiscus), the sediment contained fatty acids more typical of marine bacteria than marine algae. Boon and coworkers (op. cit., p.1563) concluded that "the lipids of diatoms - especially the fatty acids - are extensively

consumed by sulphate-reducing bacteria on the sediment-water interface. This leads to a replacement of algal lipids by bacterial acids in an early stage of burial The incorporation of (algal) fatty acid into protokerogen structures beyond the reach of bacteria is also a possibility for speculation".

Marine black phosphatic (as nodules) shales were the most organic-rich petroleum source-rocks (TOC = 7.1-12.3%, mean 10.1%; total hydrocarbons = 187-4090 ppm, mean 1720 ppm in the Cherokee Group (Pennsylvanian) of Kansas and Oklahoma (Baker, 1962).

Powell et al. (1975) found that, although phosphorites had an average organic carbon value (0.62% TOC) intermediate between those of shales and carbonates, like carbonates (but in contrast to shales) a substantial proportion of their organic matter was soluble bitumen. In low-rank phosphorites the EOM consisted largely of asphaltic material, pointing to the possible migration of heavy oils from such sediments at an early stage of diagenesis. The alkane distributions were indicative of organic matter derived principally from microorganisms; waxy, higher plant-derived n-paraffins, showing a marked odd/even predominance were abundant in only two cases (viz. North Carolina and a single sample from the Phosphoria Formation). The n-C₂₂ alkane, however, was prominent in the n-alkane profile of several samples, including some of relatively high rank. Generally, the oxygen, nitrogen and sulphur contents of the phosphorite kerogens were greater than in other sediments (e.g. McIver, 1967). The high sulphur values (3-16%) indicated that the kerogens formed in euxinic marine environments in which sulphate-reducing bacteria were active. Nevertheless, this post-depositional microbial activity cannot have been prolonged because the high nitrogen (>0.2%) and oxygen (up to 25%) values indicates a high degree of preservation of algal proteins and carbohydrates, prior to their incorporation into the protokerogen matrix. The build-up of free H₂S in iron-

poor carbonate sediments may have been a major factor limiting extensive in situ bacterial decay.

4.6.2 Results

The analytical data on which the following discussion is based are presented in Table 4.21 (formation or locality, phosphate content, yield and composition of EOM), Table 4.22 (kerogen elemental composition, type, carbon isotopic composition and reflectivity) and Table 4.23 (IR spectrometry). Additional information on depositional environment and burial history of the individual samples (including estimated maximum depth of burial) and X-ray diffraction patterns of representative kerogens may be found in Powell et al. (1975) (Enclosure 1).

4.6.3 Discussion

As with most sediments, the age of a phosphorite has an important bearing on the nature of its original organic content. Devonian and younger phosphorites, particularly those deposited in estuarine or other nearshore marine environments, are likely to contain at least some land-plant debris in addition to the remains of marine microorganisms. Therefore, the sediments examined in this study have been divided, according to their age, into two groups a) Upper Palaeozoic - Cainozoic b) Proterozoic - Lower Palaeozoic, each of which will be discussed separately.

Upper Palaeozoic - Cainozoic phosphorites

Kerogen

Plotting of kerogen H/C and O/C atomic ratios (Table 4.22a)

on a van Krevelen diagram (Fig. 4.22) shows that the organic matter in phosphorites of this group is predominantly of either the Type II (liptinite) or Type III (micrinite) variety. The exceptions are the two Florida samples (P3, 4) which have an intermediate composition (designated Type II-III in Table 4.22a).

Kerogen P4 has a very low reflectivity ($\bar{R}_O \text{ max} = 0.2\%$) and optically resembles a translucent gel-like huminite at the peat stage of vitrinite formation. The Phosphoria (P11-16) and Mona Vale (P7) samples have been more thermally altered than the younger phosphorites (P2-6). This is consistent with their greater degree of tectonic disturbance and estimated maximum depth of burial (Enclosure 1) which has resulted in

- 1) lower kerogen H/C atomic ratios (0.54-0.64);
- 2) higher reflectivity values ($\bar{R}_O \text{ max} = 1.3-2.2\%$) for the vitrinite-like component (or, alternatively, the 'colloidal' matrix) of the kerogens (Table 4.22a); and
- 3) development of an incipient graphite structure in the kerogen, as shown by XRD (Enclosure 1).

If, in fact, the Phosphoria and Mona Vale kerogens (Type III) are higher rank equivalents of the Type II organic matter in phosphorites from southeast U.S.A. and North Africa, then it appears that (as in the carbonates at Ashmore Reef No. 1: Section 4.4) the transition from eodiagenesis to mesodiagenesis in phosphorites may involve a liptinite coalification jump (Teichmuller, 1974).

The effect of subsequent thermal maturation of Type III (rank micrinite) organic matter is illustrated in Figure 4.22 by the Phosphoria samples which plot in a metamorphic series (P12, 15, 14, 16 and 11 in that order) along the lower portion of the micrinite evolution path.

The appearance of the Phosphoria kerogens P14 and 16 in polished section under reflected light was that of aggregates of flocculated organic matter lacking recognizable discrete grains or fragments. The

reflectivity measurements (Table 4.22a) were made on this compact 'matrix' material. The higher rank kerogen, P11, differs in that discrete grains of vitrinite ($\bar{R}_o \text{ max} = 2.2\%$) can be recognised (Plate 4.9, fig. 1). Overall, the kerogen resembles a micro-coke in its appearance under crossed nicols (A.J. Kantsler, pers. comm., 1976).

The contribution of humic plant debris to the Mona Vale (P7) kerogen was confirmed by optical examination (Plate 4.8). This is a relatively complex kerogen in which two main types of flocculated grain can be recognised:

- 1) very compact 'matrix' kerogen (Plate 4.3, fig. 1)
- 2) coaly plant fragments (inertinite, vitrinite) in a very dense groundmass of 'matrix' kerogen (Plate 4.3, fig. 2).

In Figure 4.22 kerogen P7 plots midway between the coalification tracks for vitrinite and micrinite. The reflectivity (1.4% for matrix material, 1.3% for vitrinite) indicates a rank approximating to that of a medium volatile bituminous coal.

IR analysis of three kerogens (P3, 5 and 12) (Table 4.23a, Fig. 4.23a) revealed a pattern of variation in absorption band intensities consistent with their classification (based on H/C and O/C atomic ratios) and rank. Of the two low rank samples, P5 (Type II) is richer in alkyl chains (higher I_{2900}/I_{1600} , I_{1450}/I_{1600} values; note also the 720 cm^{-1} band in Fig. 4.23a), whereas the more humic P3 kerogen (Type II-III) is richer in oxygenated (3400 cm^{-1} , OH; 1700 cm^{-1} , C=O) and aromatic (1600 cm^{-1} , aromatic C=C str) groups. The former kerogen possesses the greater potential to generate liquid hydrocarbons. The IR spectrum of the high rank kerogen P12 (Type III micrinite) is dominated by the carbonyl (1700 cm^{-1}) and aromatic (e.g. 1600 cm^{-1}) bands.

Carbon isotopic composition

The carbon isotopic composition of kerogen in the Upper Palaeozoic - Cainozoic phosphorites (Table 4.22a) falls mostly within the relatively narrow range $\delta^{13}\text{C}_{\text{PDB}} = -30.4$ to $-27.6^\circ/\text{oo}$ (mean $-29.2^\circ/\text{oo}$). The one notable exception is kerogen P2 from North Carolina ($\delta^{13}\text{C}_{\text{PDB}} = -21.2^\circ/\text{oo}$) which also happens to be the lowest rank sample in the suite (H/C atomic ratio = 1.46). As such, it may be expected to contain a high proportion of relatively unaltered carbohydrate, protein and lipid residues. The carboxyl group of biosynthetic amino acids is enriched in ^{13}C relative to the rest of the molecule (Abelson and Hoering, 1961) and the diagenetically labile carbohydrate-protein fraction of marine plankton is isotopically heavier than the whole organism (Degens et al., 1968b).

Isotopically the kerogen of the North Carolina phosphorite lies within the range for organic matter in Tertiary - Recent marine shelf sediments ($\delta^{13}\text{C}_{\text{PDB}} = -23$ to $-19^\circ/\text{oo}$: Eckelmann et al., 1962; Degens, 1969) and shows no indication of a normal terrestrial input. This directly contradicts the evidence of a significant higher plant contribution noted by Powell et al. (1975: Enclosure 1) in the associated EOM, namely, a high concentration of waxy (C_{23+}) n-paraffins, displaying a strong odd/even carbon number predominance. However, the apparent discrepancy would disappear if the organic matter in question was derived in part from desert and salt marsh vegetation and tropical grasses, a special category of higher plants identified by Smith and Epstein (1971) as having unusually high ^{13}C contents ($\delta^{13}\text{C}_{\text{PDB}} = -19$ to $-6^\circ/\text{oo}$).

The Algerian (P5) and Moroccan (P6) phosphorites are also of low enough rank (H/C atomic ratio >1.2) for their carbon isotopic composition to be essentially unaltered by diagenetic elimination reactions. Their $\delta^{13}\text{C}_{\text{PDB}}$ values (-29.5 and $-27.6^\circ/\text{oo}$, respectively) are typical of most higher plants. Again there appears to be a discrepancy between the

isotopic evidence and the earlier findings of Powell et al. (1975 : Enclosure 1) based on n-alkane distributions, as to the source of the organic matter, although they did recognise a minor contribution from land plants in the case of the Algerian deposit. (Note: the relative lack of C_{23+} n-alkanes in the total alkanes of these and other Upper Palaeozoic - Cainozoic phosphorites may be an artefact of the 'short-cut' asphaltene precipitation procedure employed - see Appendix 1.)

The carbon isotopic values of the Phosphoria kerogens ($\delta^{13}C_{PDB} = -30.4$ to $-28.6^{\circ}/\text{oo}$) coincide with the lighter end of the range (-31 to $-23^{\circ}/\text{oo}$) indicated by Degens (1969, fig. 20) for organic matter in Permian sediments. However, because of the high rank of these kerogens their $\delta^{13}C$ values cannot be used to determine whether they were of predominantly microbial (marine) or higher plant (non-marine) origin (cf. Hoefs, 1973, p. 86).

Extractable organic matter

Like the coexisting kerogen fraction, the EOM in Upper Palaeozoic - Cainozoic phosphorites (Table 4.21a) may be broadly characterized in one of two ways, depending on rank. Low-rank phosphorites (P2-6) have

- 1) a high EOM yield (> 150 mg/g C),
- 2) a low content of saturates ($< 4\%$ EOM), and
- 3) a low saturates/aromatics ratio (mean value, 2.1).

High-rank phosphorites (P7-16) by contrast have

- 1) a low EOM yield (< 100 mg/g C),
 - 2) a high saturates content ($> 15\%$ EOM), and
 - 3) a high saturates/aromatics ratio (mean value, 4.5;
- sample P16 excluded from calculation for the reason outlined below).

The gas chromatograms of the total alkanes (saturates) and the corresponding n-alkane distributions are discussed in Enclosure 1. However, some additional comments can be made. The high proportion of branched and cyclic alkanes (naphthene hump) which is evident in most samples (Enclosure 1, fig. 1) is probably a result of intense anaerobic bacterial reworking of the original planktonic detritus during the pre-lithification phase of diagenesis (Section 3.4). Pr/n-C₁₇ ratios greater than unity (Table 4.21a) are further evidence of such in situ microbial activity. Pr/ph ratios are low (<2). In the high-rank phosphorites this would normally indicate that terrigenous organic matter had been a relatively minor contributor to the depositional environment (Brooks et al., 1969; Powell and McKirdy, 1973b).

The n-alkane distributions of the low-rank phosphorites reach a maximum at either C₁₇₋₁₉ or C₂₃₋₂₅ (or both in the case of the bimodal pattern of the Algerian sample, P5) (Table 4.21a). The former feature is consistent with a microbial origin for the parent organic matter, whereas the latter suggests a land-plant source. In the case of the high-rank Mona Vale and Phosphoria phosphorites, however, the n-alkane maximum occurs at C₂₀₋₂₂. The significance of the n-C₂₂ alkane, where present as a major component, will be considered after discussion of the older suite of phosphorites.

For a sediment of its apparent rank, sample Pl5 clearly has an anomalous n-alkane profile (Enclosure 1, fig. 2). The marked OEP at C₂₇ and C₂₉ is possibly the result of contamination of the outcrop at the sample locality by recent land-plant remains. The unusually high saturates/aromatics ratio of sample Pl6 (Table 4.21a) also suggests contamination of the original sample.

Proterozoic - Lower Palaeozoic phosphorites

Kerogen

In terms of the composition of their insoluble organic matter,

Proterozoic and Lower Palaeozoic phosphorites differ significantly from those of the Permian age and younger. In four of the five phosphorites from which kerogen was isolated (Table 4.22b) the organic matter is rich in hydrogen (Type I), plotting just to the left of the alginite coalification track in Figure 4.22.

The two pelletal phosphorites from the Beetle Creek Formation appear to be relatively unaltered, consistent with an estimated maximum depth of burial of 750 m (Enclosure 1, Table 1) and a normal geothermal gradient. Their H/C atomic ratios (both 1.13) place them at the threshold of oil generation (i.e. early mesodiagenesis: Foscolos et al., 1976). Reflectivity measurements on a vitrinite-like component of kerogen P18 ($\bar{R}_O \text{ max} = 0.4\%$, cf. matrix $\bar{R}_O \text{ max} = 0.2\%$) confirm its comparatively low rank. IR analysis (Table 4.23, Fig. 4.23b) shows both the kerogens to have an aliphatic structure incorporating long alkyl chains (note band at approx. 720 cm^{-1}).

The elemental composition (high atomic H/C, low atomic O/C) of the Beetle Creek phosphorite kerogens indicates a prolific precursor biota (primarily phytoplankton, presumably in association with grazing zooplankton), the lipid-rich remains of which accumulated under strongly reducing conditions. This fits well the sedimentary environment envisaged for the Duchess Embayment of the Georgina Basin during the Middle Cambrian. Russell and Trueman (1971) postulate a shallow marine shelf environment in which bottom topography (carbonate banks) restricted water circulation and this, in concert with high organic productivity and a resultant oxygen deficiency in the water column, led to the deposition and preservation of large volumes of organic matter. The $\delta^{13}\text{C}_{\text{PDB}}$ value (-31.5‰) for sample 75670119 falls outside the range for unmetamorphosed Cambrian - Ordovician limestone (-29.5 to -26‰ ; Degens, 1969, fig. 20). This depletion in ^{13}C may reflect biological recycling, because of restricted water circulation, of ^{12}C -enriched CO_2 derived from the metabolic activity

(respiration) or decay of the algal biota.

Microscopic examination revealed that the bulk of the kerogen in sample Pl8 is comprised of flocculated 'matrix' material of low reflectance. Although Cambrian in age, it also contains (as already mentioned) discrete 'vitrinite' particles (Plate 4.9, fig. 2) that "resemble fragments of some Devonian land plants" (A.J. Kantsler, pers. comm., 1976). This might be dismissed as contamination of the kerogen during sample preparation if it were not for an earlier report (Fleming and Rigby, 1972) of fragments of possible land-plant stems found in the acid-insoluble residue of a phosphorite sample collected from the same formation some 2.4 km north of Mount Murray.

Samples A320/60 and 61 (Tables 4.21b, 4.22b) are slightly phosphatic limestones from the immediate vicinity of Mount Murray where interfingering calcareous and siliceous phosphorites occur. They contain much less organic matter ($\leq 0.1\%$ TOC) than the phosphorites and their kerogen is of a more oxygen-rich, humic composition (Type II-III and Type III). The explanation for this major difference in type of organic matter between phosphorites and associated carbonates in the Beetle Creek Formation may simply lie in the fact that, whereas the phosphorites examined were core material from below the water table, the slightly phosphatic limestones were outcrop samples and therefore from the oxidized surface zone of the deposit. The organic matter in sample A320/61 has obviously been more severely weathered (oxidized) than that in sample A320/60. It is possible, however, that oxidation of the organic matter in samples A320/60 and 61 commenced at the protokerogen stage. According to de Keyser and Cook (1972) the Mount Murray area may have been an elevated carbonate bank environment on which unconsolidated biogenic carbonates were subject to winnowing by more aerated waters. Thus, unless the algal remains were occluded in penecontemporaneous phosphate precipitated at or near the sediment-water interface and thereby protected

from further oxidation, then most of the organic detritus would have been removed, along with fine-grained carbonate, leaving behind ultimately a biopelsparite very much depleted in organic carbon. Any organic matter that remained is likely to have undergone at least partial oxidation.

In terms of elemental composition at least, the Karatau (P19) and Areyonga (P20) kerogens appear to be higher rank equivalents of the Beetle Creek samples, although somewhat richer in sulphur. This is consistent with their inferred maximum depth of burial and tectonic setting (Enclosure 1, Table 1). Their H/C atomic ratios (0.53) indicate maturation to the stage of late mesodiagenesis (i.e. gas-condensate prone: Foscolos et al., 1976).

The pelletal to nodular phosphorites of the Ordovician Stairway Sandstone (represented by samples P17 and 75670147: Tables 4.21b and 4.22b) are a particularly well documented example of phosphorite genesis in which winnowing has played a key role in upgrading what was originally a phosphatic mudstone to a higher grade lag deposit (Cook, 1967). The organic matter in these phosphorites differs markedly, in both concentration ($\leq 0.2\%$ TOC : Table 4.21b) and composition (Type III : Fig. 4.22) from that in the Beetle Creek pelletal phosphorites. Moreover, in apparent contrast to the Beetle Creek Formation, the Stairway phosphorites and associated non-phosphatic sediments have similar TOC values (Table 4.21b). These differences may reflect a more open (i.e. less restricted and less highly reducing) shallow marine environment for the Stairway deposits where winnowing was probably more intense and widespread. Evidence of this is the obvious intraclastic origin of some of the (sandy) phosphate pellets (Cook, 1972) implying not only winnowing but also subsequent reworking of the upgraded phosphorite. Phosphatic ovules, i.e. pellets lacking internal structure, constitute only a minor part of the phosphate in the Stairway Sandstone (Cook, 1972). They are nevertheless important to an understanding of possible post-depositional influences on the organic matter

in that their characteristic outer rims of dark organic-rich phosphate (Cook, 1972, Plate 10, Fig. 1) suggest possible diagenetic outward migration of organic matter.

The Stairway Sandstone at the AP 1 well locality, Amadeus Basin, has an estimated maximum depth of burial of 2500 m (Enclosure 1, Table 1) and has advanced to the early stage of mesodiagenesis, based on $\bar{R}_O \text{ max} = 0.6-0.8\%$ for graptolite fragments in the kerogen of sample 75670146. This is in reasonable agreement with a Type III kerogen H/C atomic ratio of 0.71 for phosphorite Pl7.

Extractable organic matter

Elemental analysis and reflectivity measurements showed that the kerogens of the Proterozoic - Lower Palaeozoic phosphorites range in maturation level from late eodiagenesis (Beetle Creek) through early mesodiagenesis (Stairway) to late mesodiagenesis (Karatau, Areyonga). This increase in rank of the insoluble organic matter is not reflected in any clear or systematic trend in either the yield or composition of the associated EOM (Table 4.21b). The difficulty of discerning any rank-related pattern(s) is compounded by the lack of agreement between the analyses of ostensibly similar phosphorites. There are large discrepancies between the respective values for EOM yield (mg/g C) and percent saturates of phosphorite pairs in the case of both the Beetle Creek Formation (Pl8 and 75670119) and the Stairway Sandstone (Pl7 and 75670147). The saturates values for Pl7 and Pl8 may be anomalously low, however, as a result of the 'short-cut' asphaltene precipitation procedure employed by Powell et al. (1975: Enclosure 1) (see Appendix 1). The low saturates content of A320/61, on the other hand, is consistent with the weathered state of its kerogen (cf. Leythaeuser, 1973).

Comparison of the gas chromatograms of the saturated hydrocarbons

from phosphorites and 'non-phosphorites' in the same formation shows that, in the case of Stairway Sandstone (Fig. 4.24), both are highly naphthenic, whereas in the Beetle Creek Formation (Fig. 4.25) this is true only of the phosphorite. The Beetle Creek samples are carbonates of low rank ($\bar{R}_O \text{ max} = 0.4\%$) and so clay-catalysed cracking reactions cannot account for the high proportion of branched and cyclic hydrocarbons (cf. Eisma and Jurg, 1969). By contrast, the Stairway samples are clay-rich siltstones of a higher rank ($\bar{R}_O \text{ max} = 0.6-0.8\%$) at which catalytic cracking reactions will have commenced as part of the hydrocarbon generation process. Branched and cyclic hydrocarbons are the preferred products of such reactions.

From the above we may conclude that, as in the younger phosphorite suite, a complex total alkane fraction rich in branched and cyclic hydrocarbons (i.e. depleted in n-alkanes) is an original feature of phosphorites. This is almost certainly a direct consequence of high levels of anaerobic bacterial activity in the euxinic environments of primary phosphate precipitation. Another geochemical signature of this bacterial reworking of the mainly phytoplanktonic detritus is a high pr/n-C₁₇ ratio (>1), cf. values of ≤ 1 for 'non-phosphorites' (Table 4.21b). The pr/ph ratios are uniformly low (0.5-1.6) as would be expected in view of the microbial source and marine depositional environment of the organic matter (Powell and McKirdy, 1973b; Lijmbach, 1975).

The n-alkane distributions of the pre-Devonian phosphorites examined range from C₁₅ to C₃₀ with a maximum at either C₂₁ or C₂₂ (Table 4.21b). In the case of the Stairway Sandstone and Beetle Creek Formation, the distributions differ quite distinctly from those of related but less phosphatic sediments (Figs 4.26 and 4.27, respectively). The n-alkane profile of the weathered limestone A320/61 (Fig. 4.27) has been affected by the evaporative loss of its more volatile homologues (C₁₅ to C₂₂) and probably originally resembled that of sample A320/60.

Origin and significance of the n-C₂₂ alkane

The n-C₂₂ alkane is a prominent constituent of the saturated hydrocarbon fraction in many of the phosphorites and phosphatic sediments examined in this study (Table 4.21a, b). In some (viz. P7, 12, 17, 18, 20, 75670147, A320/61) it is the major n-alkane. This is particularly true of the Proterozoic - Lower Palaeozoic samples (Table 4.21b). In others (e.g. Pl5, 75670146), although not the main n-alkane, its concentration is still enhanced (OEP < 1) relative to adjacent n-alkanes in the C₂₀ to C₂₄ range.

Attention has already been drawn (Enclosure 1) to the possibility of a specific biological precursor compound for this hydrocarbon. It is the n-C_{22:6} fatty acid, all-cis-4,7,10,13,16,19-docosahexaenoic acid, found in certain phytoplankton (Ackman et al., 1968; Lee and Loeblich, 1971) and zooplankton (Lee et al., 1971). However the question still remains as to why the n-C₂₂ alkane should so commonly occur in relatively high concentration in phosphatic sediments. Closer examination of

- 1) the plankton biota which populate areas of marine upwelling where at present phosphatic sediments are forming;
- 2) the occurrence and distribution of potential precursors of the n-C₂₂ alkane in these organisms; and
- 3) other key aspects of the phosphate-depositing environment

permits the formulation of an hypothesis to explain why, under certain circumstances, there is an apparent n-C₂₂ alkane-phosphate association. Contamination from polythene sample bags was earlier considered to be a possible source of the n-C₂₂ predominance (Enclosure 1, p. 627). The present work, particularly that on the phosphorites and associated sediments of the Stairway Sandstone (see also Section 6.4), now all but eliminates this possibility.

As mentioned previously, the principal planktonic remains in Recent phosphatic shelf sediments (e.g. off Peru, S.W. Africa) are diatoms (Bacillariophyta), dinoflagellates (Pyrrhophyta), foraminifera (protozoa) and zooplanktonic faecal pellets. Periodic algal blooms at Walvis Bay comprise diatoms (98%) and dinoflagellates (2%) (Boon et al., 1975), although so-called 'red tide' (actually blooms of the dinoflagellate, Gonyaulax polyedra) is known from this and other areas of marine upwelling (P.J. Cook, pers. comm., 1977). According to Morris and Calvert (in press) the waters off Walvis Bay have "a significant, though generally patchy and spasmodic, distribution of zooplankton", mostly copepods. Explicit fossil evidence of such planktonic algae or pelagic crustaceans in ancient phosphorites is generally lacking, although Cook (1976) has reported radiolarians (rhizopod protozoans) in the Cretaceous deposits of Morocco. The same author (in de Keyser and Cook, 1972, p. 75) suggests "upwelling producing 'blooms' of siliceous organisms with an associated abundance of phosphate" to account for the rich Middle Cambrian siliceous phosphorites of the Duchess area, Georgina Basin.

The $C_{22:6}$ fatty acid is an important component of the lipids in photosynthetic dinoflagellates (16-34% of total fatty acids) whereas in photosynthetic diatoms it comprises <1% of the total fatty acids (Lee and Loeblich, 1971). Significantly, the dinoflagellates tend to be richer in total lipids (5-28% dry weight, mean 18%) than do the diatoms (6-13% dry weight, mean 10%). The same fatty acid occurs in certain pelagic marine crustaceans, which is perhaps not surprising in view of their position immediately above phytoplankton in the food chain. Of particular interest is the fact that, in four marine copepods analysed by Lee et al., (1971), the $n-C_{22:6}$ acid occurs in highest concentration (17-49% of fatty acids) in the phospholipid fraction (comprising 8-17% of the total lipids) of the organism. Thus, a possible direct consequence of the sedimentation of zooplankton remains is that both biogenic phosphate and a precursor of

the $n\text{-C}_{22}$ alkane enter the sediment simultaneously. Because the phospholipids serve a structural function in cell membranes they are perhaps more likely than other intracellular lipids to survive bacterial degradation during passage through the water column and early diagenesis. It may also be significant, in view of the well established link between marine phosphate deposition and upwelling of cold, deep waters, that all the planktonic crustaceans in which Lee and coworkers found high levels of phospholipid-bound $\text{C}_{22:6}$ acid were either deep water (> 250 m) or cold water species.

Another potential source of the $n\text{-C}_{22}$ alkane is also to be found in zooplankton. This is the monounsaturated $n\text{-C}_{22:1}$ alcohol, one of two fatty alcohols characteristically present in the wax esters of upper-water calanoid copepods (Sargent, 1977; Morris and Calvert, in press).

Both the postulated precursors are unsaturated compounds with oxygenated functional groups. Formation of the fully saturated $n\text{-C}_{22}$ hydrocarbon presumably involves hydrogenation of the double bond(s) and hydrogenolysis of the alcohol (-OH) or carboxylic acid (-COOH) moieties. Clearly, highly reducing conditions are mandatory if these reactions are to proceed abiologically.

Hence, the necessary conditions for the development of an $n\text{-C}_{22}$ predominance in the normal alkanes of phosphatic marine sediments appear to be

1. Dense dinoflagellate blooms (e.g. red tide) in which algal growth exceeds zooplankton grazing rates; or, alternatively, high zooplankton productivity in surface waters involving predominantly cold water copepods.
2. A steady supply of planktonic remains to the seafloor.
3. A relatively shallow, oxygen-deficient water column which
 - 1) minimizes the oxidative loss of the unsaturated (and therefore labile) precursor compounds,

- 2) preserves an organic-rich substrate, and
- 3) maintains a high concentration of dissolved phosphate in anoxic porewaters below the sediment-water interface.
4. Protection of $n\text{-C}_{22}$ precursors from bacterial degradation.
5. A low input of terrigenous plant and mineral matter.

It should be emphasized that the specific mechanisms by which the $n\text{-C}_{22:6}$ acid is converted to the $n\text{-C}_{22}$ alkane are as yet unknown.

In the phosphorites studied (Table 4.21a, b) an $n\text{-C}_{22}$ predominance is best developed in the phosphorites of the Ordovician Stairway Sandstone. At the author's request, M.R. Walter (BMR) recently examined a petrographic thin section of sample 75670147 for evidence of microfossils. His examination revealed abundant, morphologically intact acritarchs (predominantly acanthomorphs of the Micrhystridium group, and some sphaeromorphs) preserved preferentially in the phosphate cementing quartz grains and in reworked phosphate fragments, but not in oolitic pellets (Plate 4.10). By contrast, microfossils are generally absent in the sparsely phosphatic siltstones (i.e. 'non-phosphorites'), although phosphatic conodont fragments are often abundant.

Although the taxonomic affinities of most acritarchs are obscure, there is general agreement that "they are for the most part the reproductive stages (spores or cysts) of marine planktonic algae", probably related to "one or other of two major groups of planktonic algae - the prasinophyceae (tasmanitids) and the dinophyceae (dinoflagellates)" (Downie, 1973, p. 24). Acritarchs of the Micrhystridium group (such as those found in the Stairway phosphorites) are very similar to cysts of living dinoflagellates.

Cramer and Diez (1974, p. 141) believe that "acritarchs may follow bloom sequences similar to those of dinoflagellates". Indeed, because certain acritarch forms "are good indicators of bloom in lagoons or similar sedimentary basins they are useful to determine source

rocks in subsurface work". It is interesting to note that Cook (1972) favoured a poorly aerated lagoonal setting for the lutites of the middle Stairway Sandstone. The presence of pyrite and organic matter in these lutites suggests a strongly reducing environment.

4.6.4 Summary

1. The organic matter preserved in phosphorites may be of Type I, II or III composition. However, aliphatic (H-rich) Type I kerogens are found only in phosphorites of Proterozoic - Lower Palaeozoic age.
2. Comparison of the elemental composition of kerogen in low-rank (H/C atomic ratio > 1.1 ; $\bar{R}_O \text{ max} < 0.5\%$) and high-rank ($H/C < 0.7$, $\bar{R}_O \text{ max} > 1.0\%$) phosphorites suggests that Type II (but not Type I) organic matter undergoes a liptinite coalification jump during early mesodiagenesis, resulting in a micrinite-like Type III residue depleted in N and (to a lesser extent) S.
3. In low-rank phosphorites, Type II organic matter is richer than Type I in both N and S.
4. Euxinic conditions prevailing during the deposition of phosphate-rich sediments give rise to
 - 1) a high proportion of asphaltic materials in the EOM
 - 2) a complex mixture of predominantly naphthenic alkanes
 - 3) low pr/ph (≤ 1.6) and high pr/n-C₁₇ (≥ 1) ratios
 - 4) kerogens rich in N and S.
5. The total alkane distributions of phosphorites differ markedly (e.g. n-alkane profile, pr/n-C₁₇) from those of associated less phosphatic (but otherwise similar) sediments in the same formation, indicating differences in the source biota.
6. The n-C₂₂ alkane in greater than usual concentration may be a biological marker, indicating input of either dinoflagellate or

cold-water zooplankton (or both) to the depositional environment.

7. Organic geochemical definition of the onset of oil generation in phosphorites, along the lines proposed by Foscolos et al. (1976) for shales, is complicated by the highly asphaltic nature of the original EOM. Nevertheless, low-rank (immature) phosphorites are in general characterized by

- 1) a high EOM yield (>130 mg/g C)
- 2) a low saturates content (<5% EOM)

whereas high-rank (mature) phosphorites have

- 1) a lower EOM yield (<125 mg/g C)
- 2) a higher saturates content (>20% EOM)

8. The composition of the EOM and kerogen in low-rank phosphorites suggests that oils generated in phosphatic source beds will be heavy, asphaltic, N-rich crudes capable of primary migration at an early stage of diagenesis (Enclosure 1).

4.7 STROMATOLITES

Stromatolites are organosedimentary structures produced by sediment trapping, binding and/or precipitating microorganisms, mainly cyanophytes (blue-green algae) (Walter, 1976). They are particularly common in Proterozoic and Lower Palaeozoic carbonate sequences where they frequently constitute the only morphological evidence of former biological activity. Sediments containing finely laminated structures attributed to algal growth occur widely throughout the Amadeus Basin, notably in the Bitter Springs Formation (Gillen and Loves Creek Members), Pinyinna Beds, Boord Formation, Inindia Beds and Pertatataka Formation (Ringwood and Julie Members), all late Proterozoic units; and in the Cambrian Hugh River Shale, Giles Creek Dolomite, Jay Creek Limestone, Shannon Formation and Goyder Formation (Wells et al., 1970; Walter, 1972).

In the present context, it is of interest to establish the concentration and composition of the organic matter preserved in stromatolites for two main reasons:

1. to provide data on the diagenesis of the organic remains of natural assemblages of a specific group of micro-organisms, viz. benthonic blue-green algae; and
2. to assess the hydrocarbon generating potential of stromatolitic carbonates such as are found in the Amadeus Basin.

Accordingly, a suite of 13 Proterozoic and Palaeozoic stromatolitic carbonates was assembled for analysis. Preliminary results of this study have already been reported in McKirdy (1976) (Enclosure 2). This section of the thesis draws on the main findings of that paper and includes discussion of additional work subsequently carried out on the kerogens.

4.7.1 Results

The analytical data presented in Tables 4.24 and 4.25 on the composition of the soluble and insoluble organic fractions, respectively, of the stromatolites have been recast from Enclosure 2 to facilitate comparison with other similar tables in this chapter. Table 4.25 also includes new reflectivity and $\delta^{13}\text{C}$ measurements, whereas Table 4.27 summarizes the results of PHGC analysis of selected kerogens.

4.7.2 Discussion

Extractable Organic Matter

The TOC content of the stromatolites ranges from 0.01% to 0.42%

but is generally very low ($<0.06\%$). The yield of EOM is extremely variable (3-659 mg/g C). The total hydrocarbon contents of the extracts range from 5-65% and, with perhaps two exceptions, appear to be related to the rank of the associated kerogen (as given by H/C atomic ratio). The least altered stromatolite (ST 8, atomic H/C = 0.82: early mesodiagenesis) has the lowest hydrocarbon yield (5% EOM). Those of higher rank (atomic H/C, 0.65-0.23: late mesodiagenesis and telodiagenesis) contain hydrocarbons which generally comprise 44-65% of the EOM. The two exceptions to this pattern (viz. ST 2 and 9, hydrocarbon yield $<40\%$ EOM) are stromatolites associated with sediments which were deposited under very shallow, marginal marine tending to evaporitic, conditions.

The relationship between percentage saturates and kerogen H/C atomic ratio is illustrated in Enclosure 2, figure 4. It shows a broad similarity with the classic Albrecht and Ourisson (1969) curve, suggesting that both parameters are at least partly a function of level of organic maturation.

The total alkane chromatograms are diverse and complex (Enclosure 2, fig. 2) but tend to have two features in common: a high proportion of branched/cyclic alkanes (see prominent naphthene hump), and a low pr/ph ratio (0.4 - 1.1). In any given sample, the n-alkanes occupy a relatively narrow carbon-number range between C_{16} and C_{27} , with a single maximum at C_{18-19} , C_{21} or C_{24-25} (Table 4.24). The maximum of the naphthene hump is generally close to that of n-alkane envelope. Contrary to the impression conveyed by the author in Enclosure 2, this pattern of variation in the saturated hydrocarbons shows no clear-cut relationship with the rank of the sediments in question. Rather, it appears to be more a function of the original mat biota and/or the environment in which they grew. This is borne out by the remarkable similarity between the alkane distributions of stromatolites ST 5 and 13 (Enclosure 2, fig. 2). Both are of the form genus Tungussia and presumably represent

- 1) a similar (or identical?) mat biota, and

- 2) a comparable imbalance between algal production and bacterial consumption (in favour of ST 5).

A lower order of congruence is evident between the saturated hydrocarbons of ?Baicalia f. (ST 13) and Conophyton f. (ST 14). Stratigraphic gradations between these two forms are common, particularly in the Middle Riphean of the Uchur - Maya region, U.S.S.R. (Serebryakov, 1976), implying common elements in their respective microbial ecosystems. The exceptionally high proportion of branched/cyclic alkanes in these two stromatolites may be a legacy of a significant population of photosynthetic bacteria in the actively growing mat, or a high level of non-photosynthetic, saprophytic bacterial activity below the mat surface (cf. Dembicki et al., 1976). An important (although apparently not obligatory) organism in modern Conophyton-like siliceous stromatolites at present growing in the hot springs of Yellowstone National Park is a filamentous photosynthetic bacterium Chloroflexus (Walter et al., 1976).

Kerogen

Elemental composition

On the basis of their elemental composition the stromatolite kerogens listed in Table 4.25 represent a broad spectrum of diagenetic alteration. In terms of equivalent coal rank, they range from sub-bituminous (atomic H/C = 0.82; percent carbon, dry ash-free basis = 72.7%) to the semi-anthracite - anthracite boundary (atomic H/C = 0.10, percent carbon, d.a.f. = 90.9%). The kerogen H/C values for stromatolites ST 4,5,6,7,10 and 13 from the Adelaide Geosyncline appear to decrease systematically with increasing depth of burial (as inferred from regional cross-section in Preiss, 1973), with the exception of ST 9 which has an anomalously high rank (see also below).

The two least altered kerogens (ST 8, 14) may be classified as

humic Type III organic matter (after Tissot et al., 1974), plotting close to the coalification track of vitrinite in Figure 4.28. It is significant that both were isolated from stromatolites which grew in a subtidal environment. By contrast, the remainder are from shallower and presumably more aerated aquatic environments. Not surprisingly, they are enriched in oxygen (allowing for their higher rank) and seemingly analogous to fusinite in coals (Fig. 4.28). In terms of their origin, these kerogens are probably closest to degradofusinite (or oxyfusinite) (Teichmuller, 1975, p. 219) in that they form from algal 'peat' via dehydration and oxidative polymerization reactions resulting from the intermittent desiccation and exposure to the atmosphere of the algal mat. The author's earlier interpretation of this oxygen-rich composition as being a reflection of carbohydrate (and perhaps unsaturated fatty acid)-type precursors (Enclosure 2, p. 184) is probably too simplistic, although there can be little doubt that the mucilaginous secretions (Shearman and Skipwith, 1965) and pectic sheath materials (Oehler, 1976) of blue-green algae have been important progenitors of stromatolite kerogen.

In coals, fusinite and associated macerals of the inertinite group usually have an appreciably higher reflectivity than vitrinite (Type III organic matter) of equivalent rank, "because of a greater degree of aromatization and condensation" (Teichmuller, op. cit., p. 217). This probably accounts for the otherwise anomalously high reflectivities of stromatolite kerogens ST 2 and 10 (Table 4.25).

The classification of sedimentary organic matter proposed by Tissot et al. (1974) does not include fusinite-like kerogens. Therefore, it is necessary to extend their classification by adding a fourth category, herein designated Type IV, to cover such organic matter. A cut-off point (atomic H/C = 0.25) is proposed to separate Type IV kerogens from 'subgraphitic' carbonaceous matter characteristic of the anchizone of burial metamorphism (see Section 4.8.2).

Work by Jackson (1973, 1975) on the spectroscopic (visible and infrared) properties of soluble humic matter in sediments of various ages and depositional environments, revealed secular variations which he tentatively attributed to major evolutionary changes in the pigmentation of the algal ecosystems populating those environments. UV solar radiation was envisaged as the underlying cause. Algal pigments perform such vital functions as mediating photosynthesis, screening out harmful radiation and preventing photo-oxidation. They include chlorophyll a and the phycobilins, all nitrogen-containing compounds, and are quantitatively the next most important part of the lipid fraction of blue-green algae after the fatty acids and associated acyl lipids (Nichols, 1973). Thus, along with amino acids (e.g. in the protein component of sheath mucopolysaccharides), pigments are likely to have been a major source of the nitrogen present in stromatolite kerogens. Because of the inferred relationship between pigment concentration and UV stress (thought to have been particularly important in the early Precambrian before an atmospheric ozone layer had developed: Cloud, 1972), the nitrogen content of such kerogens might be expected to depend, at least in part, on the water depth at which the mat microbiota grew. Theoretically in the absence of an ozone screen, prokaryotic algae lacking protective pigments would be restricted to depths of water greater than 10 m (Berkner and Marshall, 1965). Desiccation of the environment, insofar as it increases the amount of extracellular mucilage secreted to prevent dehydration of the algal colony (Fogg et al., 1973), will also affect the C/N ratio of the resultant kerogen.

In assessing the possible influence of growth environment (specifically, water depth) on the C/N atomic ratio of organic matter preserved in Proterozoic and Palaeozoic stromatolites, only the least altered (either by fusinitization or burial diagenesis) kerogens from the present study have been considered (i.e. those with atomic H/C > 0.45). For the limited number of samples available (Table 4.26) it is evident

that intertidal stromatolites have lower atomic ratios than those from subtidal environments. The latter are likely to require the least protection from incident UV radiation or, alternatively, to produce less protective mucilage. The higher nitrogen content of the more exposed intertidal stromatolites is consistent with higher levels of pigmentation and/or secretion of mucopolysaccharide. Thus although data on many more stromatolites are obviously needed to further test the hypothesis, kerogen C/N atomic ratios do appear to have potential as a geochemical tool in studies of stromatolite palaeoecology.

Carbon isotopic composition

The stable carbon isotopic composition of organic carbon preserved in stromatolites is discussed in Enclosure 2. The kerogen $\delta^{13}\text{C}$ values determined for seven of the stromatolites in Table 4.25 extend over and beyond the complete range ($\delta^{13}\text{C}_{\text{PDB}} = -33.5$ to $-19.9^\circ/\text{oo}$) reported in the literature for photosynthetic organic matter in ancient stromatolitic carbonates. Sample ST 2 ($\delta^{13}\text{C}_{\text{PDB}} = -32.8^\circ/\text{oo}$) is at the light (i.e. ^{13}C -depleted) end of the range and may represent algal growth under conditions of restricted water circulation in which biogenic CO_2 (enriched in ^{12}C) is recycled by the mat organisms. Organic carbon in outer shelf marine shales of similar early Devonian age and comparable high rank: ($\bar{R}_o \text{ max} = 2.3\text{-}5.9\%$) from the Variscan Geosyncline are somewhat less depleted in ^{13}C ($\delta^{13}\text{C}_{\text{PDB}}$ range = -28.9 to $-24.7^\circ/\text{oo}$; mean value = $-27.1^\circ/\text{oo}$; Welte et al., 1975b). The discrepancy between the $\delta^{13}\text{C}_{\text{PDB}}$ values of kerogens ST 9 ($-10.8^\circ/\text{oo}$) and ST 13 ($-24.6^\circ/\text{oo}$), both from Baicalia-type stromatolites in the Skillogalee Dolomite is somewhat puzzling. The author has previously expressed the view (Enclosure 4), that the anomalously heavy isotopic composition of ST 9 may be due to the cumulative effects of

- 1) the evaporitic environment in which the stromatolite grew, and
- 2) subsequent thermal maturation to a subgraphitic rank.

Palaeoecological studies by Preiss (1973) have shown that Baicalia is a cosmopolitan form and so it is quite conceivable that ST 13 may be from a somewhat less emergent non-evaporitic environment (although it is impossible to be certain of this because the exact locality and lithofacies relationships of the sample are not known). It is worth noting, however, that the marked discrepancy between the kerogen $\delta^{13}\text{C}$ values of ST 9 and 13 is paralleled by a significant difference in their respective n-alkane distributions (Table 4.24).

PHGC analysis

The results of PHGC analysis of selected stromatolite kerogens (Table 4.27, Fig. 4.29) generally confirm the differences and/or similarities in their elemental composition (Table 4.25, Fig. 4.28). At the same time the PHGC data shed further light on the basic structure of each kerogen and its capacity to generate petroleum hydrocarbons.

The inter-supratidal stromatolites, ST 1 (crenulate) and ST 2 (linked cumulate) from the Cavan Limestone were collected from outcrops less than 10 m apart along the same stratigraphic section and so must have had the same thermal history. Consequently, the differences in the PHGC products (and elemental composition) of their respective kerogens must stem from differences in precursor microbiotas or their environment of growth (or both). The higher TOC value of stromatolite ST 2 and its lower kerogen O/C atomic ratio both suggest a somewhat less aerated (i.e. less oxidizing) environment which is therefore more conducive to the preservation of algal lipids. This in turn appears to be reflected in the slightly more aliphatic nature of its kerogen PHGC products (n-alkanes = 32.8%, benzene/n-C₁₀ = 1.38). By comparison, kerogen ST 1 is less aliphatic (n-alkanes = 29.8%, benzene/n-C₁₀ =

2.38), although yielding a somewhat higher proportion of long alkyl structures ($n\text{-C}_{10+} = 17.2\%$). It is the latter feature of kerogen ST 1 which seems to account for its higher H/C value.

Presumably because of the more emergent nature of their palaeo-environment, both Cavan stromatolites contain organic matter which is considerably more aromatic (simple aromatics $>14\%$, benzene/ $n\text{-C}_{10} > 1$) than that preserved in two examples of the intertidal stromatolite form, genus Tungussia (see below). Extensive desiccation, oxidation and condensation of the algal remains prior to burial is likely, given the inter-supertidal origin of the Cavan algal limestones (Koluzs, 1972).

The kerogen of ST 7 (Gymnosolen cf. ramsayi, Tapley Hill Formation) plots close to ST 2 in Figure 4.28 and so it is not surprising that their PHGC products should be similar (Table 4.27, Fig. 4.29). Algal growth in a sheltered area, e.g. a quiet pond or lagoon, is envisaged for this stromatolite (M.R. Walter, pers. comm. 1977) in view of its fairly regular lamination and lack of allochthonous detrital sediment.

The marked similarity between Tungussia inna (ST 5) and Tungussia.wilkatanna (ST 10) noted in their alkane chromatograms (Enclosure 2, fig. 2) is also evident from the PHGC analysis of their kerogens (Table 4.27, Fig. 4.29). This similarity manifests itself despite the apparent higher rank of ST 10 (based on its lower H/C atomic ratio) which is consistent with the stratigraphic position of the Skillogalee Dolomite 2-3 km below the Wonoka Formation (ST 5) in the central Flinders Ranges, S.A. (Preiss, 1973). The PHGC products of the Tungussia kerogens are distinguished from the others in Table 4.27 by having

- 1) a higher proportion of n-alkanes (43-50%),
- 2) a higher proportion of $n\text{-C}_{10+}$ (26-38%), and
- 3) a lower proportion of simple aromatics (8-10%).

This, in conjunction with their low benzene/ $n\text{-C}_{10}$ ratios (0.5-0.6), indicates an essentially aliphatic structure, surprisingly rich in long

alkyl chains for 'fusinitic' organic matter at such an advanced stage of thermal maturation. Another interesting point to emerge from the PHGC analysis of these two kerogens is the predominance of odd-carbon numbered n-alkanes in the C_{15} to C_{20} range (Table 4.27, Fig. 4.29). This has important implications for the interpretation of the n-alkane profiles of sediment extracts and crude oils derived from blue-green algae.

In terms of its carbon content (90.9% d.a.f.) and H/C atomic ratio (0.10), kerogen in the second stromatolite from the Skillogalee Dolomite (ST 9: Baicalia burra) would appear to be the most altered of those examined. Nonetheless, its thermal history must be equivalent to that of ST 10 (75.3% C d.a.f., atomic H/C = 0.33) because both samples are from the same formation, within 100 m of each other stratigraphically, at the same locality (Depot Creek, S.A.). PHGC analysis shows it to be more aromatic (12.5% simple aromatics) than ST 10 (8.2% simple aromatics) but less so than stromatolites from the Cavan Limestone (ST 1, 2) and Tapley Hill Formation (ST 7). Moreover, its benzene/n- C_{10} ratio is the highest of the samples analysed. Clearly, the composition of this stromatolitic kerogen is highly unusual (cf. its anomalously low $\delta^{13}C$ value discussed earlier). The only feature which unequivocally distinguishes ST 9 from the other stromatolites in the present study is its close association with magnesite conglomerate, evidence of a desiccated evaporitic depositional environment, in the upper member of the Skillogalee Dolomite at Depot Creek (Preiss, 1973).

4.7.3 Summary

1. Stromatolites are of interest to the study of microbial diagenesis because they constitute a relatively unique type of benthonic algal deposit. They have a reasonably well defined precursor biota (mainly cyanophytes, with associated photosynthetic and saprophytic bacteria)

and are formed most commonly in carbonate (and chert) depositing environments.

2. Although the organic matter preserved in stromatolites is autochthonous, it accumulated under aquatic conditions that range from subtidal (maximum depth, approx. 150 m) to supratidal and lacustrine.
3. Water depth and hence the degree of exposure of the stromatolite to oxygenated conditions during and immediately after growth exerts a major influence on the ultimate composition of its kerogen.
4. Subtidal Proterozoic and Lower Palaeozoic stromatolites contain Type III organic matter which appears to be depleted in nitrogen relative to kerogen of equivalent rank in other stromatolites.
5. Stromatolites that grew in inter-supratidal environments contain organic matter (Type IV) which is analogous to degradofusinite in coal.
6. Two varieties of Type IV organic matter can be recognised by PHGC analysis:

- 1) aliphatic (benzene/n-C₁₀ <1, simple aromatics ≤10%)
- 2) aromatic (benzene/n-C₁₀ >1, simple aromatics >14%).

The genetic significance of this is not clear but may be related to the degree of fusinitization that algal remains comprising the dark, organic-rich laminae of the stromatolite undergo during the peat stage of diagenesis. Fusinitization probably involves mainly abiological dehydration, condensation and oxidation reactions, although aerobic bacterial decay may also be important.

7. Because algal remains may acquire a partial aromatic structure during early eodiagenesis, the aromaticity of an algal kerogen is not necessarily a function only of its level of thermal maturation.
8. Although not here analysed by PHGC, kerogens from the subtidal stromatolites (ST 6, 8 and 14) can be expected to have a somewhat more aliphatic structure, consonant with their higher atomic H/C

values (0.82 - 0.49), and hence to possess a greater (although limited) potential to generate liquid hydrocarbons.

9. In algal organic matter deposited in a peritidal environment, the use of H/C atomic ratio as an indicator of diagenetic rank may be misleading. This point is amply demonstrated by the differences in this parameter displayed by separate but stratigraphically closely related stromatolites from the one formation and locality. Certain oxygen-rich kerogens, (atomic O/C > 0.15) may have a greater liquid hydrocarbon generating potential (as measured by percentage n-C₁₀₊ alkanes in PHGC products) than would otherwise be expected from their H/C value.

4.8 OTHER STUDIES

Other work important to the development of the classification of diagenesis outlined in Chapter 5 was undertaken during the course of the thesis project. The results of these individual studies are presented here for the sake of completeness but without discussion, except for a resumé of the major points relevant to the classification. Part of this work has already been published (Enclosures 3 & 4). The remainder will receive fuller treatment elsewhere in due course.

4.8.1 Palaeozoic well sections

Cores from three petroleum exploration wells and one stratigraphic test hole, all of which bottomed in Lower Palaeozoic sediments, were sampled for source-rock analysis. The wells are from three separate intracratonic basins:

Canning Basin: WAPET Roebuck Bay No. 1 (TD 1219 m)

WAPET Kidson No. 1 (TD 4431 m)

Georgina Basin: PAP Netting Fence No. 1 (TD 2032 m)

Arrowie Basin: SADM Yalkalpo No. 2 (TD 799 m)

The locations of the basins and the well localities are shown in Figure 4.30. Recent accounts of the petroleum geology of the Canning, Georgina and Arrowie Basins may be found in Horstmann et al. (1976), Smith (1976) and Wopfner (1970), respectively. The aims of this investigation were

1. to examine both oil-prone and gas-prone sediments of early Palaeozoic age, and, if possible, to characterize each in terms of the following parameters:
 - 1) EOM yield
 - 2) % saturates in EOM
 - 3) % total hydrocarbons in EOM
 - 4) total alkane distribution
 - 5) n-alkane profile
 - 6) kerogen elemental composition; and
2. to relate these compositional variables to other indicators of organic maturity (where available) and present-day formation temperatures.

Roebuck Bay No. 1

This well was drilled as a test of Ordovician sediments on the Broome Arch. It penetrated a sequence of Middle Ordovician - Lower Devonian shallow marine carbonates (Roebuck Dolomite and Thangoo Calcarenite) overlain successively by Lower Permian glacial and marine (e.g. Dora Shale) clastics, Middle - Lower Jurassic deltaic (e.g. Wallal Formation) to marine (e.g. Jarlemai Siltstone) clastics, and finally Lower Cretaceous deltaic sands (J.D. Gorter and V.L. Passmore, pers. comm. 1977; Fig. 4.31). The units sampled and the results of their analysis are given in Tables 4.28 and 4.29.

Outline of major findings

The total alkane chromatograms of cores 8 and 13 (Fig. 4.32) and bimodal n-alkane distributions (Fig. 4.33) reveal that both contain a mixture of marine (algal) and terrigenous (higher plant) organic matter. H/C atomic ratios for their respective Type II-III kerogens (Table 4.29) indicate that maturation has not yet proceeded beyond the stage of very early mesodiagenesis (Foscolos et al., 1976). Consistent with this relative lack of thermal alteration are

- 1) EOM yields in range 50-70 mg/g C
- 2) low pr/ph ratios (2.0-2.6), and
- 3) a strong odd/even predominance in the n-C₂₃₊ alkanes (Table 4.28; Fig. 4.33).

Although of roughly equivalent rank to carbonaceous siltstone (core 13) of the deltaic Wallal Sandstone, the marine Jarlemai Siltstone (core 8) differs in the following important respects:

1. Its kerogen is richer in both hydrogen (atomic H/C = 1.09) and nitrogen (atomic C/N = 13),
2. Its EOM contains a higher proportion of saturated hydrocarbons (24.2%).
3. Hydrocarbons in the C₁₅ - C₂₂ range (max C₁₇) comprise the bulk of the n-alkanes.

These features are interpreted as a direct consequence of the higher primary input of authochthonous marine lipids (algal sapropel) to the depositional environment of the Jarlemai Siltstone. Core 33 (Dora Shale), also a marine siltstone, is marginally more mature than Core 8, as evidenced by

- 1) a lower kerogen H/C value (0.83),
- 2) a diminished odd/even predominance in the C₂₃₊ n-alkanes, and
- 3) a higher proportion of saturates (29.6%) and total hydrocarbons (34.2%) in the EOM.

It has not yet reached the principal phase of oil formation. The C_{22} n-alkane is prominent (OEP = 0.82-0.84) in the n-alkane distributions of both cores 8 and 33. In WAPET Barlee No. 1 (50 km northeast of Roebuck Bay No. 1) the Jarlemai Siltstone is phosphatic (up to 4.2% P_2O_5) over the depth interval 155.4 - 164.6 m (P.J. Cook, pers. comm., 1975; cf. Section 4.6).

A strong predominance of the n- C_{22} alkane (OEP = 0.77-0.88) similarly characterizes the hydrocarbon patterns of the underlying Devonian and Ordovician shallow marine to evaporitic carbonates (cores 44, 47 and 48). Here, however, the n- C_{22} alkane is actually the major saturated hydrocarbon (Fig. 4.32) and the n-alkane distributions are unimodal (Fig. 4.33). In Section 4.6, planktonic dinoflagellates and certain zooplankton were proposed as possible sources of the n- C_{22} alkane. Abundant chitinozoans and acritarchs, including acanthomorphs of the genus Michrystridium (believed to be related to the dinoflagellates, Downie, 1973), have been reported by Combaz and Peniguel (1972) from the Ordovician in several wells adjacent to Roebuck Bay No. 1 on the Broome Arch (Goldwyer No. 1 and Parda No. 1) and further south in the Willara Sub-basin (Willara No. 1 and Samphire Marsh No. 1). These authors noted an abundance of planktonic organic matter in the upper part of the Goldwyer Formation (in part the time-equivalent of the Roebuck Dolomite) and suggested that conditions overlying the Broome Platform at this time were extremely favourable for the development of periodic algal blooms. The low TOC values in the cores examined here may in part reflect a marginal marine tending to evaporitic environment shoreward of the areas of prolific algal growth.

In these Lower Palaeozoic samples there is also (Table 4.28)

- 1) a high EOM yield (185-404 mg/g C),
- 2) a high proportion of both saturates (45-55%), and total hydrocarbons (62-70%) in the EOM,
- 3) lower pr/ph values (0.6-1.1),

- 4) higher $pr/n-C_{17}$ values (0.9-1.4) and
- 5) a prominent peak (possibly the C_{21} isoprenoid alkane) of retention time just greater than $n-C_{19}$ in the chromatograms of cores 44 and 48 (Fig. 4.32).

The values for percentage saturates and total hydrocarbons, if found in shales, would be indicative of the oil generation stage of diagenesis (early meso-diagenesis: Foscolos et al., 1976). The comparatively shallow present depth of burial (within 200 m or so of the maximum palaeodepth: J.D. Gorter, pers. comm., 1976) is apparently compensated for by the early Palaeozoic age of the sediments in question and, the high regional geothermal gradient ($2.7-4.6^{\circ}\text{C/Km}$) on the Broome Arch. This is an area of elevated magnetic basement, where an 'oil-mature' zone is indicated for the Ordovician between present formation temperatures (based on uncorrected logging run data) of 51 and 71°C (Burne and Kantsler, in press). From their study of geothermal aspects of hydrocarbon generation in the Canning Basin, Burne and Kantsler concluded that present formation temperatures in Ordovician sequences of the Broome Arch and Kidson Sub-basin are close to the maximum palaeotemperatures.

Kidson No. 1

This well was drilled on a seismically-defined weak anticlinal closure as a test of Palaeozoic sediments in the southern part of the Kidson Sub-basin (Creevy, 1971). The Palaeozoic section penetrated (Fig. 4.30) ranged in age from Lower Permian to Lower Ordovician. The intervals selected for analysis and the resulting analytical data are set out in Tables 4.30 and 4.31. With one exception (core 7, Tandalgoo Red Beds: aeolian sandstone) all are marine. Of particular interest (in view of the widespread occurrence of barred-basin evaporites in the Amadeus Basin) are the halite, halite and anhydrite-bearing claystones, and dolomitic shales (sabkha deposits) of the

marginal marine Carribuddy Formation (? Silurian - Lower Devonian). In addition, the marine fine-grained clastics of the Ordovician Goldwyer Formation "can be correlated on a microfacies and microfaunal basis" with the Stairway Sandstone of the Amadeus Basin (Creevy, 1971), giving support to the existence of a common Canning - Amadeus Sea during the Ordovician (McTavish and Legg, 1976).

Outline of major findings

Although complete kerogen analyses were not obtained the available data (Table 4.31) for the Kidson well are interpreted as follows:

1. Both the Carribuddy and Goldwyer Formations contain probable Type III organic matter which is presumably the "micrinitized" equivalent of fluorescent sapropelic (Type II) organic matter observed in parts of the same unit in AAP Contention Heights No. 1, some 240 km to the east on the south-eastern extremity of the Broome Arch. Here the sediments in question have been less deeply buried (present depth 920-1789 m) than in Kidson No. 1. The Goldwyer (present depth 1343-1791 m) is at the appropriate stage of maturation for oil generation whereas Carribuddy (present depth 920-1343 m) is reported to be immature and moreover to have an anomalously low rank relative to the overlying Tandalgoo Red Beds. (M. Correia and G. Peniguel, in Australian Aquitaine Petroleum Pty Ltd, 1974).
2. By analogy with the palynology of the Ordovician in Contention Heights No. 1 (Correia and Peniguel, op. cit.) and in various wells on the western margin of the onshore Canning Basin (Combaz and Peniguel, 1972), the main precursors of the organic matter are likely to have been acritarchs (including Micrhystridium sp.), the alga Gloeocapsomorpha prisca (the source of kukersite:

Fig. 4.19) and chitinozoa. Tasmanitid acritarchs are present in the lower part of the Carribuddy Formation in Contention Heights No. 1 (Correia and Peniguel, op. cit.).

Measurements of vitrinite reflectivity on sediments from the upper 1600 m of Kidson No. 1 ($\bar{R}_o$ max = 0.44% at 177 m; 1.00% at 1367 m and 1.09% at 1577 m: A.J. Kantsler, pers. comm., 1976) gave a reflectivity gradient of 0.469% per km which, when extrapolated to total depth, indicates the following values for the samples examined in this study (although see above and below for evidence that cores 15 - 19 may be of somewhat lower rank than predicted here):

cores	2-8	$\bar{R}_o$ max	1.1-1.4%
"	15-22	"	2.0-2.3%

Thus, according to the classification of diagenesis proposed by Foscolos et al. (1976), cores 2-7 are gas-condensate prone (late mesodiagenesis) whereas cores 15-22 are dry gas prone (telodiagenesis). This assessment of the rank regime of the Lower Palaeozoic sequence agrees reasonably well with that predicted from the atomic H/C values (Table 4.31) for kerogens from cores 17 (0.55), 21 (0.50), and 22 (0.58). Present formation temperatures over the interval sampled fall within the range 67-116°C (based on a gradient of 1.7°C/100 m computed from uncorrected logging run temperatures). This compares with an empirically determined oil window of 50-75°C for the Palaeozoic of the Canning Basin (Burne and Kantsler, in press).

Examination of the total alkane chromatograms (Fig. 4.34) provides insight into features of saturated hydrocarbons resulting from the advanced thermal alteration of microbial organic matter in shallow marine Lower Palaeozoic sediments.

Carribuddy Formation Apart from core 15 this evaporitic unit shows little obvious variation with depth. The n-alkanes have a smooth distribution which ranges from C_{14} to C_{28} , with a maximum at C_{17} or C_{19} . Pr/ph values are low (1.6-2.1). Core 15 is unusual in that it has a bimodal n-alkane

distribution (maximum at C_{17} and C_{22}) with a slight predominance of even over odd-carbon-numbered hydrocarbons in the range $C_{18} - C_{25}$, and a considerably higher proportion of C_{23+} homologues. Note also that $pr/n-C_{17} > 1$. These are features of algal organic matter which has undergone extensive reworking by heterotrophic bacteria (Dembicki et al., 1976; Milner et al., 1977); and it is significant that they are still evident at such high rank. Nevertheless, it is pertinent to recall that the rank of organic matter in the same evaporitic interval in Contention Heights No. 1 was depressed relative to the rank trend in the overlying and underlying clastic suites.

Goldwyer Formation The alkane distributions of the three samples from this unit, made up predominantly of marine fine-grained clastics, differ from those of the overlying formation. The smooth n-alkane envelope (range $C_{15} - C_{30}$) has its maximum at a higher carbon number (C_{22}) and includes a higher percentage of C_{23+} homologues (42.9-52.9%).

The predominance of the n- C_{22} alkane (as given by OEP value, Table 4.30) in Palaeozoic marine sediments at Kidson is somewhat less marked than in corresponding sediments at Roebuck Bay, as might be expected in view of the higher rank of the former.

The chromatograms of saturated hydrocarbons from the Kidson well (Fig. 4.34) also indicate a higher proportion of normal (relative to branched/cyclic) alkanes than is the case at Roebuck Bay (Fig. 4.32: note the more pronounced naphthene humps). A comparison of the yield and composition of the EOM in the Carribuddy and Goldwyer Formations is informative. As a whole the evaporitic sediments of the Carribuddy Formation are characterized by

- 1) low TOC yield (0.03-0.50%, mean 0.14%)
- 2) high EOM yield (27-133 mg/g C, mean 97 mg/g C)
- 3) high percentage saturates (43-58% EOM)
- 4) high hydrocarbon content (45-67% EOM)
- 5) high saturates/aromatics ratio (≥ 6)
- 6) low pr/ph ratio (1.6-2.1)

- 7) intermediate pr/n-C₁₇ ratio (0.6-1.1)
- 8) low proportion of long chain n-alkanes (generally <25% C₂₃₊).

On the other hand, the shallow marine fine-grained clastics comprising the Goldwyer Formation have

- 1) higher TOC (0.19-0.26%, mean 0.33%)
- 2) lower EOM yield (<10 mg/g C, with the exception of core 22, an argillaceous sandstone which possibly contains migrated bitumen)
- 3) comparable percentage saturates (48-50% EOM)
- 4) higher hydrocarbon content (70-88%)
- 5) lower saturates/aromatics ratio (≤6)
- 6) lower pr/ph ratio (0.8-1.6)
- 7) comparable pr/n-C₁₇ ratio (0.5-0.8)
- 8) higher proportion of long-chain n-alkanes (43-53% C₂₃₊).

From the foregoing comparison it is concluded that, in carbonate/evaporitic sequences, a favourable environment exists for the preservation and retention of EOM rich in saturated hydrocarbons, past the normal stage of diagenesis at which organic matter in clastics is either expelled or destroyed by cracking processes. The high proportion of straight-chain alkanes common to the saturates fraction of all the Carribuddy extracts suggests that clay-catalysed cracking reactions, which proceed via a carbonium ion mechanism and lead preferentially to branched and cyclic products (Eisma and Jurg, 1969), have not been operative. This may be related to under-compaction, the high thermal conductivity of halite, and/or some other property of thick evaporite sequences which inhibits the expulsion of inter-layer water from expandable clays and hence retards their acquisition of acid properties that normally would enhance the catalytic cracking of hydrocarbons (Foscolos et al., 1976). Conversely, the occurrence of similar hydrocarbon patterns in the underlying argillaceous sediments of the Goldwyer Formation is quite unexpected and no explanation can be advanced here to

account for it.

Netting Fence No. 1

PAP Netting Fence No. 1 is located in the south-eastern Georgina Basin, 3.2 km east of the Queensland/Northern Territory border (Fig. 4.30). It was drilled to investigate the thickest development of Lower Palaeozoic sediments in the area and, in addition, to test for the possible presence of hydrocarbons on the crest of the Netting Fence Anticline, a positive structure within the northwest trending Toko Syncline. A sequence comprising 2010 m of Middle Cambrian - Middle Ordovician carbonates with minor interbedded shales, siltstone and sandstone was encountered overlying (?) Precambrian granite basement (Fig. 4.31). Contact metamorphism was not evident in the basal dolomitic limestone (Mines Administration Pty Ltd, 1965). There are no major erosional breaks within the sequence but at least several hundred metres (and possibly as much as 1200 m) of Ordovician sandstone may have been stripped off by erosion during post-Devonian tectonism (E.C. Druce, pers. comm., 1977). Only two temperatures were measured during logging operations, viz. 50°C at 1142 m (7 hrs after circulation ceased), and 73°C at 2032 m, (3.5 hrs). These gave a gradient of 2.58°C/100 m and a surface intercept of 20°C. Shows of solid or highly viscous bitumens impregnating porous (or fractured) siltstone and carbonate rock, were reported at five separate levels extending over the entire well section.

The 'reservoir bitumen' in cores 3 and 9 occurs within or just above porous zones in sandstones and dolomites, one of which (1072 - 1141 m) flowed fresh water during a drill stem test. An additional aim of the present study therefore was to determine the most likely source of the bitumen and to look for possible effects of flushing and/or biodegradation.

All four core samples analysed in this investigation (Tables 4.32 and 4.33) were taken from dense, fine-grained sediments immediately adjacent

to intervals in which residual bitumen had been observed.

Outline of major findings

EOM yield in the siltstone and shales is variable (16-55 mg/g C), with the highest value being obtained from core 19 (Marqua Beds) at the base of the sequence. Of the two samples from core 9 (Arrinthrunga Formation), one a calcareous shale (0.11% TOC) and the other a limestone (0.10% TOC), the latter yielded the greater amount of extract (89 mg/g C). The yield of total hydrocarbons (saturates and aromatics) showed a more regular increase with depth (8-47 mg/g C), as did percent saturates (18-78% EOM) and the saturates/aromatics ratio (1.4-10.0). These are probably true diagenetic trends (although see below for evidence of supergene alteration in the case of the two non-shale samples). The influence of the clays on the generation of hydrocarbons from kerogen and asphaltenes is reflected in the fact that in the calcareous shale of core 9 hydrocarbons comprise 74.1% of the EOM, whereas in the adjacent limestone most of the extract is made up of non-hydrocarbons (52.5% EOM).

Using EOM yield (mg/g C) and percent saturates in the shale/siltstone samples as a guide to the level of organic maturation, (after Foscolos et al., 1976) only the Marqua Beds (core 19) appear to have reached the stage of intense oil generation (i.e. EOM >50 mg/g C; saturates >50% EOM). In fact, the saturates content of the core 19 extract is unusually high (78% EOM; saturates/aromatics = 10.0). The maturity and high organic carbon content (core 19, 1.30% TOC) of shales in the Marqua Beds identifies them as the probable source of the reservoir bitumen observed higher in the sequence.

The elemental composition of kerogen in core 19 (Table 4.33) is characteristic of Type III (micrinite) organic matter, suggesting that oil generation in these Middle Cambrian shales has involved a liptinite

coalification jump (cf. Section 4.4 and 4.6). Its carbon isotopic composition ($\delta^{13}\text{C}_{\text{PDB}} = -30.3\text{‰}$) appears to be typical of unmetamorphosed organic matter in Cambrian shallow marine sediments of the Georgina Basin (cf. Table 4.22; Enclosure 4).

Total alkane chromatograms (Fig. 4.36) and n-alkane distributions (Fig. 4.37) illustrate differences that arose from the combined effects of

- 1) progressive burial diagenesis,
- 2) migration of oil from the Marqua Beds into porous carbonates, sandstones and siltstones in the overlying formation, and
- 3) invasion of these porous zones by meteoric waters, resulting in water-washing and biodegradation.

In 'oil prone' shales of the Marqua Beds (core 19), the low pr/ph (1.4) and pr/n-C₁₇ (0.4) values, the n-alkane maximum at C₁₅ and the bimodal distribution of naphthenic hydrocarbons, are all features of a marine crude oil (Powell and McKirdy, 1973b; Lijmbach, 1975; Milner et al., 1977). In the overlying Arrinthrunga and Ninmaroo Formations, respectively, limestone (core 9) and dolomitic siltstone (core 3) each contain saturated hydrocarbons (in part migrated) which show signs of partial biodegradation (viz. an enhanced lower molecular weight naphthene hump; a decreased proportion of <C₂₀ n-alkanes; and pr/n-C₁₇ and ph/n-C₁₈ values >1.).

Yalkalpo No. 2

SADM Yalkalpo No. 2 was drilled as a stratigraphic test of Cambrian sediments in the Arrowie Basin 50 km east of Lake Frome, S.A. (Fig. 4.30). The hole is of interest because it penetrated marine sediments, including dark grey limestones probably equivalent to the Cambrian Wilkavillina Limestone (B. Youngs, pers. comm., 1976), in an area of shallow crystalline basement (part of the adjacent Olary Block). The measured

BHT (58°C at 799 m) is consistent with an above average geothermal gradient for the area. The results of analyses of the organic matter in three closely spaced limestone cores (76670016, 687.7 m; 76670018, 715.0 m; and 76670013, 759.0 m) are presented in Tables 4.34 and 4.35. For comparative purposes, also included are data on three other samples of Early and Middle Cambrian carbonates from various localities in the western half of the basin.

Outline of major findings

The Yalkalpo suite illustrates the variability possible in the yield and composition of EOM in fine-grained limestones of fairly uniform lithofacies over a narrow (<75 m) stratigraphic interval. Their EOM yields (22-46 mg/g C) are significantly less than those for other samples in Table 4.34, including A320/32 from the same formation near Brachina Gorge, some 190 km WSW of Yalkalpo No. 2. However, the EOM (102 mg/g C) in this sample, a limestone packed with individual Archaeocyatha that are rimmed or partly filled by black, bituminous material (see Wopfner, 1970, fig. 4), may include migrated hydrocarbons.

The percent saturates values (26.3-33.3% EOM) for the Yalkalpo limestones are comparable with those of other carbonates in the Arrowie Basin and show a slight decrease with increasing depth. The latter feature parallels a progressive loss of lower molecular weight n-alkanes and a consequent shift in the maximum of the n-alkane distribution to higher carbon number (Fig. 4.38), indicating migration of $<C_{20}$ hydrocarbons or their destruction by thermal cracking.

Inspection of the total alkane chromatograms (not shown) also reveals a marked decrease in n-alkanes (relative to branched/cyclic alkanes) with increasing depth over the interval sampled. This is reminiscent of the effect of contact metamorphism on the saturated hydrocarbons in bituminous shales of the McMinn Formation where they overlie an intrusive dolerite

sill at the Sherwin Creek Iron Deposit, McArthur Basin (see Section 4.8.2). Thus a high heat flux from below (rather than heating due to progressive burial) is indicated as the main cause of the organic maturation in the Yalkalpo carbonates.

The predominance of even carbon-numbered n-alkanes (C_{18} , C_{20} and C_{24}) in the sample from 715.0 m (Fig. 4.38) may be an artefact of bacterial activity in the original shallow marine environment (Dembicki et al., 1976). The prominence of $n-C_{22}$ in the n-alkanes of the limestone at 759.0 m is particularly interesting because these core samples at no stage of their recovery and handling came into contact with plastics (a potential contaminative source of $n-C_{22}$ and other saturated hydrocarbons: Douglas and Grantham, 1973). Thus, rapid heating of organic matter in these marine limestones appears to have generated n-alkanes which display an even carbon-number predominance over the range $C_{18} - C_{24}$.

The rank of kerogen in sample 76670018 (atomic H/C = 0.59, Table 4.35) places the Yalkalpo carbonates at the late stage of mesodiagenesis (Foscolos et al., 1976). The corresponding hydrocarbon product capable of being generated from sediments at this rank is gas-condensate. On the basis of the limited data available (Table 4.35), the Yalkalpo kerogen is closest in composition to that from the Moodlatana Formation (A320/40) which plots adjacent to the micrinite evolution pathway on a van Krevelen diagram. Once again, hydrocarbon generation appears to have involved a liptinite coalification jump.

4.8.2 Precambrian carbonaceous shales and cherts

In order to document the behaviour of algal and/or bacterial organic matter in sedimentary rocks during the transition from late stage diagenesis to lower greenschist facies metamorphism, three suites of Precambrian rocks were assembled for analysis. Sediments of such antiquity

were deliberately chosen to ensure that their organic content was entirely free of the remains of higher plants. This is important because in Phanerozoic sediments optical discrimination between algal and land-plant detritus (even where particle - size permits their identification under the microscope) becomes increasingly difficult at advanced levels of coalification.

Collectively the three suites illustrate various aspects of the final stages of the thermal maturation of microbial organic matter before it is ultimately converted to dry gas (CH_4 , CO_2) and graphite.

McMinn Formation, Roper Group, McArthur Basin

The Roper Group, imprecisely dated at between 1300 and 1400 m.y. (McDougall et al., 1965), is the upper succession of the Proterozoic sedimentary sequence in the McArthur Basin, N.T. It comprises an association of mica-rich siltstone, shale and quartz greywacke, alternating with well-sorted quartz sandstone, which was deposited on a broad unstable epicontinental shelf. At Roper River (Fig. 4.39), the Roper Group is up to 1.9 km thick and intruded at several levels by dolerite sills (Dunn, 1963). In this area, the McMinn Formation forms part of the lutite-rich Maiwok Sub-Group. During 1958 it was the major target of test drilling by BHP Company Ltd which resulted in the delineation of two groups of oolitic iron ore deposits (Canavan, 1965). Four members are recognized in the McMinn Formation, of which the Kyalla and Sherwin Ironstone Members are now known to contain abundant and diverse microfossils (Muir et al., in prep.).

Microfossils were first discovered by M.S. Norvick (BMR Palynological File, Note 240, Dec. 1970, unpubl.) in diamond drill core of carbonaceous shale which the author (McKirdy, 1971) was using to study the organic geochemistry of the McMinn Formation. This core material came from the Kyalla Member in the 37 - 50 m interval of DDH U37 drilled in the

Hodgson Downs Iron Deposits (Fig. 4.39). Further core samples were obtained in 1972 and 1975, this time from the Sherwin Iron Deposits (Fig. 4.39), and these have been studied jointly by C.J. Peat, Royal School of Mines, London (palaeontology) and the author (organic geochemistry).

The presence of recognizable microfossils in ancient sediments is thought to depend, among other things, on the lack of metamorphic alteration (Gray and Boucot, 1975). Indeed, low grade metamorphism has been invoked to explain the poor preservation of many Precambrian microfossil assemblages (e.g. Muir and Hall, 1974; Muir and Grant, 1976; Muir et al., 1977). Rarely are morphologically-intact remains of microorganisms found in rocks metamorphosed above lower greenschist facies. To the author's knowledge, however, there has been no previous attempt to rigorously correlate the state of preservation of the microfossils in a Precambrian formation with its degree of incipient metamorphism. Preliminary organic geochemical analysis of both the EOM (Table 4.38) and kerogen (Tables 4.39 - 4.41) in 16 samples of carbonaceous shale from the fossiliferous McMinn Formation has provided quantitative evidence of their stage of diagenesis and incipient metamorphism. Both the Kyalla Member (1 sample) and the Sherwin Ironstone Member (15 samples) have been examined. The latter was sampled at four different stratigraphic levels - 18, 13, 46 and 55 m, respectively - above a dolerite sill in the Sherwin Creek area (Fig. 4.40). Hence, the organic matter in this suite may be expected to show the effects of contact metamorphism. The Kyalla sample comes from the Hodgson Downs locality some 70 km away to the south-southwest where it is less closely associated with intrusive dolerites. Field evidence suggests that at neither locality has the Roper Group been buried by more than 1 km of cover (M.D. Muir and K.A. Plumb, pers. comm., 1975).

Outline of major findings

Kyalla Member, Hodgson Downs Iron Deposits The one sample of carbonaceous shale analysed is characterized by a moderate yield (561 ppm, 44.7 mg/g C) of EOM rich in resins and asphaltenes (64.6%). Saturated hydrocarbons comprise

only 25.3% of the extract. The total alkanes range from C_{12} to C_{26} with a maximum at $n-C_{14}$. The major constituents are n -alkanes (cf. $pr/n-C_{17}$ and $ph/n-C_{18} \ll 1$) in which no preference for odd or even-carbon numbered homologues is evident. Phytane exceeds pristane ($pr/ph < 1$).

The kerogen (glycerine-jelly mount) is pale yellow - brown in colour and includes both structured (e.g. thin translucent sheets) and comminuted amorphous material. No discrete palynomorphs were recognised. Elemental analysis shows it to have a low rank (73.6% C daf), broadly equivalent to that of a high-volatile bituminous coal. On the basis of its atomic H/C and O/C ratios (Table 4.39) it would be classified as a Type II kerogen, plotting close to the liptinite coalification track in Figure 4.43). However, IR (Table 4.40) and PHGC analysis (Table 4.41) reveal a highly aliphatic structure more akin to that of a Type I (alginite) kerogen (cf. Tables 4.18 and 4.19; see also below).

Values of percent saturates (25.3% EOM), H/C atomic ratio (1.17) and reflectivity of vitrinite-like phytoclasts ($\bar{R}_o \text{ max} = 0.8\%$) together suggest that the Kyalla shales at this locality have matured to the stage of early mesodiagenesis (Foscolos et al., 1976) and hence are oil prone (i.e. actively generating petroleum hydrocarbons). The silty nature of these pyritic shales, and the fact that they are interbedded with micaceous siltstone and fine-grained sandstone, amounts to a favourable situation for primary migration (cf. Chapman, 1972; Cordell, 1977).

The stable carbon isotopic composition of the Kyalla kerogen ($\delta^{13}C_{PDB} = -30.2\text{‰}$) falls at the lighter (i.e. more negative) end of the range for unmetamorphosed Precambrian organic matter (-31 to -19‰: Eichmann and Schidlowski, 1975). Lower $\delta^{13}C_{PDB}$ values (between -30 and -40‰) have been reported from Precambrian organic matter (Hoering, 1967; Hoefs and Schidlowski, 1967; Eichmann and Schidlowski, 1974, 1975; Barghoorn et al., 1977) but in most instances these occurrences comprise (at least in part) 'mobilized' organics. The latter are enriched in ^{12}C because during diagenesis

or incipient metamorphism $^{12}\text{C} - ^{12}\text{C}$ bonds rupture more frequently than $^{13}\text{C} - ^{12}\text{C}$ bonds (see Enclosure 4 and references cited therein).

Petrographic examination of the shale in polished section under reflected light confirmed the presence of both a primary alginite component in the kerogen and secondary 'mobilized' organic matter. Indeed, most of the optically recognizable organic matter comprises either long coalified algal filaments or spherical aggregates of thucolite-type material (A.J. Kantsler, pers. comm., 1976: Plates 4.11 and 4.12). The former are preserved as alginite ($\bar{R}_O \text{ max} \approx 0.15\%$) in stringers up to $100\ \mu\text{m}$ in length (but more commonly $20\text{--}30\ \mu\text{m}$ long). Locally this algal material may coalesce to form structurally complex agglomerations (Plate 4.11, fig. 1). Short lengths of filament can be observed merging with 'thucolite' balls (Plate 4.11, fig. 2 and Plate 4.12, fig. 1). The 'thucolite' is present as spheres ($10\text{--}50\ \mu\text{m}$ in diameter) surrounding (?) zircon grains (Plate 4.11, fig. 2 and Plate 4.12). In most cases the organic matter is structureless (Plate 4.12, fig. 2) suggesting an origin from migrating liquid hydrocarbons which have been polymerized by ionizing radiation emanating from the zircons. As is clearly evident in Plate 4.11, figure 2 and Plate 4.12 the reflectance diminishes away from the centre of the sphere, from a maximum of $2.0\text{--}2.2\% \bar{R}_O \text{ max}$ adjacent to the mineral nucleus to about $0.8\text{--}1.0\% \bar{R}_O \text{ max}$ at the rim. In appearance, the thucolite-like carbonaceous matter resembles vitrinite.

Sherwin Ironstone Member, Sherwin Creek Iron Deposits As anticipated this suite of carbonaceous shales and siltstones, by virtue of its proximity to the underlying dolerite sill (Fig. 4.40), shows a contact metamorphic effect. Approaching the sill, there is a progressive increase in level of organic maturation (Tables 4.38 and 4.39). Organic matter at sample level 1 (110% sill thickness above sill contact) is the least affected (lowest rank) whereas that at sample level 4 (37% sill thickness above contact) is the most altered (highest rank), as is highlighted by trends in the following

parameters:

1) EOM yield	level 1	38-56 mg/g C
	2	16-20
	3	7-12
	4	6-9 (29-32)
2) total hydrocarbons	level 1	58-73% EOM
	2	49-69
	3	30-72
	4	27-62 (61-81)
3) saturates	level 1	47-59% EOM
	2	19-42
	3	19-32
	4	12-33 (25-74)
4) kerogen H/C ratio	level 1	0.86
	2	0.65
	3	0.53-0.59
	4	0.36-0.40
5) kerogen C content	level 1	81.2% d.a.f.
	2	81.9
	3	80.7-83.4
	4	85.5-86.8
6) kerogen matrix $\bar{R}_O$ max	level 1	0.47%
	2	0.82
	3	1.07-1.27
	4	1.17
7) kerogen colour	level 1	dark brown
	2	greyish brown
	3	grey brown
	4	brownish grey

The anomalous values (in brackets) for EOM yield, total hydrocarbons and saturates in two samples at sample level 4 (B7/167 and A10/121) indicate that they contain migrated hydrocarbons which presumably originated from shales lower in the sequence (i.e. closer to the upper sill contact).

The impact of contact metamorphism on the total alkane distributions of the shales is illustrated in Figures 4.41 and 4.42. The sequence of events appears to be as follows:

- 1) loss of high molecular weight branched/cyclic alkanes (retention time $> n-C_{20}$), accompanied by a slight decrease in the relative concentration of C_{23+} n-alkanes - between sample levels 1 and 2.
- 2) destruction of normal alkanes by catalytic cracking reactions leading to an increase in the proportion of branched/cyclic alkanes (note 4-5 fold increase in $pr/n-C_{17}$ and $ph/n-C_{18}$ ratios) and a shift in the maximum of the residual n-alkane envelope from $n-C_{21}$ to $n-C_{17-18}$ - between sample levels 2 and 3.
- 3) a further increase in the proportion of branched/cyclic hydrocarbons at the expense of n-alkanes - between sample levels 3 and 4.

The degree of coalification of the kerogen increases towards the sill (as indicated by dry ash-free carbon content, H/C value, $\bar{R}_O$ max and colour), from a rank equivalent to low volatile bituminous coal at level 1 to that of anthracite at level 4. Its composition (Table 4.29, Fig. 4.43) also changes, possibly via a series of coalification jumps, from Type II at level 1, through Type III (vitrinite) at level 2 and Type III (micrinite) at level 3, to Type IV (semifusinite) at level 4 where coking of the dispersed organic matter appears to have taken place.

Systematic changes in the chemical structure of the kerogen are also evident from the IR (Table 4.40) and PHGC (Table 4.41) data. Broadly,

these involve a progressive reduction in the length of aliphatic chains and a loss of alkyl groups, accompanied by the increased condensation and aromatization of the kerogen 'nucleus'. There is a threefold increase in simple aromatics in the PHGC products between level 1 and level 4.

At the levels sampled carbon isotopic fractionation (as a result of contact metamorphism of the kerogen) has been slight ($0.5^{\circ}/\text{oo}$), although in the expected direction, viz. enrichment of the residual kerogen in ^{13}C (see Enclosure 4). Possibly, greater metamorphic adjustment of kerogen $\delta^{13}\text{C}$ values has occurred closer to the sill.

Tindelpina Shale, Uمبرatana Group, Adelaide Geosyncline

The Adelaide Geosyncline is an elongate arcuate belt of folded but generally little altered late Precambrian (Adelaidean) sediments extending from Fleurieu Peninsula in the south, through the Mount Lofty and Flinders Ranges to the Barrier Range in the northeast and the Peake and Denison Ranges in the northwest, over a distance of some 1100 km (Enclosure 3, fig. 1). It represents what was a gently subsiding intracratonic mobile zone in which about 24 km (in total stratigraphic section) of sediments of predominantly shallow-water marine or lagoonal facies accumulated between 1400 and 570 m.y. ago (Thomson, 1969). Within this Precambrian sequence four major cycles of sedimentation are recognized. One of these, the Uمبرatana Group, is notable for its record of two major glacial episodes. Overlying and almost co-extensive with the lower glacials is the Tapley Hill Formation. Throughout the geosyncline the base of this formation is usually delineated by a black shale, the Tindelpina Shale Member. The member is a finely laminated black carbonaceous pyritic shale, with various minor thin sandstone and carbonate interbeds, less than 100 m in total thickness. The unit is a transgressive basinal marine facies comprising organic-rich muds and silts; its deposition was very slow and took place under euxinic conditions in moderately deep

water (Preiss, 1973). The organic matter is concentrated in the darker laminae of the silty shale, along with clays and pyrite and probably constitutes the remains of periodic near-surface blooms of phytoplankton which upon death settled to the bottom where they were partially degraded by anaerobic bacteria before burial.

The southern portion of the geosyncline has been divided into four metamorphic zones (Offler and Fleming, 1968). This zonation, based on the maximum areal distribution of specific index minerals (viz., chlorite, biotite, andalusite-staurolite, and sillimanite) in pelitic rocks, reveals a general increase in metamorphism from chlorite grade along the western front of the Mount Lofty Ranges eastwards into areas of biotite grade and higher. Thus, in view of its high organic content, uniform lithofacies, widespread deposition and inferred variation in metamorphic grade, the Tindelpina Shale appeared to be an ideal subject for a study of the incipient regional metamorphism of marine organic matter within a single formation.

The principal results and conclusions of this work have been reported in McKirdy et al. (1975: Enclosure 3) to which the reader is referred for an extended discussion. A complete compilation of the elemental and isotopic data obtained on 24 kerogens, together with TOC values for the original shales (see Enclosure 3, fig. 2 for sample localities) is presented in Table 4.42. In addition, X-ray diffraction analysis was employed to detect and quantify (Enclosure 3, table 1) the progressive ordering of the kerogen lattice as it approached graphite in both structure and composition. An attempt was made to isolate and analyse the associated EOM in four samples only (Table 4.43).

Outline of major findings

Differences in kerogen structure and composition were correlated with regional variations in illite crystallinity and the magnetic response of

the shale, and used to establish a two-fold metamorphic zonation of the Tindelpina Shale across the Adelaide Geosyncline (see Enclosure 3 for details). As can be seen from Table 4.42, two types of kerogen, subgraphitic and graphitic, were recognised. Each may be characterized in terms of its structure, elemental and carbon isotopic composition, as follows:

1) subgraphitic

structure d_{002} at $I_{\max} = 3.50-3.37 \text{ \AA}$
 $h/w = 1.1-3.5$
 degree of disorder = d_2 and d_{1A}

composition C content = 85-91% d.a.f.
 atomic H/C = 0.23-0.10
 $\delta^{13}\text{C}_{\text{PDB}} = -24.2 \text{ to } -18.8^\circ/\text{oo}$

2) graphitic

structure d_{002} at $I_{\max} = 3.40-3.36 \text{ \AA}$
 $h/w = 6.7-40.2$
 degree of disorder = d_{1A} and d_1

composition C content = 91-98% d.a.f.
 atomic H/C ≤ 0.10
 $\delta^{13}\text{C}_{\text{PDB}} = -17.5 \text{ to } -14.7^\circ/\text{oo}$

The graphitic kerogens are interpreted as higher rank (more metamorphosed) equivalents of the subgraphitic organic matter.

Differences in the yield and composition of the EOM associated with the two kerogen types are less striking:

1. EOM yield is low ($<15 \text{ mg/g C}$) and appears to decrease with increasing rank (as given by H/C value).
2. Hydrocarbons comprise 50-53% of the extract, and saturates 28-39%.

Total alkane chromatograms, presumably representative of the two metamorphic facies, are shown in Figure 4.44 and the corresponding n-alkane distributions in Figure 4.45. The subgraphitic sample has a bimodal naphthene distribution.

In the graphitic sample more intense catalytic cracking of heavier hydrocarbons has enhanced the lower-molecular-weight hump at the expense of heavier branched/cyclic alkanes, and depleted the n-alkanes of C_{23+} kerogens. The subgraphitic and graphitic facies of the Tindelpina Shale correspond with the chlorite and biotite (and higher) zones, respectively, of low-pressure intermediate-type metamorphism previously established (Offler and Fleming, 1968) for the Mount Lofty and Flinders Ranges.

Precambrian cherts

Carbonaceous cherts are of special interest to the study of microbial diagenesis, for several reasons:

1. Fossils of soft-bodied microorganisms, particularly algae and bacteria, are commonly preserved by silica permineralization in primary or early diagenetic chert. Such cherts in Precambrian sedimentary sequences have been a most fruitful source of palaeobiological information (Schopf, 1975; Cloud, 1976).
2. Excellent preservation of cellular detail is possible, permitting recognition of the taxonomic affinities of the microbiota and so also identification of the source of the organic matter, as well as optical monitoring of those parts of the organism that best survive fossilization and diagenesis (Oehler, 1976).
3. According to Jackson and Moore (1976) the 'primary characteristics of kerogen' are better preserved in cherts than in mudstones and carbonates, although the evidence for this (based mainly on C_R/C_T ratios, where C_T is the total carbon in the untreated kerogen and C_R is the residual carbon after pyrolysis under standard conditions) is somewhat equivocal.

Cherts from four Precambrian formations (one late Proterozoic and three Archaean) that have been the subject of previous organic geochemical and/or palaeontological investigations (see references cited below) were selected for further study. The formations are the stromatolitic Skillogalee Dolomite (approx. 800 m.y. old), part of Burra Group, Adelaide Geosyncline (Schopf and Barghoorn, 1969; Dungworth and Schwartz, 1972; Oehler et al., 1972; Preiss, 1973; Schopf and Fairchild, 1973) from the Flinders Ranges, South Australia (Enclosure 4, fig. 1); and the Kromberg, Hooggenoeg and Theespruit Formations of the 12,000 m thick Onverwacht Group (3300-3400 m.y. old), the lowest part of a succession of greenstones and related sediments (the Swaziland 'sequence') on the eastern side of the Kaapvaal Craton (Fig. 4.46) in the Barberton Mountainland, South Africa (Scott et al., 1970; Oehler et al., 1972; Brooks et al., 1973; Dungworth and Schwartz, 1974; Muir and Hall, 1974; Muir and Grant, 1976).

These cherts, by virtue of their age and thermal history, are too old and metamorphosed to have any direct relevance to petroleum genesis per se. Nor perhaps would most black cherts, even at lower rank, in the sense of being source rocks, although fractured cherts and associated siliceous shales and carbonates of the Monterey Formation (Miocene) do constitute a possibly unique source-rock and producing reservoir sequence in the Santa Maria Basin, California (Milner et al., 1977). Results of the elemental and carbon isotopic analysis of the Precambrian cherts (Tables 4.44 and 4.45) are included here to illustrate and further document an apparent major isotopic fractionation effect which occurs during geochemical maturation of algal kerogen beyond a rank equivalent to 91-93% C d.a.f. The possibility of such an isotopic effect, involving preferential loss of ^{12}C , was first recognized by the author after plotting $\delta^{13}\text{C}$ against atomic H/C values for a suite of 23 kerogens from shales (including the Tindelpina Shale: Table 4.42) and carbonates of early Proterozoic to Middle Cambrian age. The finding, and discussion of its possible significance for the interpretation of anomalously

heavy reduced carbon in ancient sediments (e.g. Theespruit Formation: Oehler et al., 1972) was published as McKirdy and Powell (1974: Enclosure 4).

Subsequent work on other pre-Devonian samples, notably the cherts in Tables 4.44 and 4.45 (but see also the relevant earlier sections of Chapter 4), has provided additional isotopic and rank data which support the general conclusions reached in that report. However, some matters of detail require clarification and further comment:

1. An amended version of the original kerogen $\delta^{13}\text{C}$ versus atomic H/C plot (Enclosure 4, fig. 2) is presented in Figure 4.47. It incorporates the new isotopic and rank data from Tables 4.44 and 4.45, together with that for the Precambrian and Cambrian sediments in Tables 4.22, 4.25, 4.33 and 4.39.
2. High ash values in kerogens isolated by HCl/HF acid digestion from cherts commonly give rise to spuriously high H/C atomic ratios (see Table 4.45, footnotes 1 and 2). Support for this assertion comes from
 - 1) comparison of the respective ash and corresponding H/C values for those Onverwacht kerogens which were examined independently by both the author and G. Dungworth (University of Nijmegen), and
 - 2) the fact that H/C and ash values lower than originally reported (Enclosure 4, table 2) were obtained for a second set of kerogens isolated from Hooggenoeg cherts 73325140, 73325141 and 73325144 using a revised procedure to minimize the formation of hydrated fluorosilicates (Kharkhanis, 1977) as artefacts of the acid digestion process.
3. The principal gaseous products of the thermal maturation (coalification) of kerogen are CH_4 and CO_2 . Relative to the parent kerogen, the methane contains more ^{12}C whereas the carbon dioxide is enriched in ^{13}C (Degens, 1969). The $\delta^{13}\text{C}$ value of kerogen seems to change little

with advancing maturation (as indicated by decreasing H/C ratio: Fig. 4.47) until a rank of about $H/C = 0.30$ (equivalent to approx. 86% C d.a.f.) is attained. Up to this point, therefore, methane generation must be balanced by loss of carbon dioxide because there is no significant net alteration to the $^{13}C/^{12}C$ ratio of the residual kerogen. In the rank range $H/C = 0.30-0.15$, however, there is an overall shift in $\delta^{13}C$ towards higher (more positive) values (Fig. 4.47), signifying enrichment of the kerogen in ^{13}C . This trend continues, and becomes most marked in kerogens with H/C values < 0.15 (equivalent to approx. 91% C d.a.f.).

4. For this metamorphic adjustment of $\delta^{13}C$ to proceed, as implied in Enclosure 4, by way of preferential thermal cracking of $^{12}CH_4$ from such hydrogen-deficient organic matter (containing less than 0.3 gram atoms of hydrogen per gram atom of carbon), an external source of hydrogen (e.g. H_2O) is required. Hoefs and Frey (1976) suggest that preferential oxidation of kerogen ^{12}C to CO_2 in the presence of water may be responsible for the observed enrichment of graphitic kerogen in ^{13}C . Hence, the presence of, for example, layer lattice silicates in the form of argillaceous laminae and interbeds may be critical. The apparent lack of metamorphic adjustment of $\delta^{13}C$ in the case of kerogen samples 10-T (Hooggenoeg: $H/C = 0.09$, $\delta^{13}C_{PDB} = -32.1^{\circ}/\text{oo}$) and 12-T (Kromberg: $H/C = 0.17$, $\delta^{13}C_{PDB} = -33.0^{\circ}/\text{oo}$) may indicate the non-availability of an external hydrogen source. Possibly these are examples of 'dry' incipient metamorphism.
5. The generally higher metamorphic grade of the Theespruit cherts (lower Onverwacht Group) as compared with those from the Hooggenoeg and Kromberg Formations (upper Onverwacht Group) was confirmed by XRD analysis of their respective kerogens (Fig. 4.48).

4.9 CONCLUDING REMARKS

The foregoing studies provided the basic data for a geochemical classification of the diagenesis and incipient metamorphism of organic matter derived from microorganisms. This classification is outlined in the next chapter. It attempts to characterize the principal types of microbial organic matter in terms of their respective algal, bacterial and other precursors, and their subsequent thermal alteration during burial. Particular attention is paid to the ability of each type to generate petroleum hydrocarbons.

CHAPTER 5 A CLASSIFICATION OF THE DIAGENESIS AND
 ANCHIMETAMORPHISM OF MICROBIAL ORGANIC MATTER

5.1 Introduction

5.2 Eodiagenesis

5.3 Mesodiagenesis

5.4 Telodiagenesis

5.5 Anchimetamorphism

5.6 Synthesis

5.1 INTRODUCTION

5.1.1 Previous classifications of organic diagenesis

During diagenesis, the organic matter contained in sedimentary rocks, and certain labile minerals such as the layer lattice silicates (clays), undergo transformations caused primarily by prolonged exposure to the elevated temperatures that obtain at depths greater than several hundred metres. The term diagenesis, as used here, encompasses all the physical and chemical changes that occur in a sedimentary rock between its deposition or precipitation as an uncompact sediment (the sedimentogenesis of Kontorovich and Trofimuk, 1976) and its passage into lower greenschist facies metamorphism (the metamorphic epizone of clay mineralogists: Dunoyer de Segonzac, 1970; or the metagenesis of Russian workers). It should be noted that the Russians and Hunt (1974) confine 'diagenesis' to the early burial stage of diagenesis, i.e. to depths less than approximately 1000 m and temperatures below 50°C.

The relation of oil generation to the thermal evolution (or maturation) of dispersed organic matter is now well known. Organic maturation has been divided into a sequence of ordered stages by numerous workers, including Landes (1967), Brooks (1970), Vassoyevich et al. (1970), Shibaoka et al. (1973) and Hood et al. (1975), largely on the basis of certain physical and chemical properties of humic coal (e.g. vitrinite reflectance: see Section 1.2). Therein lies the main reason for the inapplicability (or, at best, only limited applicability) of the resulting classification schemes to Lower Palaeozoic and Proterozoic source rocks. Humic coals and their land-plant precursors do not appear in the geological record until the late Silurian or early Devonian.

Temperature and time

Attempts have been made to place temperature limits on successive phases of the oil generation process. Thus, for example, various temperature estimates have been proposed for the "threshold of intense oil generation", to use Connan's (1974) term. These range from a low 60°C for the Paris Basin (Louis and Tissot, 1967), through 70°C for the Douala Basin (Albrecht and Ourisson, 1969), the generalized values of 80°C (Vassoyevich et al., 1970) and 93°C (Landes, 1967), to the relatively high figures of 115°C and 127°C for the Los Angeles and Ventura Basins, respectively (Philippi, 1965). However, as first pointed out in the coal literature (Huck and Karweil, 1955; Karweil, 1956; Teichmuller and Teichmuller, 1968; Lopatin, 1971; Bostick, 1973) and reiterated most recently by Cornelius (1975) and Hood et al. (1975) in the context of petroleum source-rock studies, both temperature and time are important factors in organic maturation. Hood et al. (1975, p.987) state: "The effect of time is too great to allow the use of maximum temperature alone as a general measure of organic metamorphism". The above spread of values for the threshold temperature of oil generation reflects differences in the age of the source beds, although differences in burial history (rate of subsidence, local geothermal gradient) and the predominant type of organic matter (amorphous sapropel versus humic ligno-cellulose) also contribute.

The time factor in diagenesis becomes more important as the age of the sediments increases. From a statistical analysis of published data on coal rank, type of associated hydrocarbons and present formation temperatures from some twenty sedimentary basins, Cornelius (1975) was able to show that, provided a certain minimum temperature (approx. 50°C: see also Vassoyevich et al., 1970; Hunt, 1974) had been exceeded, time may compensate for temperature in kerogen degradation (i.e. hydrocarbon generation) and liquid hydrocarbon maturation, both processes obeying

the Arrhenius equation. He produced a diagram (reproduced here in simplified form as Fig. 5.1) in which geochronotherms - lines of kerogen and crude oil 'isomaturity' that take account of temperature and time - replace the isotherms of Landes (1967) and Vassoyevich et al. (1970).

Some important general conclusions follow from Cornelius's (1975, pp.30 - 35) treatment of the problem of the thermal and temporal distribution of hydrocarbon phases in sedimentary rocks. They are as follows (see also Figs. 5.1 and 5.2):

1. The importance of time relative to temperature decreases exponentially during the first 60 m.y. of kerogen degradation. In sediments older than 150 m.y., increasing time has little influence on the temperature limits of the 'liquid window' but may lower the temperature of the condensate - dry gas boundary.
2. "The crude oil formation period makes up only approximately 1/3 of the geologic history of certain source rocks. According to the Arrhenius equation degradation in a source rock during this time interval is 27%. This change of concentration can be called the recovery factor of the source rock" (p.35).
3. "Only at temperatures above 135°C is there sufficient energy supplied to initiate the cracking of crude oil, especially of the straight chain hydrocarbons. This point marks the boundary between formation time and cooking time, the latter term here only being used for the gasification period of crude oil formation" (p.35).
4. Although some geologists consider the time of exposure to temperatures at or near the maximum burial temperature (the so-called exposure time) to be the most crucial factor in hydrocarbon generation, "experience has shown that the

liquid phase will not be totally transformed into the gas phase if the exposure time interval of the cooking period is comparatively short" (p.35).

5. "The time intervals during which kerogen is degraded ought to be distinguished from the exposure times: in most cases the geologist can only make an estimation of maximum values from the subsidence curve. The stagnation and uplift phases ('hiati') creating a reduced energy level are mostly beyond recognition: however, they should be subtracted from the period of maximum subsidence, using 'best guess' assumptions" (p.35).

Type of organic matter

The influence of sedimentary facies, particularly the nature of the depositional environment and the primary characteristics of the parent organic matter, on the course of subsequent organic maturation has been either overlooked or ignored by most geologists attempting to subdivide diagenesis and define the principal phase of oil formation. For example, the diagenetic classification of Vassoyevich et al. (1970) does not take into account the possible effects of inherent differences in the composition of the dispersed organic matter. Nevertheless, these workers did recognize four main types or facies - sapropelic (saprite), humic (humite), and mixed (saprohumite and huminosaprite) - and commented (p.1288): "Their chemical differences are fairly considerable, particularly in terms of content of chloroform bituminoids and, therefore, hydrocarbons at different substages of catagenesis".

Tissot et al. (1974) gave a more explicit account of the importance of the kind of sedimentary organic matter undergoing maturation in determining the yield and nature of its hydrocarbon products. Three

major kerogen types were characterized using H/C and O/C atomic ratios and comparative IR analysis. Type I kerogens possess an essentially aliphatic structure, have a high original H/C ratio and a low O/C ratio, and are able to generate abundant oil. With increasing burial, their maturation pathway follows the coalification track of alginite on a van Krevelen diagram. Sediments rich in recognizable algal remains (e.g. lacustrine Botryococcus, marine Tasmanites), and some of the most prolific source rocks in the Middle East, contain disseminated Type I kerogen. Kerogens with a predominantly aromatic structure were designated Type III. They have a high original oxygen content (atomic O/C = 0.2 - 0.3) and a relatively low H/C value, and their maturation pathway is comparable to that of vitrinite. According to Tissot et al. (op. cit., p.500), Type III kerogens "result from abundant contributions from higher plants and terrestrial humic material accumulated in nonmarine or paralic environments". During the early stages of diagenesis they generate mainly CO₂ and H₂O, and subsequently may produce CH₄ but little or no oil. Type II kerogens have a composition intermediate between Type I and III and, during diagenesis, evolve in a manner analogous to the exinite (liptinite) group of coal macerals. The kerogen in Silurian shales of the Sahara was cited as an example of Type II organic matter.

The recent classification of diagenesis proposed by Foscolos et al. (1976) is an advance on earlier schemes in that it supplies quantitative data for key parameters (e.g. EOM yield, hydrocarbon yield, percentage saturates in EOM) at different stages of diagenesis for two of the three main types of kerogen recognized by Tissot et al. (1974). It also uses H/C atomic ratios to define the limits of these stages (corresponding to the successive generation of biogenic methane, oil, gas condensate and dry gas) for each kerogen type.

5.1.2 The present classification

It was the classification scheme of Foscolos et al. (1976) that both guided the interpretation of the results of the individual studies reported in Chapter 4 and provided the model for the present classification.

As they stand, the particular values of the various organic indices used by Foscolos and coworkers are not necessarily valid for Lower Palaeozoic and Proterozoic sediments, for the following reasons:

1. They are based on data derived from the study of shales, mostly Devonian age or younger, and are therefore likely to be strongly influenced by the characteristics (composition, thermal stability, nature of hydrocarbon precursors etc.) of allochthonous continental vegetation.
2. They relate specifically to shales and argillaceous sediments. Carbonates and other sediments were not considered, so that no assessment of the effect of differences in the catalytic activity and thermal conductivity of contrasting source-rock lithologies was possible.
3. No information is included on the EOM associated with Type I kerogens, an important omission in the present context where algae are the major source of the organic matter under consideration.
4. Fusinitic organic matter, which may have a greater hydrocarbon generating potential than previously thought (Section 4.7; Powell et al., 1976), is not covered.

Chapter 4 and the author's contribution to Enclosure 5 (a preliminary study of source rocks in the Larapinta Group, Amadeus Basin) provide some of the additional data required to remedy these deficiencies in what is otherwise a very versatile classification, and to adapt it for use in evaluating the source rock potential of pre-Devonian sediments, including carbonates

and phosphorites as well as shales.

The same three stages of diagenesis, based originally on chemical and mineralogical changes observed by Foscolos et al. (1976) in clay minerals, are recognized here, viz. eodiagenesis (early), mesodiagenesis (middle) and telodiagenesis (late). In addition, the transition from late diagenesis into true metamorphism - the anchizone of Dunoyer de Segonzac (1970) - is defined. This is necessary because

- 1) the 'deadline for gas' appears to roughly correspond to the boundary between telodiagenesis and anchimetamorphism; and
- 2) in very old (>400 m.y.) source/reservoir-rock sequences, the likelihood of overmaturation, and hence the occurrence of dry gas-prone (or barren) rocks, is high.

5.2 EODIAGENESIS

This subdivision of organic diagenesis corresponds to the 'diagenesis' and 'protocatagenesis' of Russian workers (Vassoyevich et al., 1970; Kontorovich and Trofimuk, 1976), and encompasses the 'microbial degradation', 'condensation' and 'organic diagenesis' steps in the fossilization of organic matter described by Hunt (1974). In terms of the host sedimentary sequence, it coincides with the zone in which, under equilibrium conditions, about two-thirds of the original porewater of shales is lost by compaction (Burst, 1969; Perry and Hower, 1972).

5.2.1 Organic processes and reactions

Some of the more important processes that planktonic and benthonic microbial organic matter may undergo during sedimentation and early diagenesis have been discussed in Chapter 4 and are summarized

in Figure 1.1(a). To become incorporated into sediments, biochemical macromolecules ('biopolymers') such as carbohydrates, proteins, pigments and certain lipids must avoid or survive enzymatically-mediated degradation by bacteria and other microorganisms inhabiting the water column and the upper few metres of unconsolidated sediments (Fig. 3.2). Usually biopolymers are at least partially broken down into the 'biomonomers' (sugars, amino acids, fatty acids etc.) from which they were originally synthesized in the living organism. Some of these simple compounds are metabolized or recycled directly by saprophytic bacteria, whereas others condense (e.g. by Maillard - type reactions) to form a range of lipidic and humic complexes ('geopolymers') that are in effect protokerogens. It should be emphasized that, although photosynthetic algae (both planktonic and benthonic) and, to a lesser extent, protozoa and other microscopic crustaceans are the major microbial sources of sedimentary organic matter in aquatic environments, the remains of the degrading bacteria themselves (Fig. 3.2) also contribute significantly to this source material (Davis, 1968; Lijmbach, 1975: see also Chapter 3).

Further burial eventually removes the organic matter from the zone of intense microbiological activity and exposes it instead to progressively higher temperatures. In the temperature range 10 - 50°C, characteristic of eodiagenesis and corresponding to depths of burial of 0 - 1000 m, a number of geochemically important reactions can occur. According to Hunt (1974, p.594), these include "reduction of olefins to saturates, cleavage of the phytol group from chlorophyll, hydrogen disproportionation, aromatization, loss of oxygen, nitrogen and sulfur through formation of CO₂, NH₃, and various sulfur compounds". Decarboxylation of fatty acids begins (Johns and Shimoyama, 1972). However, apart from biogenic methane, minor ethylene and small amounts of gasoline range (C₄ to C₇) hydrocarbons (Hunt, 1975), few other hydrocarbons are actively generated at this stage of diagenesis. The potential geological

significance of so-called low-temperature methane has been discussed by Hedberg (1974). In cold, marine sediments in deep ocean troughs it may form major gas hydrate deposits (Katz, 1971).

5.2.2 Characteristics of extractable organic matter

Liquid hydrocarbons present in the EOM of thermally immature sediments are inherited directly from the lipid fraction of the precursor biota. Because their carbon skeletons have as yet undergone no substantial modification, other than perhaps decarboxylation, and minimal cyclization and aromatization, they are termed biological markers. Examples are odd-carbon-numbered normal alkanes and alkenes in the range C_{15} to C_{35} ; various singly branched and isoprenoid alkanes; and steranes and pentacyclic triterpanes (see Chapter 3; Enclosure 2, fig. 1). Thus, unlike the number and complexity of hydrocarbons in sediments of higher rank and crude oils, the hydrocarbon spectrum of sediments during eodiagenesis is relatively simple and essentially that of living organisms. Low molecular weight aromatic and naphthenic hydrocarbons are notably absent (Hunt, 1974).

The C_{15+} hydrocarbon content of the EOM during eodiagenesis is generally low: saturates <10%, total hydrocarbons (saturates plus aromatics) <20%. These values may be somewhat higher in low rank boghead coals. EOM yield (expressed as mg/g C) is variable but appears to be a function of both the type of organic matter (Table 5.1) and the host rock lithology (Table 5.2). Carbonates generally contain more EOM per gram of organic carbon than do shales; whereas low-rank phosphorites are characterized by anomalously high extract yields (150 - 750 mg/g C), possibly reflecting their euxinic environments of deposition.

5.2.3 Kerogen types

At this early stage of diagenesis, three of the four principal types of microbial kerogen (Table 5.1) become differentiated.

Type I kerogen

Type I organic matter originates only from certain lipid-rich eukaryotic algae (e.g. Botryococcus, Tasmanites) and blooms of prokaryotic algae (planktonic or benthonic cyanophytes), the remains of which accumulated under highly anoxic conditions in stagnant lakes (e.g. Green River Formation oil shale), coastal swamps and lagoons, or in areas of marine upwelling and/or restricted circulation (e.g. Beetle Creek Formation phosphorites). By virtue of their unusual oil-secreting physiology, algae like Botryococcus and the fossil Tasmanites appear to possess appreciable resistance to bacterial decay. In the case of other algae, under favourable conditions complete putrefaction may be inhibited or, alternatively, photosynthetic activity in the overlying aerated waters may be so high that saprophytic bacteria in the anaerobic zone (Fig. 3.2) are unable to keep pace with the input of algal detritus. In such circumstances, original algal structures commonly remain intact (in contrast to true sapropels) and lipids and other related hydrogen-rich cellular components (e.g. proteins, pigments) that would otherwise be readily degraded by bacteria instead survive to become incorporated in the protokerogen.

Type I kerogens are thus analogous to alginite in boghead coals. They have a highly aliphatic chemical structure, as is indicated by their H-rich elemental composition (original $H/C \geq 1.5$, $O/C < 0.15$; Fig. 5.3), IR analysis ($I_{2900}/I_{1600} \geq 1.5$) and the composition of the $C_6 - C_{20}$ PHGC products (benzene/ $n-C_{10} \leq 0.2$, n -alkanes $> 50\%$, $n-C_{10+} \geq 30\%$, simple aromatics $< 5\%$).

The yield of EOM associated with Type I kerogens during eodiagenesis is less than 45 mg/g C. The colour of Type I organic matter is typically greenish - yellow to pale yellow. Under UV light it fluoresces strongly.

Type II kerogen

Type II kerogen of microbial origin, like the less commonly occurring Type I organic matter, belongs to the liptinite group of macerals. Mostly it comprises true algal sapropel, in that the precursor algae do not remain identifiable morphologically. Rather, they are transformed by anaerobic bacteria "partly into amorphous bituminous matter (bituminite), and partly into the aliphatic constituents of vitrinites, particularly the desmocollinites" (Teichmüller, 1975, p.214).

The so-called sapropelization which gives rise to bituminite is a degradative process, but because it takes place under reducing (anoxic) conditions, either in the water column or below the sediment-water interface, the decomposition is somewhat slower and less effective than if it had occurred in the overlying aerobic zone (Fig. 3.2). Thus, a relatively high proportion of algal (and zooplanktonic) biolipids and other bacterially resistant fractions may be preserved, along with the allochthonous remains of aerobic and sulphur-bacteria from the upper levels of the water column and the bodies of the indigenous (anaerobic) saprophytic bacteria (Lijmbach, 1975). ZoBell (1963, p.10) puts it another way: "By a series of reactions involving poorly understood mechanisms, anaerobic bacteria tend to convert organic materials into substances having increased proportions of hydrogen and carbon This they do by selectively removing oxygen and nitrogen from organic compounds, thus producing compounds of more hydrocarbon-like composition."

Type II kerogens have original H/C atomic ratios in the range 1.5 - 1.25 (Fig. 5.3) and relatively low C/N atomic ratios (<35). The latter possibly indicates a high degree of incorporation of bacterial protein into sapropelic kerogens. Available data from IR analysis ($I_{2900}/I_{1600} = 0.2 - 0.5$; $I_{1450}/I_{1600} = 0.1 - 0.3$) and PHGC analysis (benzene/n-C₁₀ = 2 - 3.5; n-alkanes = approx. 40%, n-C₁₀₊ = 18 - 19%, and simple aromatics = 13 - 18% of the C₆ - C₂₀ products) show that bituminites are somewhat less aliphatic in chemical structure than Type I kerogens.

The yield of EOM associated with bituminite appears to depend on host rock lithology and is considerably higher in carbonates (<100 mg/g C) than in shales (<40 mg/g C). In general, low rank Type II organic matter is translucent and pale yellow to amber-yellow in colour. It fluoresces only very weakly but shows a strong increase in fluorescence intensity under extended blue light irradiation (Teichmuller, 1974, 1975).

Type III kerogen

At least two (and probably more) varieties of Type III organic matter (huminite) are generated from microbial sources during eodiagenesis. The first is thought to be analogous to humodetrinite in lignites and brown coals, but arises from the biochemical humification of algal cellulose (not the lignin-based residues of higher plants). Humification is followed by biochemical gelification which produces organic matter similar to detrogelinite (Teichmuller, 1975). As part of the humification and gelification processes, algal carbohydrates and amino acids condense via Maillard-type reactions to form nitrogen-rich humic complexes (Nissenbaum and Kaplan, 1972). Hence, low C/N atomic ratios (<30) are apparently typical of immature Type III kerogens (Table 5.2). In shallow,

aerated carbonate-depositing environments calcium humates (dopplerite) may form as amorphous gels from algal humic acids. Dopplerite is slightly more oxygen-rich than normal algal huminite (Cooper and Murchison, 1969) and plots at the low rank end of the micrinite coalification track (Fig. 5.3). Huminites may also include aliphatic moieties, presumably derived from bacterial lipids (Teichmüller, 1975).

Compared with liptinitic kerogens original humic Type III materials are more aromatic in composition as shown by IR ($I_{2900}/I_{1600} = 0.1 - 0.2$) and PHGC (benzene/n-C₁₀ = approx. 4; simple aromatics = approx. 20% of C₆ - C₂₀ products) data. Accordingly, atomic H/C ratios are lower (1.1 - 0.85) and kerogen colour tends to be somewhat darker. EOM yields are likewise lower than for liptinites, although the same difference between shales and carbonates is evident (Table 5.2).

The reflectivity of algal huminite (which is analogous to the higher plant-derived precursors of vitrinite in lignites and humic brown coals) is low ($\bar{R}_0 \text{ max} \leq 0.5\%$) during eodiagenesis.

Type IV kerogen

During the studies outlined in Chapter 4, no low rank Type IV organic matter was recognised. Indeed, there are good grounds for believing that the precursors of fusinite in algal sediments would be difficult to distinguish, either geochemically or optically, from huminite at the peat stage of diagenesis. That is not to say that these precursors are not present. Microbial residues which might be expected to form recognizable semifusinite and fusinite-like organic matter during late mesodiagenesis are

- 1) partially oxidized algal cellulose and sheath mucilage in algal mats from shallow, intermittently exposed aquatic environments (giving rise to degradofusinite); and

- 2) pectic tissue (e.g. algal and bacterial cell walls) protected from early diagenetic humification by tightly bound and/or impregnated lipids (giving rise to rank fusinite).

5.3 MESODIAGENESIS

The onset of mesodiagenesis (or middle diagenesis) in sediments is marked by the initial generation of liquid hydrocarbons from dispersed organic matter (kerogen plus asphaltenes). Mesodiagenesis, in fact, corresponds to the 'principal phase of oil formation' as defined by Vassoyevich et al. (1970). In the classification scheme proposed by Foscolos et al. (1976), mesodiagenesis is provisionally subdivided into two parts, early and late, which coincide with the first and second stages, respectively, in the loss of interlayer water from expandable clays (Perry and Hower, 1972).

5.3.1 Changes in extractable organic matter

The commencement of significant hydrocarbon generation is evidenced by a sharp increase in the proportion of saturates and total hydrocarbons in the EOM. By late mesodiagenesis saturates may comprise up to 60%, and total hydrocarbons as much as 75%, of the C₁₅₊ extract in shales (Table 5.2). The equivalent maximum value for each parameter in carbonates tends to be somewhat lower, possibly because of the absence of clay catalysts. Where a shale is closely associated with porous sandstone or carbonate containing oil or residual bitumen (e.g. Marqua Beds, Netting Fence No. 1, see Section 4.8.1; Horn Valley Siltstone, East Mereenie No. 1, see Enclosure 4) its hydrocarbon content may be even higher (saturates 72 - 78% of EOM, total hydrocarbon 80 - 87% of EOM).

In such cases expulsion (i.e. primary migration) of hydrocarbons from the shale has been inhibited or, alternatively, is still taking place.

Although the yield of C_{15+} extract and hydrocarbons (expressed as mg/g C) also increases during mesodiagenesis, the maximum values attained are, as noted by Foscolos et al. (1976, p.963), "heavily dependent on the type of parent organic matter". The data assembled during the course of the present work (Table 5.2) confirms this observation and, furthermore, point up the considerable differences that exist between shales and carbonates. In shales hydrogen-rich liptinitic kerogens (Type II) give higher EOM yields than do hydrogen-poor humic kerogens (Type III), a relationship which does not hold true for carbonates (nor, presumably, phosphorites). The reason why carbonates and phosphorites are characterized by much higher EOM yields than shales may lie in the different pathways along which their respective kerogens (Type I & II) evolve during mesodiagenesis (see below).

5.3.2 Kerogen evolution

Type I kerogens which have matured to the stage of early meso-diagenesis have H/C atomic ratios in the range 1.5 - 1.0 and retain a distinctly aliphatic structure ($IR, I_{2900}/I_{1600} = 1.0 - 1.5$; $I_{1450}/I_{1600} = 0.5 - 0.8$; PHGC parameters essentially unchanged from eodiagenesis). Beyond a rank equivalent to atomic H/C = 1.0, Type I kerogens (in this study represented by phosphorites P 19, 20) become chemically indistinguishable from Type III (micrinite) organic matter. This accords with the observations of O.A. Radchenko (as cited by Vassoyevich et al., 1970) who concluded that most of the sapropel (including alginite) in coal is 'volatilized' as the result of a 'carbonization jump' (no doubt equivalent to the first coalification jump of liptinite: Teichmuller, 1974, 1975) during the main period of oil formation; the carbonaceous matter that remains can no longer be identified as sapropel. This would also account

for the position of the Carboniferous boghead coal from Campine, Belgium^{177.} (sample 10) in Fig. 4.19, and may in part explain the otherwise highly anomalous composition of the Tertiary maruhunite of Brazil (sample 9) in the same figure. Both were derived from Type I organic matter.

Depending apparently on the nature of its host rock, Type II (bituminite) kerogen may mature by one of two alternative routes over the rank range, atomic $H/C = 1.25 - 0.5$, corresponding to mesodiagenesis. The first involves continuous evolution along a pathway similar to the coalification track of exinite on a van Krevelen diagram (Fig. 5.3), in the manner documented by Tissot et al. (1974) for Type II kerogens in Jurassic shales of the Paris Basin and Silurian shales of the Sahara. Type II organic matter in shales seems to preferentially follow this route.

The second mode of maturation is exemplified by the bituminite in Tertiary and Mesozoic carbonates at Ashmore Reef (Section 4.4) and, indeed, appears to be characteristic of both carbonates and phosphorites (Section 4.6). Here, the Type II organic matter undergoes what Teichmüller (1974, 1975) terms the first coalification jump of liptinites which, as described in Chapter 4, is a very rapid disproportionation reaction resulting simultaneously in liquid hydrocarbons and Type III (micrinite) organic matter. This maturation pathway is illustrated schematically in Fig. 5.3. Evidence from the Northwest Shelf of W.A. (Section 4.4.5) suggests that hydrocarbon generation from Type II (bituminite) kerogen involving the coalification jump mechanism occurs at a temperature some $10 - 15^{\circ}\text{C}$ lower than the threshold temperature for oil genesis from higher plant-derived Type II starting materials (e.g. sporinite, cutinite) via the widely accepted 'Tissot' evolutionary pathway.

The generalized colour of liptinitic kerogens changes from yellow-orange in early mesodiagenesis to orange-brown during late mesodiagenesis (Table 5.2).

Type III kerogen in the rank range $H/C = 0.85 - 0.5$ has a

dual origin:

- 1) from the 'normal' maturation of original low-rank humic algal residues (i.e. analogous to desmocollinite in coals), and
- 2) as discussed above, from the coalification and associated 'bituminization' (Teichmüller and Teichmüller, 1975) of original Type I and/or Type II organic matter (i.e. analogous to fine-grained rank micrinite in coals).

In petroleum source rock evaluation, particularly in carbonate sequences, it is obviously important to be able to distinguish between the two genetic varieties of Type III kerogen. The first category of Type III kerogen is incapable of generating significant quantities of liquid hydrocarbons, whereas the latter is a co-product of hydrocarbon generation. The EOM associated with original algal huminite is evidently characterized by a unimodal n-alkane distribution, with a maximum between C_{20} and C_{25} (Section 4.4.6).

During late stage mesodiagenesis oxygen-rich Type IV organic matter (analogous to fusinite) first becomes chemically differentiated ($H/C = 0.6 - 0.5$, $O/C = 0.25 - 0.15$: Fig. 5.3) from other humic Type III residues. PHGC analysis of such kerogens in stromatolitic carbonate (Section 4.7) unexpectedly revealed that, notwithstanding their oxygen-rich, fusinitic composition, they may possess a significant liquid hydrocarbon generating potential.

The mean maximum reflectivity in oil ($\bar{R}_O \text{ max}$) of phytoclasts comprising vitrinite-like Type III organic matter (or alternatively, of zooclasts such as graptolite fragments: Enclosure 5) increases regularly during mesodiagenesis and so may be used to define two substages (Table 5.2) that are equivalent to those recognized by Foscolos et al. (1976) on the basis of reflectance values for true vitrinite. Oil is the major product of organic maturation in early mesodiagenesis ($\bar{R}_O \text{ max} = 0.5 - 1.0\%$). It

is formed by the thermal cracking of liquid hydrocarbons from kerogen and the asphaltene component of the EOM. During late mesodiagenesis ($\bar{R}_o \text{ max} = 1.0 - 1.5\%$), as a result of the second loss of interlayer water from mixed layer silicates, the clays in argillaceous sediments acquire more acidic properties and hence facilitate the catalytic cracking of alkyl chains by a carbonium ion mechanism. Branched and cyclic alkanes are the preferred products as demonstrated by the McMinn Formation at Sherwin Creek (Section 4.8.2). Oil is transformed into gas-condensate. Kerogens may acquire a micro-coke texture (Plate 6.1). Kerogen atomic H/C values of approx. 0.5 and reflectivities of about 1.5% for vitrinite-like materials mark the oil deadline (Fig. 5.1).

5.4 TELODIAGENESIS

Telodiagenesis (or late diagenesis) is equivalent to the late mesocatagenesis and early apocatagenesis of Kontorovich and Trofimuk (1976). It is the high temperature 'dry gas zone' of diagenesis. Compared with mesodiagenesis, C_{15+} EOM yields are considerably lower, particularly in shales. The hydrocarbon content of the EOM also shows signs of decreasing from the maximum levels attained during late mesodiagenesis. The associated kerogen is grey-brown to black in colour. Atomic H/C values fall in the range 0.5 - 0.25, and Type II kerogens are no longer distinguishable from Type III. Kerogen phytoclast reflectivities of about $\bar{R}_o \text{ max} = 2.5\%$ and H/C values near 0.25 correspond to the gas deadline, signifying the exhaustion of the kerogen's inherent capacity to generate significant amounts of even methane without an external hydrogen source. It should be remembered, however, that the gas deadline in a commercial or economic sense is also a function of loss of reservoir porosity (which in quartz sandstones is likewise temperature dependent: Maxwell, 1964), and the development of jointing and slaty cleavage which may lead to the loss of

sealing characteristics in shale caprocks (Cornelius, 1975). According to Epstein et al. (1977), the upper thermal limit for commercial dry gas production may be as high as $\bar{R}_O \text{ max} = 3.6\%$.

5.5 ANCHIMETAMORPHISM

Organic matter at the anchizone of metamorphism has an atomic H/C value of between 0.25 and 0.10. XRD analysis reveals the development of an incipient graphite structure (Section 4.8.2). The yield of associated EOM is extremely low and its total hydrocarbon content has diminished to <60% (Table 5.2). Rocks containing such subgraphitic organic matter are normally barren of commercial hydrocarbons.

5.6 SYNTHESIS

The present classification of organic diagenesis is summarized in Table 5.1 and 5.2 and Figures 5.3 - 5.7. It attempts to take into account

- 1) the original (or primary) nature of the organic matter, which is dependent on both the precursor biota (algae - prokaryotic or eukaryotic, bacteria) and the physico-chemical and biochemical processes operating in the depositional environment (e.g. sapropelization, humification, gelification, fusinitization) at the time of sedimentation;
- 2) the degree of thermal alteration that the organic matter has undergone following burial and exposure to elevated temperatures;
- 3) the development of secondary kerogen types (e.g. micrinite) as a result of geothermal coalification; and
- 4) the effect of host rock lithology on the rate, course, and

hydrocarbon products of organic maturation.

The particular importance of this classification is that it makes possible the semiquantitative assessment of the hydrocarbon generating potential of sedimentary organic matter derived from microbial and other non-higher-plant sources. For this reason, it may be applied to sediments laid down prior to the evolution of the first continental floras in the late Silurian and early Devonian.

Tables 5.1 and 5.2 and Figure 5.3, which contain the essential details of the classification, have already been discussed at some length in the preceding sections of this chapter. The following remarks will therefore be addressed to aspects of the classification not yet touched upon.

First, the provisional nature of the classification must be stressed. Some obvious gaps remain and the data on which it is based are spread somewhat unevenly between the various sections of the classification. Similar geochemical data on selected additional samples is required to correct this imbalance. Statistical analysis might then be employed to define more precisely the limits of the successive diagenetic stages for each of the four types of organic matter, in terms of the parameters listed in Table 5.2.

Although the van Krevelen H/C versus O/C diagram (Fig. 5.3) is widely used to determine the type and maturation level of dispersed organic matter, its usefulness is frequently limited by the difficulty of obtaining a reliable value for the O/C atomic ratio. To obviate this problem, an alternative diagram has been prepared (Fig. 5.4) which uses instead the percentage carbon content (dry, ash-free basis) of the kerogen.

The relationship between the two commonly employed rank indicators, kerogen H/C atomic ratio and reflectivity of vitrinite-like phytoclasts is shown in Figure 5.5. Again, because of the extremely small particle size of the kerogen in shales and carbonates, it is frequently impossible to obtain reflectance measurements on discrete phytoclasts $>2\mu\text{m}$ in diameter. In such cases, provided the kerogen is closely packed in the cold-setting resin

mount, an approximate indication of rank may be gained from 'matrix' reflectivities. Examples of such measurements are included in Figure 5.5. The curve for kerogen H/C versus phytoclast $\bar{R}_0$ max appears to comprise two distinct segments. Their intersection (at H/C approx. 0.7, $\bar{R}_0$ max approx. 1.6%) may represent a coalification break at which the reflectivity of liptinites first surpasses that of vitrinite-like organic matter (cf. Teichmuller, 1974; Teichmuller and Teichmuller, 1975).

To this point in the discussion, the stable carbon isotopic composition of microbial kerogens has not been considered. The reason for this is that $\delta^{13}\text{C}$ values are in fact a relatively poor discriminator of kerogen type, although they do display some evidence (Fig. 5.6) of

- 1) early diagenetic alteration (probably due to decarboxylation, involving loss of $^{13}\text{CO}_2$) and
- 2) metamorphic adjustment during telodiagenesis and incipient metamorphism (as discussed in Section 4.8.2) corresponding to cracking of $^{12}\text{CH}_4$ from the kerogen matrix.

Using the isotopic data presented in Chapters 4 and 6, and Enclosure 4, the range and mean values of $\delta^{13}\text{C}_{\text{PDB}}$ were calculated for each of the four principal types of microbial kerogen (plus sub-graphitic and graphitic varieties):

	Range	Mean
Type I (n = 5)	-31.5 to - 23.3 $^{\circ}$ /oo	-27.4 $^{\circ}$ /oo
Type II (n = 18)	-32.5 to - 18.8 $^{\circ}$ /oo	-26.2 $^{\circ}$ /oo
Type III (n = 34)	-32.5 to - 14.7 $^{\circ}$ /oo	-25.7 $^{\circ}$ /oo
Type IV (n = 8)	-32.8 to - 20.9 $^{\circ}$ /oo	-26.4 $^{\circ}$ /oo

	Range	Mean
Sub-graphitic (n = 16)	-33.0 to - 10.8 ⁰ /oo	-24.7 ⁰ /oo
Graphitic (n = 5)	-32.1 to - 14.3 ⁰ /oo	-22.0 ⁰ /oo

Features of sedimentary alkane distribution patterns which appear to be indicative of a microbial source include:

- 1) n-alkane maximum at C₁₇ (blue-green algae), C₂₁ (diatoms) or C₂₂ (dinoflagellates);
- 2) a significant predominance of odd over even-carbon-numbered n-alkanes in the C₁₅ - C₂₀ range (fats of marine microorganisms and invertebrates);
- 3) a slight predominance of even over odd-carbon-numbered n-alkanes in the C₂₀ - C₂₆ range (bacteria);
- 4) low pr/ph ratio (≤ 2); and
- 5) high pr/n-C₁₇, ph/n-C₁₈ ratios (≥ 1) in conjunction with a prominent naphthene hump (bacterial reworking of algal remains).

Finally, it is appropriate to specify those parameters which appear to be the best indicators of hydrocarbon generating potential. They are

- 1) H/C atomic ratio;
- 2) the IR peak intensity ratios, I_{2900}/I_{1600} and I_{1450}/I_{1600} (see Fig. 5.7); and
- 3) the PHGC parameters, benzene/n-C₁₀ and the percentages of n-alkanes and simple aromatics in the C₆ to C₂₀ products.

All relate directly to the hydrogen content of the kerogen, which in turn is dependent on the degree of aromatic condensation of the basic kerogen structure. A supplementary measure of the ultimate liquid hydrocarbon

potential of low rank (immature) carbonates and phosphorites is the non-hydrocarbon content of their EOM.

" it is only by using good basic geological information on the history of a sedimentary basin, together with data on the geochemistry of the organic matter, specifically kerogen, that the true petroleum potential can be determined".

B. Hitchon (1974, p. 519)

PART III - HYDROCARBON GENERATING POTENTIAL OF PROTEROZOIC AND
LOWER PALAEOZOIC SEDIMENTS, AMADEUS BASIN

CHAPTER 6 PETROLEUM SOURCE-ROCK STUDIES, AMADEUS BASIN

6.1 Introductory review

- 6.1.1 Geological setting
- 6.1.2 Oil and gas occurrences
- 6.1.3 Previous geochemical work
- 6.1.4 Some problems

6.2 Proterozoic rocks

- 6.2.1 Mount Charlotte No. 1
- 6.2.2 Erldunda No. 1
- 6.2.3 Ooraminna No. 1
- 6.2.4 Alice Springs No. 3

6.3 Cambrian rocks (Pertaoorrta Group)

- 6.3.1 Mount Charlotte No. 1
- 6.3.2 Highway Anticline No. 1
- 6.3.3 Alice No. 1

6.4 Cambro-Ordovician rocks (Larapinta Group)

- 6.4.1 Pacoota Sandstone
- 6.4.2 Horn Valley Siltstone
- 6.4.3 Stairway Sandstone

6.5 Correlation of reservoir hydrocarbons with source rocks

- 6.5.1 Gas
- 6.5.2 Oil and condensate

6.6 Preliminary regional assessment of hydrocarbon potential

- 6.6.1 Southern area
- 6.6.2 Central folded belt
- 6.6.3 Northern area

6.7 Epilogue

6.1 INTRODUCTORY REVIEW

Despite ample evidence that petroleum generation has occurred in the Amadeus Basin (Fig. 1.3), no systematic geochemical study of the reservoir hydrocarbons themselves, nor of the sediments considered to be their source, has previously been undertaken. This is surprising, particularly in view of the increasingly important role being played by organic geochemistry in the current worldwide search for oil, both onshore and offshore (Welte, 1972; Bailey et al., 1974; Hitchon, 1974; Powell, 1975). Geochemical data on fine-grained sediments containing dispersed organic matter, and oil or gas shows found early in the exploration of a sedimentary basin, can be of considerable help in assessing the amount and type of hydrocarbons present and their likely distribution within the basin. In the case of the Amadeus Basin, insufficient organic geochemical information is available to provide a clear regional picture of source-rock quality, volume and thermal maturity, all essential ingredients of any quantitative estimate of a basin's petroleum potential (McDowell, 1975).

Apart from being an area in which the principal factors that controlled the genesis and present distribution of oil and gas have still to be identified and assessed, there are other aspects of the Amadeus Basin which are of interest to the organic geochemist. It is the only basin in Australia where oil of exclusively marine origin has been discovered. All its known hydrocarbon accumulations and shows are confined to Ordovician and older rocks which antedate the appearance in the geological record of abundant continental floras. Thus their source material cannot have included organic matter derived from land plants which is a major progenitor of younger oils found in other parts of the continent. This probably explains why the composition of the Mereenie crude is unique among Australian oils (Powell and McKirdy, 1972, 1975, 1976). The oldest bituminous sediments in the basin belong to the Bitter Springs Formation (Ranneft, 1963), the

same formation which contains a great variety of stromatolites and several of the world's best preserved and most diverse assemblages of late Precambrian microfossils (Schopf, 1968; Schopf and Blacic, 1971; Walter, 1972). These microbiotas are found in primary carbonaceous chert and provide rare and important clues to the type of organisms that were the earliest precursors of petroleum (Tappan, 1971).

6.1.1 Geological setting

The geology of the Amadeus Basin is described in detail by Wells et al. (1970), and summarized in Wells (1976). Recent outlines of the petroleum geology of the basin have been presented by Devine (1975) and Pearson and Benbow (1976). The following brief account draws heavily on these publications.

The Amadeus Basin is an elongate easterly trending, intracratonic depression, asymmetrical in cross section, which extends for 800 km across the southern part of the Northern Territory and into Western Australia between latitudes 23° and 26° S (Fig. 1.2). It covers an area of about $150,000 \text{ km}^2$ and contains up to 9000 m of mainly Upper Proterozoic and Palaeozoic sediments (Wells et al., 1970). A summary of the stratigraphy is shown in Figure 6.1, together with maximum thicknesses of the individual formations. The basin is bounded on the north and south by igneous and metamorphic rocks of the Arunta Block and the Musgrave-Mann Block, respectively. These Precambrian crystalline rocks for the most part form the basement which slopes northward into a deep trough underlying the Missionary Plain (Froelich and Kreig, 1969). To the east the sedimentary sequence is overlain by Permo-Triassic sediments of the Pedirka Basin, whereas to the west it thins markedly and is obscured by recent sand cover. During the Ordovician, the Amadeus and Canning Basins were probably connected (Cook, in Wells et al., 1970; McTavish and Legg, 1976; see also Section 4.8.1).

Marine sedimentation commenced on a stable epicontinental shelf in late Proterozoic time (probably about 1000 m.y. B.P.) and continued, with local interruptions from at least three diastrophic episodes (Fig. 6.2), until finally terminated by the Rodingan Movement in the Late Ordovician. Depositional environments ranged from periglacial and open marine shelf, through deltaic and lagoonal, to shallow evaporitic. Evidence that conditions of restricted circulation prevailed from time to time is afforded by dark pyritic shales and siltstones (commonly phosphatic), and the thick saline deposits (halite, gypsum, anhydrite) of the Bitter Spring Formation (Proterozoic) and Chandler Limestone (Cambrian).

Proterozoic

The first cycle of marine sedimentation started with the deposition of blanket sands (Heavitree and Dean Quartzites). These were followed, after mild epeirogenic movements, by the equally extensive shallow marine evaporites of the Bitter Springs Formation and equivalent Pinyinna Beds. Wells (in Wells et al., 1970, p. 25) writes:

"The Bitter Springs Formation is characterized by a marked cyclical repetition of beds which represent stages in the restriction of a seaway and in the concentration of soluble salts. The presence of glauconite, phosphate, pyrite and bituminous matter indicates shallow anaerobic conditions ranging from a saline environment in a silled basin to a marine environment. The beds of shale and siltstone ... represent periods when detrital material was introduced. Halite and rhythmic interbeds of anhydrite dolomite and anhydrite were deposited in an initially highly saline sea; the saline deposits were followed by penesaline deposits of fine laminated dolomite and anhydrite (together comprising

the Gillen Member), and finally by marine algal dolomite and fine detrital material (Loves Creek Member)".

Source-rock potential has been ascribed to foetid carbonates (Ranneft, 1963) and black shales (Wells et al., 1970; Pearson and Benbow, 1976) of the Bitter Springs Formation.

The first phase of intracratonic subsidence (Areyonga Movement: Fig. 6.2) served to localize sedimentation. The Areyonga Formation (sandstone-conglomerate-carbonate-phosphorite facies) was deposited in the north, and the Inindia Beds (sandstone-shale-chert-stromatolitic dolomite facies) in the south adjacent to areas of uplift. Both formations accumulated under conditions that ranged from shallow marine (in part euxinic, as indicated by dark pyritic shales and siltstones) to periglacial. The area of greatest sedimentation and subsidence in the southwest and south was separated from a northern shelf area by an east-west hinge line near the centre of the basin (Fig. 6.4). A similar hinge-line (Fig. 6.4) and a second period of late Proterozoic diastrophism (the Souths Range Movement, Fig. 6.2) controlled the deposition of the overlying Pertatataka Formation and Winnall Beds. The thickest deposits (siltstone and sandstone of the predominantly arenaceous Winnall Beds) accumulated in a southern subsiding depression whereas a thinner sequence of lutites and carbonates (Pertatataka Formation) was laid down on a northern shelf. A subsidiary basin developed in the northeast where a thick lobe (1800 m) of Pertatataka Formation includes both algal dolomites and limestones (Julie and Ringwood Members) and diamictites of probable glacial origin (Olympic Member). According to Wells et al., (1970), the basal siltstone of the Winnall Beds was "laid down in slightly stagnant water" (p. 38) whereas the fine-grained clastics of the Pertatataka Formation were "deposited in a predominantly reducing environment under quiet conditions" (p. 41). Dark pyritic silty shales within the Pertatataka sequence were considered by Siller et al. (1963, p. 190) to have "favourable petroleum source rock

characteristics" (see also Ranneft, 1963).

At the close of the Proterozoic or in early Cambrian time, during the Petermann Ranges Orogeny, the southwest portion of the Amadeus Basin was uplifted and overfolded. The intensity of the folding decreased northward and, north of the Proterozoic hinge-line, its effect was almost negligible.

The relationship of the Proterozoic formations is shown schematically in Figure 6.5.

Cambrian (Pertaoorrta Group)

Isostatic uplift of the southwestern margin of the Amadeus Basin following the Petermann Ranges Orogeny shed coarse, continental, clastics into a depression that developed in front of the newly formed mountain ranges. This foredeep was separated by a ridge from the main basin to the north where deltaic sediments (Arumbera Sandstone) were deposited without a major break on the Pertatataka Formation in the east. In the west, the equivalent Eninta Sandstone and Quandong Conglomerate unconformably overlies the Pertatataka Formation (Fig. 6.5). These Lower Cambrian clastic sediments thin noticeably over a north-south structural zone (the Illamurta Diapiric Complex: Cook, 1971) near the centre of the basin (Fig. 6.10). This growth structure had a profound effect on subsequent sedimentation in the northern Amadeus Basin. The existence of two centres of sedimentation in an otherwise long, shallow basin of the embayment type is evident from both the isopachous map (Fig. 6.6), and facies distribution (Fig. 6.7) of the Pertaoorrta Group. Input of detrital sediment was from the west and north, and on its eastern side the basin opened to the sea. In the western sub-basin, the locus of generally coarse clastic sedimentation, deltaic sands of the Cleland Sandstone overlie the marine siltstone dolomite and glauconitic sandstone of the Tempe Formation, and interfinger with a sequence of

paralic to continental redbeds (sandstone, siltstone and shale of the Illara Sandstone, Deception Formation and Petermann Sandstone). In the eastern sub-basin, mainly carbonates, evaporites and lutites were deposited. In the northeast corner of the Amadeus Basin the basal Arumbera Sandstone is overlain successively by carbonate (Todd River Dolomite), evaporites (Chandler Limestone), and penesaline to marine stromatolitic carbonates and siltstones (Shannon Formation and Jay Creek Limestone). The Hugh River Shale comprising apparently non-fossiliferous shales and siltstones straddles the Illamurta structure along the present northern margin of the basin. It is an intermediate or transitional facies, interfingering with paralic coarser clastics to the west and marine carbonates to the east. The top of the Pertaoorrtta Group is marked by the widespread transgressive sands, calcareous silts and interbedded limestones of the Goyder Formation. The unit displays little facies variation across the central structural zone (Fig. 6.7), indicating more uniform subsidence of the basin during early and middle Late Cambrian time. Together the sediments of the Pertaoorrtta Group document two broad cycles of regression and transgression. Like the underlying Proterozoic sediments (Fig. 6.5) they display a complex interdigitation of facies (Fig. 6.7). Extensive marine transgressions took place in the lower Middle Cambrian (Tempe Formation, Giles Creek Dolomite, Jay Creek Limestone) and in the Upper Cambrian (Goyder Formation).

An oil show in the Giles Creek Dolomite, residual hydrocarbons in the Goyder Formation and Jay Creek Limestone, and the black foetid limestones of the Chandler Limestone (Ranneft, 1963; Pearson and Benbow, 1976) are all indicative of the presence of source beds within the Pertaoorrtta Group. To this list of possible source rocks, Wells et al. (1970) added the siltstones and carbonates of the Shannon Formation, Hugh River Shale, Todd River Dolomite and Tempe Formation.

Cambro-Ordovician (Larapinta Group)

The Larapinta Group is of late Cambrian to late Ordovician age and comprises the basal Pacoota Sandstone, overlain successively by the Horn Valley Siltstone, the Stairway Sandstone, the Stokes Siltstone and the Carmichael Sandstone (Fig. 6.1). The subsurface lithology of each formation is described in Enclosure 5. Clastic rocks (sandstone, siltstone and silty shale) predominate. Carbonates are relatively rare. Phosphorites occur sporadically throughout the sequence but are most abundant in the middle and upper units of the Stairway Sandstone (Cook, 1972).

Sedimentation was initially confined to the northern half of the basin where the Pacoota Sandstone was deposited conformably on the Goyder Formation. It is here that the greatest thickness of Larapinta Group sediments (2500 m) is preserved (Fig. 6.8b). During the Ordovician, the shallow epeiric sea spread progressively farther south (Fig. 6.8a) so that in the south and west of the present basin the younger formations of the Larapinta Group unconformably overlie Proterozoic rocks.

The Pacoota Sandstone is a transgressive shallow marine medium to coarse-grained sand with silt and shale interbeds in which four lithological units (in ascending order P4 to P1) are recognized. The shale content of the formation increases upwards. Glauconitic intervals are present in units P2 and P1. The uppermost unit (P1) is highly bioturbated and the shales are generally dark grey to black, and pyritic.

The black, fossiliferous shales, siltstones and minor carbonates of the Horn Valley Siltstone were deposited in a nutrient-rich marine environment which supported a prolific fauna. Cook in Wells et al. (1970, p. 71) states: "The abundance of graptolites suggests that the upper waters were well aerated and able to support a prolific fauna; the lack of indigenous fauna and the extremely good preservation of the numerous fossils suggests euxinic conditions on the sea bottom. The presence of

pyrite also suggests strongly reducing bottom conditions as do the foetid smell, the black colour, and the abundance of organic carbon." Near the close of Horn Valley time a regressive phase of deposition set in. The presence of anhydrite and gypsum in the Palm Valley area indicates development of restricted marine conditions.

Cook (1972) favoured a barrier island-coastal lagoon model for the regressive - transgressive shallow marine environment in which the Stairway Sandstone accumulated. The lower and upper arenites were deposited under higher energy conditions than the intervening lutites for which a poorly aerated lagoonal setting is indicated. The presence of pyrite, organic matter, and phosphorites in the lutites suggests a strongly reducing environment, although more oxidizing conditions prevailed to the southeast where carbonates and redbeds occur.

Shallow marine (intertidal to supratidal) conditions prevailed during the deposition of the Stokes Siltstone. Larapinta Group sedimentation ended with a regressive phase of estuarine or deltaic sedimentation (Carmichael Sandstone). Before the deposition of the overlying aeolian and fluviatile Mereenie Sandstone (Fig. 6.3), extensive uplift and erosion of the eastern half of the basin occurred as a result of the Rodingan Movement (Fig. 6.2).

Geological opinion favours the Horn Valley Siltstone as the main source rock for the large accumulations of hydrocarbons in the Mereenie and Palm Valley fields (see e.g. Froelich and Krieg, 1969; Wells et al., 1970; Devine, 1975; Pearson and Benbow, 1976). Other units in the Larapinta Group to which hydrocarbon source potential has been attributed include the Stokes Siltstone (Ranneft, 1963; Wells et al., 1970) and fine-grained pyritic facies of the Stairway and upper Pacoota Sandstones (Wells et al., 1970; Devine, 1975; Pearson and Benbow, 1976).

Structural evolution

The principal pre-Devonian (late Proterozoic and early Palaeozoic) diastrophic events have been mentioned previously in this discussion and are summarized in Figure 6.2.

The Pertnjara Movement (Fig. 6.2) was a Middle to Upper Devonian upwarping that led to extensive erosion of the Mereenie Sandstone in the central-northern and northeastern parts of the Amadeus Basin. It also initiated the deposition of the Parke Siltstone, the lowermost of three non-marine formations comprising the Pertnjara Group (Figs 6.1 and 6.3; Jones, 1972). The uppermost formation in the group, the Brewer Conglomerate, is restricted to the northern margin of the basin, where it accumulated as a synorogenic wedge of coalescing alluvial fan deposits during uplift associated with the Alice Springs Orogeny. An assemblage of spores recovered from the Undandita Member of the Brewer Conglomerate establishes the age of the main uplift phase of the orogeny as Late Devonian (Playford et al., 1976). The predominantly Early Carboniferous metamorphic events recorded by isotope age datings of rocks in the Arunta Block (Armstrong and Stewart, 1975; Woodford et al., 1975) apparently reflect a later, more northerly deformation.

It was during the Alice Springs Orogeny that the Amadeus Basin acquired most of its present structural expression (Fig. 6.9). Seismic and gravity data from the northern part of the basin indicate that regional folding was facilitated by detachment and plastic flowage within evaporites of the Bitter Springs Formation (Gillen Member) and Chandler Limestone (Froelich and Krieg, 1969). Some structures (e.g. the Goyder Pass Diapir, Fig. 6.10; McNaughton et al., 1968), may have been caused by sedimentary loading and diapirism of the Bitter Springs salt layer (but see Wells, 1976). Others appear to have been the result of thrusting or a combination of thrusting and diapirism. Examples of the latter type of structure include

- 1) the Ringwood Dome, situated in the Ringwood-Olympic Thrust Zone (A.J. Stewart in Wells, 1976),
- 2) the Illamurta Diapiric Complex (Fig. 6.10; Cook, 1971), and
- 3) the Gardiner Range Anticline (Forman, in Wells et al., 1970).

The dominant regional pattern of surface folding is one of broad, flat-bottomed synclines and tight, often asymmetric anticlines. Fold axes describe a gently convex arc parallel to the southern margin of the basin. As stated by Pearson and Benbow (1976, p. 221) the "frequency and amplitude of the folds decreases gradually from south to north, apparently as a function of the thickness of section involved and the depth to the inferred Bitter Springs detachment plane". Crestal stratigraphic convergence and possible gravitational sliding, features consistent with growth during sedimentation, are associated with individual structures in the Goyder structural zone (Fig. 6.10) and the Tyler-Gardiner arch (Fig. 6.9). It is significant that both are transverse structural zones which lie at approximately 90° to the younger folds produced by the Alice Springs Orogeny. The importance of such early Palaeozoic growth structures is, that they "constitute potential primary petroleum traps for hydrocarbons generated at that time" (Pearson and Benbow, 1976, p. 220).

Williams et al. (1965) reported coarse-grained, unusually well sorted reservoir sands in the Pacoota Sandstone along the culmination of the Mereenie anticline, and attributed them to differential submarine winnowing on a palaeotopographic high. The inference of structural growth during deposition of the Pacoota Sandstone is, however, no longer tenable. The latest seismic data "suggests that the present NW-SE Mereenie anticline is a relatively young structure that was not in existence at the time of Pacoota deposition" (D.A. McNaughton, written comm., 1976).

The tectonic history of the Amadeus Basin to the end of the Carboniferous is summarized diagrammatically in Figure 6.11. The horizontal axis represents geological time. The top curve in each diagram shows the

variation in position of the sedimentary surface with respect to sea level. The rate of sedimentation, or erosion is indicated by the slope of the lower curves (representing respectively the base of the Heavitree Quartzite and the Proterozoic/Palaeozoic boundary). The vertical separation of the top and bottom curves at any point along the horizontal axis is a measure of the cumulative thickness of Proterozoic and Palaeozoic sediments deposited at that time. It is apparent from Figure 6.11 that sedimentation was more or less continuous from the Proterozoic through to the end of the Devonian in the north of the basin, but elsewhere was more intermittent, especially in the Palaeozoic. The basin has remained relatively stable since the close of the Alice Springs Orogeny.

6.1.2 Oil and gas occurrences

To date, twenty-five petroleum exploration wells have been drilled in the Amadeus Basin, all on structural targets. The locations of the wells are shown in Figure 1.2. An indication of the wide stratigraphic and geographic distribution of hydrocarbon discoveries and shows within the basin is given in Figure 1.3.

Cambro-Ordovician

In 1963, an oil-saturated core was taken in the lower Stairway Sandstone in the shallow phosphate test hole BMR AP No. 1. This was the first authenticated discovery of crude oil in the subsurface of the Amadeus Basin. Subsequently the hydrocarbon potential of the Ordovician was confirmed by major discoveries of oil and gas at Mereenie in 1964, and gas condensate at Palm Valley in 1965. A brief case history of each field is presented by Pearson and Benbow (1976). The Pacoota Sandstone is the main reservoir formation in both fields, although during testing of the

Palm Valley No. 1 and 2 wells, gas condensate also flowed from the Horn Valley Siltstone and lower Stairway Sandstone. Estimates of oil in place in the Mereenie field range between 300 and 500 million bbls., of which 60 million bbls. is currently thought to be recoverable (Devine, 1975). Combined recoverable reserves of gas and gas liquids for the two fields are 1.9 Tcf and 15 million bbl., respectively. Brown residual hydrocarbons and fluorescence were reported from the Pacoota Sandstone and Horn Valley Siltstone in East Johnny Creek No. 1. Gas shows were recorded from Ordovician rocks in Gosses Bluff No. 1 and West Waterhouse No. 1.

Cambrian

The most significant occurrence of hydrocarbons so far recorded in Cambrian rocks of the Amadeus Basin is the oil and gas which bled from cores taken in the Giles Creek Dolomite during drilling of Alice No. 1. In the same well, and in East Johnny Creek No. 1, residual oil was present in the Goyder Formation. Other wells in which porous Cambrian rocks contained traces of residual hydrocarbons and some fluorescence are Highway Anticline No. 1, James Range "A" No. 1, Waterhouse No. 1 and Ochre Hill No. 1.

Proterozoic

Reference has already been made (Section 1.4) to the minor flow of dry gas recorded during a drill-stem test of the Areyonga Formation (Proterozoic) in Ooraminna No. 1. To the south in Mount Charlotte No. 1, black shales of the Bitter Springs Formation registered small wet gas shows and fluorescence. Traces of black residual bitumen and slight fluorescence were observed in sandstones of the Bitter Springs and Areyonga Formations penetrated by the East Johnny Creek No. 1 well.

6.1.3 Previous geochemical investigations

In what was the first published report to incorporate geochemical data on source rocks in the Amadeus Basin, Siller et al. (1963) presented the results of an analysis of a single core sample of pyritic black shale from the Pertatataka Formation in Ooraminna No. 1. The sample contained 0.94% TOC and 780 ppm EOM, and was considered by Olexcon International of The Hague (who actually performed the analysis) to "represent a commercial oil source rock of a moderate quality".

Most of the early organic geochemical work on sedimentary rocks from the Amadeus Basin, has remained unpublished. Schrayner (1962, unpubl.) examined the extractable organic matter in a sample of limestone from outcrop of the Pertatataka Formation at Alalgara Yard (35 km NW of Henbury homestead), using liquid chromatography. Upon solvent extraction, the sample (0.34% TOC) yielded 96 ppm (or 28 mg/g C) EOM, comprising hydrocarbons, 53.5%, resins, 41.5% and asphaltenes, 2.8%. The hydrocarbons were of low aromaticity (saturates/aromatics ≈ 6) and predominantly paraffinic in character. Schrayner concluded that a substantial portion of the extractable organic matter resembled a low wax, paraffinic crude oil.

In a subsequent study, Schrayner (1963, unpubl.) analysed a suite of 18 outcrop samples for total organic carbon. The results are summarized in Table 6.1. Whereas the carbonates were noted to have near average organic carbon values, the shales were considered to be "too poor in organic matter to be suggestive of good source rocks".

A similar geochemical survey was carried out by Esso Exploration, Australia, Inc. (1965, unpubl.), this time involving core samples of Proterozoic, Cambrian and Ordovician shales from 6 exploration wells (Table 6.2). Although no interpretative comments were appended to the report, it is evident that

- 1) the majority of the samples contained less than the minimum

amount of organic carbon (viz. 0.5% TOC) regarded by Dickey and Hunt (1972) as necessary for a shale to qualify as a potential source rock; and

- 2) the four samples with TOC values $>0.5\%$ (viz., Jay Creek Limestone, Alice No. 1; Pertatataka Formation, Ooraminna No. 1; and Bitter Springs Formation, Mount Charlotte No. 1) yielded very little EOM (<30 mg/g C).

Stevaux et al. (1964, unpubl.) examined twenty samples of black shale from BMR AP 1-4 and reported TOC values for the Stairway Sandstone (0.1-0.7%) and the Horn Valley Siltstone (BMR AP 1 only: 0.4-2.7%). In BMR AP 1 a high yield of EOM characterized the shales from both formations, and their n-alkane distributions (range, C_{17} to C_{32} ; maximum, C_{23} or C_{24}) lacked any predominance of odd or even-carbon-numbered homologues. The authors suggested an algal origin for the organic matter and concluded that the Horn Valley Siltstone was "a possible or even probable" source of the hydrocarbons in the underlying Pacoota Sandstone.

Brooks (1969, unpubl.) determined the concentration and n-alkane profile of the saturated hydrocarbon (total alkane) fraction in each of 14 core samples from the Ordovician - Proterozoic sequence penetrated by Mount Charlotte No. 1. Alkanes were present in highest concentrations in siltstones of the Jay Creek Limestone (core 4, 159 ppm) and dolomite of the Bitter Springs Formation (core 26, 143 ppm); in both cases, the ratio of paraffinic to naphthenic hydrocarbons was low. The maximum of the n-alkane distributions was in the range $C_{17} - C_{19}$ or at C_{22} . A predominance of n- C_{17} and n- C_{19} over the adjacent even-carbon-numbered n-alkanes was evident in core 3 (shale, Stairway Sandstone) and core 4 (siltstone, Jay Creek Limestone) and, to a lesser degree, in cores 16 and 17 (dolomite, Bitter Springs Formation). A predominance of n- C_{22} over the adjacent odd-carbon-numbered homologues characterized cores 3 and 4, cores 5 and 6 (dolomite and shale, respectively, Jay Creek Limestone) and cores 15, 19

and 26 (dolomite, shale and dolomite respectively, Bitter Springs Formation). Brooks considered the hydrocarbons to be derived from the fats of marine algae and bacteria.

In a more recent investigation, Welte et al. (1975a) demonstrated a moderate to good correlation between the Mereenie oil and extractable organic matter in the Horn Valley Siltstone from two wells in the Mereenie field (Table 6.3), on the basis of the similarity in composition of their respective C_{15+} normal and isoprenoid alkanes, and C_{27+} cyclic alkanes. In terms of their carbon isotopic composition, however, the oil-source rock pairs were non-correlative. According to Welte and coworkers, the Horn Valley kerogens have a "somewhat peculiar composition". By comparison with kerogens from younger source rocks examined in the same study, they are unusually rich in non-fluorescent bituminite and vitrinite (although identification of vitrinite in the Horn Valley kerogen is open to question: see Section 6.4, Enclosure 5, and below).

The Mereenie oil (46.9° API gravity) was analysed by Powell and McKirdy (1972, 1975, 1976) and found to be highly paraffinic to paraffinic, low in sulphur (<0.1%) and wax. It has a carbon isotopic composition ($\delta^{13}C_{PDB} = -31.0^{\circ}/\text{oo}$) that is typical of early Palaeozoic marine oils (Section 3.5.3). Its low ratio of pristane to phytane (1.5), and unusual n-alkane distribution, in which the C_{17} and C_{19} homologues are predominant (Enclosure 5, fig. 9), were interpreted by Powell and McKirdy (1972) as indicating an origin from the fats of aquatic microorganisms (cf. Section 3.5.3).

Gas analysis data for the Amadeus Basin have been collated by Konecki and Blair (1970).

6.1.4 Some problems

Taken as a whole the previous organic geochemical studies of fine-grained sediments and reservoir hydrocarbons in the Amadeus Basin (Section 6.1.3) afford, at best, only a very sketchy picture of the source-rock potential of the sediments, and provide no explicit information on their thermal history and present maturation level.

Although the Horn Valley Siltstone (Ordovician) is probably the main source formation for the hydrocarbons in the Mereenie and Palm Valley fields, other sources (particularly within the Stairway Sandstone) may also have been present in the Larapinta Group. In addition, the various fine-grained units in the underlying Cambrian and Proterozoic sequences may have had some potential as source rocks. If so, are they more likely to have been generative of gas or liquids? Thus, one of the tasks of a regional source-rock study of the Amadeus Basin would be to determine the organic richness and maturation level of the individual formations comprising the Proterozoic - Ordovician sedimentary sequence. Other important aspects of the formation of oil and gas in the Amadeus Basin are still only poorly known or understood. They include

- 1) the composition and origin of the precursor organic matter;
- 2) the temperature of initial oil generation;
- 3) the timing of primary migration in relation to trap formation and the destruction of reservoir porosity;
- 4) the role of maturation (and other in situ alteration processes) in determining the type of hydrocarbons found in the major reservoirs; and
- 5) the location and extent of immature, oil-prone, gas-prone and barren areas.

As it happens, all these topics are amenable to organic geochemical

investigation, in that each relates in some way to the diagenesis of organic matter dispersed in either non-reservoir or reservoir rocks. Taken together they illustrate both the nature and scope of the problem being tackled in this part of the thesis study.

For the Amadeus Basin it is a reasonable assumption that terrestrial plant material is not a variable in the 'source rock - crude oil' equation. However, because marine organisms are therefore the only available progenitors of sedimentary organic matter of Proterozoic - early Palaeozoic age, it does not necessarily follow that the source material for petroleum hydrocarbons was completely homogeneous or uniform in composition. If, for example, consistent geochemical differences were to be found between the organic contents of the main marine lithofacies in the basin, this may reflect differences in the biota, the level of bacterial activity, or other physical and chemical properties of the unconsolidated sediment and the environment in which it was deposited. Several related questions then arise:

1. How does the organic matter preserved in non-clastic sediments (e.g. the carbonates and evaporites of the Bitter Springs Formation and the Pertaoorrtta Group; and the phosphorites of the Areyonga Formation and the Stairway Sandstone) compare with that in shales and siltstones throughout the section in terms of composition and hydrocarbon-generating capability?
2. If the Mereenie oil has a marine origin, why is it so highly paraffinic (and not naphthenic-aromatic)?
3. Why does a marked predominance of odd over even-carbon-numbered n-alkanes in the C_{10} - C_{20} range appear to characterize the Mereenie crude (Powell and McKirdy, 1972) and other pre-Silurian oils (Martin et al., 1963; Williams, 1974; Kontorovich et al., 1974) in view of their great age and expected thermal maturity?

Answers to these particular questions require the interpretation of

geochemical and palaeontological data on the sediments themselves in terms of predictions based on the biochemistry of extant microorganisms (Sections 3.4 and 4.2), mechanisms of organic decay in marine environments (Sections 3.4, 4.2, 4.3, 4.6, 4.7 and 5.2), and geochemical reactions involved in organic maturation (Sections 3.5, 4.4, 4.6 and 5.3).

6.2 PROTEROZOIC ROCKS

Core samples have been examined from thick Proterozoic sections in three exploration wells, namely, Mount Charlotte No. 1, Erldunda No. 1 and Ooraminna No. 1 (Fig. 6.12). In addition, cores of the Bitter Springs Formation from a shallow BMR evaporite test hole, Alice Springs No. 3, drilled in the Ringwood Dome, were also analysed. The locality of each well is shown in Figure 1.2.

6.2.1 Mount Charlotte No. 1

The results of organic geochemical analyses of the Bitter Springs Formation (Gillen and Loves Creek Members) and the Pertatataka Formation are shown in Table 6.4. The main potential source rock types represented are shale, dolomite and salt (halite). Organic carbon values are well below average for both shales (0.03-0.28%, mean 0.13%) and carbonates (0.02-0.14%, mean 0.08%). The richest intervals sampled are the shales of the Gillen Member (cores 19, 21 and 24). The two halite beds are notably deficient in indigenous organic matter (TOC = 0.01-0.03%).

Extractable organic matter

Shales

BOM ranges from 20 to 62 ppm in the Pertatataka Formation, and

from 37 to 318 ppm in the Gillen Member, Bitter Springs Formation. The yield of EOM per gram of organic carbon (31-73 mg, Pertatataka; 25-111 mg, Bitter Springs) shows no systematic variation with increasing depth. However, in the Bitter Springs Formation below 1650 m, the proportion of both saturated hydrocarbons (17-37%) and total hydrocarbons (32-54%) in the EOM is considerably higher than in the overlying Pertatataka Formation (saturates $\leq 13\%$, total hydrocarbons $\leq 20\%$). This suggests that hydrocarbon generation has occurred in shales of the Gillen Member, Bitter Springs Formation, but not in those of the Pertatataka Formation. With the exception of cores 13 and 24, saturates exceed aromatics by as much as 4 to 1.

The n-alkane distributions of the Pertatataka shales (Fig. 6.13) show evidence of maturation with increasing depth, namely

- 1) loss of the even carbon-number predominance at C_{22} and C_{24} in core 10,
- 2) progressive shift of maximum from C_{24} to C_{18} , and
- 3) progressive decrease in pr/n- C_{17} and ph/n- C_{18} ratios.

By comparison, the n-alkane distributions of the Bitter Springs shales (Fig. 6.14)

- 1) extend over a wider carbon-number range (C_{13} to C_{31}),
- 2) have a maximum at lower carbon-number (C_{16} or C_{17}), and
- 3) display a progressive increase in pr/n- C_{17} and ph/n- C_{18} with increasing depth.

The last feature is paralleled by an increase in the predominance of n- C_{22} (OEP value = 1.01 in core 19, 0.93 in core 21 and 0.60 in core 24). Both probably reflect the change in sedimentary environment, from restricted evaporitic to penesaline marine (Wells et al., 1970), that occurred during the deposition of the Gillen Member. In situ bacterial activity (of the type described by Dembicki et al., 1976) appears to have been more intense in the lower part of the unit.

The competing effects of burial diagenesis (maturation) and depositional environment on the composition of the saturated hydrocarbons in Proterozoic shales at Mount Charlotte are illustrated in Figures 6.15 - 6.17. The hydrocarbons of the immature Pertatataka shale (Fig. 6.15) comprise mostly high molecular weight branched/cyclic alkanes, represented by a pronounced naphthene hump centred on the $n\text{-C}_{26}$ position. With increasing diagenesis, catalytic cracking of the longer branched/cyclic alkanes into smaller molecules, gives rise to a bimodal naphthene distribution (Fig. 6.16) comprising a lower-molecular-weight mode at $n\text{-C}_{18}$ and a much reduced 'hump' at $n\text{-C}_{26}$. The influence of a highly saline, dolomite-depositing, partly anoxic environment on the resulting saturated hydrocarbons may be seen in Figure 6.17. In this case the maximum of the naphthene hump is located near the $n\text{-C}_{21}$ position, and the ratio of branched and cyclic to normal alkanes is greater than for shales deposited under less saline marine conditions.

Finally, shales of the Bitter Spring Formation have ratios of pristane to phytane that are consistently higher ($\text{pr/ph} = 1.1\text{-}1.2$) than those of the Pertatataka shales ($\text{pr/ph} = 0.7\text{-}0.9$). This could be a function of a difference in maturation level, or environment (Powell and McKirdy, 1973b), or a combination of both.

Carbonates

EOM yields are generally low (≤ 26 ppm, ≤ 26 mg/g C) throughout the Bitter Springs Formation, except for core 19 (45 ppm, 53 mg/g C) and core 26 (91 ppm, 91 mg/g C). Similarly, the proportion of saturates in the extract remains uniformly low ($\leq 10\%$ EOM), over the interval 1450-2050 m, but increases to 35% EOM in core 26 at the base of the sequence. The saturates/aromatics ratio also increases sharply from 0.2 above 2000 m to 4.4 at 2115 m. Thus the onset of hydrocarbon generation in carbonates

appears to lag behind that in shales and is located some 500 m lower in the sequence. The carbonate n-alkane profiles (Fig. 6.18) show little systematic change over the interval sampled, except perhaps for a similar (although less marked) increase in predominance of the n-C₂₂ alkane to that observed in the shales of the Bitter Spring Formation (cf. Fig. 6.14). The dolomite at 2115 m (core 26), in terms of its n-alkane distribution, is strikingly similar to the shale at 1772 m (core 21). The pr/n-C₁₇ and ph/n-C₁₈ values of the two rocks are identical.

Comparison of the respective n-alkane (and isoprenoid) distributions of the dolomite (Fig. 6.18) and shale (Fig. 6.14) from core 19, illustrates the major effect source-rock lithology may have on the resulting hydrocarbon pattern (cf. Powell and McKirdy, 1973a). These two samples, only 0.3 m apart in the original core, clearly have had the same burial history. In carbonates, the maximum of the n-alkane profile is typically located at higher carbon number than in shales of equivalent diagenetic rank.

Both the foregoing comparisons bear a further testimony to the stratigraphic separation of the zones of hydrocarbon generation in Proterozoic shales and carbonates in Mount Charlotte No. 1.

The saturated hydrocarbons in the dolomite of core 26 (Fig. 6.19), like those in the shales of cores 21 and 24 (Fig. 6.17), consist predominantly of branched and cyclic alkanes (note the pronounced naphthene hump).

Salt (halite)

Halite beds at 1872 m (core 22) and 2059 m (core 25) in the Gillen Member are lean in both organic carbon (see previously) and extractable organic matter (11-26 ppm).

Their organic content appears to be derived largely from intra-

clasts (or 'rafts') of shale and/or dolomite. Thus, halite containing dolomite rafts (core 22) has an n-alkane distribution (maximum at $n\text{-C}_{24}$; Fig. 6.20) and saturated hydrocarbon chromatogram (Fig. 6.21) typical of a dolomite. Similarly, the skewed bimodal n-alkane (major maximum at $n\text{-C}_{17}$; Fig. 6.20) and total alkane (Fig. 6.22) distributions of the halite of core 24 reflect the presence of shale and dolomite intraclasts.

Kerogen

The available geochemical and petrographic data on kerogens from Proterozoic rocks in the Mount Charlotte No. 1 well section are summarized in Table 6.8. Those kerogens isolated from black shales in the thick shale-siltstone sequence of Pertatataka Formation (e.g. core 12) and the poorly developed sandstone facies of the Bitter Springs Formation (e.g. core 21) fall into the Type III category (Table 5.2; Fig. 5.3). Their hydrogen-poor (atomic $\text{H/C} = 0.76\text{--}0.70$), condensed aromatic structure precludes the generation of hydrocarbons other than gas and perhaps small amounts of condensate.

On the other hand, the kerogen in shales which occur as relatively thin interbeds throughout the carbonate-evaporite part of the sequence (e.g. cores 19 and 25) is richer in hydrogen (atomic $\text{H/C} = 0.85\text{--}0.81$) and has a more aliphatic, Type II composition. Given an adequate thermal history, such organic matter is capable of generating oil. The contrast in composition and hence hydrocarbon generating potential of the organic matter in cores 19 and 21 is clearly shown by the PHGC data in Table 6.8. The volatile matter yield from core 19 kerogen is nearly twice that from the more aromatic core 21 kerogen.

The Type III organic matter (atomic $\text{H/C} = 0.73$; matrix $\overline{R}_o \text{ max} = 1.06\%$) in the dolomite of core 26 appears to be similar to rank micrinite. The kerogen is extremely finely divided, lacks any particulate

matter $>2\ \mu\text{m}$ in size, and has presumably undergone a coalification jump similar to that depicted in Figure 5.3. This would be consistent with the observed yield and composition of the associated EOM which indicated that generation of liquid hydrocarbons has occurred in carbonates at this level in the formation. Probable Type II kerogen in core 16 (dolomite, Loves Creek Member) may be a lower rank equivalent (atomic H/C = 0.80; phytoclast $\bar{R}_o\text{max} = 1.05\%$) of the organic matter in core 26.

Reflectivity measurements ($\bar{R}_o\text{max} = 1.05\text{--}1.19$) on vitrinite-like phytoclasts in kerogen concentrates, together with kerogen H/C values in the range 0.85–0.70, show that the sediments of the Bitter Springs Formation are at the halfway stage of mesodiagenesis (Table 5.2). In other words their maturation level is appropriate for oil generation. Thus, in terms of both rank and dominant type of organic matter, the Bitter Springs shales and carbonates in Mount Charlotte No. 1 are oil prone.

However, the only indications of petroleum in the well were fluorescence and shows of wet gas associated with black shales of the Gillen Member (McTaggart et al., 1965, unpubl.). Analysis of gas (C_1 to C_4) desorbed from black shale of core 19 (1653.5 m) contained 74.5% wet gas (C_{2+}) components.

6.2.2 Erldunda No. 1

Seven cores were selected for geochemical analysis (Table 6.5). Proterozoic formations sampled were the Bitter Springs Formation (Gillen and Loves Creek Members), Inindia Beds, and Winnall Beds (Fig. 6.12). With the exception of a siliceous dolomite (core 10) from the Gillen Member, all samples were taken from clastic units. Coarse-grained, potential reservoir rocks (sandstone and conglomerate) were included in the study because Pemberton and McTaggart (1965, p. 20, unpubl.) had reported finding "traces of pinpoint blue fluorescence and black residual hydrocarbon"

in sands at the top of the Winnall Beds.

Organic carbon values are low ($\leq 0.25\%$) throughout the well section, except for shale at the base of the Winnall Beds (core 6, 0.60% TOC). On average, the shales and siltstones of the Winnall Beds (mean TOC = 0.32%) are appreciably richer in organic matter than their stratigraphic and lithological equivalents in the Pertatataka Formation (mean TOC = 0.09%) at Mount Charlotte. This is probably a reflection of deeper water conditions at the Erldunda locality during Winnall-Pertatataka time (see Section 6.1.1).

Extractable organic matter

EOM is present in extremely small concentrations (2-14 ppm). The yield of extract per gram of organic carbon is also very low (≤ 14 mg). As a proportion of the extract, saturates are highest in core 3 (40.0% EOM) and decrease towards the bottom of the hole. Total hydrocarbons (53.3% EOM in core 3) show a similar decrease with increasing depth below 600 m. The high ratio of saturates to aromatics in core 5 (6.5:1), in conjunction with the highest EOM yield in the section, indicates that the conglomerate (not unexpectedly) contains migrated bitumen. This 'reservoir bitumen' probably originated in the surrounding shales of the Winnall Beds.

The total alkane chromatograms of the shales and siltstone in the Proterozoic sequence at Erldunda are exemplified by that of core 6 (Fig. 6.23). They are characterized by a high proportion of branched and cyclic hydrocarbons and are strikingly similar to the hydrocarbon patterns obtained from Proterozoic shales of the McMinn Formation adjacent to a dolerite sill (Fig. 4.41; Section 4.8.2). As in the McMinn shales, the relative lack of n-alkanes is probably the end result of extensive catalytic cracking which would also account for the low EOM yields.

The saturated hydrocarbons of the Winnall conglomerate (core 5) are even more depleted in n-alkanes (Fig. 6.24) and appear to be partially

biodegraded. Bacterial alteration (which involves preferential removal of straight-chain paraffins) may have occurred soon after the migration of oil into what, at that stage, was presumably a quite porous conglomerate. Fresh water carrying bacteria could have been introduced as a result of uplift and erosion of the area during the Petermann Ranges Orogeny (Fig. 6.2).

Higher $pr/n-C_{17}$ and $ph/n-C_{18}$ values ($\gg 1$), and a predominance of the even-carbon-numbered n-alkanes in the range C_{22} to C_{26} (Fig. 6.25), are further evidence of the involvement of bacteria in the origin and/or alteration of these hydrocarbons.

The n-alkane distributions of shales from the Winnall Beds (cores 4 and 6) have a maximum at C_{20} or C_{21} (Fig. 6.25). The corresponding $pr/n-C_{17}$ and $ph/n-C_{18}$ values are relatively high (0.7-1.0).

Kerogen

Although only one Proterozoic kerogen has been examined from the Erldunda well, the resulting geochemical and petrographic data (Table 6.8) provides pertinent clues to the nature and diagenetic rank of the organic matter preserved in shales of the Winnall Beds.

On the basis of its elemental composition, kerogen from core 6 may be classified as Type III-IV organic matter (Table 5.2; Fig. 5.3). Isotopically ($\delta^{13}C_{PDB} = -32.5\text{‰}$) it is almost identical to kerogen from the Pertatataka Formation in Ooraminna No. 1, but is quite distinct from dispersed organic matter in the Bitter Springs Formation. Its low H/C atomic ratio (0.55) means that it has matured at least to the stage of late mesodiagenesis (Table 5.2). This is consistent with the highly aromatic structure indicated by the PHGC ratios in Table 6.8.

Petrographic examination of the shale (Plate 6.1) and the kerogen concentrate (Plate 6.2, figure 1) in polished section by A.J. Kantsler

(pers. comm., 1976) revealed the presence of particulate organic matter resembling vitrinite ($\bar{R}_O \text{ max} = 2.18\%$). The variable reflectance of some of the vitrinite-like material indicates that it has undergone a process akin to fusinitization. Many phytoclasts of the resulting semifusinite have a definite micro-coke texture (illustrated in Plate 6.1). $\bar{R}_O \text{ max}$ for the micro-cokes is 3.15%. Some interstitial algal material is also present and this may account for the relatively high volatile matter content (V.M. = 39.9%) of the kerogen.

The reflectivity of the vitrinite-like component of the kerogen suggests a rank equivalent to semi-anthracite (i.e. telodiagenesis). This level of organic maturation is somewhat higher than that inferred from its atomic H/C value, but in good agreement with

- 1) the low yield of associated EOM (Table 6.5),
- 2) "the extraction of small amounts of methane from cuttings and core No. 6 over the interval 3420' - 3743'" (Pemberton and McTaggart, 1965, unpubl.), and
- 3) the pelitic nature of the shales and the dense, glassy siliceous matrix of the sandstones in the Winnall and Inindia Beds.

It seems reasonable to conclude that the Winnall Beds in Erldunda No. 1 are dry gas prone.

The fact that cuttings gas (C_1 to C_4) from black shales (1261.8 - 1274.1 m) in the underlying Loves Creek Member contains 23.5% wet gas (C_{2+}) components (calculation based on a single analysis reported by Pemberton and McTaggart, op. cit.) appears to be slightly at odds with above conclusions. However, this discrepancy (if real) may simply reflect a difference in kerogen type (the Loves Creek organic matter is likely to be more sapropelic) and/or the higher thermal conductivity of the Bitter Springs sequence. Heating due to depth of burial alone is unlikely to have been sufficient to produce the advanced levels of organic maturation,

evident in both the EOM and kerogen, of Proterozoic sediments at Erldunda. A high heat flux associated with the Petermann Ranges Orogeny (Fig. 6.2) probably also contributed.

6.2.3 Ooraminna No. 1

Source-rock analyses have been carried out on eleven core samples, four from the Bitter Springs Formation, two from the Areyonga Formation and five from the Pertatataka Formation (Fig. 6.12). Seven shales, three carbonates and one evaporite were examined. TOC values for the shales range from 0.02 to 0.77% (mean 0.27%). The carbonates and evaporite are very lean in organic matter ($\leq 0.04\%$ TOC) and therefore have negligible source-rock potential. They are nevertheless of interest because their hydrocarbon patterns show an unusual diagenetic trend (see below). In terms of organic richness, the most prospective intervals are dark, pyritic silty shales in the Pertatataka Formation (cores 9 and 11) and the Areyonga Formation (core 13).

Extractable organic matter

Shales

EOM is present in low concentrations (5-16 ppm; 3-20 mg/g C) throughout the section, with the notable exception of core 9 (412 ppm; 54 mg/g C).

Saturates comprise 33-37% of the EOM above 720 m, a proportion that increases to a maximum of 73% at 823 m (core 9), before decreasing to a low of 18% at 1270 m. Both total hydrocarbons (as a percentage of EOM) and the ratio of saturates to aromatics show a similar trend with increasing depth in the sequence.

Normal alkane distributions (Figure 6.26) have a maximum in the range $C_{15} - C_{18}$ and taper off towards higher carbon numbers. With increasing depth, the proportion of C_{23+} n-alkanes decreases. In profile the n-alkane distribution of core 9 is somewhat broader and flatter than those of the other shales and its maximum is located at lower carbon number ($n-C_{15}$). Core 9 is also distinguished from the other shales by its low $pr/n-C_{17}$ and $ph/n-C_{18}$ values. In cores 7 and 8, $pr/n-C_{17}$ and $ph/n-C_{18}$ values of >1 are consistent with a lower degree of maturation and apparently also reflect the euxinic depositional environment of the Pertatataka Formation. The naphthene hump in the total alkane chromatogram (Fig. 6.27a) is further evidence of highly reducing conditions. In core 14, increasing maturation has enhanced the concentration of the two n-alkanes (C_{17} and C_{18}) in relation to the adjacent isoprenoids (Figs 6.26 and 6.27c).

The total alkane pattern of core 9 (Fig. 6.27b) is distinctly crude oil-like in appearance. This accords with the high EOM yield and high proportion of saturates in the extract noted earlier.

Carbonates and evaporite

The EOM content of the non-argillaceous sediments ranges from 23 to 138 ppm. The yield of EOM is 123-391 mg/g C, showing no orderly variation with depth. In core 6 (478 m) at the top of the sequence saturates (58.5% EOM), total hydrocarbons (70.7% EOM), and saturates/aromatics (4.8) are all high. The values of each parameter, however, decrease steadily through core 17 (1505 m) and core 20 (1792 m), before increasing slightly in the evaporite (core 21, 1855 m) at total depth. A similar depth-related trend is seen in the n-alkane distributions (Fig. 6.28). The profile maximum shifts from C_{22} in core 6, through C_{23} in core 17, to C_{29} in core 20, but reverts to C_{18} in core 21. Inspection of the corresponding total alkane chromatograms (Fig. 6.29)

reveals that the proportion of branched and cyclic alkanes (as indicated by the size of the naphthene hump) also decreases in the carbonates with increasing depth, before increasing again in the basal evaporite.

The compositional variation in the hydrocarbon content of Proterozoic carbonates at Ooraminna is understandable in terms of progressive maturation with increasing depth of burial, except for the anomalous behaviour of the n-alkane patterns. No explanation can be offered for the latter at this time.

The saturates/aromatics ratio of core 6 is unusually high for a carbonate. This, in conjunction with an extremely low TOC content ($<0.01\%$) and a high yield of EOM per gram of organic carbon, indicates that core 6 probably contains migrated hydrocarbons. To a lesser degree, the same may be true of the salt in core 21. The saturated hydrocarbons in both cases are characterized by very high $pr/n-C_{17}$ and $ph/n-C_{18}$ values (≥ 2). If the latter feature is attributed to bacterial modification of the hydrocarbons during or following their migration into the rocks in question, this would in turn imply the influx of fresh-water at some stage prior to the loss of reservoir porosity. In this connection, it may be significant that the sample of core 6 was taken just 12 m below the contact with the overlying Arumbera Sandstone. The Arumbera Sandstone is a major fresh-water aquifer in the Amadeus Basin, and in Ooraminna No. 1 (core 5) has a porosity of 21-22% and a horizontal permeability of 251 millidarcies (md) (Planalp and Pemberton, 1963, unpubl.).

Kerogen

Kerogen concentrates were prepared from black shales of the Pertatataka Formation (core 9) and the Areyonga Formation (core 13) (Table 6.8). Both comprise Type III organic matter (Table 5.2; Fig. 5.3), similar in carbon isotopic composition ($\delta^{13}C_{PDB} = -32.2$ and $-30.6^{\circ}/\text{oo}$,

respectively) to kerogen from black shale of the Winnall Beds in Erldunda No. 1.

The H/C atomic ratio of the Areyonga kerogen (0.59) is lower than that of the Pertatataka organic matter (0.66), which is as expected (assuming a similar original composition) since the latter has been less deeply buried. In each case a rank within the range corresponding to late mesodiagenesis (Table 5.2) is indicated (but see below). The likely hydrocarbon product at such levels of maturation is gas condensate. This agrees reasonably well with an $\bar{R}_O \text{ max} = 1.40\%$ for phytoclasts of vitrinite-like material in the kerogen from the Pertatataka shale (core 9). Examination of the shale in polished section by A.J. Kantsler (pers. comm., 1976) also revealed several grains of thucolite ($\bar{R}_O \text{ max} = 1.70\text{--}1.80\%$) with zircons at their centre (Plate 6.3, fig. 1), and some algal balls with a much lower reflectivity. The thucolite and algal material may, in part, explain the unexpectedly aliphatic nature of the pyrolysis (PHGC) products (Table 6.8). Type III kerogens of comparable rank (e.g. Mount Charlotte No. 1, core 21: Table 6.8) are usually somewhat more aromatic in composition. Thus the original classification of the Pertatataka (core 9) kerogen as Type III organic matter, based as it was on elemental data, is possibly misleading, and may even be in error. Moreover, in view of the high yield and hydrocarbon-rich composition of its associated EOM, this particular kerogen may not be typical of the organic matter preserved in shales elsewhere in the sequence. For example, a more truly humic Type III composition is likely for kerogen in the Areyonga shales (e.g. core 13), particularly in view of the very low yield of associated EOM.

A non-commercial flow of dry gas was obtained from impermeable dolomitic limestone during a drill-stem test of the interval 1146-1191 m in the Areyonga Formation (Planalp and Pemberton, 1963, unpubl.). Inspection of analytical data on the gas (Konecki and Blair, 1970) shows that it contained only 4.3% wet gas. Its most likely source is the

underlying pyritic dark grey shale of the Areyonga Formation. The extreme depletion in C_{2+} components is here interpreted as a dual function of the humic composition of the kerogen and its high degree of thermal alteration. The latter probably corresponds more closely to telodiagenesis than to the late stage of mesodiagenesis indicated by the H/C value of the kerogen isolated from core 13.

Finally, the preservation of oil-like saturated hydrocarbons in core 9 (Fig. 6.27b), significantly located near the centre of a thick, monotonous shale sequence, may be a relic of original undercompaction and overpressuring of the Pertatataka Formation.

6.2.4 Alice Springs No. 3

In order to characterize more fully the organic matter associated with evaporitic sediments of the Gillen Member, Bitter Springs Formation, six core samples from this shallow (259.7 m T.D.) air-drilled BMR hole were selected for analysis (Fig. 6.30, Table 6.7). The well penetrated the evaporite core of the Ringwood Dome. Of the five main evaporite rock types in the well section (Stewart, 1974, unpubl.), three were examined in the present study: dolomite-gypsum breccia (cores 1, 38 and 42), bituminous dolomite (cores 9 and 54) and dololutite (core 24).

Organic carbon values are generally low (0.04-0.11% TOC), although higher concentrations of organic matter, sufficient to indicate significant source-rock potential, are present in the bituminous gypsiferous dolomite of core 9 (0.22% TOC) and the pyritic dololutite with vein gypsum of core 24 (0.84% TOC).

Extractable organic matter

The composition of extractable organic matter is extremely

variable (15-214 ppm; 24-368 mg/g C). Saturates range from 21.5% to 59.6% of the EOM. The ratios of saturates to aromatics are unusually high for carbonate rocks. Nevertheless, some regularities and trends can be discerned in the organic geochemical data.

The highest saturates/aromatics values (5.2-7.8) are found in brecciated or recrystallized samples (cores 1, 38 and 54), which also yield the greatest amount of extract per gram of organic carbon (54-368 mg/g C). This suggests that all three cores in question contain migrated bitumen. The fact that both organic variables (saturates/aromatics and EOM yield) increase with depth in the section is consistent with an upward direction of migration, from the generally more bituminous and pyritic lower half of the evaporitic sequence (Fig. 6.30).

The remaining three cores appear to contain mostly indigenous bitumen. Presumably their EOM yield (24-49 mg/g C) and composition (saturates, 21.5-58.3%; total hydrocarbons, 27.9-75.0%; saturates/aromatics, 2.2-3.5) in these samples is a truer reflection of the source and diagenetic history of their organic content.

Chromatograms of the saturates and hydrocarbons in every core examined from the lower part of the sequence (Figs 3lc-f) have a high molecular weight naphthene hump extending from approximately $n\text{-C}_{23}$ to the $n\text{-C}_{32}$ position. A second naphthene hump (between $n\text{-C}_{15}$ and C_{23}) may also be present (cores 24 and 42: Figs 6.3lc and e), in which case n -alkanes ($\text{C}_{15} - \text{C}_{30}$) are somewhat more prominent than in those samples with a unimodal naphthene distribution (cores 38 and 54: Fig. 6.3ld,f). On the whole, however, n -alkanes are markedly depleted. In fact, a second series of hydrocarbons (as yet unidentified, but possibly iso and anteiso alkanes) is present in greater concentration than the n -alkanes in the C_{23+} range. $\text{Pr}/n\text{-C}_{17}$ and $\text{ph}/n\text{-C}_{18}$ ratios are high (≥ 1) and, in core 54, there is distinct even-carbon-number predominance among the $\text{C}_{20} - \text{C}_{30}$

n-alkanes (Fig. 6.32). All these features are indicative of the involvement of bacteria in the production and/or alteration (saproelization) of the organic matter preserved in this part of the Ringwood evaporite sequence. Stewart (1974, unpubl.) noted the relatively high concentration of organic matter and pyrite in the basal interbedded dolomite and anhydrite and attributed it to deposition in a barred basin or stagnating lagoon.

The upper half of the sequence accumulated under generally less reducing conditions. Here anhydrite was the dominant evaporitic precipitate and the abundant pyrite and organic matter seen lower in the sequence are missing. Not unexpectedly, then, the total alkane patterns (Fig. 31a,b) are different. They are characterized by

- 1) a single predominant naphthene hump between $n\text{-C}_{15}$ and $n\text{-C}_{25}$,
- 2) an envelope of $\text{C}_{15} - \text{C}_{26}$ n-alkanes with a maximum at $\text{C}_{17} - \text{C}_{19}$ (Fig. 6.32), and
- 3) intermediate $\text{pr}/n\text{-C}_{17}$ and $\text{ph}/n\text{-C}_{18}$ values (0.6-1.0).

It seems reasonable to postulate a very shallow, intermittently exposed environment in which aerobic bacteria subsisted on the remains of planktonic or benthonic algae. Bacterial reworking of the algal debris was extensive (as evidenced by the relatively high proportion of branched and cyclic alkanes, and intermediate $\text{pr}/n\text{-C}_{17}$, $\text{ph}/n\text{-C}_{18}$ ratios), but insufficient to completely obliterate the original algal n-alkanes (or their lipid precursors).

Kerogen

Differences between the upper and lower evaporites are also apparent in the composition of their respective kerogens (Table 6.8). The kerogens from core 9 and core 42 are both highly aromatic, oxygen-rich

(semi-fusinitic) Type IV organic matter (Table 5.2; Fig. 5.3). However, they differ significantly in their degree of aromaticity. Kerogen from the upper evaporites (core 9) is clearly the more aromatic, as is shown by its lower atomic H/C value (0.28) and higher PHGC ratios. It also has a higher volatile matter content than kerogen in core 42, but much of this is probably CO_2 .

The semi-fusinitic nature of the organic matter in the Ringwood evaporites is reminiscent of the kerogens found in inter-supratidal stromatolites (Section 4.7), and no doubt has much the same genetic significance. Of the two kerogens examined, the extent of fusinitization is greater in the one from core 9. This is probably a direct reflection of the shallower, more aerated conditions that obtained during the precipitation of the upper evaporites, and of the participation of aerobic (as distinct from anaerobic) bacteria. Exposure of the Ringwood Dome by erosion has allowed meteoric water to penetrate the upper levels of the deposit (Stewart, 1974, unpubl.). This may have contributed further to the oxidation (or fusinitization) of the organic matter in core 9.

Microscopic examination of core 9 kerogen in transmitted light revealed that it consists of extremely fine particles of medium-dark olive brown organic matter (Plate 6.4, fig. 3). Thermal maturation appears to have involved micrinitization. Rare larger fragments (Plate 6.2, fig. 2) have a reflectivity in oil ($\bar{R}_o \text{ max}$) which ranges from 1.95 to 3.20% (A.J. Kantsler, pers. comm., 1976). Reflectance values at the lower end of the range were probably obtained from particles that have undergone the least fusinitization, and are therefore considered to provide the best indication of rank.

The available geochemical data (EOM yield, and composition, cores 9, 24 and 42; kerogen H/C atomic ratios, cores 9 and 42) and petrographic data (core 9) are reasonably consistent in indicating (cf. Table 5.2) that the organic matter in the Ringwood evaporites has

evolved to the stage of telodiagenesis. In other words the Gillen Member, Bitter Springs Formation, in the northeastern corner of the basin, is dry gas prone.

6.3 CAMBRIAN ROCKS (PERTAOORRTA GROUP)

Cores from Cambrian sections in three exploration wells - Mount Charlotte No. 1, Highway Anticline No. 1 and Alice No. 1 (Fig. 6.33) - have been sampled for source-rock analysis. The well locations are given in Figure 1.2.

6.3.1 Mount Charlotte No. 1

Organic geochemical data on evaporites of the Chandler Formation and shales and carbonates of the Jay Creek Limestone are summarized in Table 6.9. Organic carbon values for both formations are uniformly very low ($\leq 0.06\%$ TOC). If the intervals sampled are representative of each formation, neither can be considered to possess significant potential as a source of petroleum hydrocarbons at this locality.

Extractable organic matter

Shales

EOM yields of 43-57 mg/g C for cores 4 and 5, in conjunction with a saturates value of 8.5% EOM in cores, is typical of shales at or near the threshold of oil generation. The higher saturates content (22.2% EOM) and correspondingly high saturates/aromatics value (5.2) of core 4, a silty shale, suggests that it contains migrated hydrocarbons. This is confirmed by the appearance of its total alkane chromatogram

(Fig. 6.34). The relative lack of n-alkanes and high pr/n-C₁₇ and ph/n-C₁₈ values (>1) are signs of biodegradation. In addition, the anomalous concentration of n-C₂₂ in the n-alkane profile (Fig. 6.35) may be the result of contamination from the polythene bag in which the core was stored (Douglas and Grantham, 1974).

Carbonates and evaporites

EOM yields in the range 29-439 mg/g C are considerably higher than those for the associated shales. As for the Proterozoic evaporites of the Bitter Springs Formation, the bitumen in the halite deposits of the Chandler Limestone is partly allochthonous. The saturated hydrocarbons comprise mostly branched and cyclic alkanes (Fig. 6.36). Normal alkanes (Fig. 6.35) fall in the range C₁₅ to C₂₆, with a maximum at C₂₁ or C₂₂.

Kerogen

No kerogens were isolated to provide information on the type and rank of the organic matter in the Pertaoorrtta Group in the southeast corner of the Amadeus Basin. Nevertheless, on the basis of the level of organic maturation displayed by the underlying Proterozoic sequence (Section 6.2.1), and the yield and composition of the EOM in shales of the Jay Creek Limestone, we may conclude that Cambrian rocks in Mount Charlotte No. 1 are at best only marginally mature.

6.3.2 Highway Anticline No. 1

Four cores have been analysed (Table 6.10), all from the Jay Creek Limestone. Rock types sampled were siltstone, argillaceous limestone and dolomite.

Total organic carbon values range from 0.02 to 0.15%. Although somewhat richer in organic matter than the Jay Creek limestone in the Mount Charlotte well section, these sediments (with the possible exception of the argillaceous limestone of core 1) are still too lean to be rated as potential source rocks.

Extractable organic matter

EOM yields are low (14-31 ppm, 9-32 mg/g C). Saturated hydrocarbons account for 21.3-47.4% of the extract. The high ratio of saturates to aromatics in core 1 suggests migration of hydrocarbons, possibly from basal sands of the overlying Goyder Formation, into the upper part of the Jay Creek Limestone. Gas chromatography of the saturates (Fig. 6.37) showed that they comprise a complex mixture of predominantly branched and cyclic alkanes in both siltstones and carbonates. Hydrocarbons in the siltstones of cores 3 and 4 (Fig. 6.37a & b, respectively) probably represent successive phases in the burial diagenesis of the same (or similar) detrital organic matter. Core 4 has the lower proportion of n-alkanes consistent with catalytic cracking being the dominant mechanism of thermal maturation. Normal alkane distributions (Fig. 6.38) range from C_{16} to C_{29} and have a maximum between C_{18} and C_{21} . $Pr/n-C_{17}$ and $ph/n-C_{18}$ values are intermediate to high (0.6-1.2).

Kerogen

Elemental analysis of kerogen from core 4 showed it to be Type III organic matter (Fig. 5.3) which has attained a rank (atomic H/C = 0.71) equivalent to the boundary between early and late mesodiagenesis (Table 5.2). This means, the organic matter in argillaceous sediments of the Jay Creek Limestone at 740 m in Highway Anticline No. 1 has realized its optimum

liquid hydrocarbon generating potential. The PHGC peak ratios of the Jay Creek kerogen are similar to those of the Type III organic matter in shale of the Gillen Member, Bitter Spring Formation, Mount Charlotte No. 1 (Table 6.8).

Although the Jay Creek Limestone in Highway Anticline No. 1 is oil prone in terms of level of organic maturation, the humic (Type III) composition and generally low concentration of the dispersed organic matter severely reduces its source-rock potential.

6.3.3 Alice No. 1

Fine-grained rocks have been examined from each of the five Cambrian formations that comprise the thickest well section of the Pertaoorrtta Group in the Amadeus Basin (Fig. 6.33). A total of thirteen core samples were analysed (Table 6.11).

TOC values are below average for all the rock types sampled (viz., shale and siltstone, 0.02-0.32%; carbonate and evaporite, <0.01-0.10%). The most carbonaceous intervals are in the Goyder Formation (shale, core 11: TOC = 0.30%), Shannon Formation (dolomitic shale, core 15: TOC = 0.24%) and Giles Creek Dolomite (dolomitic shale, core 23: TOC = 0.32%), but even these fall short of the minimum 0.4-0.5% TOC generally considered necessary for an argillaceous sediment to qualify as a source rock.

Extractable organic matter

Shales and siltstones

EOM in shales ranges from 28 to 128 ppm. The yield of extract per gram of organic carbon increases with depth, from 18 mg in core 11

(1089.1 m), through 53 mg in core 15 (1379.2 m), to a maximum of 178 mg in core 25 (2060.4 m). The low yield of EOM from the dolomitic shale of core 23 (1868.7 m) does not fit this apparent trend. Siltstone in the Arumbera Sandstone at 2292.1 m has evidently been flushed, although the low EOM concentration (4 ppm, 6 mg/g C) could also be a primary feature of redbeds.

With the exception of core 11, the proportion of saturates in the extract (5-9% EOM) and the saturates/aromatics value (0.2-0.7) are both unusually low for Cambrian shales whose depth of burial reached an estimated maximum of 2200-3300 m in the late Devonian and has always exceeded 1000 m since that time. The proportion of total hydrocarbons is also low (18-36% EOM), and shows no systematic variation with depth.

The picture of EOM yield and composition that emerges for shales is rather confused. Part of the reason for this may be variation in the type of precursor organic matter (Table 6.12).

The proportion of saturates (23.3%) and total hydrocarbons (35.5%) in the EOM of core 11 suggests that hydrocarbons have been generated in shales at this level of the sequence. Such shales are likely to have been the source of the "black asphaltic oil", which gave rise to a dull gold fluorescence, in sandstones and dolomites between 1052 and 1110 m in the Goyder Formation (Pemberton et al., 1963, unpubl.). Recovery of fresh water (495 ppm NaCl) during a drill-stem test of the interval 1061 - 1076 m is consistent with the reservoir bitumen being an indigenous, residual, water-washed, crude.

By virtue of their deeper burial relative to the Goyder Formation, dolomitic shales of the Shannon Formation, Giles Creek Dolomite and Chandler Limestone would normally be expected to contain saturated hydrocarbons in somewhat higher concentrations (as a percentage of EOM) than in fact they do. The extremely low proportion of saturates in the EOM of cores 23 and 25 is particularly puzzling. For want of a reasonable alternative

explanation, one is forced to conclude that saturated hydrocarbons have preferentially migrated from these shales into the adjacent dolomites. Dark brown, high gravity (43° API) oil which bled from tight dolomite over the interval 1864.2 - 1868.4 m (Pemberton et al., 1963, unpubl.) is strong evidence that migration of hydrocarbons has occurred in this part of the section.

Normal alkane distributions in the range C_{14} to C_{27} , with a single maximum at C_{17} or C_{18} , characterize the dolomitic shales (Fig. 6.39). That of core 23, Giles Creek Dolomite, displays a slight predominance of the $n-C_{22}$ alkane (OEP value = 0.83). $Pr/n-C_{17}$ and $ph/n-C_{18}$ values are low to intermediate (0.4-0.8). Gas chromatography of the saturated hydrocarbons isolated from the shales (Fig. 6.41a,c,d) showed they comprise an extremely complex mixture of mostly branched and cyclic alkanes.

Carbonates and evaporites

The absolute concentration of EOM in carbonates and evaporites is 10-41 ppm. The yield of extract per gram of organic carbon varies erratically between 21 and 113 mg over the depth range 950 to 1865 m. Below 1865 m, higher yields were obtained from the anhydritic dolomite of core 23 (116 mg/g C) and the salt (halite) of core 26 (415 mg/g C) but the corresponding saturates/aromatics values are also high (12.2 and 5.0, respectively), indicating that the EOM in these two intervals is largely allochthonous (i.e. migrated). This accords with the fact that oil was bleeding from core 23 when first recovered (Pemberton et al., 1963, unpubl.). Excluding cores 23 and 26, the proportion of saturates in the extract decreases steadily from 21% in core 9 to 8% in core 22.

No depth related trend is evident in the shape of the n-alkane profiles (Fig. 6.40). The maximum of most distributions is located at $n-C_{20}$ or $n-C_{21}$, the two exceptions being core 9 (glaucinitic sandy dolomite, $n-C_{17}$ maximum) and core 22 (anhydritic dolomite, $n-C_{22}$ maximum). The

predominance of the $n\text{-C}_{22}$ alkane, most strikingly developed in the anhydritic dolomite of core 22 (OEP value = 0.56), is also evident in other samples of the Giles Creek Dolomite (core 20, silty anhydritic dolomite, OEP = 0.76; core 23, anhydritic dolomite, OEP = 0.89; core 23 dolomitic shale, OEP = 0.83) and appears to be a feature of that formation. Comparison of Figures 6.41b and 6.35 reveals the close similarity between

- 1) the n -alkane distributions of core 22, Alice No. 1 and core 7, Mount Charlotte No. 1, the latter also from a Cambrian anhydritic dolomite; and
- 2) the n -alkane distributions of core 26, Alice No. 1 and core 8, Mount Charlotte No. 1, both from salt (halite) of the Chandler Limestone.

Gas chromatograms of the saturated hydrocarbons present in carbonates of the Alice No. 1 sequence (Fig. 6.41a-d) are dominated by a naphthene hump centred on the $n\text{-C}_{20}$ or $n\text{-C}_{21}$ position. $\text{Pr}/n\text{-C}_{17}$ and $\text{ph}/n\text{-C}_{18}$ values are consistently higher (0.6-1.7) than in the interbedded shales, and the maximum of the naphthene hump is located one to three carbon numbers closer to the high-molecular-weight end of the chromatogram.

The occurrence of highly naphthenic alkane patterns in shales and carbonates alike is probably an original feature related to the predominantly carbonate-depositing environment in which the Cambrian sequence at Alice No. 1 accumulated. However, prior to the loss of primary porosity and permeability in the carbonates partial biodegradation of their hydrocarbons may have occurred, thereby enhancing the original preponderance of naphthenes over normal and isoparaffins. Porous intervals are still present in the Giles Creek Dolomite (Pemberton et al., 1963, unpubl.), and some contain fresh water (e.g. 1849 - 1871 m, 743 ppm NaCl) in which bacteria may have been introduced.

Kerogen

Elemental analyses of kerogens isolated from shales of the Goyder Formation (Type II-III, $H/C = 0.99$), Shannon Formation (?Type II, $H/C = 0.91$) and Giles Creek Dolomite (Type III, $H/C = 0.84$) (Table 6.12) indicates that they have evolved only to the stage of early mesodiagenesis (cf. Table 5.2). In terms of level of organic maturation, therefore, the Cambrian at Alice No. 1 is oil prone.

The higher organic carbon content of the shales suggests that they (and not the carbonates) have been the major source of the oil shows in the sequence (but see Section 6.5). This assessment is supported by the probable liptinitic (Type II) composition and high volatile matter content (60.7%) of the kerogen from the Shannon Formation (Table 6.12). Kerogen in the Giles Creek Dolomite appears to have been micrinitized as the result of a liptinite coalification jump. This would explain its lower volatile matter content (32.2%). Both the Shannon and Giles Creek kerogens are highly aromatic. The Goyder kerogen is somewhat more humic (Type II-III) and this reduces its potential to generate liquid hydrocarbons.

6.4 CAMBRO-ORDOVICIAN ROCKS (LARAPINTA GROUP)

As will be evident from a reading of Section 6.1.2, the Larapinta Group is the primary exploration objective in the Amadeus Basin. Accordingly, the coverage afforded the Cambro-Ordovician in this study was somewhat more extensive than that given to the Proterozoic and Cambrian. Source-rock analyses were undertaken on cores from six exploration wells - East Mereenie Nos. 1, 2 and 4, Tyler No. 1, and Palm Valley Nos. 1 and 3 - and four BMR phosphate test holes - AP 1-4. The locality of each well is shown in Figure 1.2. A well correlation diagram may be found in Enclosure 5, figure 2, on which the wells sampled have been marked with asterisks.

Preliminary results and discussion of this work were published in Kurylowicz et al. (1976), which forms Enclosure 5 of this thesis. Formations identified as having significant source-rock potential were the Pacoota Sandstone, Horn Valley Siltstone and Stairway Sandstone. The availability of core from 10 well sections in the central northern area of the basin has made possible an examination of the regional variation in composition, type, and degree of maturation of the organic matter in each formation.

6.4.1 Pacoota Sandstone

Organic geochemical analyses of fine-grained lithofacies (shale, siltstone, argillaceous sandstone) of the Pacoota Sandstone in wells from the Mereenie and Palm Valley fields are given in Table 6.13. Organic carbon values range from 0.07% to 0.89% (mean 0.34%) and tend to be higher at Mereenie than in the Palm Valley area.

Extractable organic matter

EOM concentration is variable in the Mereenie wells (39-1633 ppm) but uniformly low (1-25 ppm) at Palm Valley.

On the basis of their yield of extract per gram of organic carbon, shales of the Pacoota Sandstone in the Mereenie oil and gas field fall into one of three categories:

source facies	180-198 mg/g C
intermediate facies	83 mg/g C
non-source facies	19-45 mg/g C

In the source facies, saturates comprise 44.6-58.8% of the EOM and the ratio of saturated to aromatic hydrocarbons is high (saturates/aromatics = 7.1-10.1). The corresponding values are somewhat lower for the non-source

facies (saturates, 25.3-46.2% EOM; saturates/aromatics, 1.7-3.0). The intermediate facies is represented by core 10, East Mereenie No. 1 (saturates, 35.2% EOM; saturates/aromatics, 5.8). Each facies has a characteristic total alkane pattern and n-alkane distribution. The n-alkane profile of the Pacoota source facies (e.g. core 10, East Mereenie No. 1, Fig. 6.42) has a maximum at C_{15-17} and a marked odd/even predominance at C_{17} and C_{19} . In the case of the non-source facies, the maximum is located between C_{21} and C_{25} and the odd/even predominance in the $< C_{20}$ range is missing. The intermediate facies has an n-alkane maximum at C_{20} and displays a slight predominance of the n- C_{17} and n- C_{19} alkanes (see core 10, East Mereenie No. 1, Fig. 6.42). The total alkane chromatograms of the non-source and intermediate facies (Fig. 6.44) have a more pronounced naphthene hump than those of the source facies (Fig. 6.43). Pr/ph values (0.7-2.0) and pr/n- C_{17} and ph/n- C_{18} values (≤ 0.2) are low for all three facies.

In the Palm Valley gas field, EOM yields (≤ 11 mg/g C) for argillaceous intervals of the Pacoota Sandstone are much lower than at Mereenie. This, no doubt, is a consequence of the higher rank of the sediments at Palm Valley (see following discussion on kerogen). Nevertheless, despite their advanced level of diagenetic alteration, it is still possible to discriminate between source and non-source shales:

	<u>Source</u>	<u>Non-source</u>
EOM yield (mg/g C)	2-11	3
saturates (% EOM)	32.4-48.5	12.9-36.7
saturates/aromatics	2.0-5.5	1.0-2.0
n-alkane profile, maximum	C_{18-19}	C_{22}
pr/n- C_{17}	0.4-0.7	0.6-1.1

Typical n-alkane distributions for the source and non-source facies of the Pacoota Sandstone in the Palm Valley No. 1 well section are illustrated in Figure 6.45.

Kerogen

A limited amount of geochemical and petrographic information has been obtained on the particulate organic matter preserved in the Pacoota Sandstone (Table 6.14; see also Enclosure 5, table 8).

At Mereenie, the source facies contains aliphatic Type II kerogens (Fig. 5.3). The H/C atomic ratio (0.78) of this organic matter shows that it has evolved to the stage of late mesodiagenesis (Table 5.2). This in turn indicates that the Pacoota source facies in the Mereenie area is light oil prone, a conclusion that is consistent with

- 1) the yield and saturates content of the associated EOM (see above), and
- 2) the reflectivity of graptolite fragments ($\bar{R}_o \text{ max} = 1.40\%$) identified in the kerogen.

Graptolites, a common component of the insoluble organic matter in the Larapinta Group sediments, are thought by Kantsler and Cook (see Enclosure 5, p. 61) to respond to coalification in much the same manner as vitrinite. Lack of elemental data precludes characterization of the kerogen in the intermediate facies, although its isotopic composition ($\delta^{13}\text{C}_{\text{PDB}} = -31.1^\circ/\text{oo}$) closely matches that of condensate produced from the Pacoota Sandstone (Units P1 to P4) in East Mereenie No. 1 ($\delta^{13}\text{C}_{\text{PDB}} = -30.3^\circ/\text{oo}$), and oil from the same formation (Unit P3) in East Mereenie No. 4 ($\delta^{13}\text{C}_{\text{PDB}} = -31.0^\circ/\text{oo}$) (see Table 6.19).

In the Palm Valley field, the Pacoota kerogen (both source and non-source facies) is of Type III composition. Atomic H/C values (source, 0.65; non-source, 0.60-0.63) suggests a level of organic maturation equivalent to late mesodiagenesis, but this is in poor agreement with the observed EOM yields (see above) and measured graptolite reflectivities ($\bar{R}_o \text{ max} = 2.00\text{-}2.26^\circ/\text{oo}$) which correspond to ranks more indicative of telodiagenesis (cf. Table 5.2). Another discrepancy is the presence of optically recognizable alginite, as

small 'algal balls' (similar to, but smaller than, those found in the Horn Valley Siltstone at East Mereenie No. 1: Plate 6.5), in the Pacoota Sandstone at Palm Valley No. 3 (2072.3 m) (A.J. Kantsler, pers. comm., 1976).

Analysis of a non-source kerogen (Palm Valley No. 3, 2077.2 m) revealed an aromatic structure (PHGC ratios >1: Table 6.14), and an isotopic composition ($\delta^{13}\text{C}_{\text{PDB}} = 28.8\text{‰}$) surprisingly similar to that of condensates from the three Palm Valley wells ($\delta^{13}\text{C}_{\text{PDB}} = 29.9$ to -28.9‰ : Table 6.21). There are two possible explanations for this close isotopic correspondence between non-source kerogen and condensate in the Palm Valley field.

1. The condensate formed by thermal cracking in the reservoir of a Mereenie-type crude ($\delta^{13}\text{C}_{\text{PDB}} \approx -31.0\text{‰}$); loss of ^{12}C -enriched, low molecular weight hydrocarbons via preferential rupture of $^{12}\text{C} - ^{12}\text{C}$ bonds led to an increase of $1\text{--}2\text{‰}$ in the $\delta^{13}\text{C}$ value of the resulting condensate.
2. At the advanced maturation levels which obtain in the Palm Valley area, the limited liquid hydrocarbon-generating potential of the 'non-source' kerogen became increasingly significant as that of the 'source' kerogen neared exhaustion.

The first explanation is favoured because it

- 1) accords with the highly paraffinic to ultraparaffinic composition of the Palm Valley condensate; and
- 2) avoids the problem inherent in the latter hypothesis, of late-stage migration of liquid hydrocarbons into the reservoir.

6.4.2 Horn Valley Siltstone

Core samples of the Horn Valley Siltstone from BMR AP 1-3, East Mereenie No. 1 and Palm Valley No. 1 have been analysed (Table 6.15).

With the exception of BMR AP 3, 311.6 m (argillaceous sandstone: 0.51% TOC) and Palm Valley No. 1, core 14 (dolomitic limestone: 0.07% TOC), all are shales with organic carbon contents in the range 0.29 - 1.81% (mean 0.79%). Again, as for the shales of the Pacoota Sandstone, the highest organic carbon values are obtained from the Mereenie area.

Extractable organic matter

Source and non-source facies shales exist in the Horn Valley Siltstone and may be differentiated (Table 6.15) in the same way as those of the Pacoota Sandstone (viz., on the basis of EOM yield and n-alkane profile).

Within the source facies, the concentration (ppm), yield (mg/g C) and composition (% saturates, % total hydrocarbons) of the EOM changes in a manner which reflects a northeasterly increase in the level of organic maturation across the central northern part of the basin. At the BMR AP 2 well locality (Fig. 1.2), the Horn Valley is marginally mature (EOM 83 mg/g C; saturates, 14.5% EOM), i.e. hydrocarbon generation has only just begun.

In BMR AP 1, the extract yield has increased to 150-221 mg/g C, and saturates to 40-45% of the EOM, typical of early mesodiagenesis (Table 5.2). The formation here is oil prone, a conclusion that is borne out by the presence of oil saturated sands in the overlying lower Stairway Sandstone and the underlying upper Pacoota Sandstone (Unit P1), immediately adjacent to their contacts with the Horn Valley Siltstone (Barrie, 1964; see also Section 6.3.4). Gas chromatograms of the saturated hydrocarbons in source and non-source shales are compared in Figure 6.46. The marked predominance of the C₁₇ and C₁₉ n-alkanes which characterizes the source facies appears to be related to the fossil content (notably trilobites, graptolites) of the shale.

Extract yields (175-225 mg/g C) and saturates contents (72-74% EOM)

are highest in East Mereenie No. 1. These values are indicative of late mesodiagenesis (Table 5.2). The expected hydrocarbon product, gas condensate, was in fact recovered during testing of the Pacoota Sandstone (gross interval 1118.3-1371.9 m) in this well. The high saturates/aromatics values (5.6-10.4) suggests that primary migration of hydrocarbons from the shale is still taking place (or has been arrested). The saturated hydrocarbons of the source facies are again characterized by a marked odd/even predominance in the $<C_{20}$ range (Figs 6.42 and 6.43). Pr/ph ratios (2.3-2.5) are the highest observed in the Horn Valley Siltstone, whereas the corresponding pr/n- C_{17} and ph/n- C_{18} values (<0.1) are the lowest.

At Palm Valley No. 1, EOM yield has diminished to <10 mg/g C and the proportion of saturates in the extract has fallen to 19-20%. Gas chromatography of the saturated hydrocarbons shows them to be a complex mixture of branched and cyclic alkanes, with few n-alkanes. Prominent naphthene humps and relatively high pr/n- C_{17} and ph/n- C_{18} values (0.6-0.9) are artefacts of extensive catalytic cracking during telodiagenesis. All this reflects the higher rank of the Horn Valley Siltstone in the Palm Valley area, where the source rocks of the Larapinta Group have matured beyond the stage at which they are capable of generating significant quantities of liquid hydrocarbons.

Kerogen

The results of analyses carried out on the insoluble organic fraction of the Horn Valley Siltstone are presented in Table 6.16. Additional graptolite reflectivity values may be found in Enclosure 5, table 8.

Aliphatic Type II organic matter appears to be present in both source and non-source facies at BMR AP 1 and 2 and East Mereenie No. 1. Kerogen rank is lowest in BMR AP 2 (H/C atomic ratio = 1.11) and is only

slightly higher at BMR AP 1 (H/C atomic ratio = 1.01 - 1.10; graptolite $\bar{R}_O \text{ max} = 0.68\%$). This confirms the oil-prone nature of the shales noted earlier. In appearance, the kerogen is largely amorphous (sapropelic) matrix material, with rare small graptolite fragments. Some translucent algal debris is also present (Plate 6.4, figs 1 and 2). Its colour in transmitted white light ranges from amber-yellow (BMR AP 2, 162.3 m) to yellow-orange (BMR AP 1, 209.4 m).

The Horn Valley Siltstone at East Mereenie No. 1 contains kerogen that is still recognizable as aliphatic Type II organic matter, although its maturation level has advanced to late mesodiagenesis (H/C atomic ratio = 0.75; graptolite $\bar{R}_O \text{ max} = 1.19 - 1.42\%$). The formation is, therefore, light oil or gas condensate prone (Table 5.2). The kerogen contains much particulate organic matter, 'mostly graptolite fragments and some algal balls' (A.J. Kantsler, pers. comm., 1976: Plate 6.5).

By virtue of its higher rank (equivalent to graptolite $\bar{R}_O \text{ max} = 2.37\%$), kerogen in the source facies of the Horn Valley Siltstone at Palm Valley No. 1, has acquired a distinctly more aromatic structure, as evidenced by PHGC benzene/ $n\text{-C}_6$ and toluene/ $n\text{-C}_7$ ratios >1 (Table 6.16). It is again surprising to find discrete 'algal balls' persisting in rocks (e.g. core 15, Palm Valley No. 1: A.J. Kantsler, pers. comm., 1976) that are ostensibly dry gas prone (cf. Pacoota Sandstone in Palm Valley No. 3). Also present are localized aggregates of thucolite around zircon grains (Plate 6.3, fig. 2).

Finally, there appears to be a clear-cut distinction between the carbon isotopic composition of source ($\delta^{13}C_{\text{PDB}} = -32.5$ to $-29.1^\circ/\text{oo}$) and non-source ($\delta^{13}C_{\text{PDB}} = -28.1$ to $-26.8^\circ/\text{oo}$) kerogens in the Horn Valley Siltstone (Fig. 6.56).

6.4.3 Stairway Sandstone

The results of source-rock analyses of core material from the Stairway Sandstone in BMR AP 1-4, East Mereenie No. 1, Tyler No. 1 and Palm Valley Nos. 1 and 3 are presented in Table 6.17. The rock types examined are predominantly lutites (shales, siltstones), some of which are phosphatic enough ($>4\% \text{P}_2\text{O}_5$) to be termed phosphorites. Most samples came from the middle unit of the formation which comprises illitic mudstone and phosphorite. Organic carbon contents are low (0.02-0.31%, mean 0.18%) and, solely on the grounds of organic richness, the formation rates as only marginally prospective. Phosphorites (0.13-0.28%, mean 0.20% TOC) differ little in this respect from the whole suite of samples.

Extractable organic matter

The yield of extract per gram of organic matter in the Stairway Sandstone displays a similar pattern of regional variation to that evident in the underlying Horn Valley Siltstone. EOM yield increases from 19 mg/g C in BMR AP 4, through 36-44 (mean 40) mg/g C at BMR AP 2, to a maximum of 38-127 (mean 75) mg/g C in the BMR AP 1 well section. In the East Mereenie No. 1 the yield has decreased to 23-57 (mean 39) mg/g C. It declines further through 14-47 (mean 29) mg/g C in BMR AP 3, 13-34 (mean 24) mg/g C in Tyler No. 1 and 11 mg/g C in Palm Valley No. 3, to a low of ≤ 8 (mean 4) mg/g C at Palm Valley No. 1. It is possible to draw through these well localities (refer Fig. 1.2) iso-yield lines which conform with a general northeasterly (Mereenie area) to east-northeasterly (Palm Valley area) increase in level of organic maturation. Generally EOM yields from the Stairway Sandstone (both lutites and phosphorites) are lower than those from shales of the Horn Valley Siltstone and Pacoota Sandstone at the same locality (except in the vicinity of Palm Valley). This can be explained

by what appears to have been an original difference in the composition of their organic detritus (see discussion of kerogen).

The saturates content of the EOM is somewhat erratic, ranging from 3.9% to 51.5% (mean 29.6%) in the lower-rank well sections (BMR AP 1, 2 and 4, East Mereenie No. 1), and from 7.7% to 50.9% (mean 26.4%) in the higher-rank area (BMR AP 3, Tyler No. 1, Palm Valley Nos. 1 and 3). In other words, no rank-related trend is evident in the proportion of saturated hydrocarbons in the EOM of the Stairway Sandstone (and this is true also of the total hydrocarbons). In the Stairway Sandstone at BMR AP 1, phosphorites have saturates/aromatics ratios (3.7-10.2) that are considerably higher than those of the less phosphatic lutites (1.0-2.7) in the same drill hole. The same feature characterizes the phosphorites in BMR AP 3, but not those at BMR AP 2 and 4. The Stairway Sandstone in the latter two well sections is of lower rank (see above). This suggests that the release of saturated hydrocarbons from kerogen and asphaltenes at the onset of oil generation occurs more readily in the phosphorites than in the lutites (cf. Section 4.6.3); or alternatively that the phosphorites contain hydrocarbons which are in part allochthonous (migrated).

The total alkane (saturated hydrocarbon) chromatograms are generally characterized by prominent naphthene humps (e.g. Figs 6.47 and 6.48). In Palm Valley No. 1 (cores 11 and 12) the saturates are particularly depleted in n-alkanes. Preferential generation of branched and cyclic alkanes by catalytic cracking during late mesodiagenesis and telodiagenesis is indicated. Notable exceptions to this rule are shales (cores 4 and 5: Fig. 6.44) in East Mereenie No. 1. Pr/ph ratios are generally low (<2.5) but tend to be slightly higher in the vicinity of the Palm Valley field (0.7-2.4, mean 1.3) than elsewhere in areas of lower rank (0.6-1.3, mean 1.0).

Normal alkane distributions in the Stairway Sandstone are of two types. One has a maximum at C_{17-19} , whereas in the other the maximum is located at C_{22} (but may shift to C_{21} or C_{20} in higher rank samples).

A feature of the n-alkane profiles is the invariable predominance of the n-C₂₂ alkane (OEP = 0.63 - 1.00: values close to unity come from higher rank samples), and this is believed to be related to the phosphatic nature of the Stairway Sandstone as a whole (cf. Section 4.6.4). However, in light of the analysis of further samples (see e.g. Figs 6.47 and 6.48) the distinction made earlier (Section 4.6.3) between phosphorites and non-phosphorites from the Stairway Sandstone, on the basis of their respective total alkane distributions (Fig. 4.24) and corresponding n-alkane profiles (Fig. 4.26), is evidently not universally applicable. Nevertheless, within the middle member of the formation, there appears to be a systematic change in hydrocarbon pattern with increasing phosphate content, namely,

- 1) shift of n-alkane maximum from C₁₇ to C₂₂,
- 2) broadening of n-alkane envelope from C₁₅ - C₂₄ to C₁₆ - C₃₀,
and
- 3) concomitant shift in position of naphthene hump to
higher carbon number.

These changes are partially illustrated in Figures 6.47 and 6.48.

Recognition of source and non-source facies in the Stairway Sandstone is complicated by the fact that there are no indigenous reservoir hydrocarbons with which to compare the EOM. (Note - The biodegraded oil impregnating tight sands of the Lower Stairway Sandstone in BMR AP 1 appears to be derived from the Horn Valley Siltstone: see Section 6.4). Moreover the odd/even predominance at n-C₁₇ and n-C₁₉ which characterizes the n-alkane profiles of the Pacoota and Horn Valley source facies is not observed in the Stairway Sandstone. Among the most crude oil-like total alkane patterns are those of shales from East Mereenie No. 1 (core 4, 820.8 m and BMR AP 3, 97.2 m). Condensate-like patterns were obtained from Tyler No. 1 (core 7, 3832.7 m) and Palm Valley No. 3 (core 1, 1855.3 m). All have n-alkane profiles with a maximum at C₁₇ and pr/n-C₁₇ values ≤ 0.4 (see e.g. core 4 in Fig. 6.42). Examples of n-alkane profiles from non-source

facies shales are shown in Figure 6.42 (East Mereenie No. 1, core 3, 811 m) and Figure 6.45 (Palm Valley No. 1, core 11, 1407 m).

Kerogen

Results of the partial geochemical and petrographic analysis of kerogens isolated from selected core samples of the Stairway Sandstone are summarized in Table 6.18.

Atomic H/C ratios decrease more or less regularly from 0.90-0.87 (eodiagenesis to early mesodiagenesis) in the vicinity of BMR AP 4 and 2, to 0.66-0.41 (late mesodiagenesis to telodiagenesis) in the Tyler-Palm Valley area. This trend conforms with the regional pattern of variation in organic maturation evident in the yield of associated EOM (mg/g C). PHGC analysis of three non-phosphorite kerogens (BMR AP 1, 78.3 m; BMR AP 3, 97.2 m; and Tyler No. 1, 3832.7 m) revealed a corresponding increase in the degree of aromatic condensation of the kerogen structure.

The graptolite reflectivity value of $\bar{R}_o \text{ max} = 0.6\text{-}0.8\%$ obtained from graptolite fragments in BMR AP 1 (78.3 m) confirms that the middle Stairway Sandstone at this locality is oil prone. However, the average yield of saturated hydrocarbons (32.4% EOM) from this part of the section is lower than that from the underlying Horn Valley Siltstone (42.6% EOM), suggesting that the Stairway kerogen (the presence of some Type II organic matter notwithstanding) is a less prolific source of liquid hydrocarbons. Moreover, the carbon isotopic composition of kerogen in the 'source facies' of the Stairway Sandstone ($\delta^{13}\text{C}_{\text{PDB}} = -26.5 \text{ to } 24.5\text{‰}$) is clearly different from that of the Horn Valley (and Pacoota) source facies kerogen ($\delta^{13}\text{C}_{\text{PDB}} = -32.5 \text{ to } -29.1\text{‰}$).

6.5 CORRELATION OF RESERVOIR HYDROCARBONS WITH SOURCE ROCKS

6.5.1 Gas

Analyses of gases from the various shows and discoveries in the Amadeus Basin are tabulated in Konecki and Blair (1970).

Gas in both the Mereenie and Palm Valley fields has a very low CO₂ content (range 0.00 - 0.53%, mean 0.10%). This is consistent with the original oxygen-poor (Type II) composition of the Horn Valley - Pacoota source kerogen.

Within the Pacoota Sandstone the wet gas (C₂₊) content of the reservoir gas (C₁ to C₄) decreases eastward, as expected, in the direction of increasing level of organic maturation (Table 6.19; cf. Fig. 1.2). In the two Mereenie wells for which analyses are available, gas in the Lower Stairway is wetter than that in both the Upper Stairway and the Pacoota. The existence of three discrete reservoirs in the Mereenie field is indicated. Moreover, compared with the gas in the Pacoota Sandstone, that in the Stairway Sandstone is on average wetter. This implies a somewhat milder thermal history for the Stairway gas. Because the stratigraphic separation of the lower Stairway and upper Pacoota sands at Mereenie is only 76-100 m (the thickness of the intervening Horn Valley Siltstone), a later date of entrapment must be postulated for the gas in the Stairway Sandstone. The compositional difference between the gases in the Stairway and Pacoota reservoirs is unlikely to be source-related because the kerogen in the Stairway lutites was originally more humic than that in the Horn Valley and Pacoota shales and therefore would have tended to generate drier gas, not wetter as observed.

As mentioned previously (Section 6.2.3), the extreme dryness of the Proterozoic gas (4.3% C₂₊) in Ooraminna No. 1 is not a true indication of regional maturation level. It probably also reflects the humic (Type III) composition of the parent kerogen in the Areyonga Formation.

6.5.2 Oil and condensate

Analytical data on the oils and condensates examined in this study (Table 2.3) are presented in Tables 6.20 and 6.21.

Proterozoic rocks

No oil has been found in Proterozoic reservoir beds. The formation with the greatest potential as a source of liquid hydrocarbons is the Bitter Springs Formation. Its kerogen appears to be richer in hydrogen than kerogen of comparable rank from the Pertatataka Formation (Table 6.8). In Mount Charlotte No. 1, both shales and dolomites of the Gillen Member are oil-mature. Their respective total alkane patterns (Figs. 6.50 and 6.51) are a guide to the characteristics one might expect to find in Proterozoic oils (>250°C fraction) if and where they have accumulated. Shale-derived oils will have an n-alkane profile with a maximum of C₁₇₋₁₉ (Fig. 6.50). In oils with dolomite source beds, the n-alkane maximum is located at n-C₂₂ and the naphthene hump is more pronounced (Fig. 6.51).

Isotopically, kerogens in the Bitter Springs Formation ($\delta^{13}\text{C}_{\text{PDB}} = -28.4$ to $-18.6^\circ/\text{oo}$) are considerably heavier than those in younger Proterozoic formations ($\delta^{13}\text{C}_{\text{PDB}} = -32.5$ to $-30.6^\circ/\text{oo}$) (Table 6.8, Fig. 6.56). This suggests that it should be possible to distinguish oils generated in the predominantly shallow marine carbonate-evaporite sequence of the Bitter Springs Formation, from any petroleum hydrocarbons which may have originated in the generally deeper-water shales and siltstones of the overlying Areyonga Formation and Pertatataka Formation (and its stratigraphic equivalent in the southwestern part of the basin, the Winnall Beds).

Cambrian rocks (Pertaoorrtta Group)

The most positive evidence of indigenous hydrocarbons in the Cambrian sequence of the Amadeus Basin is the core of oil-saturated dolomite

taken in the Giles Creek Dolomite in Alice No. 1. Although of only slightly lower gravity (43° API: Table 6.20) than the Mereenie oil (Table 6.21), the Alice oil has a quite distinctive composition. Saturates comprise a low 45.6% of the oil ($>250^{\circ}\text{C}$ fraction). The small size of the original sample precluded distillation and calculation of USBM correlation indices. Nevertheless, we may infer from the high resins plus asphaltenes content (41.5%) that the oil is naphthenic (tending to aromatic) in composition and immature. The sulphur content of the Alice oil is 0.19%, only marginally higher than that of the Mereenie crude (0.15%, $>267^{\circ}\text{C}$ fraction: Magellan, unpubl. data).

Additional indications of an apparent lack of maturity are displayed by the total alkane chromatogram of the oil (Fig. 6.52). The n-alkanes show a marked predominance of odd carbon-numbered homologues in the C_{15} - C_{20} range (OEP values: $\text{C}_{15} = 1.65$, $\text{C}_{17} = 1.55$, $\text{C}_{19} = 1.21$). Furthermore, the C_{22} n-alkane is also prominent (OEP = 0.79). Apart from being signs of immaturity, the presence of both compositional features in the one oil suggests that it had a mixed shale-carbonate source. As noted earlier (Section 6.3.3), a marked predominance of the n- C_{22} alkane appears to be common in the Giles Creek Dolomite, and is most strongly and consistently developed in anhydritic dolomite. The correlation between n- C_{22} and anhydritic dolomite is a second example of the close relationship between this hydrocarbon and a particular lithology (cf. the n- C_{22} - phosphorite association: Section 4.6). It also, of course, argues against the enhanced concentration of n- C_{22} being the result of contamination by plastic (cf. Douglas and Grantham, 1973). In any event, the saturated hydrocarbon distribution of the Alice oil shows that it was generated (at least in part) within the same formation in which it presently occurs. The odd/even predominance of the $<\text{C}_{20}$ n-alkanes is more pronounced in the oil than in shales of the Shannon Formation and Giles Creek Dolomite (Fig. 6.39). This is an indication that cracking of hydrocarbons has been more efficient in

the source shales (catalytic cracking) than in the reservoir dolomite (thermal cracking).

Finally, the $\delta^{13}\text{C}_{\text{PDB}}$ value of the oil ($-28.8^{\circ}/\text{oo}$: Table 6.20) is intermediate between those of kerogens isolated from shales in the Shannon Formation ($-28.0^{\circ}/\text{oo}$) and Giles Creek Dolomite ($-30.8^{\circ}/\text{oo}$) (Table 6.12). The oil, isotopically at least, has a somewhat closer affinity with the former kerogen, suggesting that dolomitic shale of the Shannon Formation may have been an important part of the source-bed sequence.

Cambro-Ordovician rocks (Larapinta Group).

The light oil ($45\text{--}47^{\circ}\text{API}$) found in the Pacoota Sandstone of the Mereenie field is highly paraffinic to paraffinic in composition (Fig. 6.49). By comparison, the condensates ($52 - 64^{\circ}\text{API}$) at Palm Valley and Mereenie are ultra-paraffinic to highly paraffinic, consistent with them being products of the progressive thermal maturation of oil in the reservoir. The USBM correlation indices of the oil from East Mereenie No. 3 are lower than those of the oil in East Mereenie No. 4 over the complete boiling range. This is probably due to the more highly evolved maturation state of the former oil. In this regard, it may be significant that the oil column in East Mereenie No. 3 is located in a more argillaceous section of the Pacoota reservoir (Unit P1) than is the case for East Mereenie No. 4 (Unit P3). The sulphur contents of oils and condensates alike are very low ($<0.07\%$).

A feature of both oils and condensates is the high saturates content ($82\text{--}89\%$) of their high-boiling fraction (Table 6.21). Conversely, the concentration of resins plus asphaltenes is low ($<15\%$, and mostly $<9\%$). This contrasts with the oils extracted from sands of the lower Stairway Sandstone and upper Pacoota Sandstone (P1) in BMR AP 1 (Table 6.20). In

these two oils saturated hydrocarbons account for only 32-37% of the total oil. Analysis by gas chromatography shows that they comprise a complex mixture of branched and cyclic alkanes (Fig. 6.55). Normal alkanes are highly depleted in the Pacoota oil and almost completely absent in the Stairway sample, a sign that both oils have been degraded in situ by bacteria (Bailey et al., 1973). The Stairway Sandstone is breached in the core of the anticline on which BMR AP 1 is located, permitting the entry of meteoric waters. The isotopic composition of the residual oil ($\delta^{13}\text{C}_{\text{PDB}} = 30.8^{\circ}/\text{oo}$) closely matches that of both kerogen and EOM in the source facies of the underlying Horn Valley Siltstone (Fig. 6.56).

A strong predominance of the C_{17} and C_{19} n-alkanes characterizes the total alkane chromatograms of the oils recovered from wells in the Mereenie field (Figs. 6.53 and 6.54). In the oil from East Mereenie No. 4, n- C_{17} is slightly more prominent (OEP = 1.23) than at East Mereenie No. 3 (OEP = 1.14). This discrepancy, and the larger naphthene hump of the former oil, accords with the apparent difference in oil maturity (noted above) between Units P1 and P3 in the Pacoota reservoir. As discussed in Sections 6.3.1 and 6.3.2, the Mereenie crude oil may be correlated with 'source shales' in the Horn Valley Siltstone and Pacoota Sandstone, primarily on the basis of its carbon isotopic composition ($\delta^{13}\text{C}_{\text{PDB}} = -31.0^{\circ}/\text{oo}$; Table 6.21) and unusual n-alkane distribution.

The characteristic n-alkane profile of the Mereenie oil(s) is nowhere seen in oil-mature lutites of the Stairway Sandstone. Should Stairway-source oils be found as a result of future exploratory drilling, it is reasonable to predict that their alkane pattern (cf. Figs. 6.47 and 6.48) and carbon isotopic composition (cf. Table 6.18, Fig. 6.56) will differ significantly from those of oils generated in the Pacoota Sandstone and Horn Valley Siltstone.

6.6 PRELIMINARY REGIONAL ASSESSMENT OF HYDROCARBON POTENTIAL

Wells et al., (1970) divided the Amadeus Basin into three areas of different character and petroleum potential: southern area, central folded belt and northern area (Fig. 6.57). The results of the present study throw further light on the prospectivity of each area by providing new information on the concentration, type and maturation of the organic matter in potential source rocks.

6.6.1 Southern area

Samples from three wells in this area were examined. Thick sequences (1180 - 1287 m) of Proterozoic sedimentary rocks were penetrated by Mt. Charlotte No. 1 and Erldunda No. 1, whereas BMR AP 4 tested a thin sequence of Ordovician clastics. In addition, at the Mt. Charlotte well location, the Proterozoic was overlain by 467 m of Cambrian marine shales, dolomites and evaporites.

In the fine-grained sediments analysed from the Mt. Charlotte sequence, the concentration of organic matter was generally low (<0.3% TOC), although higher organic carbon values (up to 1.37% TOC) have been reported previously from two intervals in the Gillen Member of the Proterozoic Bitter Springs Formation (Table 6.2). This unit appears to be the most attractive source rock in the area. It contains organic matter which, in terms of both composition (probable Type II) and rank (kerogen atomic H/C = 0.85-0.80; vitrinite-like phytoclast $\bar{R}_o$ max = 1.05-1.19%; 74.5% C₂₊ in cuttings gas), is appropriate for the generation of oil.

Kerogen in the overlying Pertatataka Formation is thermally somewhat less mature. It is also more humic in composition (Type III) and hence incapable of generating significant quantities of liquid hydrocarbons. Elsewhere, given an adequate thermal history, this formation may have some potential as a source of gas.

At Erldunda, the shale-siltstone lithofacies of the Winnall Beds contains up to 0.6% TOC. The dispersed organic matter, because of its highly aromatic (Type III-IV) composition, is dry gas prone. However, the high reflectivity of the vitrinite-like component ($\bar{R}_{O\max} = 2.18\%$) indicates that even the limited inherent hydrocarbon generating capacity of the kerogen may be nearly exhausted. Thus, in the southern part of the Amadeus Basin, the major limitations on hydrocarbon generating potential of the fine-grained sediments are the low concentration of dispersed organic matter, and its humic composition. Only certain black shales and dolomites within the Gillen Member in the vicinity of Mt. Charlotte have any significant capacity to generate liquid hydrocarbons. These factors, in conjunction with a lack of permeable reservoir beds of either Proterozoic or Cambrian age, serves to downgrade the petroleum prospects of the area. Levels of maturation range from immature in the Stairway Sandstone at BMR AP 4, through mature (oil prone) in the Gillen Member at Mt. Charlotte No. 1 to post-mature (dry gas prone) in the Winnall Beds at Erldunda No. 1.

6.6.2 Central folded belt

Six wells from this area of the basin (Fig. 6.57) were sampled for source rock evaluation: BMR AP 1-3, Highway Anticline No. 1, Ooraminna No. 1 and BMR Alice Springs No. 3.

In the eastern part of the central folded belt, Proterozoic formations penetrated by Ooraminna No. 1 and BMR Alice Springs No. 3 include several organic-rich intervals. At Ooraminna, black shales of the Pertatataka and Areyonga Formations contain 0.3-0.9% TOC whereas, in the core of the Ringwood Dome, evaporitic bituminous carbonates of the Gillen Member, Bitter Springs Formation, contain up to 0.8% TOC. Such organic carbon values are adequate to impart significant (although not abundant) source-rock potential to the formation in question. With the possible

exception of kerogen from the middle of the thick shale sequence which comprises the Pertatataka Formation, Proterozoic shales in Ooraminna No. 1 apparently contain humic organic matter that is unsuitable for the generation of oil. In terms of rank, the Pertatataka-Areyonga shales have evolved to the stage of late mesodiagenesis (vitrinite-like phytoclast $\bar{R}_o$ max = 1.40%). The likely hydrocarbon product is therefore gas condensate. The highly aromatic organic matter in the Gillen Member at BMR Alice Springs No. 3 has attained a rank corresponding to telodiagenesis (vitrinite-like phytoclast $\bar{R}_o$ max = 1.95%), and is dry gas prone. However, because this well was drilled in an allochthonous wedge of the Bitter Springs Formation in the structurally complex Ringwood-Olympic Thrust Zone, the organic geochemical data obtained may not provide a true indication of regional level of organic maturation for the Bitter Springs Formation at the eastern end of the central folded belt. The only source-rock data on Cambrian sediments in the central folded belt were obtained from Highway Anticline No. 1. Here the Jay Creek Limestone has reached the oil-generating phase of its diagenetic history, but lacks sufficient organic matter to be a good source rock. Previous work by Esso on Cambrian shales in East Johnny Creek No. 1 also revealed low organic carbon values (0.2-0.3%: Table 6.2).

In the area of the central folded belt which extends from Highway Anticline No. 1 in the east to East Johnny Creek No. 1 in the west (Fig. 6.57), three shallow BMR stratigraphic holes have tested the Stairway Sandstone and underlying Horn Valley Siltstone, both Ordovician formations. Lutites of the Stairway Sandstone (0.1-0.3% TOC) are less organic-rich than the Horn Valley Siltstone (0.3-0.8% TOC), which therefore has the greater source-rock potential.

This assessment is confirmed by the hydrogen-rich, sapropelic nature of its kerogen (atomic H/C = 1.01-1.11; cf. Stairway, 0.83-0.87) and the generally higher yield of associated EOM (14-221 mg/g C; cf. Stairway, 14-127 mg/g C). Although it is possible to recognize 'source' and 'non-

source' facies within each formation, the Stairway Sandstone, where thermally mature, is less likely to generate oil than is the Horn Valley Siltstone. Reflectivity measurements on graptolite remains in the Horn Valley Siltstone and Stairway Sandstone at BMR AP 1 ($\bar{R}_O \text{ max} = 0.6-0.8\%$) indicate that both formations are mature enough for the main phase of hydrocarbon generation to have begun. The level of organic maturation is slightly higher in the Ordovician sediments intersected by BMR AP 3, whereas those at BMR AP 2 are still immature.

Thus, along the northern edge of the central folded belt the thermal history of the preserved Ordovician sequence has been adequate for oil generation.

6.6.3 Northern area

The deep northern region of the Amadeus Basin incorporates the large hydrocarbon-bearing Mereenie and Palm Valley Anticlines (Fig. 6.57). It is here also that the thickest succession of sediments is preserved. Drilling has established the presence of productive reservoir sands and potential source rocks in the Larapinta Group (Cambro-Ordovician). In addition, a show of oil was encountered at depth in Alice No. 1, implying the existence of mature Cambrian source beds beneath the Brewer Plain north of the Ooraminna Anticline (Fig. 6.9). Source-rock and/or maturation data were obtained from the Cambrian section in Alice No. 1, and from 7 other wells which tested rocks of the Larapinta Group. Of the latter wells, all but two (Tyler No. 1 and West Waterhouse No. 1) were located within the Mereenie and Palm Valley Fields.

The most prospective Cambrian source beds in the area appear to be dolomitic shales of the Giles Creek Dolomite which contain up to 0.96% TOC (Table 6.2). Field observations of the Chandler Limestone by P.J. Cook (pers. comm., 1977) and others (see Wells et al., 1970) suggest that the

core samples of this formation examined in the present study may not be indicative of its true source-rock potential. Elsewhere the organic carbon content of the Chandler Limestone is likely to be considerably higher than the very low TOC values reported in Tables 6.9 and 6.11. Just how much higher is shown by the analysis of a single sample of dark foetid bituminous limestone (collected by A.T. Wells) from an outcrop in the Todd River area which assayed at 2.38% TOC. Notwithstanding their aromatic structure, kerogens from the Shannon Formation and Giles Creek Dolomite below 1100 m in Alice No. 1 appear to be still in the oil generation phase of their diagenetic history.

West of longitude 133° in the northern sector of the basin, the main zone of hydrocarbon generation is located within Ordovician rocks at present depths of 1000-1400 m (based on observations in the Mereenie field). Dark grey to black, pyritic, fossiliferous shales and siltstones in the Pacoota Sandstone (notably Unit P1: maximum TOC = 0.9%) and Horn Valley Siltstone (maximum TOC = 1.8%) are the most attractive source rocks in the Amadeus Basin. Much of their organic content is in the form of hydrogen-rich algal sapropel which, under appropriate thermal conditions, is capable of generating abundant oil.

Regional differences in level of organic maturation have been crucial in determining the type and present distribution of hydrocarbons in Ordovician reservoirs throughout the northern prospective area of the Amadeus Basin. As indicated in Figure 5.2, thermal maturity is related to the burial history of the sediments in question. A comprehensive analysis of the relationship between time, temperature and depth of burial as it pertains to oil and gas generation in the Amadeus Basin has yet to be undertaken, although a start was made by Kantsler and Cook (in Enclosure 5). The present study has shown that the Palm Valley and Mereenie fields differ appreciably in the thermal maturity of their respective source rocks and associated reservoir hydrocarbons. At Mereenie, where the levels of organic

maturation correspond to late mesodiagenesis (atomic H/C, Type II kerogen = 0.75-0.78; graptolite $\bar{R}_O$ max = 1.22-1.42%; C_{2+} = 21-32% of C_1 to C_4 in reservoir gas), source beds are light oil (or gas condensate) prone. At Palm Valley, the degree of maturation is close to that expected for telodiagenesis (atomic H/C, Type III kerogen = 0.60-0.65; graptolite $\bar{R}_O$ max = 2.00-2.37%; C_{2+} = 9-13% of C_1 to C_4 in reservoir gas) and hence the Pacoota-Horn Valley sequence is here capable of generating and/or conserving only relatively dry gas. In areas to the northeast of the Palm Valley field, even higher levels of organic maturation, and reservoir porosities of less than 4% (Kurylowicz and Ozimic, in Enclosure 5), can be anticipated.

Despite the great age of the source and reservoir rocks, and uncertainties in their history of burial and uplift prior to and following the Alice Springs Orogeny, the contrast in maturation level between the two main fields in the northern Amadeus Basin is at least consistent with the fact that the present depth of burial and reservoir temperature of the Pacoota Sandstone at Palm Valley (1717-2048 m; 84°C) are greater than at Mereenie (1021-1494 m; 60°C). These features are interpreted by Kantsler and Cook (Enclosure 5) to be relics of the deeper burial and more intense thermal history of the Palm Valley terrain.

Finally, it is considered to be significant that, for both source formations, organic carbon values are higher at Mereenie than in the Palm Valley area. This might be related to the fact that the Mereenie structure appears to be closer to the inferred depocentre of the basin for late Pacoota-Horn Valley time (see Wells et al., 1970, Fig. 23). Thus, more persistently euxinic bottom conditions, favouring a higher degree of organic preservation, may have characterized the Mereenie locality at that time. The lower TOC values at Palm Valley are compatible with the more humic nature of the organic matter, which would have accumulated under less reducing conditions. It follows from this hypothesis that the occurrence of light oil at Mereenie, as opposed to gas with minor condensate at Palm Valley, may in

part be source-related and not simply a function of the more intense thermal history of the source-reservoir sequence in and around the Palm Valley field. In any event, from the standpoint of both source-rock richness and maturation, future exploration for liquid hydrocarbons (oil and/or condensate) should be concentrated in the area to the immediate north and northeast of the Mereenie Anticline, in the vicinity of M Solitary, the Gardiner Range Anticline and the Carmichael Structure.

6.7 EPILOGUE

The results of these source-rock studies have certain implications for the petroleum prospects of the Amadeus Basin. Although both Proterozoic and Cambrian sediments have generated hydrocarbons their prospectivity is downgraded by the spasmodic occurrence of organic-rich (ie. >0.5% TOC) intervals through the section and an apparent absence of potential traps. The younger Larapinta Group lacks the carbonates which characterize the Proterozoic and Cambrian sequences, but more importantly it contains thick and extensive reservoir sands. It comprises sandstones, siltstones, and shales which include the best source rocks in the basin. These range from immature in the south to light oil prone in the Mereenie area and gas prone at Palm Valley. The most promising area for future discoveries of liquid hydrocarbons lies immediately north and northeast of the Mereenie field.

Development of the presently known oil and gas deposits at Mereenie and Palm Valley awaits the finding of suitable markets. Undoubtedly the discovery of further commercial quantities of hydrocarbons in the Amadeus Basin would enhance the development prospects of these two fields. Most of the major unbreached structures with good surface expression have already been drilled. Any remaining hydrocarbons will be found in smaller anticlinal traps, combination dip and fault structures, or stratigraphic plays, all of which are harder and more expensive to locate.

In documenting the quality and stratigraphic distribution of source rocks within the basin, this study has provided information essential both to reassessment of the general prospectivity of the region and, ultimately, to the selection of specific drilling targets.

Use of the proposed classification of microbial diagenesis materially assisted the recognition, characterization and evaluation of source rocks within the Proterozoic-Lower Palaeozoic succession of the Amadeus Basin. Differences in both kerogen type and thermal maturity, which are related respectively, to the source and depositional environment of the organic matter and its subsequent thermal history, emerged as the principal reasons for the observed variations in source-rock quality throughout the basin.

Incomplete elemental analysis prevented the unequivocal characterization of many kerogens in terms of their H/C and O/C atomic ratios, although, in some cases, PHGC data (benzene/n-C₆, toluene/n-C₇ and ethylbenzene/n-C₈ ratios) provided a supplementary measure of aliphatic versus aromatic character. Kerogen H/C atomic ratio and reflectivity of vitrinite-like phytoclasts and/or zooclasts were found to be the most useful indicators of diagenetic rank.

Hydrocarbon generating potential was assessed on the basis of EOM yield (mg/g C) and composition (% saturates, % total hydrocarbons); and kerogen composition (H/C atomic ratio, % volatile matter on pyrolysis, relative concentration of aliphatic hydrocarbons in PHGC products). In addition, geochemical 'fingerprinting' (using total alkane chromatogram, n-alkane profile and $\delta^{13}\text{C}$ value) proved to be an effective means of correlating the oils found in the basin with their respective source-rocks.

As a test of the preliminary classification of diagenesis described in Chapter 5, the results of this 'pilot' study are sufficiently encouraging to suggest that a similar approach to source-rock evaluation might fruitfully be employed in other onshore regions of Australia where

sedimentary rocks of late Proterozoic and/or early Palaeozoic age occur, such as the Canning, Officer, Arrowie and Georgina Basins.

APPENDIX

ANALYTICAL METHODS

Preface

General

Sample preparation

Analysis of sediments and rocks

Organic carbon

Phosphate

Extractable organic matter

Kerogen

Analysis of oils and condensates

PREFACE

As indicated in Chapter 2, two analytical schemes were employed in this study, one for fine-grained sediments and sedimentary rocks (Fig. 2.1) and the other for oils and condensates (Fig. 2.2). The purpose of this appendix is to supply details of the individual procedures and techniques specified in the flow-charts (Figs. 2.1 and 2.2). Where this information has been published the reader is referred to the appropriate reference or enclosure.

GENERAL

All solvents (mostly Unilab L.R. grade, Ajax Chemicals Ltd.) were distilled through the 91.5 cm x 25 mm Heligrid packing of a Podbielniak Hypercal Series 3700 fractional distillation unit. Periodic injections of distilled solvents and their rotary evaporation residues into the gas chromatograph (instrumental settings as for analysis of saturated hydrocarbon fraction of EOM) revealed no detectable impurities.

The routine precautions taken to minimize the introduction of contamination during the course of rock sample preparation, Soxhlet extraction, and EOM analysis were similar to those described by Eglinton et al. (1966). Only one case of significant contamination by hydrocarbons occurred and this was traced to the liners of screw-caps in a new batch of sample vials. These were replaced by Teflon liners.

SAMPLE PREPARATION

The materials investigated in the thesis study were of the following types:

1. freeze-dried cultures of algae and bacteria
2. rubbery algal mat
3. unlithified calcareous sediments
4. rock samples from surface outcrops
5. rock samples from drill-hole cores
6. oils and condensates

Samples in category 1 (Botryococcus braunii, Desulfovibrio gigas) were analysed for C, H, N, S and ash as received. The coorongite (category 2) was first freed of obvious foreign matter (sand grains, twigs etc.) by hand picking. Then, because of its rubbery nature, it was either reduced to a coarse powder (suitable for elemental and PHGC analysis) by abrading with a metal file, or cut into 5 mm pieces ready for homogenization (under chloroform) in a Sorvall Omnimixer, prior to solvent extraction in a Soxhlet apparatus. Core material from DSDP Site 262 was calcareous mud and ooze (category 3) which had been squeezed in a modified hydraulic press to remove interstitial water, dried at 60°C, and ground to approximately 100 mesh (0.149 mm) (P.J. Cook pers. comm., 1974). This material was sufficiently finely divided not to require further grinding before Soxhlet extraction. The torbanites, tasmanite shale, phosphorites (except Beetle Creek and Stairway), stromatolites, Tindelpine Shale suite, and carbonaceous cherts fell into category 4. Outside surfaces were removed with a water-lubricated diamond saw. The samples were then broken into chips (5-15 mm) by hammering on a clean steel surface. The chips were washed ultrasonically in benzene-methanol (3:1, 1 x 2 min), drained, air-dried and finally pulverized in a Siebtechnik disc mill to less than 200 mesh (0.074 mm). The powdered rock was stored in solvent-washed screw-top glass pomades while awaiting analysis. The remaining samples were drill-hole core material (category 5). Cores were sampled by slabbing with the diamond saw, or cutting small cylindrical plugs. Exposed surfaces were trimmed from the slabs or plugs before washing in solvent and crushing. The oils and condensates (category 6) were stored under refrigeration but otherwise received no special treatment prior to analysis.

ANALYSIS OF SEDIMENTS AND ROCKS

Total organic carbon

The procedure is outlined in Enclosure 1. The nominal weight of powdered rock taken for digestion in 4N HCl varied according to lithology, thus:

shale, siltstone, chert	4 g
carbonate, phosphorite	8 g
rock salt	12 g

The acid-digestion residue was isolated by centrifugation, washed with distilled water, oven-dried at 75°C and weighed. Before analysis, the residue was homogenized by gentle grinding in an agate mortar and pestle and a portion pelletized in a stainless steel die (13 mm i.d.; load, 10 tonnes). The actual analysis for organic carbon was performed in triplicate on accurately weighed aliquots (7-9 mg) of the pelletized carbonate-free sediment.

Phosphate

See Enclosure 1.

Extractable organic matter

EOM was isolated and analysed as described in Enclosure 1, with the following modifications and exceptions:

1. The powdered rock or sediment was extracted with benzene-methanol(3:2) for 50 hr (or, in the case of stromatolites and DSDP Hole 262 sediments, for 100 hr).
2. Coorongite and rock samples containing gypsum, anhydrite or halite were extracted with chloroform.
3. Elemental sulphur, where present in the crude extract (or saturated hydrocarbon fraction), was removed by reaction with colloidal copper.

4. The 'short-cut' asphaltene precipitation procedure described in Enclosure 1 was abandoned when, during analysis of the first DSDP extracts, it was found that waxy (C_{23+}) n-alkanes co-precipitated with the asphaltenes. Thereafter, the standard Institute of Petroleum method (IP 143/57) was used (McKirdy and Horvath, 1976: Enclosure 6), but only when the crude extract exceeded 20 mg in weight. Otherwise, the asphaltenes were not removed and the complete extract was transferred to the alumina column for liquid chromatography.
5. The standard temperature programme for capillary gas chromatography was 80-250°C at 4°C/min.
6. Towards the end of the thesis project, the Apiezon L column was replaced with a stainless steel, SE-30 coated capillary column of similar dimensions.

For liquid chromatography, alumina: sample ratios were in the range 200-500:1. The volume of each eluting solvent was 3.5 x alumina-bed volume. Extracts and the various fractions resulting from liquid chromatography were stored under refrigeration in solvent-washed glass vials with Teflon or Alfoil-lined screw caps.

Normal alkane profiles and pristane/phytane ratios were obtained by measuring peak areas (peak height above background x width at half peak height) directly from the gas chromatogram of the total alkane (i.e. saturated hydrocarbon) fraction. As a visual representation of pr/n- C_{17} and ph/n- C_{18} ratios, pristane and phytane (represented by dashed lines) were usually included in the n-alkane profile. The identification of nor-pristane was based only on comparison of its retention time with published values and hence must be regarded as tentative. The ratio of odd to even-carbon-numbered n-alkanes was computed for selected alkanes using the OEP formula of Scalan and Smith (1970).

Kerogen

Details of the techniques employed in the isolation and analysis of kerogen may be found in Enclosures 1, 3 and 4. Information on IR analysis, PHGC analysis and microscopic examination of the kerogens, not provided in the enclosures, is set out below.

IR analysis Infra-red spectra of kerogen concentrates were obtained from potassium bromide (KBr) disc mounts. Spectroscopic KBr (200 mg) was ground with kerogen (0.1-0.5% w/w) in a small agate ball mill for 2 min. The powdered mixture was pressed into a translucent disc in an evacuable KBr die (D-01, 13 mm i.d., Research and Industrial Instruments Co.). The die was evacuated with a backing pump for 1-5 min., and a load of 8 tonnes applied for a further 2-3 min. The resulting disc was mounted in a stainless steel sample holder and placed in the reference beam of a Shimadzu IR 27-G Recording Infrared Spectrophotometer. The majority of the spectra were run with a blank KBr disc in the reference beam. All discs were prepared under a heating lamp to minimize absorption of moisture by the KBr. The areas of the 2900, 1700, 1600 and 1450 cm^{-1} absorption bands on the recorder chart were measured with a planimeter.

PHGC analysis The basic apparatus and experimental parameters have been described by McHugh et al. (1976). For the present work, the equipment and operating conditions were modified as follows:

Sample size	0.2 - 2 mg
Pyrolysis temperature	600°C
Pyrolysis time	5 min.
H ₂ flow rate through pyrolyser	30 ml/min.
Gas chromatograph	Perkin-Elmer Model F30
Column	40 m x 0.5 mm i.d. glass SCOT, with SE-30 as stationary liquid phase
Carrier gas	He
Flow rate through column	2 ml/min.

After leaving the pyrolyser, the pyrolysis products passed through the

hydrogenator (750 x 3 mm i.d. stainless steel tube containing 1% Pd on Chromosorb W, heated to 300°C by a heating tape) and into a cold trap (150 x 1.4 mm i.d. stainless steel U-tube packed with 80-100 mesh chromosorb W, immersed in liquid nitrogen). Upon completion of the pyrolysis, the cold trap was quickly removed from the end of the hydrogenator and placed (via Swagelok fittings) in the oven of the gas chromatograph between the injection port and SCOT column. Rapid heating of the trap by direct application of a low-voltage current volatilized the hydrogenated pyrolysis products and facilitated their flushing on to the column. The oven door was then closed and the chromatograph temperature programmed from 50-300°C at 10°C/min., with a final heating time of 10 min. Major peaks in the C₄-C₂₀ range of the resulting chromatogram were identified by comparison with a reference PHGC trace of the Greta coal (courtesy J.W. Tardif). In this trace, obtained under the same experimental conditions, the major component peaks had been characterized by mass spectrometry. Periodic blanks were run and appropriate corrections applied to the kerogen PHGC's when measuring peak heights.

Microscopic examination Glycerine jelly mounts of selected kerogens (with 18 x 18 mm glass cover slips) were prepared for microscopic examination under plane polarized transmitted light. The instrument used was a Zeiss Photomicroscope III with x 63 planapochromat oil immersion objective (x 1000 magnification) and automatic exposure. Photomicrographs (Plates 4.1, 4.2, 4.3, 4.13 and 6.4) were taken with Kodacolor II, C135 film (80 ASA). Acritarchs in the Stairway Sandstone (Plate 4.1) were identified and photographed by M.R. Walter (B.M.R). All petrographic work (viz. maceral identification, reflectivity measurements and photography) on sediments and kerogen concentrates in polished section was undertaken by A.J. Kantsler (University of Wollongong).

ANALYSIS OF OILS AND CONDENSATES

Stable carbon isotopic analyses were performed by Geochron Laboratories Inc., Cambridge, Massachusetts. All other tests and analyses were carried out as described in Powell and McKirdy (1972, 1975, 1976) and summarized in Enclosure 6.

BIBLIOGRAPHY

Note: references omitted from the original compilation
are listed separately on pages 299 & 300.

BIBLIOGRAPHY

- ABELSON, P.H., 1967. Conversion of biochemicals to kerogen and n-paraffins. In, Researches in Geochemistry, 2. (ed. P. H. Abelson), Wiley, New York, N.Y., pp. 63-86.
- ACKMAN, R.G., TOCHER, C.S. & McLACHLAN, J., 1968. Marine phytoplankter fatty acids. J. Fish. Res. Bd Can., 25, 1603-1620.
- AIZENSHTAT, Z., BAEDECKER, M.J. & KAPLAN, I.R., 1973. Distribution and diagenesis of organic compounds in JOIDES sediment from Gulf of Mexico and western Atlantic. Geochim. Cosmochim. Acta, 37, 1881-1898.
- ALBAIGES, J. & TORRADAS, J.M., 1974. Significance of the even-carbon n-paraffin preference of a Spanish crude oil. Nature, 250, 567-568.
- ALBRECHT, P. & OURISSON, G., 1969. Diagenèse des hydrocarbures saturés dans une série sédimentaire épaisse (Douala, Cameroun). Geochim. Cosmochim. Acta, 33, 138-142.
- ALBRO, P.W. & DITTMER, J.C., 1970. Bacterial hydrocarbons: occurrence, structure and metabolism. Lipids, 5(3), 320-325.
- ALBRO, P.W. & HUSTON, C.K., 1964. Lipids of Sarcina lutea II. Hydrocarbon content of the lipid extracts. J. Bacteriol., 88, 981-986.
- ALLAN, J. & DOUGLAS, A.G., 1974. Alkanes from the pyrolytic degradation of bituminous vitrinites and sporinites, In, Advances in Organic Geochemistry 1973 (eds.B. Tissot & F. Bienner), Editions Technip, Paris, pp. 203-206.

- ANHAUESSER, C.R. & BUTTON, A., 1974. A review of southern African stratiform ore deposits - their position in time and space. Inf. Circ. Econ. Geol. Res. Unit, Univ. Witwatersrand, Johannesburg, 85.
- ARMSTRONG, R.L. & STEWART, A.J., 1975. Rubidium-strontium dates and excess argon in the Arltunga Nappe Complex, Northern Territory. J. Geol Soc. Aust., 22, 103-115.
- AUSTRALIAN AQUITAINE, 1974. Contention Heights No. 1 well, W.A. Well completion report. Australian Aquitaine Petroleum Pty. Ltd., (unpubl.).
- BAILEY, N.J.L., JOBSON, A.M. & ROGERS, M.A., 1973. Bacterial degradation of crude oil: comparison of field and experimental data. Chem. Geol., 11, 203-221.
- BAILEY, N.J.L., EVANS, C.R. & MILNER, C.W.D., 1974. Applying petroleum geochemistry to search for oil: examples from Western Canada Basin. Bull. Am. Ass. Pet. Geol., 58, 2284-2294.
- BAKER, D.R., 1962. Organic geochemistry of Cherokee Group in Southeastern Kansas and Northeastern Oklahoma. Bull. Am. Ass. Pet. Geol., 46, 1621-1642.
- BAKER, E.G., 1967. A geochemical evaluation of petroleum migration and accumulation. In, Fundamental Aspects of Petroleum Geochemistry (eds. B. Nagy & U. Colombo), Elsevier, Amsterdam, pp. 299-329.
- BARBAT, W.N., 1967. Crude-oil correlations and their role in exploration. Bull. Am. Ass. Pet. Geol., 51, 1255-1292.
- BALDUCCHI, A. & POMMIER, G., 1970. Cambrian oil field of Hassi Messaoud, Algeria. In, Geology of Giant Petroleum Fields (ed. M.T. Halbouty), Am. Ass. Pet. Geol., Mem. 14: pp. 477-488.
- BANKS, M.R., 1962. The geology of Tasmania-Permian. J. Geol. Soc. Aust., 9, 189-215.

BARGHOORN, E.S., MEINSCHIN, W.G. & SCHOPF, J.W., 1965.

Paleobiology of a Precambrian shale. Science, 48, 461-472.

BARGHOORN, E.S., KNOLL, A.H., DEMBICKI, H., Jr. & MEINSCHIN,

W.G., 1977. Variation in stable carbon isotopes in organic matter from the Gunflint Iron Formation.

Geochim. Cosmochim. Acta, 41, 425-430.

BARRIE, J., 1964. Phosphate drilling, Amadeus Basin. Bur.

Miner. Resour. Aust. Rec., 1964/195 (unpubl.).

BECKER, L.E. & PATTON, J.B., 1968. World occurrence of

petroleum in pre-Silurian rocks. Bull. Am. Ass. Pet.

Geol., 52, 224-245.

BERKNER, L.V. & MARSHALL, L.C., 1965. On the origin and rise

of oxygen concentration in the earth's atmosphere.

J. Atmos. Sci., 22, 225-261.

BERNER, R.A., 1971. Principles of Chemical Sedimentology.

McGraw-Hill, New York, N.Y., 240 pp.

BESTOUGEFF, M., BYRAMJEE, R. & VASSE, L., 1969. Classification

and characterization of high-sulphur crude oils. In,

Advances in Organic Geochemistry 1968 (eds. P.A. Schenck

& I. Havenaar), Pergamon, Oxford, pp. 331-344.

BIRCH, F. & CLARK, H., 1940. The thermal conductivity of rocks

and its dependence on temperature and pressure. Am. J.

Sci., 238, 529-558, 613-635.

BIRD, C.W., LYNCH, J.M., PIRT, S.J. & REID, W.W., 1971a.

The identification of hop-22(29)-ene in prokaryotic organisms. Tetrahedron Lett., 3189-3190.

BIRD, C.W., LYNCH, J.M., PIRT, S.J., REID, W.W., BROOKS, C.J.W.

& MIDDLEDITCH, B.S., 1971b. Steroids and squalene in

Methylococcus capsulatus grown on methane. Nature, 230,

473-474.

- BLACKBURN, K.B. & TEMPERLEY, B.N., 1936. Botryococcus and the algal coals. Trans. R. Soc. Edinburgh, 58(3), 841-868.
- BLUMER, M., 1970. Dissolved organic compounds in sea water: saturated and olefinic hydrocarbons and singly branched fatty acids. In, Organic Matter in Natural Waters (ed. D.W. Hood), Inst. Mar. Sci., Univ. of Alaska, Occas. Publ. 1, 153-167.
- BLUMER, M. & THOMAS, D.W., 1965a. Phytadienes in zooplankton. Science, 147, 1148-1149.
- BLUMER, M. & THOMAS, D.W., 1965b. "Zamene" isomeric C₁₉ monoolefins from marine zooplankton, fishes, and mammals. Science, 148, 370-371.
- BLUMER, M. & SNYDER, W.D., 1965. Isoprenoid hydrocarbons in recent sediments: Presence of pristane and probable absence of phytane. Science, 150, 1588-1589.
- BLUMER, M., ROBERTSON, J.C., GORDON, J.E. & SASS, J., 1969. Phytol-derived C₁₉ di-and triolefinic hydrocarbons in marine zooplankton and fishes. Biochemistry, N.Y., 8, 4067-4074.
- BLUMER, M., GUILLARD, R.R.L. & CHASE, T., 1971. Hydrocarbons of marine phytoplankton. Mar. Biol., 8(3), 183-189.
- BOCAL, 1972. Source rock report. Bocal Pty. Ltd. (unpubl.).
- BOCAL, 1975. Formation temperature data as an aid to the evaluation of hydrocarbon prospects on the Australian Northwest Shelf. Bocal Pty. Ltd. (unpubl.).
- BODE, G.W., 1974. Carbon and carbonate analyses, Leg 27. In, J. J. Veevers et al., Initial Reports of the Deep Sea Drilling Project. Vol. 27, U.S. Govt. Printing Office, Washington, pp. 499-502.

- BOON, J.J., DE LEEUW, J.W. & SCHENCK, P.A., 1975. Organic geochemistry of Walvis Bay diatomaceous ooze -1. Occurrence and significance of the fatty acids. Geochim. Cosmochim. Acta, 39, 1559-1565.
- BOON, J.J., DE LEEUW, J.W., VAN DER HOEK, G.J. & VOSJAN, J.H., 1977. Significance and taxonomic value of iso and anteiso monoenoic fatty acids and branched β -hydroxy acids in Desulfovibrio desulfuricans. J. Bacteriol., 129, 1183-1191.
- BORDOVSKIY, O.K., 1965. Accumulation and transformation of organic substances in marine sediments. Marine Geol., 3, 3-114.
- BORNHAUSER, M., 1950. Oil and gas accumulation controlled by sedimentary facies in Eocene Wilcox to Cockfield Formations, Louisiana Gulf Coast. Bull. Am.Ass. Pet. Geol., 34, 1887-1896.
- BOSTICK, N.H., 1973. Time as a factor in thermal metamorphism of phytoclasts (coaly particles). Congr. Int. Stratigraphie et Géologie Carbonifère, 7th, Krefeld, 1971, Compte Rendu, 2, 183-193.
- BRADLEY, W.H., 1970. Green River oil shale - concept of origin extended: an inter-disciplinary problem being attacked from both ends. Bull. Geol. Soc. Am., 81, 985-1000.
- BRADLEY, W.H., 1973. Oil shale formed in desert environment: Green River Formation, Wyoming. Bull. Geol. Soc. Am., 84, 1121-1123.
- BRAY, E.E. & EVANS, E.D., 1961. Distribution of n-paraffins as a clue to recognition of source beds. Geochim. Cosmochim. Acta, 22, 2-15.
- BRONGERSMA-SANDERS, M., 1966. The fertility of the sea and its bearing on the origin of oil. Advancement of Sci., 23 (107), 41-46.

- BROOKS, J.D., 1969. Hydrocarbon composition in cores from Mt. Charlotte No. 1 well. C.S.I.R.O., Division of Mineral Chemistry, Investigation Rept.304R, (unpubl.).
- BROOKS, J.D., 1970. The use of coals as indicators of the occurrence of oil and gas. Aust. Pet. Explor. Ass. J., 10(1), 35-40.
- BROOKS, J.D. & SMITH, J.W., 1967. The diagenesis of plant lipids during the formation of coal, petroleum and natural gas - I. Changes in the n-paraffin hydrocarbons. Geochim. Cosmochim. Acta, 31, 2389-2397.
- BROOKS, J.D., GOULD, K. & SMITH., J.W., 1969. Isoprenoid hydrocarbons in coal and petroleum. Nature, 222, 257-259.
- BROOKS, J. & SHAW, G., 1972. Geochemistry of sporopollenin. Chem. Geol., 10, 69-87.
- BROOKS, J., MUIR, M.D. & SHAW, G., 1973. Chemistry and morphology of Precambrian microorganisms. Nature, 244, 215-217.
- BROOKS, P.W. & MAXWELL, J.R., 1974. Early stage fate of phytol in a recently deposited lacustrine sediment. In, Advances in Organic Geochemistry 1973 (eds. B. Tissot & F. Bienner), Editions Technip, Paris, pp. 977-991.
- BROWN, A.C., KNIGHTS, B.A. & CONWAY, E., 1969. Hydrocarbon content and its relationship to physiological state in the green alga, B. braunii. Phytochemistry, 8(3), 543-547.
- BROWN, F.S., BAEDECKER, M.J., NISSENBAUM, A. & KAPLAN, I.R., 1972. Early diagenesis in a reducing fjord, Saanich Inlet, British Columbia - III. Changes in organic constituents of sediment. Geochim. Cosmochim. Acta, 36, 1185-1203.

- BURGESS, J.D., 1974. Microscopic examination of kerogen (dispersed organic matter) in petroleum exploration. In, Carbonaceous Materials as Indicators of Metamorphism (eds. R.R. Dutcher, P.A. Hacquebard, J.M. Schopf & J.A. Simon), Geol. Soc. Am., Spec. Pap. 153, pp. 19-30.
- BURLINGAME, A.L., WSZOLEK, P.C. & SIMONEIT, B.R., 1969. The fatty acid content of Tasmanites. In, Advances in Organic Geochemistry 1968 (eds. P.A. Schenck & I. Havenaar), Pergamon, Oxford, pp. 131-155.
- BURNE, R.V. & KANTSLER, A.J., (in prep.). Geothermal constraints on the hydrocarbon potential of the Canning Basin, Western Australia. Bur. Miner. Resour. J.
- BURST, J.F., 1969. Diagenesis of Gulf Coast sediments and its possible relation to petroleum migration. Bull. Am. Ass. Pet. Geol., 53, 73-93.
- BYRAMJEE, R. & VASSE, L., 1969. Geochemical interpretation of Libyan and North-Saharan crude oil analysis. In, Advances in Organic Geochemistry 1968 (eds. P.A. Schenck & I. Havenaar), Pergamon, Oxford, pp. 319-330.
- CANE, R.F., 1967. The constitution and synthesis of oil shale. World Pet. Congr. Proc., 7th, Mexico City, 3, 681-689.
- CANE, R.F., 1968. The nature of Tasmanian oil shale. Proc. R. Soc. Tasmania, 102, 65-68.
- CANE, R.F., 1969. Coorongite and the genesis of oil shale. Geochim. Cosmochim. Acta, 33, 257-265.
- CANE, R.F. & ALBION, P.R., 1971. The phytochemical history of torbanites. J. Proc. R. Soc. New South Wales, 104, 31-37.
- CANE, R.F. & ALBION, P.R., 1973. The organic geochemistry of torbanite precursors. Geochim. Cosmochim. Acta, 37, 1543-1549.

- CANAVAN, F., 1965. Iron ore deposits of Roper Bar. In, Geology of Australian Ore Deposits (ed. J. McAndrew), 8th Commonw. Min. Metall. Congr. Publ., 1, 233-246. 266.
- CHAPMAN, R.E., 1972. Primary migration of petroleum from clay source rocks. Bull. Am. Ass. Pet. Geol., 56, 2185-2191.
- CLARK, R.C. Jnr. & BLUMER, M., 1967. Distribution of n-paraffins in marine organisms and sediment. Limnol. Oceanogr., 12, 79-87.
- CLOUD, P.E., 1972. A working model of the primitive Earth. Am. J. Sci., 272, 537-548.
- CLOUD, P., 1976. Beginnings of biospheric evolution and their biogeochemical consequences. Paleobiology, 2, 351-387.
- COMBAZ, A., 1971. Thermal degradation of sporopollenin and genesis of hydrocarbons. In, Sporopollenin (eds. J. Brooks, P.R. Grant, M.D. Muir, P. Van Gijzel and G. Shaw), Academic Press, London, pp. 621-653.
- COMBAZ, A., 1974. La matière algaire et l'origine du pétrole. In, Advances in Organic Geochemistry 1973 (eds. B. Tissot, & F. Bienner), Editions Technip, Paris, pp. 423-438.
- COMBAZ, A. & PENIGUEL, G., 1972. Etude palyno-stratigraphique de l'Ordovicien dans quelques sondages du Bassin de Canning (Australie Occidentale). Bull. Cent. Rech. Pau - SNPA, 6, 121-167.
- CONACHER, H.R.J., 1938. Coorongite and its occurrence. In, Oil Shale and Cannel Coal, Inst. Petroleum, pp. 42-49.
- CONNAN, J., 1974. Time - temperature relations in oil genesis. Bull. Am. Ass. Pet. Geol., 58, 2516-2521.

- COOK, P.J., 1967. Winnowing - an important process in the concentration of the Stairway Sandstone (Ordovician) phosphorites of central Australia. J. Sediment. Petrol., 37, 818-828.
- COOK, P.J., 1971. Illamurta Diapiric complex and its position on an important central Australian structural zone. Bull. Am. Ass. Pet. Geol., 55, 64-79.
- COOK, P.J., 1972. Sedimentological studies on the Stairway Sandstone of central Australia. Bur. Miner. Resour. Aust., Bull., 95, 73 p.
- COOK, P.J., 1974. Geochemistry and diagenesis of interstitial fluids and associated calcareous oozes, Deep Sea Drilling Project, Leg 27, Site 262, Timor Trough. In, J.J. Veevers et al., Initial Reports of the Deep Sea Drilling Project, Vol. 27, U.S. Govt. Printing Office, Washington, pp. 463-480.
- COOK, P.J., 1976. Sedimentary phosphate deposits. In, Handbook of Strata-bound and Stratiform Ore Deposits. (ed. K. H. Wolf), Elsevier, Amsterdam, pp. 505-535.
- COOPER, B.S. & MURCHISON, D.G., 1969. Organic geochemistry of coal. In, Organic Geochemistry: methods and results (eds. G. Eglinton & M.T.J. Murphy), Springer-Verlag, New York, N.Y., pp. 699-726.
- CORDELL, R.J., 1973. Colloidal soap as proposed primary migration medium for hydrocarbons. Bull. Am. Ass. Pet. Geol., 57, 1618-1643.
- CORDELL, R.J., 1977. How oil migrates in clastic sediments. Part 4. World Oil, 184 (2), 36-38.
- CORNELIUS, C.D., 1975. Geothermal aspects of hydrocarbon exploration in the North Sea area. Norges geol. Unders., 316, 29-67.

- CORREIA, M., 1971. Diagenesis of sporopollenin and other comparable organic substances: application to hydrocarbon research. In, Sporopollenin, (eds. J. Brooks, P.R. Grant, M.D. Muir, P. Van Gijzel & G. Shaw). Academic Press, London, pp. 569-620.
- CORREIA, M. & CONNAN, J., 1974. Analyses physico-chimiques et observations microscopiques de la matiere organique de schistes bitumineux australiens. In, Advances in Organic Geochemistry 1973 (eds. B. Tissot & F. Biennner), Editions Technip, Paris, pp. 153-161.
- CORREIA, M. & PENIGUEL, G., 1975. Etude microscopique de la matiere organique - ses applications a l'exploration petroliere. Bull. Centre Rech. Pau - SNPA, 9(1), 99-127.
- CRAMER, F.H. & DIEZ, M.d.C.R., 1974. Silurian acritarchs: distribution and trends. Rev. Palaeobot. Palynol., 18, 137-154.
- CREEVY, K., 1971. Recent information and prospects in the Kidson Sub-basin. Aust. Pet. Explor. Ass. J., 11, 53-58.
- CUMMINS, J.J. & ROBINSON, W.E., 1964. Normal and isoprenoid hydrocarbons isolated from oil-shale bitumen. J. Chem. Eng. Data, 9, 304-307.
- DAVIS, J.B., 1968. Paraffinic hydrocarbons in the sulfate-reducing bacterium Desulfovibrio desulfuricans. Chem. Geol, 3, 155-160.
- DEGENS, E.T., 1969. Biogeochemistry of stable carbon isotopes. In, Organic geochemistry: methods and results. (eds. G. Eglinton & M.T.J. Murphy), Springer-Verlag, New York, N.Y., pp. 304-329.
- DEGENS, E.T., GUILLARD, R.R.L., SACKETT, W.M. & HELLEBUST, J.A., 1968a. Metabolic fractionation of carbon isotopes in marine plankton, Part I: temperature and respiration experiments. Deep-Sea Res., 15, 1-9.

- DEGENS, E.T., BEHRENDT, M., GOTTHARDT, B. & REPPMANN, E., 1968b. Metabolic fractionation of carbon isotopes in marine plankton -II. Data on samples collected off the coasts of Peru and Ecuador. Deep - Sea Res., 15, 11-20.
- DE KEYSER, F. & COOK, P.J., 1972. Geology of the Middle Cambrian phosphorites and associated sediments of Northwestern Queensland. Bur. Miner. Resour. Aust. Bull., 138, 79 p.
- DE LEEUW, J.W., CORREIA, V.A. & SCHENCK, P.A., 1974. On the decomposition of phytol under simulated geological conditions and in the top-layer of natural sediments. In, Advances in Organic Geochemistry 1973 (eds. B. Tissot & F. Bienner), Editions Technip, Paris, pp. 993-1004.
- DEMAISON, G.J. & SHIBAOKA, M., 1975. Contribution to the study of hydrocarbon generation from hydrogen-poor kerogen. Proc. World Pet. Congr., 9th, Tokyo, 2, 195-197.
- DEMBICKI, H. Jr., MEINSCHEN, W.G. & HATTIN, D.E., 1976. Possible ecological and environmental significance of the predominance of even-carbon number $C_{20}-C_{30}$ n-alkanes. Geochim. Cosmochim. Acta, 40, 203-208.
- DEROO, G., 1976. Correlations of crude oils and source rocks in some sedimentary basins. Bull. Centre Rech, Pau - SNPA, 10, 317-335.
- DE ROSA, M., GAMBACORTA, A., MINALE, L. & BU'LOCK, J.D., 1973. Isoprenoids of Bacillus acidocaldarius. Phytochemistry, 12, 1117-1123.
- DEVINE, S.B., 1975. An assessment of the onshore petroleum potential of Central and South Australia. Aust. Pet. Explor. Ass. J, 15(2), 60-71.
- DICKEY, P.A., 1975. Possible primary migration of oil from source rock in oil phase. Bull. Am. Ass. Pet. Geol., 59, 337-345.

- DICKEY, P.A. & HUNT, J.M., 1972. Geochemical and hydrogeologic methods of prospecting for stratigraphic traps. In, Stratigraphic Oil and Gas Fields - classification exploration methods and case histories (ed. R.E. King), Am. Ass. Pet. Geol., Mem. 16, 136-167.
- DOTT, R.H. Sr. & REYNOLDS, M.J., 1969. Sourcebook for Petroleum Geology. Am. Ass. Pet. Geol., Mem. 5, 471 pp.
- DOUGLAS, A.G. & GRANTHAM, P.J., 1973. Docosane in rock extracts: a possible contaminative source. Chem. Geol., 12, 249-255.
- DOUGLAS, A.G. & GRANTHAM, P.J., 1974. Fingerprint gas chromatography in the analysis of some native bitumens, asphalts and related substances. In, Advances in Organic Geochemistry 1973 (eds. B. Tissot & F. Bienner), Editions Technip, Paris, pp. 261-276.
- DOUGLAS, A.G., EGLINTON, G. & MAXWELL, J.R., 1969. The hydrocarbons of coorongite. Geochim. Cosmochim. Acta, 33, 569-577.
- DOW, W.G., 1974. Application of oil-correlation and source-rock data to exploration in the Williston Basin. Bull. Am. Ass. Pet. Geol., 58, 1253-1262.
- DOWNIE, C., 1973. Observations on the nature of the Acritarchs. Palaeontology, 16, 239-259.
- DREWS, G. & GOLLWITZER, W., 1965. Untersuchungen an der Polysaccharidfraktion der Zellwände von Anacystis nidulans. Arch. Mikrobiol., 51, 179-185.
- DROBOT, D.I. & PRESNOVA, R.N., 1975. Organic sulphur compounds in oils of the Vendian and Lower Cambrian of the Siberian Platform. Geol. Nefti Gaza, 1, 47-52.
- DULHUNTY, J.A., 1944. Origin of the New South Wales torbanites. Proc. Linnean Soc. N.S.W., 69, 26-48.

- DUNGWORTH, G. & SCHWARTZ, A.W., 1972. Kerogen isolates from the Precambrian of South Africa and Australia: analysis for carbonised micro-organisms and pyrolysis gas liquid chromatography. In, Advances in Organic Geochemistry 1971 (eds. H. R. von Gaertner & H. Wehner), Pergamon, Oxford, pp. 699-706.
- DUNGWORTH, G. & SCHWARTZ, A.W., 1974. Organic matter and trace elements in Precambrian rocks from South Africa. Chem. Geol., 14, 167-172.
- DUNN, P.R., 1963. Urapunga, N.T. - 1:250 000 Geological Series. Bur. Miner. Resour. Aust. Explan. Notes, SD/53-10.
- DUNOYER DE SEGONZAC, G., 1970. The transformation of clay minerals during diagenesis and low-grade metamorphism: a review. Sedimentology, 15, 281-346.
- DURAND, B. & ESPITALIÉ, J., 1973. Evolution de la matière organique au cours de l'enfouissement des sédiments. Comptes Rendu Acad. Sci. Paris, Ser. D., 276, 2253-2255.
- EADIE, B.J. & JEFFREY, L.M., 1973. $\delta^{13}\text{C}$ analyses of oceanic particulate organic matter. Mar. Chem., 1, 199-209.
- ECKELMANN, W.R., BROECKER, W.S., WHITLOCK, D.W. & ALLSUP, J.R., 1962. Implications of carbon isotopic composition of total organic carbon of some recent sediments and ancient oils. Bull. Am. Ass. Pet. Geol., 46, 699-704.
- EDGAR, N.T., SAUNDERS, J.B., et al., 1973. Initial Reports of the Deep Sea Drilling Project, Vol. 15, U.S. Govt. Printing Office, Washington.
- EGLINTON, G., SCOTT, P.M., BELSKY, T., BURLINGAME, A.L., RICHTER, W. & CALVIN, M., 1966. Occurrences of isoprenoid alkanes in a Precambrian sediment. In, Advances in Organic Geochemistry 1964 (eds. G.D. Hobson & M.C. Louis), Pergamon, Oxford, pp. 41-74.

- EICHMANN, R. & SCHIDLOWSKI, M., 1974. Isotopic composition of carbonaceous matter from the Precambrian uranium deposits of the Blind River district, Canada. Naturwissenschaften, 61(10), 449.
- EISMA, E. & JURG, J.W., 1969. Fundamental aspects of the generation of petroleum. In, Organic Geochemistry: methods and results (eds. G. Eglinton & M.T.J. Murphy), Springer-Verlag, New York, pp. 676-698.
- ENSMINGER, A., VAN DORSSELAER, A., SPYCKERELLE, Ch., ALBRECHT, P. & OURISSON, G., 1974. Pentacyclic triterpenes of the hopane type as ubiquitous geochemical markers: origin and significance. In, Advances in Organic Geochemistry 1973 (eds. B. Tissot & F. Bienner), Editions Technip, Paris, pp. 245-260.
- EPSTEIN, A.G., EPSTEIN, J.B. & HARRIS, L.D., 1977. Conodont color alteration - an index to organic metamorphism. U.S. Geol. Surv., Prof. Pap., 995, 27 pp.
- ESSO 1965. Organic geochemical analysis of twelve shale cores from the Amadeus Basin, Australia. Esso Exploration, Aust., Inc. (unpubl.).
- EVANS, C.R. & STAPLIN, F.L., 1971. Regional facies of organic metamorphism. Can. Inst. Min. & Metall. Spec. Vol., 11, 517-520.
- EVANS, C.R., ROGERS, M.A. & BAILEY, N.J.L., 1971. Evolution and alteration of petroleum in Western Canada. Chem. Geol., 8, 147-170.
- FERGUSON, J. & BUBELA, B., 1974. Concentration of Cu(II), Pb(II), and Zn(II) from aqueous solutions by particulate algal matter. Chem. Geol., 13, 163-186.

- FLEMING, P.J.G. & RIGBY, J.F., 1972. Possible land plants from the Middle Cambrian, Queensland. Nature, 238, 266.
- FORSTER, H.J., BIEMANN, K., HAIGH, W.G., TATTRIE, N.H. & COLVIN, J.R., 1973. The structure of novel C₃₅ pentacyclic terpenes from Acetobacter xylinum. Biochem.J., 135, 133-143.
- FOSCOLOS, A.E., POWELL, T.G. & GUNTHER, P.R., 1976. The use of clay minerals and inorganic and organic geochemical indicators for evaluating the degree of diagenesis and oil generating potential of shales. Geochim. Cosmochim. Acta, 40, 953-966.
- FROELICH, A.J. & KREIG, E.A., 1969. Geophysical-geologic study of northern Amadeus Trough, Australia. Bull. Am. Ass. Pet. Geol., 53, 1978-2004.
- GASKELL, S.J., MORRIS, R.J., EGLINTON, G. & CALVERT, S.E., 1975. The geochemistry of a recent marine sediment off northwest Africa. An assessment of source of input and early diagenesis. Deep-Sea Res., 22, 777-789.
- GELPI, E. ORÓ, J., SCHNEIDER, H.J. & BENNETT, E.O., 1968. Olefins of high molecular weight in two microscopic algae. Science, 161, 700-702.
- GELPI, E., SCHNEIDER, H., MANN, J. & ORÓ, J., 1970. Hydrocarbons of geochemical significance in microscopic algae. Phytochemistry, 9, 603-612.
- GIBERT, J.M., DE ANDRADE-BRUNIGG, I.M.R., NOONER, D.W. & ORÓ, J., 1975. Predominance of isoprenoids among the alkanes in the Irati oil shale, Permian of Brazil. Chem. Geol., 15, 209-215.
- GIRAUD, A., 1970. Application of pyrolysis and gas chromatography to geochemical characterization of kerogen in sedimentary rock. Bull. Am. Ass. Pet. Geol., 54, 439-455.

GOLDHABER, M.B. & KAPLAN, I.R., 1974. The sulfur cycle.

In, The Sea, Vol. 5, Marine Chemistry (ed. E.D. Goldberg),
Wiley, New York, pp. 569-655.

GURKO, N.N. & STEPINA, L.F., 1974. Isoprenoid hydrocarbons
in the Lower Palaeozoic oils of the Baltic region.

Geol. Nefti Gaza, 7, 62-65.

GUTJAHR, C.C.M., 1966. Carbonization of pollen grains and
spores and their application. Leidse Geol. Meded., 38,
1-30.

HACQUEBARD, P.A. & DONALDSON, J.R., 1970. Coal metamorphism
and hydrocarbon potential in the Upper Palaeozoic of
the Atlantic Provinces, Canada. Can. J. Earth Sci., 7,
1139-1163.

HALBOUTY, M.T., MEYERHOFF, A.A., KING, R.E., DOTT, R.H. Sr.,
KLEMME, H.D. & SHABAD, T., 1970. World's giant oil and
gas fields, geologic factors affecting their formation,
and basin classification. In, Geology of Giant Petroleum
Fields (ed. M.T. Halbouty), Am. Ass. Pet. Geol. , Mem. 14,
pp. 502-555.

HAN, J. & CALVIN, M., 1969. Hydrocarbon distribution of
algae and bacteria, and microbiological activity in
sediments. Proc. Natl. Acad. Sci. U.S., 64, 436-443.

HAN, J. & CALVIN, M., 1970. Branched alkanes from blue-green
algae. Chem. Comm., 1490-1491.

HAN, J., MCCARTHY, E.D., CALVIN, M. & BENN, M.H., 1968a.
Hydrocarbon constituents of the blue-green algae Nostoc
muscorum, Anacystis nidulans, Phormidium luridum and
Chlorogloea fritschii. J. Chem. Soc.(C), 2785-2791.

- HAN, J., MCCARTHY, E.D., VAN HOEVEN, W., CALVIN, M. & BRADLEY, W.H., 1968b. Organic geochemical studies, II. A preliminary report on the distribution of aliphatic hydrocarbons in algae, in bacteria, and in a recent lake sediment. Proc. Natl. Acad. Sci. U.S., 59, 29-33.
- HEDBERG, H.D., 1968. Significance of high-wax oils with respect to genesis of petroleum. Bull. Am. Ass. Pet. Geol., 52, 736-750.
- HILLS, I.R., SMITH, G.W. & WHITEHEAD, E.V., 1970. Hydrocarbons from fossil fuels and their relationship with living organisms. J. Inst. Pet., 56, 127-137.
- HITCHON, B., 1974. Application of geochemistry to the search for crude oil and natural gas. In, Introduction to Exploration Geochemistry (ed. A.A. Levinson), Applied Publishing, Calgary, pp. 509-545.
- HO, T.Y., ROGERS, M.A., DRUSHEL, H.V. & KOONS, C.B., 1974. Evolution of sulfur compounds in crude oils. Bull. Am. Ass. Pet. Geol., 50, 2338-2348.
- HODGSON, G.W., HITCHON, B., TAGUCHI, K., BAKER, B.L. & PEAKE, E., 1968. Geochemistry of porphyrins, chlorins and polycyclic aromatics in soils, sediments and sedimentary rocks. Geochim. Cosmochim. Acta, 32, 737-772.
- HOEFS, J., 1973. Stable Isotope Geochemistry. Springer-Verlag, Berlin, 140 pp.
- HOEFS, J. & FREY, M., 1976. The isotopic composition of carbonaceous matter in a metamorphic profile from the Swiss Alps. Geochim. Cosmochim. Acta, 40, 945-951.
- HOEFS, J. & SCHIDLOWSKI, M., 1967. Carbon isotope composition of carbonaceous matter from the Precambrian of the Witwatersrand System. Science, 155, 1096-1097.

- HOERING, T.C., 1967. The organic geochemistry of Precambrian rocks. In, Researches in Geochemistry, 2, (ed. P.H. Abelson), Wiley, New York, N.Y., pp. 87-111.
- HOERING, T.C., 1976. Molecular fossils from the Precambrian Nonesuch shale. Carnegie Inst. Wash., Yearb., 75, 806-813.
- HOLM-HANSEN, O., 1968. Ecology, physiology, and biochemistry of blue-green algae. Ann. Rev. Microbiol., 22, 47-70.
- HOOD, A., GUTJAHR, C.C.M. & HEACOCK, R.L., 1975. Organic metamorphism and the generation of petroleum. Bull. Am. Ass. Pet. Geol., 59, 986-996.
- HORSTMAN, E.L., LYONS, D.A., NOTT, S.A. & BROAD, D.S., 1976. Canning Basin: on-shore. In, Economic Geology of Australia and Papua New Guinea 3. Petroleum (eds. R.B. Leslie, H.J. Evans & C.L. Knight), Australian Inst. Min. Metall., Parkville, pp. 170-184.
- HUCK, G. & KARWEIL, J., 1955. Physikalisch-chemische Probleme der Inkohlung. Brennst.-Chem., 36, 1-11.
- HUNT, J.M., 1953. Composition of crude oil and its relation to stratigraphy in Wyoming. Bull. Am. Ass. Pet. Geol., 37, 1837-1872.
- HUNT, J.M., 1967. The origin of petroleum in carbonate rocks. In, Carbonate Rocks: Physical and chemical aspects (eds. G.V. Chilingar, H.J. Bissell & R.W. Fairbridge), Developments in Sedimentology, 9B. Elsevier, Amsterdam, pp. 225-251.
- HUNT, J.M., 1974. Organic geochemistry of the marine environment. In, Advances in Organic Geochemistry 1973 (eds. B. Tissot & F. Biennner), Editions Technip, Paris, pp. 593-605.

- HUNT, J.M., 1975a. An examination of petroleum migration processes. In, Papers on Geochemical and Physico-chemical Problems Related to Crude Oil and Gas Research and Exploration (eds. A. Balazs & G. Milley), Oil and Gas Industrial Research Lab. (OGIL), Budapest, pp. 219-229.
- HUNT, J.M., 1975b. Origin of gasoline range alkanes in the deep sea. Nature, 254, 411-413.
- IKAN, R., BAEDECKER, M.J. & KAPLAN, I.R., 1975. Thermal alteration experiments on organic matter in recent marine sediments -II. Isoprenoids. Geochim. Cosmochim. Acta, 39, 187-194.
- JACKSON, T.A., 1973. 'Humic' matter in the bitumen of ancient sediments: variations through geologic time. A new approach to the study of Pre-Palaeozoic (Precambrian) life. Geology, 1, 163-166.
- JACKSON, T.A., 1973. 'Humic' matter in the bitumen of pre-Phanerozoic and Phanerozoic sediments and its paleobiological significance. Am. J. Sci., 275, 906-953.
- JACKSON, T.A. & MOORE, C.B., 1976. Secular variations in kerogen structure and carbon, nitrogen and phosphorus concentrations in pre-Phanerozoic and Phanerozoic sedimentary rocks. Chem. Geol., 18, 107-136.
- JOHNS, W.D. & SHIMOYAMA, A., 1972. Clay minerals and petroleum forming reactions during burial and diagenesis. Bull. Am. Ass. Pet. Geol., 56, 2160-2167.
- JOHNSON, R.W. & CALDER, J.A., 1973. Early diagenesis of fatty acids and hydrocarbons in a salt marsh environment. Geochim. Cosmochim. Acta, 37, 1943-1955.
- JONES, B.G., 1972. Upper Devonian to Lower Carboniferous stratigraphy of the Pertnjara Group, Amadeus, Basin, central Australia. J. Geol. Soc. Aust., 19, 229-249.

- JONES, J.G. & YOUNG, B.V., 1970. Major paraffin constituents of microbial cells with particular reference to Chromatium sp.. Arch. Mikrobiol., 70, 82-88.
- JONES, T.S. & SMITH, H.M., 1965. Relationships of oil composition and stratigraphy in the Permian basin of West Texas and New Mexico. In, Fluids in Subsurface Environments (eds. A. Young & J.E. Galley), Am. Ass. Pet. Geol., Mem. 4, pp. 101-224.
- KANEDA, T., 1967. Fatty acids in the genus Bacillus, I. Iso and anteiso fatty acids as characteristic constituents of ten species. J. Bacteriol., 93, 894-903.
- KARWEIL, J., 1956. Die Metamorphose der Kohlen vom Standpunkt der physikalischen Chemie. Zeitschr. Deutsch. Geol. Gesell., 107, 132-139.
- KATES, M., 1964. Bacterial lipids. In, Advances in Lipid Research, 2, (eds. R. Paoletti & D. Kritchevsky), Academic Press, New York, pp. 17-90.
- KATZ, D.L., 1971. Depths to which frozen gas fields may be expected. J. Pet. Tech., 23, 419-423.
- KELLER, B.M. (ed.), 1963. Stratigraphy of the U.S.S.R. Upper Precambrian, Moscow, pp. 655-657.
- KENDALL, C.G.St.C. & SKIPWITH, P.A.d'E., 1968. Recent algal mats of a Persian Gulf lagoon. J. Sed. Petrol., 38, 1040-1058.
- KARKHANIS, S.N., 1977. Artifacts produced by chemical processing of samples for micropalaeontology and organic geochemistry - a note of caution. Precambrian Res., 4, 229-236.

- KIMBLE, B.J., MAXWELL, J.R., PHILP, R.P., EGLINTON, G.,
ALBRECHT, P., ENSMINGER, A., ARPINO, P. & OURISSON, G.,
1974. Tri-and tetraterpenoid hydrocarbons in the Messel
oil shale. Geochim. Cosmochim. Acta, 38, 1165-1181.
- KNIGHTS, B.A., BROWN, A.C., CONWAY, E. & MIDDLETON, B.S., 1970.
Hydrocarbons from the green form of the freshwater alga,
Botryococcus braunii. Phytochemistry, 9, 1317-1324.
- KOLUZS, P.J., 1972. Sedimentary and environmental reconstruction
of the Cavan Limestone, Taemas District, N.S.W. M. Sc.
Thesis, A.N.U. (unpubl.).
- KONECKI, M.C. & BLAIR, K., 1970. Preliminary analysis of
natural gases encountered in exploration and development
drilling Australia and Papua New Guinea. Bur. Miner.
Resour. Aust. Rec., 1970/76 (unpubl.).
- KONTOROVICH, A.E. & TROFIMUK, A.A., 1976. Lithogenesis and
oil and gas generation. Int. Geol. Congr., 25th, Sydney,
Abstracts, 1, 245-246.
- KONTOROVICH, A.E., DROBOT, D.I. & PRESNOVA, R.N., 1974.
Normal alkanes in oils of the Vendian and Cambrian of the
Siberian Platform. Geol. Nefti Gaza, 5, 48-53.
- KREJCI-GRAF, K., 1963. Origin of oil. Geophys. Prospecting,
11, 244-275.
- KURYLOWICZ, L.E., OZIMIC, S., McKIRDY, D.M., KANTSLER, A.J.
& COOK, A.C., 1976. Reservoir and source rock potential
of the Larapinta Group, Amadeus Basin, Central Australia.
Aust. Pet. Explor. Ass. J., 16(1), 49-65.
- KVENVOLDEN, K., 1970. Evidence for transformation of normal
fatty acids in sediments. In, Advances in Organic
Geochemistry 1966 (eds. G.D. Hobson & G.C. Speers),
Pergamon, Oxford, pp. 355-366.

- LANDES, K.K., 1967. Eometamorphism, and oil and gas in time and space. Bull. Am. Ass. Pet. Geol., 51, 828-841.
- LEE, R.F. & LOEBLICH, A.R., 1971. Distribution of 21:6 hydrocarbon and its relationship to 22:6 fatty acid in algae. Phytochemistry, 10, 593-602.
- LEE, R.F., HIROTA, J. & BARNETT, A.M., 1971. Distribution and importance of wax esters in marine copepods and other zooplankton. Deep-Sea Res., 18, 1147-1165.
- LEVCHENKO, I.G., 1975. Oil-gas prospects of the Cambrian of the Tunguska Synclize and surrounding areas. Geol. Nefti Gaza, 1, 1-9.
- LEYTHAEUSER, D., 1973. Effects of weathering on organic matter in shales. Geochim. Cosmochim. Acta, 37, 113-120.
- LIJMBACH, G.W.M., 1975. On the origin of petroleum. World Pet. Congr. Proc., 9th, Tokyo, 2, 357-369.
- LOPATIN, N.V., 1971. Temperature and geologic time as factors in coalification. Akad. Nauk SSSR Izv., Ser. Geol., 3, 95-106 (in Russian); English transl. by N.H. Bostick, Illinois State Geol. Survey, 1972.
- LOUIS, M. & TISSOT, B., 1967. Influence de la temperature et de la pression sur la formation des hydrocarbures dans les argiles a kerogene. World Pet. Congr. Proc., 7th, Mexico City, 2, 47-60.
- MCCASLIN, J.C., 1976. Geologists appraise Southwest U.S. Oil and Gas J., 74(18), 307.
- MCDOWELL, A.N., 1975. Estimates of basin oil potential. AAPG-SEPM Annu. Mtg. Abstr., 2, 47-48.
- McHUGH, D.J., SAXBY, J.D. & TARDIF, J.W., 1976. Pyrolysis-hydrogenation-gas chromatography of carbonaceous material from Australian sediments, Part I: Some Australian coals. Chem. Geol., 17, 243-259.

- McIVER, R.D., 1967. Composition of kerogen: clue to its role in the origin of petroleum. World Pet. Congr. Proc., 7th, Mexico City, 2, 25-36.
- McIVER, R.D., 1974. Methane in canned core samples from Site 262, Timor Trough. In, J.J. Veevers et al., Initial Reports of the Deep Sea Drilling Project, Vol. 27, U.S. Govt. Printing Office, Washington, pp. 453-454.
- McKELVEY, V.E., 1959. Relation of upwelling marine waters to phosphorite and oil (abstr.). Bull. Geol. Soc. Am., 70, 1783-1784.
- McKIRDY, D.M., 1971. An organic geochemical study of Australian Cambrian and Precambrian sedimentary rocks. M. Sc. Thesis, Univ. of Adelaide. (unpubl.).
- McKIRDY, D.M., 1974. Organic geochemistry in Precambrian research. Precambrian Res., 1, 75-137.
- McKIRDY, D.M., 1976. Biochemical markers in stromatolites. In, Stromatolites (ed. M.R. Walter), Developments in Sedimentology, 20. Elsevier, Amsterdam, pp. 163-191.
- McKIRDY, D.M. & HORVATH, Z., 1976. An integrated scheme for the laboratory analysis of oil, natural gas, and petroleum source-rocks. Sci. Aust. Technol., 14(2), 12-16.
- McKIRDY, D.M. & 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.
- McNAB, J.G., SMITH, P.V. & BETTS, R.L., 1952. The evolution of petroleum. Ind. Eng. Chem., 44, 2556-2563.
- McNAUGHTON, D.A., QUINLAN, T., HOPKINS, R.M. & WELLS, A.T., 1968. Evolution of salt anticlines and salt domes in the Amadeus Basin, central Australia. Geol. Soc. Am., Spec. Pap. 88, pp. 229-247.

- McTAGGART, N.R., PEMBERTON, R.L. & PLANALP, R.N., 1965. Well completion report, Mount Charlotte No. 1. Tronsoil (N.T.) Pty. Ltd. (unpubl.).
- McTAVISH, R.A. & LEGG, D.P., 1976. The Ordovician of the Canning Basin, Western Australia. In, The Ordovician System (ed. M.G. Bassett), University of Wales Press, Cardiff, pp. 447-478.
- MAGELLAN, 1975. Annual Report. Magellan Petroleum Aust. Ltd.
- MANHEIM, F., ROWE, G.T. & JIPA, D., 1975. Marine phosphorite formation off Peru. J. Sed. Petrol., 45, 243-251.
- MARCHAND, A., LIBERT, P. & COMBAZ, A., 1969. Essai de caracterisation physico-chimique de la diagenese de quelques roches organiques biologiquement homogenes. Rev. Inst. Fr. Pet., 24, 3-20.
- MARTIN, R.L., WINTERS, J.C. & WILLIAMS, J.A., 1963. Distribution of n-paraffins in crude oils and their implications to origin of petroleum. Nature, 199, 110-113.
- MAXIMOV, S.P. & MUROMTSEVA, V.A., 1975. Formation of oil pools in Cambrian sediments on the southern margin of the Baltic Synclize. Geol. Nefti Gaza, 3, 20-27.
- MAXIMOV, S.P., RODINOVA, K.F., GOLOVANOVA, S.I. & MUROMTSEVA, V.A., 1974. The evaluation of oil source-rock characteristics in Cambrian sediments of the Baltic Basin using geochemical criteria. Zeitschr. Angew. Geol., 20(8), 343-351 (in German).
- MAXWELL, J.R., DOUGLAS, A.G., EGLINTON, G. & McCORMICK, A., 1968. The botryococcenes - hydrocarbons of novel structure from the alga Botryococcus braunii, Kutzinger. Phytochemistry, 7, 2157-2171.
- MAZLIAK, P., 1969. Chemistry of plant cuticles. In, Progress in Phytochemistry, (eds. L. Reinhold & Y. Liwochitz), Interscience, London, pp. 49-111.

- MEYERHOFF, A.A., 1974. Geological principles of world oil occurrence: a summary. Bull. Can. Pet. Geol., 22, 413-419.
- MILLAIS, R. & MURCHISON, D.G., 1969. Properties of the coal minerals: infra-red spectra of alginites. Fuel, 48, 247-258.
- MILNER, C.W.D., ROGERS, M.A. & EVANS, C.R., 1977. Petroleum transformations in reservoirs. J. Geochém. Explor., 7, 101-153.
- MINES ADMINISTRATION PTY. LTD. 1965. P.A.P. Netting Fence No. 1 well, Queensland. Well completion report. Rep. for the Papuan Apinaipi Petroleum Co. Ltd. (unpubl.).
- MOLLAN, R.G., CRAIG, R.W. & LOFTING, M.J.W., 1970. Geologic framework of continental shelf off northwest Australia. Bull. Am. Ass. Pet. Geol., 54, 583-600.
- MOORE, L.R., 1968. Cannel coals, bogheads and oil shales. In, Coal and Coal-bearing Strata (eds. D.G. Murchison & T. S. Westoll), Oliver and Boyd, Edinburgh, pp. 19-29.
- MORRIS, R.J. & CALVERT, S.E., in press. Geochemical studies of organic-rich sediments from the Namibian Shelf I. The organic fractions. Deep-Sea Res.
- MUIR, M.D. & GRANT, P.R., 1976. Micropalaeontological evidence from the Onverwacht Group, South Africa. In, Early History of the Earth (ed. B.F. Windley), Wiley, London, pp. 595-604.
- MUIR, M.D. & HALL, D.O., 1974. Diverse microfossils in Precambrian Onverwacht group rocks of South Africa. Nature, 252, 376-378.

- MUIR, M.D., GRANT, P.R., BLISS, G.M., DIVER, W.L. & HALL, D.O., 1977. A discussion of biogenicity criteria in a geological context with examples from a very old greenstone, a Late Precambrian deformed zone and tectonized Phanerozoic rocks. In, Chemical Evolution of the Early Precambrian (ed. C. Ponnampertuma), Academic, New York, N.Y., pp. 155-170.
- MUIR, M.D., PLUMB, K.A., PEAT, C.J., NORVICK, M.S. & McKIRDY, D.M., (in prep.). Microorganisms from shales of the mid-Proterozoic McMinn Formation, Roper Group, Northern Territory. Bur. Miner. Resour. J.
- MURRAY, G.E., 1965. Indigenous Precambrian petroleum? Bull. Am. Ass. Pet. Geol., 49, 3-22.
- NICHOLS, B.W., 1973. Lipid composition and metabolism. In, The Biology of Blue-green Algae (eds. N. Carr & B. Whitton), Blackwell, Oxford, pp. 144-161.
- NISSENBAUM, A. & KAPLAN, I.R., 1972. Chemical and isotopic evidence for the in situ origin of marine humic substances. Limnol. Oceanogr., 17, 570-582.
- NISSENBAUM, A., BAEDECKER, M.J. & KAPLAN, I.R., 1972. Organic geochemistry of Dead Sea sediments. Geochim. Cosmochim. Acta, 36, 709-727.
- OEHLER, J., 1976. Experimental studies in Precambrian paleontology: Structural and chemical changes in blue-green algae during simulated fossilization in synthetic chert. Bull. Geol. Soc. Am., 87, 117-129.
- OEHLER, D.Z., SCHOPF, J.W. & KVENVOLDEN, K.A., 1972. Carbon isotopic studies of organic matter in Precambrian rocks. Science, 175, 1246-1248.
- OFFLER, R. & FLEMING, P.D., 1968. A synthesis of folding and metamorphism in the Mt. Lofty Ranges, South Australia. J. Geol. Soc. Aust., 15, 245-266.

ORÓ, J., TORNABENE, T.G., NOONER, D.W. & GELPI, E., 1967.

Aliphatic hydrocarbons and fatty acids of some marine and freshwater microorganisms. J. Bacteriol., 93, 1811-1818.

PEARSON, T.R. & BENBOW, D.D., 1976. Amadeus Basin. In, Economic Geology of Australia and Papua New Guinea 3. Petroleum (eds. R.B. Leslie, H.J. Evans & C.L. Knight), Australian Inst. Min. Metall., Parkville, pp. 216-225.

PEMBERTON, R.L. & McTAGGART, N.R., 1965. Well completion report, Erldunda No. 1. Exoil (N.S.W.) Pty. Ltd. (unpubl.).

PEMBERTON, R.L., CHAMBERS, S.S., PLANALP, R.N. & WEBB, E.A., 1963. Well completion report, Alice No. 1. Exoil (N.T.) Pty. Ltd. (unpubl.).

PERRY, E.A. Jr. & HOWER, J., 1972. Late-stage dehydration in deeply buried pelitic sediments. Bull. Am. Ass. Pet. Geol., 56, 2013-2021.

PEVEAR, D.R., 1966. The estuarine formation of United States coastal plain phosphorite. Econ. Geol., 61, 251-256.

PHILIPPI, G.T., 1965. On the depth, time and mechanism of petroleum generation. Geochim. Cosmochim. Acta, 29, 1021-1049.

PHILIPPI, G.T., 1974. Influence of marine and terrestrial source material on the composition of petroleum. Geochim. Cosmochim. Acta, 38, 947-966.

PHILP, R.P. & CALVIN, M., 1975. Kerogen structures in recently-deposited algal mats at Laguna Mormona, Baja California: a model system for the determination of kerogen structures in ancient sediments, In, Environmental Biogeochemistry, Vol. 1 (ed. J.O. Nriagu). Proc. 2nd. Int. Symp. Environ. Biogeochem., Ann Arbor Science, Ann Arbor, Mich., pp. 131-148.

- PHILP, R.P. & CALVIN, M., 1976. Possible origin for insoluble organic (kerogen) debris in sediments from insoluble cell-wall materials of algae and bacteria. Nature, 262, 134-136.
- PLANALP, R.N. & PEMBERTON, R.L., 1963. Well completion report, Ooraminna No. 1. Exoil N.L. (unpubl.).
- PLAYFORD, G., JONES, B.G. & KEMP, E.M., 1976. Palynological evidence for the age of the synorogenic Brewer Conglomerate, Amadeus Basin, central Australia. Alcheringa, 1, 235-243.
- POWELL, D.E., 1976. The geological evolution of the continental margin off northwest Australia. Aust. Pet. Explor. Ass. J., 16(1). 13-23.
- POWELL, T.G., 1975. Geochemical studies related to the occurrence of oil and gas in the Dampier Sub-basin, Western Australia. J. Geochem. Explor., 4, 441-466.
- POWELL, T.G. & McKIRDY, D.M., 1972. Geochemical characterization of Australian crude oils. Aust. Pet. Explor. Ass. J., 12(1), 125-131.
- POWELL, T.G. & McKIRDY, D.M., 1973a. The effect of source material, rock type and diagenesis on the n-alkane content of sediments. Geochim.Cosmochim. Acta, 37, 623-633.
- POWELL, T.G. & McKIRDY, D.M., 1973b. Relationship between ratio of pristane to phytane, crude oil composition and geological environment in Australia. Nature Phys. Sci., 243, 37-39.
- POWELL, T.G. & McKIRDY, D.M., 1973c. Crude oil correlations in the Perth and Carnarvon Basins. Aust. Pet. Explor. Ass. J., 13(1), 81-85.

- POWELL, T.G. & McKIRDY, D.M., 1975. Geologic factors controlling crude oil composition in Australia and Papua New Guinea. Bull. Am. Ass. Pet. Geol., 59, 1176-1197.
- POWELL, T.G. & McKIRDY, D.M., 1976. Geochemical character of crude oils from Australia and Papua New Guinea. In, Economic Geology of Australia and Papua New Guinea. 3. Petroleum (eds. R.B. Leslie, H.J. Evans, & C.L. Knight), Australian Inst. Min. Metall., Parkville, pp. 18-29.
- POWELL, T.G., COOK, P.J. & McKIRDY, D.M., 1975. Organic geochemistry of phosphorites: relevance to petroleum genesis. Bull. Am. Ass. Pet. Geol., 59, 618-632.
- POWELL, T.G., DOUGLAS, A.G. & ALLAN, J., 1976. Variations in the type and distribution of organic matter in some Carboniferous sediments from northern England. Chem. Geol., 18, 137-148.
- PREISS, W.V., 1973. Palaeoecological interpretations of South Australian Precambrian stromatolites. J. Geol. Soc. Aust., 19, 501-531.
- PREISS, W.V., 1977. The biostratigraphic potential of Precambrian stromatolites. Precambrian Res., 5, 207-219.
- PRICE, L.C., 1976. Aqueous solubility of petroleum as applied to its origin and primary migration. Bull. Am. Ass. Pet. Geol., 60, 213-244.
- PUSEY, W.C., 1973. How to evaluate potential gas and oil source rocks. World Oil, 175(5), 71-75.
- RANNEFT, T.S.M., 1963. Amadeus Basin petroleum prospects Aust. Pet. Explor. Ass. J., 3, 42-52.

- REED, W.E. & HENDERSON, W., 1972. Proposed stratigraphic controls on the composition of crude oils reservoired in the Green River Formation, Uinta Basin, Utah. In, Advances in Organic Geochemistry 1971 (eds. H.R. von Gaertner and H. Wehner), Pergamon, Oxford, pp. 499-515.
- REITZ, R.C. & HAMILTON, J.G., 1968. The isolation and identification of two sterols from two species of blue-green algae. Comp. Biochem. Physiol., 25, 401-416.
- RHEAD, M.M., EGLINTON, G., DRAFFEN, G.H. & ENGLAND, P.J.E., 1971. The conversion of oleic acid to saturated fatty acids in Severn Estuary sediments. Nature, 231, 327-330.
- RICHARDS, F.A., 1970. The enhanced preservation of organic matter in anoxic marine environments. In, Organic Matter in Natural Waters (ed. D.W. Hood), Inst. Mar. Sci., Univ. of Alaska, Occas. Publ. 1, 399-411.
- RJABUCHIN, G.E., 1976. Oil and gas deposits in Early Palaeozoic and Precambrian successions of beds. Zeitschr. Angew. Geol., 22(2), 56-59 (in German).
- ROBINSON, W.E., 1969. Isolation procedures for kerogens and associated soluble organic materials. In, Organic Geochemistry: methods and results (eds. G. Eglinton & M.T.J. Murphy), Springer-Verlag, New York, N.Y., pp. 181-195.
- ROBINSON, W.E. & DINNEEN, G.U., 1967. Constitutional aspects of oil-shale kerogen. World Pet. Congr. Proc., 7th, Mexico City, 3, 669-680.
- ROBINSON, W.E., CUMMINS, J.J. & DINNEEN, G.U., 1965. Changes in Green River oil-shale paraffins with depth. Geochim. Cosmochim. Acta, 29, 249-258.

- ROGERS, M.A. & KOONS, C.B., 1969. Organic carbon $\delta^{13}\text{C}$ values from Quaternary marine sequences in the Gulf of Mexico: a reflection of paleotemperature changes. Trans. Gulf Coast Ass. Geol. Socs., 19, 529-534.
- ROGERS, M.A., BAILEY, N.J.L. & EVANS, C.R., 1971. A plea for inclusion of basic sample information when reporting geochemical analyses of crude oils. Geochim. Cosmochim. Acta, 35, 632-636.
- ROGERS, M.A., VAN HINTE, J.E. & SUGDEN, J.G., 1972. Organic carbon $\delta^{13}\text{C}$ values from Cretaceous, Tertiary and Quaternary marine sequences in the North Atlantic. In, A.S. Laughton et al., Initial Reports of the Deep Sea Drilling Project, Vol. 12, U.S. Govt. Printing Office, Washington, pp. 1115-1126.
- ROGERS, M.A., KOONS, C.B. HO, T.Y. & PERRY, D., 1973. Geologic controls on the hydrocarbon source potential of young sediments. Paper presented to 23rd Ann. Mtg. Gulf Coast Ass. Geol. Socs., Houston, Texas, Oct. 24-26.
- ROGERS, M.A., McALARY, J.D. & BAILEY, N.J.L., 1974. Significance of reservoir bitumens to thermal maturation studies, Western Canada Basin. Bull. Am. Ass. Pet. Geol., 58, 1806-1824.
- ROMANKEVICH, Y.A. & BATURIN, G.N., 1972. Composition of the organic matter in phosphorites from the continental shelf of southwest Africa. Geochem. Int., 6, 464-470.
- RONOV, A.B. & MIGDISOV, A.A., 1971. Geochemical history of the crystalline basement and the sedimentary cover of the Russian and North American platforms. Sedimentology, 16, 137-185.

- RUSSELL, R.T. & TRUEMAN, N.A., 1971. The geology of the
Duchess phosphate deposits, northwestern Queensland,
Australia. Econ. Geol., 66, 1186-1214.
- SACKETT, W.M., 1964. The depositional history and isotopic
organic carbon composition of marine sediments.
Marine Geol., 2, 173-185.
- SACKETT, W.M. & RANKIN, J.G., 1970. Paleotemperatures for
the Gulf of Mexico. J. Geophys. Res., 75, 4557-4559.
- SARGENT, J.R., 1977. Waxes for survival. Sci. and Technol.,
14(4), 11-13.
- SAXBY, J.D., 1972. Organic matter in Red Sea sediments.
Chem. Geol., 9, 233-240.
- SCALAN, R.S. & SMITH, J.E., 1970. An improved measure of
the odd-even predominance in the normal alkanes of
sediment extracts and petroleum. Geochim. Cosmochim.
Acta, 34, 611-620.
- SCHENCK, P.A., 1969. The predominance of the C₂₂ n-alkanes
in rock extracts. In, Advances in Organic Geochemistry
1968 (eds. P.A. Schenck & I. Havenaar), Pergamon,
Oxford, pp. 261-267.
- SCHIDLOWSKI, M., 1969. Critical remarks on a postulated
genetic relationship between Precambrian thucolite and
boghead coal. In, Advances in Organic Geochemistry 1968
(eds. P.A. Schenck & I. Havenaar), Pergamon, Oxford,
pp. 579-592.
- SCHNEIDER, H., GELPI, E., BENNETT, E.O. & ORO, J., 1970.
Fatty acids of geochemical significance in microscopic
algae. Phytochemistry, 9, 613-617.
- SCHOPF, J.W., 1968. Microflora of the Bitter Springs
Formation, Late Precambrian, Central Australia.
J. Paleont., 42, 651-688.

- SCHOPF, J.W., 1970. Precambrian micro-organisms and evolutionary events prior to the origin of vascular plants. Biol. Rev. Cambridge Phil. Soc., 45, 319-352.
- SCHOPF, J.W., 1975. Precambrian paleobiology: problems and perspectives. Annu. Rev. Earth and Planet. Sci., 3, 213-249.
- SCHOPF, J.W. & BARGHOORN, E.S., 1969. Microorganisms from the Late Precambrian of South Australia. J. Paleont., 43, 111-118.
- SCHOPF, J.W. & BLACIC, J.M., 1971. New micro-organisms from the Bitter Springs Formation (Late Precambrian) of the north-central Amadeus Basin, Australia. J. Paleont., 45, 925-960.
- SCHOPF, J.W. & FAIRCHILD, T.R., 1973. Late Precambrian microfossils: a new stromatolitic biota from Boorthanna, South Australia. Nature, 242, 537-538.
- SCHRAYER, G.J., 1962. Chemical composition of the extractable organic matter in a sample of Proterozoic Pertatataka limestone from the Amadeus Area, Northern Territory, Australia. Gulf Research & Development Co. (unpubl.).
- SCHRAYER, G.J., 1963. Organic carbon content of selected Australian rock samples. Gulf Research & Development Co. (unpubl.).
- SCHULTZ, D.J. & CALDER, J.A., 1976. Organic carbon $^{13}\text{C}/^{12}\text{C}$ variations in estuarine sediments. Geochim. Cosmochim. Acta, 40, 381-385.
- SCOTT, W.M., MODZELESKI, V.E. & NAGY, B., 1970. Pyrolysis of Early Pre-Cambrian Onverwacht organic matter ($> 3 \times 10^9$ yr old). Nature, 225, 1129-1130.

- SEKI, H., 1970. Microbial biomass on particulate organic matter in seawater of the euphotic zone. Appl. Microbiol., 19, 960-962.
- SENIOR, B.R. & SMART, J., 1973. Oil traces in the Toolebuc Limestone, Carpentaria and Eromanga Basins, Queensland. Oil and Gas, 19(10), 11-12.
- SEREBRYAKOV, S.N., 1976. Biotic and abiotic factors controlling the morphology of Riphean stromatolites. In, Stromatolites, (ed. M.R. Walter), Developments in Sedimentology, 20. Elsevier, Amsterdam, pp. 321-336.
- SHEARMAN, D.J. & SKIPWITH, P.A.d'E., 1965. Organic matter in recent and ancient limestones and its role in their diagenesis. Nature, 208, 1310-1311.
- SHIBAOKA, M., BENNETT, A.J.R. & GOULD, K.W., 1973. Diagenesis of organic matter and occurrence of hydrocarbons in some Australian sedimentary basins. Aust. Pet. Explor. Ass. J., 13(1), 73-80.
- SILLER, C.W., MURRAY, G.E., HOPKINS, R.M. & McNAUGHTON, D.A., 1963. Aussie strike attracts interest. Oil and Gas J., 61(32), 189-191.
- SILVERMAN, S.R., 1964. Investigations of petroleum origin and evolution mechanisms by carbon isotope studies. In, Isotopic and Cosmic Chemistry (eds. H. Craig, S.L. Miller & G.J. Wasserburg), North-Holland, Amsterdam, pp. 92-102.
- SILVERMAN, S.R., 1971. Influence of petroleum origin and transformation on its distribution and redistribution in sedimentary rocks. World Pet. Congr. Proc., 8th, Moscow, 2, 47-54.

- SIMONEIT, B.R. & BURLINGAME, A.L., 1972. Preliminary organic analyses of the DSDP (JOIDES) cores, Legs V-IX. In, Advances in Organic Geochemistry 1971 (eds. H.R. von Gaertner & H. Wehner), Pergamon, Oxford, pp. 189-228.
- SIMONEIT, B.R. & BURLINGAME, A.L., 1973. Carboxylic acids derived from Tasmanian tasmanite by extractions and kerogen oxidations. Geochim. Cosmochim. Acta, 37, 595-610.
- SIMONEIT, B.R. & BURLINGAME, A.L., 1974. Study of the organic matter in the DSDP (JOIDES) cores, Legs 10-15. In, Advances in Organic Geochemistry 1973. (eds. B. Tissot & F. Bienner), Editions Technip, Paris, pp. 629-648.
- SMITH, H.M., 1964. Hydrocarbon-type relationships of eastern and western hemisphere high-sulfur crude oils. U.S. Bur. Mines Rep. Inv., 6542.
- SMITH, K.G., 1976. Georgina Basin. In, Economic Geology of Australia and Papua New Guinea 3. Petroleum (eds. R.B. Leslie, H.J. Evans & C.L. Knight), Australian Inst. Min. Metall., Parkville, pp. 231-236.
- SMITH, B.N. & EPSTEIN, S., 1971. Two categories of C^{13}/C^{12} ratios for higher plants. Plant Physiol., 47, 380-384.
- SNOWDON, L.R. & ROY, K.J., 1975. Regional organic metamorphism in the Mesozoic strata of the Sverdrup Basin. Bull. Can. Pet. Geol., 23, 131-148.
- STACH, E., 1975. The microscopically recognizable constituents of coal. In, Stach's Textbook of Coal Petrology (eds. E. Stach, M. Th. Mackowsky, M. Teichmuller, G.H. Taylor, D. Chandra & R. Teichmuller), Gebruder Borntraeger, Berlin, pp. 54-121.

- STAHL, W.J. & CAREY, B.D.Jr., 1975. Source-rock identification by isotope analyses of natural gases from fields in the Val Verde and Delaware Basins, West Texas. Chem. Geol., 16, 257-267.
- STAPLIN, F.L., 1969. Sedimentary organic matter, organic metamorphism, and oil and gas occurrence. Bull. Can. Pet. Geol., 17, 47-66.
- STEVAUX, J., KULBICKI, G. & VAN DER WEIDE, B., 1964. Etude geochemique de quelques enchantillons provenant de la region du Johnny's Creek, Bassin de l'Amadeus. Cent. Rech. Pau - SNPA, Note R/GS No. 6988 (unpubl.).
- STEWART, A.J., 1974. Petrographic and geochemical study of the Ringwood evaporite deposit. Bur. Miner. Resour. Aust. Rec., 1974/145 (unpubl.).
- STONE, D.S., 1967. Theory of Paleozoic oil and gas accumulation in Big Horn Basin, Wyoming. Bull. Am. Ass. Pet. Geol., 51, 2056-2114.
- SWARBRICK, C.F.J., 1974. Oil shale resources of Queensland. Geol. Surv. Qld. Rep, 83, 23-29.
- TAPPAN, H., 1968. Primary production, isotopes, extinctions and the atmosphere. Palaeogeography, Palaeoclimatol., Palaeoecol., 4, 187-210.
- TAPPAN, H., 1971. Microplankton, ecological succession and evolution. North Am. Paleontol. Conv., Chicago, 1969, Proc., H, 1058-1103.
- TAPPAN, H. & LOEBLICH, A.R.Jr., 1972. Fluctuating rates of protistan evolution, diversification and extinction. Int. Geol. Congr., 24th, Montreal, Proc., Sect. 7, 205-213.
- TAYLOR, G.H., 1966. The electron microscopy of vitrinites. Coal Science, Adv. Chem. Ser., 55, Washington, D.C., pp. 274-283.

- TEICHMULLER, M., 1974. Generation of petroleum-like substances in coal seams as seen under the microscope. In, Advances in Organic Geochemistry (eds. B. Tissot & F. Bienner), Editions Technip, Paris, pp. 379-407.
- TEICHMULLER, M., 1975. Origin of the petrographic constituents of coal. In, Stach's Textbook of Coal Petrology (eds. E. Stach, M.Th. Mackowsky, M. Teichmuller, G.H. Taylor, D. Chandra & R. Teichmuller), Gebruder Borntraeger, Berlin, pp. 176-238.
- TEICHMULLER, M. & TEICHMULLER, R., 1968. Geological aspects of coal metamorphism. In, Coal and Coal-Bearing Strata (eds. D.G. & T.S. Westoll), Oliver and Boyd, Edinburgh, pp. 233-267.
- TEICHMULLER, M. & TEICHMULLER, R., 1975. The geological basis of coal formation. In, Stach's Textbook of Coal Petrology (eds. E. Stach, M.Th. Mackowsky, M. Teichmuller, G.H. Taylor, D. Chandra & R. Teichmuller), Gebruder Borntraeger, Berlin, pp. 5-53.
- THAYER, P.S., HOSTETTLER, J. & SMITH, S., 1974. Grain-size distribution of sediments from the eastern Indian Ocean: Deep Sea Drilling Project, Leg 27. In, J.J. Veevers et al., Initial Reports of the Deep Sea Drilling Project, Vol. 27. U.S. Govt. Printing Office, Washington, pp. 507-522.
- THOMSON, B.P., 1969. Precambrian basement cover: the Adelaide System. In, Handbook of South Australian Geology (ed. L.W. Parkin), Geol. Surv. S.Aust., Adelaide, pp. 49-83.
- TISSOT, B., CALIFET-DEBYSER, Y., DEROO, G. & OUDIN, J.L., 1971. Origin and evolution of hydrocarbons in Early Toarcian shales, Paris Basin, France. Bull. Am. Ass. Pet. Geol., 55, 2177-2193.

TISSOT, B., DURAND, B., ESPITALIÉ, J. & COMBAZ, A., 1974.

Influence of nature and diagenesis of organic matter in formation of petroleum. Bull. Am. Ass. Pet. Geol., 58, 499-506.

TISSOT, B., ESPITALIÉ, J., DEROO, G., TEMPERE, C. & JONATHAN, D., 1974. Origine et migration des hydrocarbures dans le Sahara oriental (Algerie). In, Advances in Organic Geochemistry 1973 (eds. B. Tissot & F. Bienner), Editions Technip, Paris, pp. 315-334.

TORNABENE, T.G., GELPI, E. & ORÓ, J., 1967. Identification of fatty acids and aliphatic hydrocarbons in Sarcina lutea by gas chromatography and combined gas chromatography - mass spectrometry. J. Bacteriol., 94, 333-343.

TORNABENE, T.G., MORRISON, S.J. & KLOOS, W.E., 1970. Aliphatic hydrocarbon contents of various members of the family Micrococcaceae. Lipids, 5, 929-937.

VANDENBROUCKE, M., ALBRECHT, P. & DURAND, B., 1976. Geochemical studies on the organic matter from the Douala Basin (Cameroon) - III. Comparison with the Early Toarcian shales, Paris Basin, France. Geochim. Cosmochim. Acta, 40, 1241-1249.

VAN KREVELEN, D.W., 1961. Coal. Elsevier, Amsterdam, 514 pp.

VASSOYEVICH, N.B., KORCHAGINA, Y.I., LOPATIN, N.V. & CHERNYSHEV, V.V., 1970. Principal phase of oil formation. Int. Geol. Rev., 12, 1276-1296.

VASSOYEVICH, N.B., VYSOTSKIY, I.V., SOKOLOV, B.A. & TATARENKO, T.I., 1971. Oil-gas potential of Late Precambrian deposits. Int. Geol. Rev., 13, 407-418.

VEEVERS, J.J., HEIRTZLER, J.R. et al., 1974. Site 262. In, J.J. Veevers et al., Initial Reports of the Deep

Sea Drilling Project, Vol. 27. U.S. Govt. Printing Office, Washington, pp. 193-278.

WALTER, M.R., 1972. Stromatolites and the biostratigraphy of the Australian Precambrian and Cambrian. Spec. Pap. Palaeontology, 11, 256 pp.

WALTER, M.R. (ed.), 1976. Stromatolites. Developments in Sedimentology, 20. Elsevier, Amsterdam, 790 pp.

WALTER M.R., BAULD, J. & BROCK, T.D., 1976. Microbiology and morphogenesis of columnar stromatolites (Conophyton, Vacerrilla) from hot springs in Yellowstone National Park. In, Stromatolites (ed. M. R. Walter), Developments in Sedimentology, 20. Elsevier, Amsterdam, pp. 273-310.

WANG, F.F.H., 1975. Submarine phosphorite. Committee for Co-ordination of Joint Prospecting for Mineral Resources in Asian Offshore Areas (CCOP), Background Paper, 20 pp.

WEBB, G.W., 1976. Oklahoma City oil - second crop from preserved subunconformity source rocks. Bull. Am. Ass. Pet. Geol., 60, 115-122.

WEETE, J.D., 1972. Aliphatic hydrocarbons of the fungi. Phytochemistry, 11, 1201-1205.

WELLS, A.T., 1976. Geology of the Late Proterozoic - Palaeozoic Amadeus Basin. Int. Geol. Congr., 25th, Sydney, Excursion Guide, No. 48A, 28 pp.

WELLS, A.T., FORMAN, D.J., RANFORD, L.C. & COOK, P.J., 1970. Geology of the Amadeus Basin, Central Australia. Bur. Miner. Resour. Aust. Bull., 100, 222 pp.

WELTE, D.H., 1972. Petroleum exploration and organic geochemistry. J. Geochem. Explor., 1, 117-136.

WELTE, D.H. & EBHARDT, G., 1968. Distribution of long chain n-paraffin and n-fatty acids in sediments from the Persian Gulf. Geochim. Cosmochim. Acta, 32, 465-466.

- WELTE, D.H. & WAPLES, D.W., 1973. Über die Bevorzugung geradzahliger n-Alkane in Sedimentgesteinen. Naturwissenschaften, 11, 516-517.
- WELTE, D.H., HAGEMANN, H.W., HOLLERBACH, A., LEYTHAEUSER, D. & STAHL, W., 1975a. Correlation between petroleum and source rock. World. Pet. Congr. Proc., 9th, Tokyo, 2, 179-191.
- WELTE, D.H., KALKREUTH, W. & HOEFS, J., 1975b. Age-trend in carbon isotopic composition in Paleozoic sediments. Naturwissenschaften, 62, 482-483.
- WILLIAMS, J.A., 1974. Characterization of oil types in Williston Basin. Bull. Am. Ass. Pet. Geol., 58, 1243-1252.
- WILLIAMS, G.K., HOPKINS, R.M.Jr. & McNAUGHTON, D.A., 1965. Pacoota reservoir rocks, Amadeus Basin, N.T., Australia. Aust. Pet. Explor. Ass. J., 5, 159-167.
- WINTERS, K., PARKER, P.L. & VAN BAALEN, C., 1969. Hydrocarbons of blue-green algae: geochemical significance. Science, 163, 467-468.
- WOODFORD, P.J., MATEEN, A., GREEN, D.C. & WILSON, A.F., 1975. $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology of a high-grade polymetamorphic terrain, northeastern Strangways Range, central Australia. Precambrian Res., 2, 375-396.
- WOLK, C.P., 1973. Physiology and cytological chemistry of blue-green algae. Bacteriol. Rev., 37, 32-101.
- WOPFNER, H., 1970. Early Cambrian paleogeography, Frome Embayment, South Australia. Bull. Am. Ass. Pet. Geol., 54, 2395-2409.

- ZOBELL, C.E., 1963. Geochemical aspects of the microbial modification of carbon compounds. In, Advances in Organic Geochemistry 1962 (eds. U. Columbo & G.D. Hobson), Pergamon, Oxford, pp. 339-356.
- ABELSON, P.H. & HOERING, T.C., 1961. Carbon isotope fractionation in formation of amino acids by photosynthetic organisms. Proc. Natl. Acad. Sci. U.S., 47, 623-632.
- COOPER, W.J. & BLUMER, M., 1968. Linear, iso and anteiso fatty acids in Recent sediments of the North Atlantic. Deep-Sea Res., 15, 535-540.
- DE LEEUW, J.W., SIMONEIT, B.R., BOON, J.J., RIJPSTRA, W.I.C., DE LANGE, F., VAN DER LEEDEN, J.C.W., CORREIA, V.A., BURLINGAME, A.L. & SCHENCK, P.A., 1976. Phytol-derived compounds in the geosphere. Unpubl. manuscript.
- EGLINTON, G., 1969. Hydrocarbons and fatty acids in living organisms and recent and ancient sediments. In, Advances in Organic Geochemistry 1968 (eds. P.A. Schenck & I. Havenaar), Pergamon, Oxford, pp. 1-24.
- EICHMANN, R. & SCHIDLOWSKI, M., 1975. Isotopic fractionation between coexisting organic carbon-carbonate pairs in Precambrian sediments. Geochim. Cosmochim. Acta, 39, 585-595.
- FOGG, G.E., STEWART, W.D.P., FAY, P. & WALSBY, A.E., 1973. The Blue-Green Algae, Academic, London, 459 pp.
- GOLDHABER, M.B. & KAPLAN, I.R., 1975. Controls and consequences of sulfate reduction rates in recent marine sediments. Soil Sci., 119, 42-55.

- GRAY, J. & BOUCOT, A.J., 1975. Color changes in pollen and spores: a review. Bull. Geol. Soc. Am., 86, 1019-1033.
- HOEFS, J. & SCHIDLOWSKI, M., 1967. Carbon isotope composition of carbonaceous matter from the Precambrian of the Witwatersrand System. Science, 155, 1096-1097.
- McDOUGALL, I., DUNN, P.R., COMPSTON, W., WEBB, A.W., RICHARDS, J.R. & BOFINGER, V.M., 1965. Isotopic age determinations on Precambrian rocks of the Carpentaria region, Northern Territory. J. Geol. Soc. Aust., 12, 67-90.
- McKIRDY, D.M., SUMARTOJO, J., TUCKER, D.H. & GOSTIN, V., 1975. Organic, mineralogic and magnetic indications of metamorphism in the Tapley Hill Formation, Adelaide Geosyncline. Precambrian Res., 2, 345-373.
- PARSONS, T.R., 1963. Suspended organic matter in sea water. In, Progress in Oceanography, 1. (ed. M. Sears), Pergamon, Oxford, pp. 205-239.
- ROGERS, M.A. & KOONS, C.B., 1971. Generation of light hydrocarbons and establishment of normal paraffin preferences in crude oils. In, Origin and Refining of Petroleum (ed. R.F. Gould), Advances in Chemistry Series, 103. Am. Chem. Soc., Washington, D.C., pp. 67-80.
- SIMONEIT, B.R., SCOTT, E.S., HOWELLS, W.G. & BURLINGAME, A.L., 1972. Preliminary organic analyses of Deep Sea Drilling Project cores, Leg 11. In, C.D. Hollister et al., Initial Reports of the Deep Sea Drilling Project, Vol. 11, U.S. Govt. Printing Office, Washington, pp. 1013-1045.
- VAN ANDEL, T.H. & VEEVERS, J.J., 1967. Morphology and sediments of the Timor Sea. Bur. Miner. Resour. Aust. Bull., 83, 173pp.