ORIGIN OF LIGHT HYDROCARBONS IN RECENT CARBONATE OOLITES IN RELATION TO THE PROBLEM OF PETROLEUM GENESIS IN CARBONATE ROCKS

by

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Dedicated to my parents,

LUCY AND JUSTUS IBE

as an inadequate, but sincere, expression
of affection and filial gratitude

ABSTRACT

One of the problems of petroleum geology is the origin of the petroleum stored in carbonate rocks. Even those authors who admit of a restricted source bed role for carbonates seek, in general, to distinguish between the effective source beds like the fine grained carbonate facies and 'porosity providers' such as oolites and reefs.

However, analyses of light hydrocarbons from over 200 samples of Recent marine oolites have revealed the presence of C_1-C_5+ compounds which are believed to be authigenic products of early diagenetic biochemical and low temperature chemical reactions.

Determination of organic carbon content of these sediments showed values between 1.23 and 4.13 wt.%, which are well above the 0.3 wt.% organic carbon minimum requirement (0.5 wt.% for clastic facies) for carbonate sediments to be considered potential source beds. Characterisation of both the bitumen and kerogen fractions of the organic matter by standard optical and chemical means showed that, although it is immature, it has a very high potential for generating hydrocarbons. There is strong evidence that, with deeper burial and exposure to higher temperatures and perhaps to catalytic influence of the host sediments, this organic matter of algal - amorphous facies will, through time, generate commercially significant hydrocarbons which will accumulate as petroleum in the porosity of the oolites.

A scheme for in-situ formation of petroleum in oolites is advanced and the geological-geochemical conditions for its fulfilment are examined. It is suggested that the indigenous origin of petroleum in oolites which precludes an extensive and largely inefficient primary migration process may provide another explanation for the enormous petroleum accumulations in such inherently porous carbonates.

From exploratory data obtained in this study on various other Recent carbonates, the probability is that, for many petroleum bearing carbonate rocks, the petroleum forming materials were deposited at the same time and place as the reservoir materials; therefore there are no separate source beds but rather integrated source-reservoir beds. This proposal is consistent with the known structural and stratigraphic habitats of many oil and gas pools in carbonate rocks.

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ABBREVIATIONS USED IN TEXT

C_2+	hydrocarbons heavier than methane; generally include gas and gasoline range hydrocarbons
$C_{15}+$	all hydrocarbons containing 15 or more carbon atoms
CPI	carbon preference index
CR (FC)	residual or fixed carbon
CT (C_{TOC})	total organic carbon
Corg	organic carbon
DSDP	Deep Sea Drilling Project
Eh	redox potential - a measure of the oxidising or reducing intensity of the environment
EPB	ethane, propane, butane
FID	flame ionisation detector
g	gram
GC	gas chromatograph
ng	nanogram
pH	the negative logarithm of the hydrogen ion concentration

ABBREVIATIONS USED IN TEXT contd ...

ppb	parts per billion
ppm	parts per million
OEP	odd even preference
SEM	scanning electron microscope
TOE	total organic extract

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CHAPTER I

INTRODUCTION

'Time after time hypotheses have been formed, each apparently well founded and incontrovertible, yet each in turn found wanting when put to the test or when further field evidence accumulated'.

Lees, 1934
"The Source Rocks of Persian Oil".

I. 1 THE PROBLEM

Closely associated with the ascendancy, in the early part of this century, of the source bed theory of the organic origin of petroleum, was the concept of argillaceous sediments as universal source beds. This was a logical and convenient extension of the long known association of oil with shales in oil shales, a fact reflected in part by the subsequent designation of every bituminous rock ranging from limestones through marls to shales as 'oil shales'. A glaring example is the much investigated Green River Formation of North America which is generally referred to as 'shale' but is in fact limestone (with subordinate quartz and feldspar).

The influence of this paradigm was so strong that even obvious evidence of carbonate source beds (Hunt, 1863; Orton, 1888; Hedberg, 1931; Adams, 1934; Howard, 1934; Muir, 1934), hardly attracted more than cursory reference in general discussions of petroleum source beds. In a state-of-the-art review, Dott and Reynolds (1969,p.78) commented: 'so firmly entrenched is the doctrine of carbonaceous shales as source beds that most reports on oil fields, petroliferous areas, or new petroleum prospects routinely include sections attempting to identify the most likely candidates'. Earlier, Snider (1934,p.51) had analysed opinions regarding source beds as expressed in publications of the American Association of Petroleum Geologists (AAPG) and concluded : 'the preponderant view is that source beds are marine shales --- in contact with or near the reservoir.'

However, it soon became increasingly evident from field stratigraphic relationships in carbonate petroliferous provinces that this exclusive doctrine of argillaceous source beds could not be admitted. In such regions as the Middle East, especially in and around the Persian Gulf, there are practically no source shales; besides the impervious nature of the rocks surrounding limestone reservoirs, makes it unlikely that oil migrated into them the same way as it is believed to have entered sandstones. This was probably realised by Lees (1934) who, on the problem of the origin of Middle East petroleum, wrote of 'an embarrassment of possibilities' and went on to propose a mixed origin that was part in-situ and part migrated (through fractures) for the Oligocene-L.Miocene Asmari Limestone oil and similar accumulations.

The publications that followed on the subject (eg. Lees, 1938; Lees and Richardson, 1940; Gibson, 1948), though brilliant in their conception, were equally equivocal and contributed little in real terms to establishing the 'truth' about the origin of the oil and gas in the carbonate reservoirs of the Middle East. The major hinderance was underscored by Link (1950) who noted that such interpretations from field data were commonly influenced by pre-conceived notions and faulty geological prejudices. He declared: 'thus data may be presented in favour of a plausible interpretation which is diametrically opposite to the true or correct deduction' (ibid p.286). Link (op cit) then offered, as 'food for thought', a postulation of an indigenous origin for the petroleum found in coral reefs and bioherms adding, 'when one considers that in coral reefs and bioherms conditions exist, ideal for growth, death and accumulation of countless generations of inumerable organisms, why is it necessary to look for outside sources to explain the oil found in them?' (ibid p.286). This idea was not entirely new. Earlier, Bergmann and Lester (1940) had combined the results of their chemical studies on coral reefs with the data on organic matter in various corals published by Silliman (1846) and Clark and Wheeler (1922) and called attention to coral reefs as 'one possible source of petroleum'.

Based on the facts of the formation of carbonate deposits, Link extended his hypothesis of in-situ generation of petroleum in reefs to most limestones and dolomites that possess adequate porosity for the petroleum hydrocarbons to accumulate. This proposal was to receive a boost from a series of papers published in the 1950's; for example, agreeing with a previous suggestion by Richardson (1924), Thomas (1950) noted that much of the Asmari Limestone were laid down in environments suitable for oil formation and that its organic content was adequate to account for the present oil accumulation. Henson (1951 p.128) and Baker and Henson (1952 p.1859) stated that the oil and gas in bands of porous, detrital and oolitic limestone and sacchroidal dolomites of Jurassic - L. Cretaceous age that occur between persistent anhydrite bands, is indigenous. The conclusion reached by Steineke et al (1958) on the origin of the oil in the Jurassic oolitic carbonate rocks of Saudi Arabia was identical.

Wengerd (1958) studied the Mississippian and Pennsylvanian oils of Rattlesnake, Hogback and Table Mesa fields in the San Juan Basin, U.S.A. and concluded that they originated virtually in-situ in the carbonate porosity. On the basis of the sedimentation pattern in the limestone province of the Madison Group in the Williston Basin, Andrichuk (1958) supported the idea of a source for the Madison oil in the sediments themselves. In a review of the geology of the giant Ghawar oil field, Aramco Staff (1959) believed that the Upper Jubaila and Arab -D oil originated in the oolitic limestones in which it is now found. Other examples could be cited ad infinitum from producing fields the world over but these few will suffice to demonstrate the importance of the local or indigenous origin of the petroleum found in carbonate rocks.

At the experimental level, Hunt (1961), Gheman (1962) and Baker (1962) found that despite much lower organic matter contents, ancient pure limestones had more extractable hydrocarbons than equivalent shales presumed to be source beds. Although these authors did not exactly say so, their data afforded tacit support to the concept of petroleum hydrocarbon generation in carbonate beds.

In 1964, the whole question of the universality of shale scoure beds was brought into sharp focus by Edgar Owen when he observed that 'one of the prevalent dogmas is that oil in dolomite or limestone reservoirs cannot be indigenous to the rocks in which it is stored.' (ibid p.1727). He examined the assertions behind this dogma vis-a-vis the geological concepts in favour of carbonates as source beds and declared that the stratigraphic and structural habitats of many oil and gas pools in carbonate rocks indicate indigenous origin of their hydrocarbons. He cited, as an example, the occurrence, in many fields, of productive oolitic or coquina reservoirs as local facies completely enclosed within impermeable limestones. The arguments of Hedberg (1964) and Tiratsoo (1967) in favour of the in-situ origin of oil in carbonate beds were along similar lines.

From studies of Recent sediment facies from locations stretching from the Caspian Sea through the Indian Ocean and Cuba to the shelf of Australia and New Zealand, Veber and Gorskaya (1965) and Ali-Zade and Shoikhet (1967) observed that the phenomenon of neogenesis and transformation of bitumen in the direction of oil formation is as intense in carbonate facies of deposits as in corresponding argillaceous facies. The authors concluded that the results of their research confirmed the conjecture that ancient carbonate rocks may be syngenetically oil bearing. Back in 1928, Trask had come to the same conclusion based on studies of Recent carbonate facies from Cuba.

In a timely review paper on the origin of petroleum in carbonate rocks, Hunt (1967) noted that, 'it has frequently been assumed that petroleum does not originate in carbonate rocks'. His discussion on the subject which included examples of carbonate source beds ended with the declaration: 'the fact that 40% of the petroleum in major oil fields is in carbonate reservoirs many of which are completely surrounded by carbonate rocks, indicates that carbonates can be oil source rocks ' (ibid,p.225).

Along related lines, Andreev et al (1968) argued that the fact of petroleum occurrence in areas of carbonate rocks where it is impossible to find clay beds that could be regarded as source for petroleum, excludes the possibility of considering shales as the only type of source beds. In a rather scathing remark, the authors concluded: 'the idea of such a universal role for clays has never had a definite or reasonable basis, and the mere fact of this concept only serves to illustrate the inertia and stagnation in theoretical geology.'(ibid, p.14).

Such declarations, however, represent mere flashes of illumination in a largely twilight zone and there is still widespread prejudice against the concept of carbonates as source beds. It is, perhaps, in this light that one appreciates the fact that the intensive organic geochemical investigations since the 1960's have been heavily biased in favour of argillaceous beds. In contrast, carbonate sediments have remained the cinderella of the petroleum industry deserving perfunctory attention and, then, only in those circumstances where lithologic associations permit no other alternative. Consequently, very little experimental data are available as to the effectiveness of carbonates as source beds of petroleum.

This was vividly manifested in the patchy,controversial and inconclusive discussion on this subject by a very distinguished panel of petroleum geologists and geochemists at the 9th World Petroleum Congress in 1975 (Vol.2 of Proceedings, pp.201-203) which prompted the Panel Chairman, Mr. J. A. Momper to observe that, 'little worthwhile information has been published on the important subject of carbonates as effective oil and gas source beds.' Yet, in relative terms, carbonates are quantitatively the most important petroleum bearing rocks. As Weeks (1958) pointed out, carbonates represent only about 16% of the sediments of the basins of the continents and continental shelves (compared to 50% for clays and shales) but house at least 40% (50% : Blatt et al, 1972) of the world's petroleum.

In summarising the proceedings of the Discussion Panel, the Scientific Secretary remarked: 'As revealed by the prolonged discussion [on source beds], carbonates provide another intriguing problem of profound interest requiring further study' (Vol.2. Proc.9th World Pet. Cong., 1975; p.205).

I. 2 OBJECTIVES OF STUDY

This combined organic geochemical and geological study of the implications of light hydrocarbon occurrence in Recent carbonate oolite was undertaken in the hope of contributing to the rather limited data currently available on the petroleum generating capacity of carbonates.

The objectives were : a) to verify the fact of occurrence and distribution of light hydrocarbons in Recent oolites reported by Ferguson (1975) and to account for its origin; b) if (a) was promising, to determine the values of organic carbon in oolite and to characterise the organic matter from the point of view of its petroleum generating potential; c) if (b) proved prospective, to propose a scheme of petroleum generation and accumulation in oolites and to test the geological - geochemical chances for its fulfilment.

An ultimate goal was to relate the results to the overall problem of the origin of petroleum in carbonate rocks.

Attention was focussed on Recent carbonate sediments on the principle of the present as a key to the past. Although a broad interest was maintained in a variety of carbonate sediments, a choice was made of oolite facies as the main investigative material. This preference seemed particularly appropriate for the following reasons :

a) Oolites which occur repeatedly in the stratigraphic record are familiar host rocks for petroleum.

b) Despite divided opinions about their origin, oolites (at least those found in any one set of environments) are comparatively homogenous in texture, structure, mineral composition and their diagenetic and porosity relationships are fairly well established (Illing, 1954; Ginsburg, 1957; Friedman, 1964; Robinson, 1967; Coogan, 1970).

c) Even those authors (eg, Hedberg, 1964; Hunt, 1967) who admit of a limited source bed role for carbonates seek, in general, to distinguish between the effective source beds such as the fine grained carbonate facies and the 'porosity providers' like oolite, reefs, coquina beds et cetera. Yet stratigraphic relationships in most petroleum bearing oolitic rocks preclude any other suggestion than in-situ origin for their contained hydrocarbons.

Despite the concentration on one carbonate facies, it is hoped that this investigation would act as a model to help establish some general principles on modes of petroleum generation and accumulation in carbonate beds. Happily, essential supplementary data were acquired on other Recent carbonate facies and provide the background to some generalisations made in the concluding discussions.

I. 3 THEORETICAL FRAMEWORK

The light hydrocarbons (also called low molecular weight hydrocarbons) and in particular their saturated members through C_5 form the bulk of natural gas and a characteristic portion of crude oils.

Of these hydrocarbons only the lowest member, Methane, has been recognised as a natural product due to the fermentative degradation of organic matter by bacteria in anoxic environments (Emery and Hoggan, 1958; Erdman, 1961; Claypool et al., 1971; McIver, 1973; Rashid et al., 1977). Despite sporadic literature references to the association of C_2 - C_5 hydrocarbons with anoxic mud and sewage sludge (Zobell, 1951; Davis and Squires, 1954; Bokova, 1959; Malyshek, 1962; Veber and Maximov, 1976), the ethane through butanes have generally not been reported as constituents of living things or as metabolic products. In fact, the lowest aliphatic hydrocarbon known to be a constituent of living organisms is n-heptane (Erdman, 1961). Herein lies the geochemical significance of light hydrocarbons; that unlike the heavier hydrocarbons (generally, C_{15}+) which are synthesised by living organisms and are found in Recent sediments, the C_2+ hydrocarbons are generated at depth by thermo-chemical reactions over geologic time and are practically absent in Recent sediments (Louis, 1964; Phillipi, 1965; Vassoyevich et al, 1970; Sokolov: in Kartsev, 1971; Tissot, et al, 1974; Tissot and Welte, 1978).

For a long time, therefore, the presence of C_2+ hydrocarbons in surface or shallow sediments has been interpreted to be diagnostic of migration of gas from a deep seated source of hydrocarbons. This is the basis of geochemical exploration for petroleum which seeks to identify anomalous C_1 - C_4 (or C_5) gas concentrations in surface or shallow sediments as a clue to the existence, at some depth, of a gas or oil accumulation (Laubmeyer, 1933; Sokolov, 1933; Horvitz, 1939, 1972, 1980; Andreev et al, 1968; Fedynsky et al, 1975).

Thus, during the ongoing DSDP (Deep Sea Drilling Project), C_2+ hydrocarbons have been routinely monitored on the shipboard and their presence in any hole has been used as one of the criteria adopted, to shut down drilling because of the possibility of encountering a pressured oil or gas deposit (Whelan, 1979).

However, subsequent organic geochemical analyses of DSDP shallow sediment cores (from 10 meters and deeper) revealed the presence of light hydrocarbons, up through 7 carbon atoms, that were not petroleum derived. Such hydrocarbons were found to occur in concentrations greater than geochemists had been accustomed to believing (Hunt, 1974, 1975, 1978; McIver, 1971, 1974, 1975; Rogers and Koons, 1971; Whelan and Hunt, 1978; Whelan, 1979). In a comparative study of surface gravity cores of calcareous sediments from shallow water areas of the Persian Gulf and Arabian Sea, Hunt and Whelan (1979) encountered a similar suite of hydrocarbons as in the DSDP sediments except that the surface samples showed higher concentrations of alkenes (and non hydrocarbons) which, however, decreased with depth (ibid, p.223). Other current data on C_2+ light hydrocarbon occurrence in Recent sediments include those of Rumeau and Sourisse (1972), Ferguson (1975), Bernard et al (1978) and Kvenvolden et al (1980).

Tables I.1 and I.2 show some relevant data. Such results raised fresh questions about low molecular weight hydrocarbon generation and migration in sedimentary basins. In general, the new data demonstrate that C_2+ light hydrocarbons are not only present in Recent shallow sediments but that; a) they generally increase with

TABLE I.1 HYDROCARBON GASES, SHELF, SLOPE AND BASIN, BERING SEA CONCENTRATIONS
(nl/l interstitial water)* (after Kvenvolden et al (1980)

Sta-Core	Interval (cm)	C_1	C_2	$C_{2:1}$	C_3	$C_{3:1}$	i-C_4	n-C_4	$C_2/C_{2:1}$	$C_1/(C_2+C_3)$
Bering Shelf										
2-01	0-10	1500	56	70	27	22	-	-	0.8	18
	50-60	8700	86	61	39	12	9	15	1.4	70
	92-102	10000	130	95	78	30	13	21	1.4	48
3-02	0-10	1500	31	41	20	10	-	-	0.8	29
	42-52	3700	76	55	38	16	11	14	1.4	33
4-04	0-10	1800	50	68	21	32	-	14	0.7	25
	55-65	6300	80	68	39	24	-	15	1.2	53
5-06	0-10	1800	49	73	31	21	-	4	0.7	23
	50-60	7800	100	62	52	18	9	16	1.6	51
6-07	0-10	1300	42	41	23	10	-	-	1.0	20
	27-37	3400	89	95	54	31	15	18	0.9	24
7-10	0-10	1300	27	49	14	16	-	-	0.6	32
	34-44	4100	68	76	40	27	-	-	0.9	38
8-11	0-10	3300	87	91	43	27	8	14	1.0	25
	50-60	5000	57	38	30	17	8	14	1.5	58
9-12	0-10	13000	510	131	150	33	33	43	3.9	20
	50-60	4700	180	10	42	9	-	-	18.0	21
	100-110	6800	490	10	130	26	15	11	49.0	11
10-13	0-10	2100	87	79	43	27	12	14	1.1	16
	50-60	4500	52	15	14	17	-	-	3.5	68
	100-110	5000	130	16	10	49	-	-	8.1	36
	150-160	5400	230	19	11	77	-	-	12.0	22
Bering Slope										
15-15	0-10	1100	31	65	17	19	5	9	0.5	23
	100-110	1200	56	91	34	37	6	10	0.6	13
16-18	0-10	900	27	44	17	19	-	6	0.6	21
	50-60	3300	28	33	15	12	-	-	0.9	77
	100-110	5000	33	42	15	16	-	7	0.8	100
17-21	0-10	1300	33	40	24	10	4	8	0.8	23
	50-60	1700	19	22	9	7	-	-	0.9	61
	100-110	2100	19	18	4	7	-	-	1.1	91
	150-160	4200	25	11	9	-	-	-	2.3	120
20-25	10-20	1300	15	39	11	13	-	-	0.4	50
	70-80	5900	23	22	8	9	-	-	1.1	190
	110-120	6800	30	22	11	13	-	-	1.4	170
	160-170	9900	30	30	11	17	-	-	1.0	240
	200-210	9100	41	32	12	23	-	-	1.3	170
21-27	0-10	5100	21	26	9	7	-	-	0.8	170
	50-60	4800	18	18	4	7	-	-	1.0	220
	102-112	8400	22	22	7	0	-	-	1.0	290

Sta-Core	Interval (cm)	C_1	C_2	$C_{2:1}$	C_3	$C_{3:1}$	i-C_4	n-C_4	$C_2/C_{2:1}$	$C_1/(C_2+C_3)$
Bering Slope contd/.										
22-28	0-10	1200	19	22	11	7	-	-	0.9	40
	50-60	700	12	22	7	7	-	-	0.6	37
	100-110	1600	25	25	13	87	340	14	1.0	42
	150-160	2500	63	95	43	63	160	14	0.7	24
	200-210	8000	45	22	12	11	43	6	2.1	140
Aleutian Basin										
1 G 1	16-24	3500	14	38	13	14	-	8	0.4	130
	64-71	6100	38	38	16	16	-	9	1.0	110
2 G 1	2-10	1100	9	16	5	13	8	-	0.6	79
	34-44	5600	31	150	24	31	-	5	0.2	100
	61-71	12000	22	31	16	15	-	-	0.7	320
	87-97	21000	33	37	19	15	-	-	0.9	400
2 G 3	108-118	5900	16	33	10	8	-	-	0.5	230
3 G 1	2-12	900	14	37	6	7	-	-		45
	36-46	3300	18	25	14	-	-	-		100
	61-72	5500	16	26	13	-	-	-	0.6	190
	100-110	6700	11	21	8	-	-	-	0.5	350
	140-150	7100	18	21	8	-	-	-	0.9	270
	180-190	6900	18	21	4	-	-	-	0.9	310
	220-230	8600	26	39	11	14	-	-	0.7	230
4 G 1	2-12	300	7	12	-	-	-	-	0.6	43
	64-74	2500	22	94	21	28	2	9	0.2	58
	129-139	4500	-	-	10	14	-	-	-	450
	181-191	5400	7	9	-	-	-	-	0.8	770
6 G 2	0-10	2400	13	16	9	6	-	5	0.8	110
	60-70	5000	16	14	7	15	-	-	1.1	220
	120-130	5100	13	10	5	12	-	-	1.3	280
	167-177	11000	19	9	7	40	-	-	2.1	420
7 G 4	65-75	4700	25	26	16	18	4	8	1.0	120
8 G 2	1-11	500	10	20	10	14	-	5	0.5	25
	29-39	1600	22	26	17	11	-	6	0.9	41
	63-73	1600	20	18	14	12	-	6	1.1	47
9 G 2	1-11	1000	14	25	15	11	-	-	0.6	35
	60-70	2000	11	21	9	7	-	-	0.5	100
	115-125	2500	10	16	10	11	-	-	0.6	130

* Values are semi-quantitative having been based on analyses of interstitial waters rather than directly on sediments.

TABLE I.2

C_4 - C_7 HYDROCARBONS IN BLACK SEA CORES,
DSDP HOLE 380/380A, LEG 42B (after Hunt, 1979)

	Hydrocarbon yield (ng/g dry sediment)	
	175 m Depth	356 m Depth
Isobutane	3.6	5.1
n-Butane	2.5	4.0
Isopentane	4.9	10.9
n-Pentane	0.7	2.6
2.2-Dimethylbutane	0.3	4.5
Cyclopentane	0.2	0.7
2.3-Dimethylbutane	0.2	3.7
2-Methylpentane	0.3	10.0
3-Methylpentane	0.5	11.7
n-Hexane	0.3	123
Methylcyclopentane	1.0	19.8
2.2-Dimethylpentane	1.7	0
Benzene	0.6	10.8
Cyclohexane	1.7	12.0
3.3-Dimethylpentane	0.3	0
2-Methylhexane	0.3	1.5
2.3-Dimethylpentane	1.5	3.2
3-Methylhexane	1.0	2.7
1-trans-3-Dimethylcyclopentane	0.5	1.8
1-trans-2-Dimethylcyclopentane	0.8	5.0
n-Heptane	0.2	3.2
Methylcyclohexane	3.2	8.3
Toluene	2.0	25.2
Total	28.4	270

depth; b) there is a decrease and ultimately absence of unsaturated hydrocarbons and non hydrocarbons with depth; c) there is some correlation between amounts of the hydrocarbons detected and organic matter content of samples.

On the basis of these and other evidence, most investigators are agreed that, except for a few isolated cases where C_2+ light hydrocarbons could be considered as seeps from other sediments, their occurrence in Recent or shallow sedimentary beds represent the onset of in-situ thermal (low temperature) diagenesis of organic matter in the sediments (Rumeau and Sourisse, 1972; Hunt, 1974, 1975, 1978; McIver, 1974, 1975; Bernard et al, 1978; Hunt and Whelan, 1979; Whelan, 1979; Kvenvolden et al 1980 and others). This is a part of the oil forming process (Phillipi, 1965, 1968; McIver, 1974) and signifies that conditions favourable for hydrocarbon generation exist in the sediments (Hunt, 1979).

It must be quickly added that these sediments do not constitute effective source beds at this stage; but the indication is that given adequate conditions of burial and temperature and aided, perhaps, by catalysis, the organic matter in these sediments would proceed along the path of thermal maturation to form petroleum. This is consistent with the generation, at depth, of the vast bulk of petroleum forming hydrocarbons.

In those Recent sediments where unsaturated hydrocarbons were detected along with saturated ones, a biochemical influence has been inferred.

I. 4 PREVIOUS WORK

The problem of the origin of the petroleum found in carbonate rocks has provoked a vast interest among petroleum geologists. However, against this background, comparatively little work has been done along the lines of the present investigation, namely, approaching the problem from the standpoint of light hydrocarbon analysis. It is conceded that some petroleum companies have shown some interest in such an approach (R.N. Ginsburg, personal communication,1979) but due to the confidential nature of commercial company operations, there is usually a considerable time lag before results of such investigations are made public. As a result, the published work on the problem of the origin of petroleum in carbonate rocks has been mostly confined to interpretation or deductions based on field observations and largely supplemented by geological intuition.

However, the positive effect of carbonate content on gas concentrations detected in samples taken in the course of geochemical exploration for petroleum has been recognised by many workers. Long et al (1964) have noted the enhanced gas concentrations in carbonate bearing argillaceous sediments. They had considered that 'naphthanogenic clays' (i.e. clays with large amounts of organic matter) should contain larger hydrocarbon concentrations than other samples; instead the results showed greater abundance of gaseous hydrocarbons in the carbonate fractions mixed with the sediments. The authors pointed out that the hydrocarbons are released from the carbonates during acid extraction. As to the origin of the hydrocarbons they suggested 'as a pure speculation' that the gases are linked to the biochemical genesis of the carbonate and that the close link between the calcareous support and the living organisms which generated it, may have helped in the trapping of gaseous hydrocarbons during subsequent fermentation of the organic matter.

A similar effect was recognised by Neglia et al (1964) who recommended that sample degassing techniques used in geochemical exploration should be designed to minimise the breakdown of carbonates and the consequent development of spurious hydrocarbons. McCrossan et al (1972) also observed enhanced gas concentrations due to the presence of carbonates in the samples and noted that dark coloured carbonates contained more hydrocarbons than light coloured ones; they, however, concluded that no simple relationship existed between carbonate and gas contents.

More related investigations devoted to light hydrocarbon occurrence in carbonate sediments and its implications on petroleum formation have been reported by Degens et al (1964) who detected various concentrations of $C_1 - C_8$ hydrocarbons in freshwater carbonate concretions. In accounting for the origin of these hydrocarbons, the authors preferred an explanation involving migration from the surrounding fine grained organic shales while admitting the possibility that they were formed from the entrapped organic matter within the concretions. Thompson and Creath (1966) studied the $C_1 - C_5$ hydrocarbon concentrations in Recent carbonate shells and concluded that the principal source of the hydrocarbons detected is the organic matter in the shell structure. On the basis of a parallel investigation of Pleistocene and fossil shells (of the same taxa as the Recent shells), the authors proposed that light hydrocarbons start forming soon after the deaths of the organisms and increase in amounts with increasing geological age of the specimens.

The initiation of the DSDP in 1968 brought about a renewed geochemical interest in questions about when and how light hydrocarbons form in relation to petroleum generation in sedimentary beds. While these studies were not specifically directed at carbonate sediments, they have served an invaluable purpose in revealing something of the nature and implications of light hydrocarbon generation in Recent sediments (see Section I.3).

Veber et al (1977) and Veber and Maximov (1976) have detected $C_1 - C_6$ hydrocarbons in a variety of Recent sediments which they attributed to early diagenetic reactions and remarked that, of particular interest is the fact that hydrocarbon gas generation takes place not only in terrigenous facies but also in carbonate facies with organic matter of mainly autochtonous type.

Hunt and Whelan (1979) reported light hydrocarbons believed to be early biologic and low temperature chemical reaction products in Recent carbonate sediments of the Persian Gulf and Arabian Sea.

It was, however, the work of Ferguson (1973a, b, c, 1974, 1975) that inspired the present study. Following a detailed mathematical and statistical treatment of geochemical exploration data acquired by the British Gas Corporation over the Locton Natural Gas Reservoir, Ferguson established a strong correlation between the percentage carbonate and, in particular oolites, in the samples and the amounts of light hydrocarbons detected. This led to doubts about the validity of the gas anomaly map prepared from the data. As part of an effort to resolve the suspected lithologic influence, Ferguson sampled as a 'blank trial' for the Locton Survey, a carbonate area in Weardale in County Durham, England, underlain by granite, a generally accepted non-source rock and noted a correlation trend similar to that for the Locton Survey. This led him to believe that the source of the hydrocarbons was in the carbonates. Next,. he addressed himself to the origin of the hydrocarbons in carbonates by investigating light hydrocarbon distribution in Recent delta and dune oolites from the Persian Gulf.

Commenting on the results, Ferguson (1975, p.24) observed: 'a fact which was unexpected is the occurrence of ethane and propane in the samples of ooliths studied. The ratio of $C_1 : C_2 : C_3$ of approximately 2 : 1 : 0.6 is abnormal, since the recorded composition of Recent natural gases suggests that methane is generated, with only traces of higher hydrocarbons.' [see Table I.3a] He concluded: 'Clearly this result is significant and when the origins of natural gas is considered, may be of some importance' (loc.cit). In follow up experiments the author demonstrated that oolites have a capacity to adsorb petroleum hydrocarbons (Table I.3b). Thus the stage was set for the present investigation.

Prior to the work of Ferguson, the only published mention of investigations along related lines was a negative reference by Mitterer (1972, p.1418) to the work of Frishman (Unpublished Masters Thesis, 1969) who failed to detect hydrocarbons (range not specified) or, for that matter, organic material in oolites from Baffin Bay, Texas. Unfortunately, Frishman's work is not accessible to the present writer who therefore cannot assess the validity of this claim. However, it is instructive that in a recent paper published by Frishman in conjunction with others (Land, Behrens and Frishman, 1979) the Baffin Bay oolitic coatings were reported as containing 0.6 wt.% organic matter (ibid.,p.1273).

TABLE I.3a HYDROCARBON GAS IN RECENT CARBONATE SEDIMENTS
Values given in ppb w/w (after Ferguson, 1975)

MATERIAL	HYDROCARBONS		
	METHANE	ETHANE	PROPANE
Delta ooliths	328	144	76
Delta ooliths	305	144	101
Dune ooliths	500	241	160
Dune ooliths	514	251	158
Dune ooliths	489	245	157
Dune ooliths	520	222	150
Fresh, recent) 1.	925	315	195
carbonate material) 2.	880	270	168
with some ooliths) 3.	805	230	150

TABLE I.3b SUMMARY OF EXPERIMENTAL RESULTS ON ADSORPTION OF LIGHT HYDROCARBONS ON SEDIMENTS (VALUES GIVEN IN pp b w/w). (after Ferguson, 1975)

MATERIAL	BLANK			MAX.ADSORPTION*		
	METHANE	ETHANE	PROPANE	METHANE	ETHANE	PROPANE
Delta Ooliths	316	144	88	7491	1617	833
Dune Ooliths (1)	507	246	159	6175	1521	714
Dune Ooliths	504	233	153	7767	1860	980
Precipitated Chalk	180	4.1	Nil	317	17.8	Nil
Natural Chalk Rock	741	202	Nil	1017	286	81
Sandstone	79	7.0	Nil	580	185	216

* Natural Gas passed over samples for an average of 18 hours.

I. 5 PRESENT STUDY

The work evolved through several stages. At the start of the project, it was considered necessary to build up data on light hydrocarbon occurrence in ancient oolites and other carbonate types which would serve as comparative reference data for the expected results from the proposed work on Recent sediments.

The first step involved a laboratory study to develop a method of hydrocarbon extraction that will be common to both investigations and which would be effective without producing any artifacts. Details of this stage are presented in Chapter IV. Following the development of a desorption technique, several outcrop samples of ancient carbonates were collected at various sites from carboniferous and Jurassic exposures in Britain and France between March and September 1978 and analysed for C_1 - C_5+ hydrocarbons.

The results of these investigations are presented in Appendix I. Although the results and their corresponding organic carbon values were initially intended to be quantitative, it must be stressed that, as presented here, they have only a qualitative significance. Despite the fact that every effort was made to obtain unweathered samples including the use of a diamond saw to chip off suspected altered surfaces before crushing (to 1-2mm) samples for analysis, subsequent literature survey revealed that near surface samples lose up to 50% of their C_{15}+ hydrocarbons down to a depth of 10 meters (Leythaeuser, 1973; Clayton and Swetland, 1978). Understandably, such loss will be even greater for the light hydrocarbons. For example, Thompson and Creath (1966) found that weathered and recrystallised pelecypod carbonate shells contained about 92% less C_1 - C_5 hydrocarbons as the non weathered and non recrystallised specimens from the same piece of rock.

The next stage was the analysis of subtidal to intertidal Recent oolites from the United Arab Emirates, Kuwait and Egypt.

The results which showed the presence of C_2+ hydrocarbons in even greater concentrations than obtained by Ferguson (1975) were only dimmed by the fact of the collection and storage of the samples.

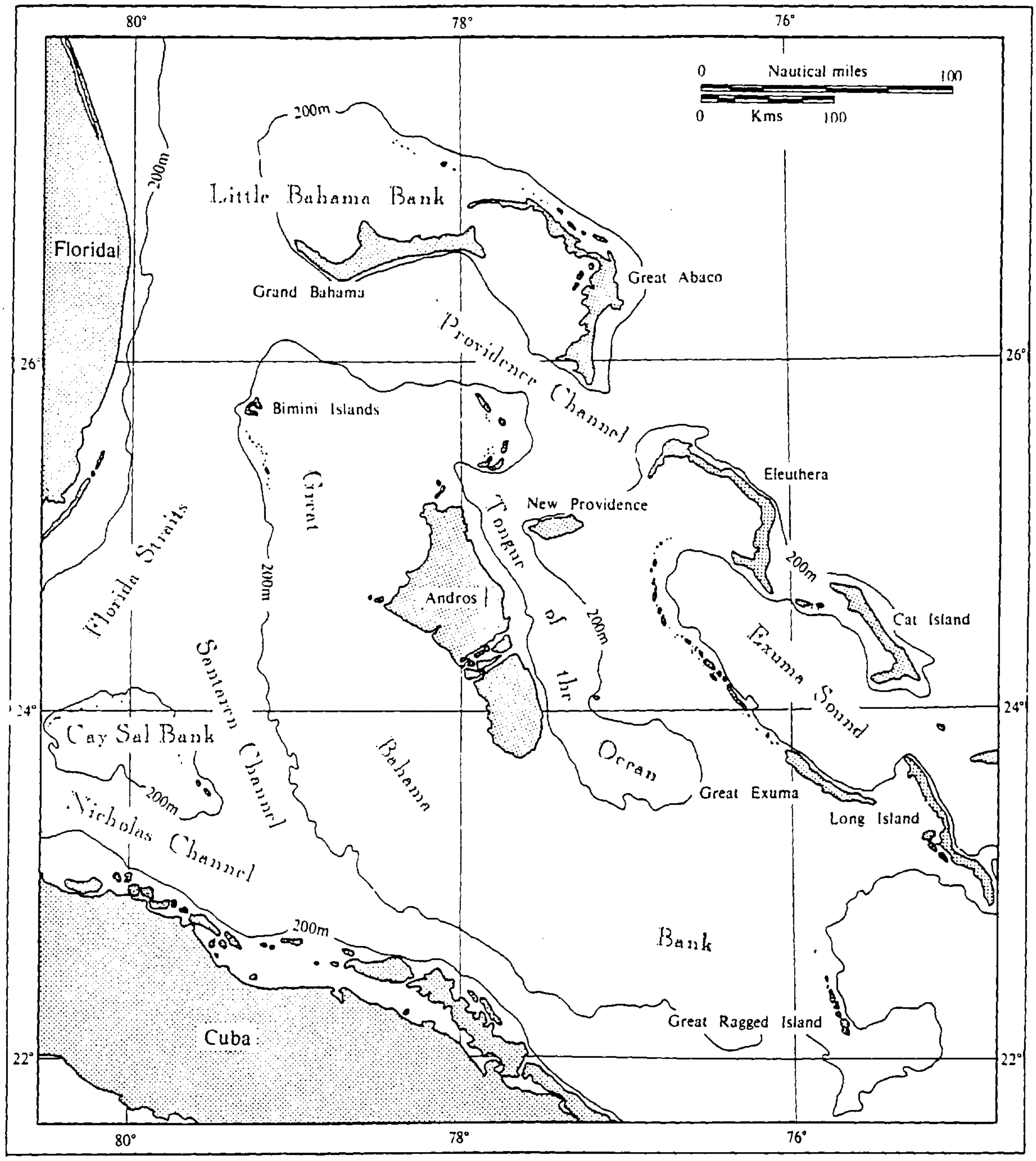


FIG. I.1 CHART OF THE BAHAMAS (from Bathurst, 1975). THE SCHOONER CAYS TIDAL BAR BELT IS AT THE NORTH END OF THE EXUMA SOUND.

Because the samples had been collected (by other people) for purposes other than organic geochemical studies, no precautions had been taken to prevent either the loss of light hydrocarbons or contamination during the transportation and storage of the samples. Nevertheless, the results proved vital to the formation of certain preliminary views that pointed to the need for further controlled investigations.

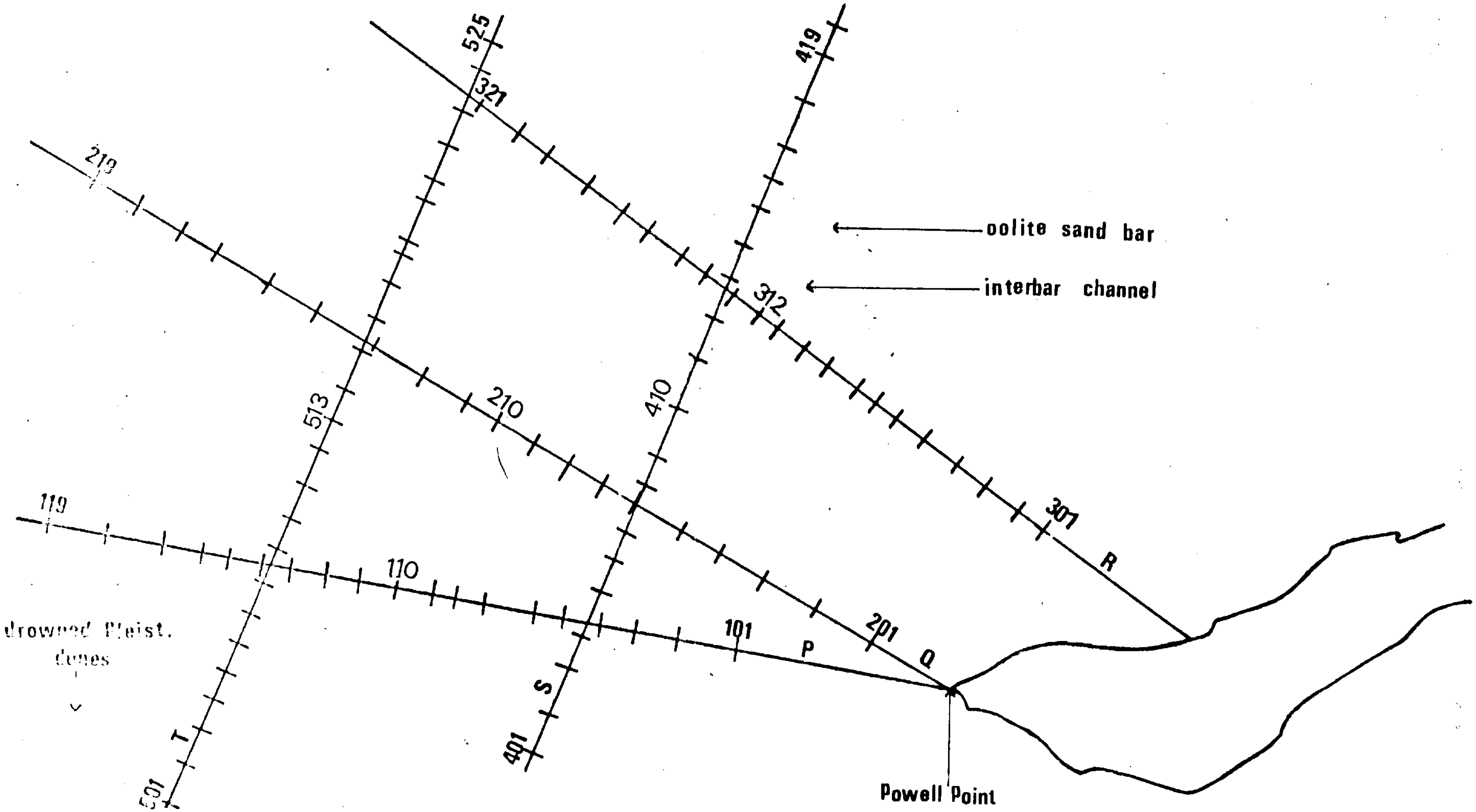
I. 6 FIELD WORK AND SAMPLE HANDLING

The Bahama Banks, a shallow irregularly shaped, flat topped platform, was selected for sample collection not only because of thier almost pure carbonate sediments but also because, together with the adjacent Florida Keys (see fig.I.1), they constitute a vast 'carbonate rock factory' which is actively producing most modern equivalents of carbonate rocks found in the geologic record.

Also important in the selection of the Bahama Banks was the fact of a recommendation by Sissler (in Cloud, 1962; p.69) that, 'the Bahama Banks may afford a site of unusual interest for investigation of petroleum genesis.' In his report of a specially commissioned study on the microbiology and biochemistry of the sediments and overlying waters from the Bahama Banks, Sissler noted that carbonate sediments and cores showed gas evolution. Based on the highly saline waters, high organic productivity including the abundance in sediments of micro-organisms capable of producing H_2 gas as well as evidence of biochemical heating et cetera, Sissler concluded that the area was ideal for 'further studies of conditions possibly leading to the formation of petroleum hydrocarbons'.(loc.cit.)

Much of the fieldwork was done in June, 1979. Bearing in mind that the analytical results and deductions made from them will be viewed against the background of the environment in which the sediments were deposited, importance was attached to field observations and measurements. 208 oolite samples, 4 short cores and 48 water samples were collected from 104 stations along five traverses (fig. I.2) designed, with the aid of aerial photographs, to gain a valid spread of sediment characteristics and environmental parameters.

Sediment samples were obtained by special 'grab' technique using purpose made inert containers that were then hermetically sealed.



525
321
419
219
oolite sand bar
interbar channel
312
513
210
410
119
110
301
R
drowned Pleist. dunes
101
P
201
Q
S
T
401
501
Powell Point

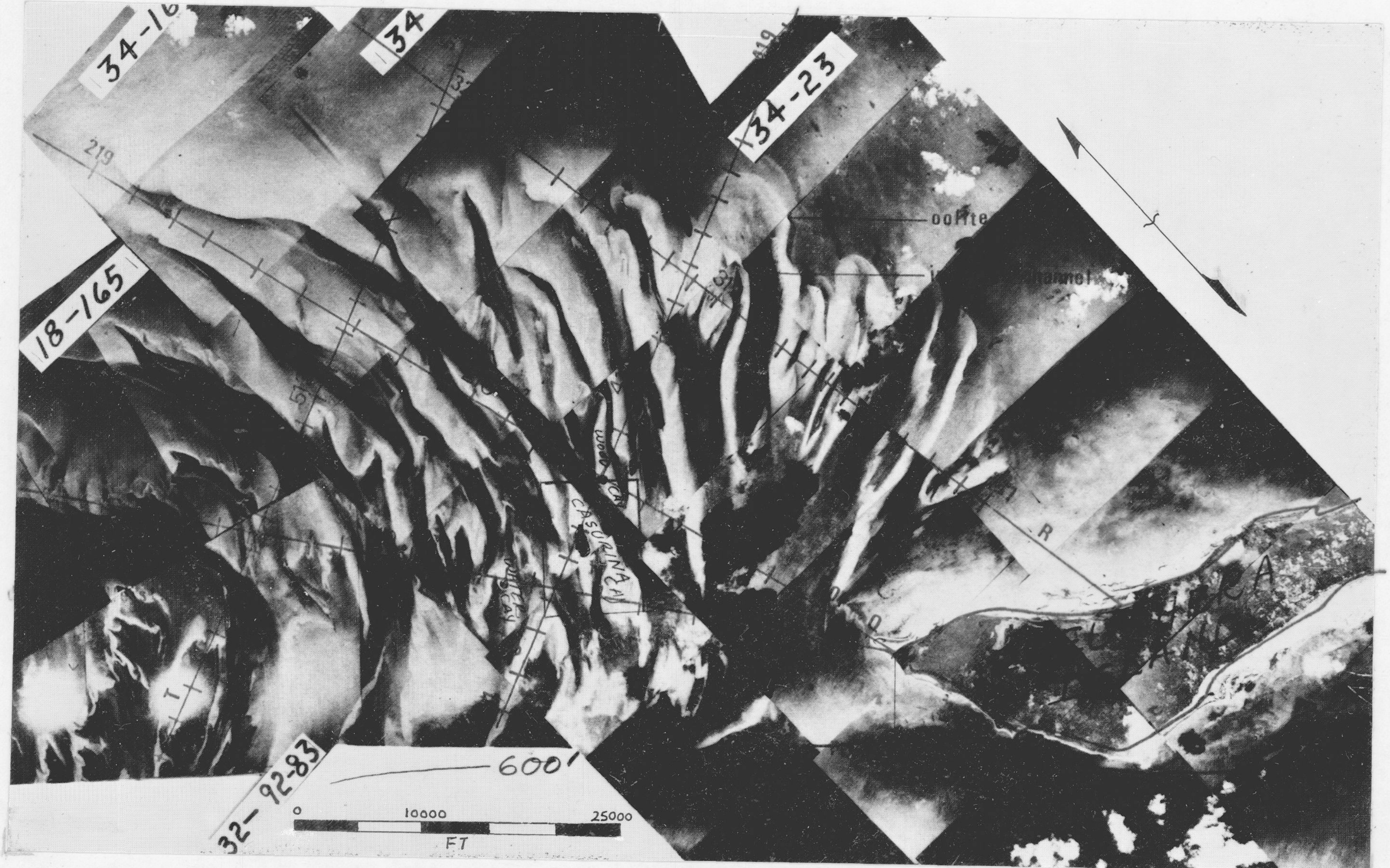


FIG.I.2. Aerial Photograph of the Schooner Cays tidal bar belt. Overlay shows sampling locations along 5 traverses. Photograph: Courtesy of Professor R.N. Ginsburg.

The cores were taken by manually pushing lengths of 10cm diameter, thick walled aluminium tubes equipped with slips and having inert linings into the sediments by hand (see figs. I.3a and b). The cores were sealed with pvc caps and cloth tape. In deeper waters, sampling was achieved with the aid of snorkel apparatus. Water was collected with small water samplers.

At each station, various environmental parameters like pH, Eh and salinity of surface and pore waters were measured from the moored boat.

Depth from the surface water to the top of the sediments was determined by sounding with a long and robust measuring stick. Temperature was recorded to the nearest .1°C with a fractional celcius thermometer and salinity values obtained with a salinity meter. A Beckman model G meter with a glass-calomel combination electrode was used to measure the hydrogen ion concentration (pH); the same instrument, because of its extended scale, but with a platinum-calomel electrode, was used for the oxidation - reduction potential (Eh) determination. The measurements of pH and Eh have inherent problems. For dependable results, these parameters should be determined 'in situ' since disturbances in the environment would result in anomalous values. However, since it was unavoidable to remove the sediments before measurements, the sample collection technique was designed not to disturb the sediment unduly and measurements were made for the pH on the sample reaching the surface; for the Eh, after the sediment had regained equilibrium (generally 5 - 10 minutes) as described by Zobell (1946) and Swain (1970). The values reported here should therefore more nearly characterise 'in situ' conditions.

To inhibit any further microbial activity or atmospheric alteration of labile organic constituents, all sample bearing containers were immediately refrigerated , following the completion of measurements, in large Thermos ice chests specially packed with dry ice. These were subsequently kept in cold storage at the University of Miami. From Miami, the containers were flown to London where they were stored in the deep freeze until analyses. In general, analyses were completed in the first six months after collection.

FIG. I.3a Coring at Crane Key, Florida.

FIG. I.3b. Coring at Wood Cay, Eleuthera, Bahamas.

A parallel field trip was made to the Florida keys to observe and sample the Recent carbonate environment along the lines reported above but no formal account of this or the sampling of the sedimentary facies adjacent to the oolite deposits on the Eleuthera Bank are presented. However, data from them, have been reported where relevant and proved important as a basis of some generalisations made in this study.

I.7 EXPERIMENTAL

Most analytical procedures of this study follow common practices often employed in sedimentological and organic geochemical studies. This section is necessarily brief; only broad outlines of methods are given here. It was considered more appropriate to present details of instrument conditions, particular precautions taken and any assumptions made along with the results of each experiment in the relevant sections. Procedural blank determinations were made for all reaction systems.

Degassing of the samples was effected by heat and C_1 - C_4 analysis was carried out under isothermal conditions using a Perkin Elmer F.30 gas chromatograph. The FID response for C_1, C_2, C_3, i C_4 and n C_4 as well as their unsaturated members were computed against known standards. The C_5+ compounds were backflushed and integrated as single peaks.

A Perkin Elmer 240 Elemental Analyser was used for organic carbon determinations as well as elemental analysis of the Kerogen. Soluble organic matter (bitumen) was soxhlet extracted with azeotropic 3 : 2 benzene-methanol mixture for 22 hours. Kerogen isolation was by the use of 10% HCl to destroy the mineral fraction of the sediment. Cold HF follow up treatment was found not to be necessary for pure carbonates.

Organic matter characterisation was achieved by a combination of standard optical and chemical analyses.

The main petrologic information was acquired through

a) petrographic examination of thinned and polished sections using conventional low power microscope and high power Scanning Electron microscope respectively; b) Mineral identification by x-ray diffraction analysis backed up by staining technique; and c) Trace elements which were determined by the Inductively Coupled Plasma method and their possible relationships studied by qualitative microprobe analysis.

Thermal conductivity measurements were made at the Imperial College Geophysical laboratories. The grain densities of ooids were determined as part of the procedure for thermal conductivity measurements.

Radiocarbon dating of the ooids had been conducted by the University of Miami Radiocarbon Dating laboratory and published by Dravis (1979).

I. 8 PRESENTATION

The organisation of this thesis is as follows : Part I details the geological-geochemical conditions that bear on this study. The broad features of the sampling environment including sediment characteristics are presented followed by the proposal of a new theory on the origin of ooids.

Part II reports the results, and discusses the implications, of light hydrocarbon occurrence and origin in oolite along with the account of work carried out to evaluate the petroleum generating potential of oolites.

A model for in situ generation and accumulation of petroleum hydrocarbons in oolites is presented in Part III along with case studies to test the validity of the proposal. In the concluding remarks, an attempt is made to relate the findings of the study to the overall problem of the origin of petroleum in carbonate rocks.

The original field designations are used throughout this report. Thus El (for Eleuthera) is retained to designate samples from the Eleuthera Banks, Bahamas and Fl for those from Florida Keys.

As far as possible, measurements have been given in the metric system. The scale of the aerial photograph is, however, in feet. Important abbreviations are explained at the beginning of the Thesis. All diagrams and photographs are referred to as figures and, as in the case of the tables, numbered sequentially within each Chapter.

PART 1

BROAD FEATURES OF THE SAMPLING ENVIRONMENT, SEDIMENT DISTRIBUTION AND PETROLOGY

CHAPTER II

GEOLOGY OF THE OOLITE FACIES OF THE SCHOONER CAYS TIDAL BELT

II. 1 INTRODUCTION

Oolite facies such as those that occur repeatedly in the stratigraphic record are accumulating at several sites in the Bahamas; i) on many platform margins of the Great Bahama Bank; ii) along the northern and western margins of the Little Bahama Bank; iii) along the southern and eastern margins of the Cul-de-Sac at the southern end of Tongue of the Ocean [TOTO] iv) around the Berry Islands along the northern margin of Northwestern Channel of TOTO; v) along the western margin of TOTO north of Andros Island; and vi) around the northern rim of Exuma Sound. The overall geology of these deposits has been the subject of a vast literature from the early records of the British nautical surveys of 1836 and 1848; these were followed by the scientific writings of Vaughan (1914, 1918) Thorpe (1936) and Black (1938) among others. More recent publications include: Illing (1954),Newell et al(1960), Purdy(1963 a, b) and Harris (1979).

However, for the purposes of the present study it is necessary to make a few comments regarding the specific sampling site. In addition, features of the oolite which are considered relevant to later discussions on petroleum generation in these deposits are presented.

On the advice of Professor R. N. Ginsburg of the Rosentiel School of Marine and Atmospheric Science, University of Miami (written communication, 1978) the oolitic sand environment on Eleuthera Bank, off Eleuthera Island and known locally as the Schooner Cays tidal bar belt was selected as the area of study and sampling. Situated between 24° 50-56 N and 76° 19-25°W (see fig. 1.1) it is bordered on its southern margin by the deep water embayment of Exuma Sound and bounded to the North by a shelf Lagoon (after the terminology of Purdy, 1963a). Many ancient oolitic host rocks for oil and gas are generally interpreted to have been deposited under circumstances similar to those operating in the formation of present day oolitic tidal bars. For example, the 'reservoirs' of the Arab Zone in the Middle East are thought to have been deposited on a broad shelf as offshore bars of oolite flanked on the northeast by 'deeper' water sediments and on the southwest by lagoonal facies (Steineke et al, 1958; Aramco Staff, 1959; Powers, 1962). This was the predominant reason for selecting this environment as a suitable contemporary system to investigate the problem of the origin of petroleum in carbonate rocks.

II. 2 REGIONAL SETTING

The regional hydrographic setting, a slope-break at the end of an embayment into the platform, is responsible for the formation of the oolitic tidal bars. Four other adjoining surface sedimentary environments have been delineated by Dravis (1979) on the Eleuthera Bank (fig.II.1).

Wind, tide, current and topography are the principal factors which affect water movement and chemistry as well as organic associations. The tidal bar belt is an active physicochemical and biochemical environment characterised by a very high sedimentation rate (Martin and Ginsburg, 1965, p.714; equivalent to 72.6cm per 1000 years). The bank is inundated twice daily by strong tidal currents of up to 0.51 metres per second (approximately 3 knots) generated in Exuma Sound (Ball, 1967).

The shelf break occurs in about 20 metres of water. Variations in the geometry and morphology of recent sand accumulation as typified by the presence of shoal and channel development has resulted in a complex bathymetric pattern in this tidal belt. The bars are covered by about 1 metre of water and some shoal crests are exposed at Mean Low tide; but the channels, which on the average are 5 metres below the surface waters, are almost always under water. A more detailed description of the tidal bar system has been presented by Ball (1967).

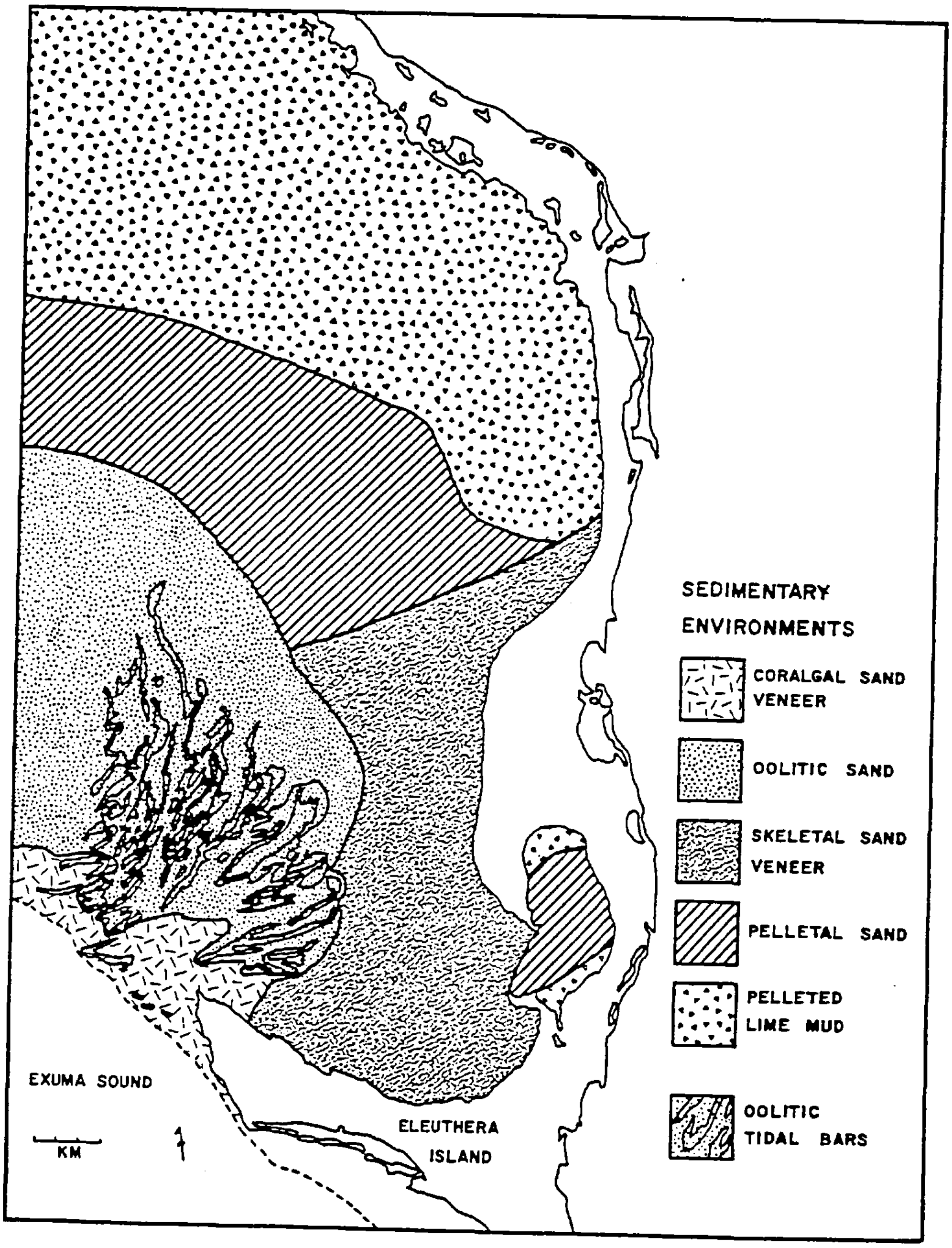


FIG. II.1 HOLCENE SURFACE SEDIMENTARY ENVIRONMENTS ON ELEUTHERA BANK (after J. Dravis, 1979)

II. 3 SEDIMENT DISTRIBUTION AND PETROGRAPHY

Fig. I.2 shows that the oolites occur in fairly equal sized and spaced linear sand bars (5-7 metres wide) oriented obliquely to the shelf break with intervening channels on the floors of which are large subdued sand bodies. Also, large carbonate sand waves occur near to and parallel to the shelf break in about 10 metres of water.

Observations by the writer are in agreement with those of Dravis (1979) who further subdivided the oolite environment into active and stabilised sand zones. Active sand areas which stretch an average of 16 km from the near shelf margin bankwards are marked by intermittent bottom agitation which promotes the most rapid development of thick coated oolitic grains. The stabilised sand zone is a 2 - 4km. wide belt bankward of the active ooid environment and is characterised by a near total lack of agitation and by implication shows almost zero ooid growth.

Uncontaminated ooid accumulation occurs only along the seaward margin of the shoal. Most Holocene oolite sequences actually consist of a mixture of ooids and non skeletal grains like peloids with varying contribution by skeletal grains such as foraminifera and caralline algae. Correspondingly, the ooid deposits range from well sorted to 'fairly'sorted.

The composition of the constituent particles was determined in thin section by point count analysis based on 500 recognisable grains and supplemented by qualitative examination of whole samples using a binocular microscope. This was the method adopted by Purdy (1963a). The mud content, < 63 microns, which varied between < 2 and > 10 wt. per cent, was determined independently by sieving. As a result, five main compositional types [A-E] have been delineated (Table II.1) and serve as a useful means of characterising the sediments collected along the five traverses.

In general, marginal shoal or bar crest sands are by and large clean, polished and well sorted with a small admixture of peloids and skeletal grains. The carbonate mud content is less than

TABLE II.1 CONSTITUENT PARTICLE COMPOSITION+ OF RECENT OOLITIC SANDS FROM THE SCHOONER CAYS TIDAL BAR BELT, BAHAMAS

Constituent Particles	A	B	C	D	E
	Seaward Margin Shoal Sediments	Inner Platform Bar Sediments	Tidal Channel Sediments	Stabilised Sand Flats. Algal Scum Bottom Sediments	Outer Platform Margin. Shelf sediments
Total Non-Skeletal	97.8	92.3	87.4	74.1	46.4
Ooids	93.2	79.9	57.9	39.7	17.1
Aggregates	1.5	3.6	9.8	16.8	19.8
Peloids	3.1	8.7	19.7	17.6	9.5
Total Skeletal	2.2	6.7	12.6	25.9	53.6
<u>Halimeda</u>	0.7	0.8	2.4	3.6	11.7
Foraminifera	0.8	1.4	3.5	7.9	11.3
Mollusc	0.3	1.7	1.9	3.7	13.4
Coral	-	-	-	-	4.5
Coraline Algae	-	-	-	-	2.3
Unknown Skeletal	0.4	2.8	4.7	10.7	10.4
*Mud (wt.%)	1.2	3.7	10.2	13.5	7.6

+ Values are averages of multiple determinations
* Determined independently by sieving (< 63 microns)

2%. The percentage of ooids in the bar sands decreases while other constituents increase away from the margin. The tidal channel ooids are dull in appearance and the sediments have a higher skeletal, peloidal and mud (about 10%) content. The stabilised sand flat, beyond the area of shoal and channel development, have large proportions of skeletal constituents and mud. Where this subenvironment borders the adjacent skeletal sand veneer for example, the total skeletal content exceeds the non skeletal and the percentage of oolite is as low as 14% on the average with another 20% of aggregates and more than 10% mud. Stabilisation is effected by algal 'scum' mats.

Oolitic crust formation as a result of sub-marine cementation is active in this tidal bar belt and has been cited by Dravis (1979) as a modern example of oolitic hardground development. Synsedimentary lithification is discussed more fully in the section on diagenesis.[see Section II.9]

II. 4 AGE

Dating by the University of Miami Radiocarbon Dating Laboratory published by Dravis (1979) has shown that the oolite of this environment are 'juvenile' sediments ranging from 457 ± 76 years to 1516 ± 86 years (see Table II.2)

II. 5 MINERALOGY

Mineralogical identification was by X-ray diffraction analysis of pulverised (< 63 microns) 'whole rock' samples backed up by microchemical staining techniques as described by Friedman (1959). Samples were scanned on a broad X-ray spectrum between 5° and 75° (degrees in 2θ, Copper target tube) to allow for the detection of carbonate minerals and possibly, a broad suite of other minerals; for example, clay minerals as reported by Eardly (1938) and Sandberg

TABLE II.2 Radiocarbon dating* results for Eleuthera Bank oolitic crusts and clasts (after Dravis, 1979)

SAMPLE	SETTING	WATER DEPTH (m)	MATERIAL DATED*	APPARENT AGE (YRS)	DENDROCHRONOLOGY (YRS)
SC-182 (Crust)	Surface - Oolite Shoal Crest	0.43	Cement and extraneous material less than 177 microns	2% greater than modern	-
SC-202 (Crust)	Surface - Oolite Shoal Crest	0.50	Outer 13% of laminae of spherical ooids (500-250 microns)	457 ± 76	443 ± 147
E-29 (Crust)	Surface - Flank of Oolite Shoal	4.90	Outer 14% of laminae of spherical ooids (500-250 microns)	849 ± 79	825 ± 146
E-29 (Crust)	Surface - Flank of Oolite Shoal	4.90	Fragment of *Porites porites furcata* in growth position	919 ± 71	933 ± 143
E-29 (Clast)	Surface - Flank of Oolite Shoal	4.90	Outer 16% of laminae of spherical ooids (500-250 microns)	1516 ± 86	1473 ± 150
SC-89 (Clast)	Surface - Subdued Oolite Sand Wave Parallel to Shelf Margin	5.20	Unaltered *Strombus* sp. Fragment	Less than 173	-
SC-36 (Crust)	Surface - Large Submerged Cemented Sand Ridge	2.50	Unaltered *Strombus* sp. Fragment	600 ± 82	572 ±150

* Radiocarbon dating conducted by the University of Miami Radiocarbon Dating Laboratory.

(1975) in Great Salt Lake ooids. However, only carbonate minerals were found to be present. This was not totally unexpected as the sampling area is marked by almost pure $CaCO_3$ deposits.

All of the Recent subaqueous oolitic sands are nearly pure aragonite with only 1-4% of high magnesian calcite. The latter reflects the extent of admixture of skeletal debris. A similar correlation was also noted by Friedman (1964). Samples from the extreme seaward margin, which are uncontaminated ooid sand, have a mineralogical composition of virtually 100 per cent aragonite.

Sub-aerially exposed uncemented oolites, with evidence of rim leaching, show 5-8 per cent low Mg-calcite content. The mineralogy of the cemented Recent oolite is presented in the discussion on diagenesis later in this Chapter.

II. 6 TRACE ELEMENT ANALYSES

Bearing in mind the objective of the research, some attention was paid to the trace element assemblage present in the oolites. The Inductively Coupled Plasma Detector was used for the determination of Ba, Ti, V, Mn, Fe, Cu, Zn, Al, K and Ag; (see Table II.3a). A special two stage-digestion technique was adopted, which involved initial HCl dissolution - SDDC (Sodium Diethyldithiocarbonate) extraction of unpulverised samples followed by $HF/HNO_3/HClO_4$ digestion of the HCl insoluble fraction. More conventional digestion technique involving the use of crushed samples yielded no useful results, probably due to the masking (interference) effect of Ca (M.Thompson, personal communication, 1979). The two fractions were analysed separately and the results totalled. This approach had the additional advantage of revealing possible trace element associations. For example, Al^{+3} and K^+ showed by far greater concentrations in the insoluble fraction, and this suggests their possible association with some residual clays. However, from a separate HCl dissolution of oolites, the insoluble fraction was judged, from microscopic study, to be dominantly organic matter. The distributions of certain other

TABLE II.3a Selected Trace Element composition of Recent ooids (ppm)

Sample Location	Ba	Ti	V	Mn	Fe	Cu	Zn	Al	K	Ag
El-P-101	3	32	1	10	200	4	4	355	180	Not detected (< 1ppm)
El-Q-208	8	101	3	28	745	6	6	1190	533	
El-R-314	4	53	1	12	274	4	3	501	230	
El-S-407	11	70	3	20	460	4	2	1311	452	
El-T-512	16	188	5	50	1259	1	5	2632	1080	
El-T-525	7	103	3	28	703	1	3	1574	568	

TABLE II.3b Trace Element composition of modern marine ooids (ppm) - from Milliman (1974; p.46)

Sample Location	Sr	Na	Ba	Si	P	Mn	Fe	Cu	S	Al	K	Cr
Great Bahama Bank	8000	2300	N/D	N/D	N/D	80	1290	<50	N/D	N/D	<20	N/D*
"	9000	2400	<65	376	70	3	300	<20	1000	<300	11	N/D
Bimini Lagoon, Bahamas	9600	N/D	9	730	N/D	5	14	N/D	N/D	<100	N/D	<3

* N/D - Not Determined.

trace elements like, V, Mn and Cu, which were expected to be concentrated in the insoluble fraction because of their known association with living organisms, were not definitive enough to indicate any preferred trends. It is suggested that this lack of correlation is related to the HCl solubility of organic matter in Recent sediments (Roberts et al, 1973; Hunt, 1979) which would serve to distort the intrinsic distribution of the trace elements. However, a subsequent qualitative electron microprobe study, revealed the expected preferred concentration of certain trace elements in the organic lamellae of the ooids. In general, however, trace elements in carbonates could either be associated with their contained organic matter or be present as impurities from the precipitating medium. At the time of analysis, the ICP was being used on a trial basis and had limited 'lines'; so that it was not possible to investigate a broader suite of trace elements. This omission has been made up by the compilation in Milliman (1974 p.46) of results of elemental analysis of oolites by various workers (Table II3.b). This is presented alongside the results from the present work. (fig.II.3a).

The role of these various trace elements in petroleum generating reactions in oolites is dealt with in later discussions [Chapters IV and VI].

II. 7 BANK WATERS

Field measurements at each station included temperature, salinity, pH and Eh of surface and interstitial waters.

Appendix II summarises the results; these values were determined in June and should be regarded as a rough approximation for the environment since it is obvious that seasonal variations do occur. Therefore, the discussion that follows is necessarily brief and along very broad lines.

The temperatures averaged about 29.5°C,being slightly higher on the platform proper and lower about the region of the shelf break. This average temperature agrees with summer temperatures reported by other workers on the Bahama Banks (Smith, 1940; Cloud, 1962; Purdy, 1963a; Siebold, 1962) who noted that temperatures of the shallow waters of this bank are strongly dependent on air temperatures. This dependence is not reflected by the slight increase recorded in temperatures of interstitial waters. This may be due to the influence of biochemical heating as reported by Sissler (in Cloud, 1962 p.67).

Salinity varied from about 35.5 p.p.t. near the shelf break to about 38 p.p.t. in the platform proper. There was a general increase in the salinity of interstitial waters. This might have no real significance; it is suggested that such differences may be due to the time lag between the mixing of interstitial and surface waters particularly after rains. Salinity, like temperature,is dependent on seasons and reported salinities elsewhere on the Bahama Banks vary from 32 p.p.t. (Newell et al, 1959) to 43 p.p.t. (Smith, 1940).

The pH shows a slight general decrease from about 8.2 at the shelf break where they reflect more or less the hydrogen ion concentration in the Exuma Sound, to 8.1 about the center of the platform. It falls to 8.0 in the stabilised sand flat. There is a fractional decrease in pH from surface to interstitial waters. Locally, the pore waters of the channel sands show lower pH values, of 7.9. In general, the pH of a sediment is controlled by organic activity (Oppenheimer and Kornicker, 1958; Baas Becking et al, 1960; Oppenheimer, 1960). The pH pattern in this environment broadly accords with this view.

Oxidation - reduction potentials (Eh) of the waters showed high positive values averaging +380 m.volts. Locally, slight differences exist between the Eh values of the pore waters of the shoal sand and that of the channel sediments. Broadly, lowest Eh was found at sites of low pH. Oxidation - reduction potentials are difficult to measure as has been pointed out but even more difficult to interpret. At best, Eh readings are only a rough indication of the oxidising or reducing ability of a sedimentary environment. Oxidation and reduction may or may not involve oxygen in natural systems (Swain, 1970). For example, experiments have indicated that variation in molecular oxygen content in sea water does not have any direct influence on Eh potentials, except at very low oxygen tensions (Baas Becking et al; 1960). Reduction potentials are controlled by organic activity, in particular, microbial action (Zobell, 1946; Oppenheimer, 1960; Baas Becking et al, 1960; Kaplan and Rittenberg, 1963). Apart from the null value of +245 mv (corrected Eh), the other limits of Eh used for characterising an environment are fairly fluid. Swain (1970 p.54) regards a value of +347mv as denoting a weakly oxidising environment. Applying this judgement, the oolite environment of Schooner Cays is described as weakly oxidising.

II. 8 ECOLOGIC COMMUNITIES

Owing to the writer's lack of expertise in this field, no attempt was made at a detailed analysis of entire biotas and ecosystems. Observations on which this discussion is based are therefore of a restricted nature but draws additionally from exploratory ecologic study of the area by Dravis (1979).

Compared with the adjacent sediment areas where platform bottoms are covered by dense growth mainly of Thalassia, the oolitic environment supports a sparse floral cover confined for the most part to the bottoms of broad tidal channels.

However, a variety of encrusting and endolithic organisms considered anomalous to a mobile sand environment are present. Encrusters include serpulid worm tubes, bryozoans, foraminifera (especially _Homotrema rubra_ and _Gypsina_ sp.), coralline algae and Clionid sponges. _Lithophaga_ sp. is a common boring mollusc and several other varieties of microborers also inhabit this environment. Most of the crusts and clasts serve as bases of attachments for several sclerectinian corals, alcyonarians, _Millepora_ sp., sponges and bivalves.

As was noted by Dravis (1969), this anomalous biological community through death and subsequent trituration of their skeletal hard parts, provides an additional source of potential nuclei for the ongoing generation of ooids.

More important from the view point of this research is the existence of algal scum in this environment. The mats are normally composed of intertwining algal filaments coated by their gelatinous sheaths (Sorensen and Conover, 1962). Their role in sediment stability has been noted elsewhere (Section II.2).

The dominant contributing algae are the numerous blue green species (Cyanophyta) which owe their dominance to an ability to tolerate a wide variety of adverse environments. However, they grow in mat communities only in optimum or near optimum conditions for their growth (Fagerstrom, 1967). The inference is obvious of a favourable environment for active biologic life. Associated with the blue-green algae would be diatoms which also deposit their own mucilages, and cysts of flagellates and green algae, bacteria, et cetera (Black, 1933a, p.168).

Except in the shoals where constant agitation retards biocorrosion, there is widespread evidence of microborings by endolithic algae. In addition, petrographic examination reveals the concentration of colonial algae, bacteria and fungi in well layered organic membranes sandwiched by aragonite lamellae. In culture studies carried out at the request of the writer by Dr. Alan Pentecost of the Department of Applied Biology, Chelsea College, two main types of Cyano-bacteria were recognised. The cosmopolitan blue green algae Entophysalis deusta reported by other workers (Newell et al, 1960; Shearman et al, 1970) constituted only 10% of the biomass whereas the vast bulk was made up of Hyella balari (A. Pentecost, written communication, 1979). Various other endolithic, chasmolithic and epilithic organisms have been identified by other workers in similar deposits (Margolis and Rex, 1970; Golubic, et al 1975; Kobluk and Risk, 1977a; Harris, 1977), and point to the intense organic productivity of this type of environment.

In conclusion, the writer would want to note that a variety of the organisms and micro-organisms either identified or inferred to be present in this high energy environment would be considered anomalous if viewed from the standpoint of the traditional beliefs about preferred biologic/environmental associations; this raises doubt about the exactness of such views particularly when applied rigidly. While not denying the basic concept, it is suggested that other associated parameters confer elasticity to generally recognised environmental limits. If, for example, the other requirements like sunlight and nutrients are satisfied, the fact of 'high energy' alone cannot deprive an environment of its biologic communities. At least,it is recognised that agitation would favour regular upwellings of water which serve to boost the supply of nutrient vital to the survival and growth of floating organisms. Perhaps, nothing emphasises the intense biological activity in the present environment more than the phenomenon of crust formation by algal filament calcification (Dravis, 1979).

II. 9 EARLY DIAGENESIS IN OOLITE AND ITS IMPLICATIONS

Diagenetic studies have been made of oolitic sediments, notably by Ginsburg (1957), Friedman (1964), Robinson (1967), and Harris (1977, 1979). These works have provided a useful insight into the sequence of diagenetic changes in Recent and Pleistocene sediments as they affect ultimate reservoir characteristics in ancient oolites. Consequently, this account will concentrate on diagenetic features specific to the present environment of study. Diagenesis was estimated by alteration in sediment texture and mineralogy.

Early diagenetic effects in this environment range from simple boring by endolithic algae to near complete obliteration of primary porosity in dune oolites.

Outside of the mobile sand areas, ooids are actively bored by endolithic algae which disrupt their cortex (Newell et al, 1960; Margolis and Rex, 1971; see fig.III.6). The association of micro borings with micritisation has been documented by Illing (1954), Bathurst (1966), Purdy (1968), Shearman et al (1970) and Golubic et al. (1975) among others. Cementation occurs in vacated micro borings resulting in changes in crystal size, fabric and, rarely, mineralogy of the cortex. Two styles of cementation are apparent :

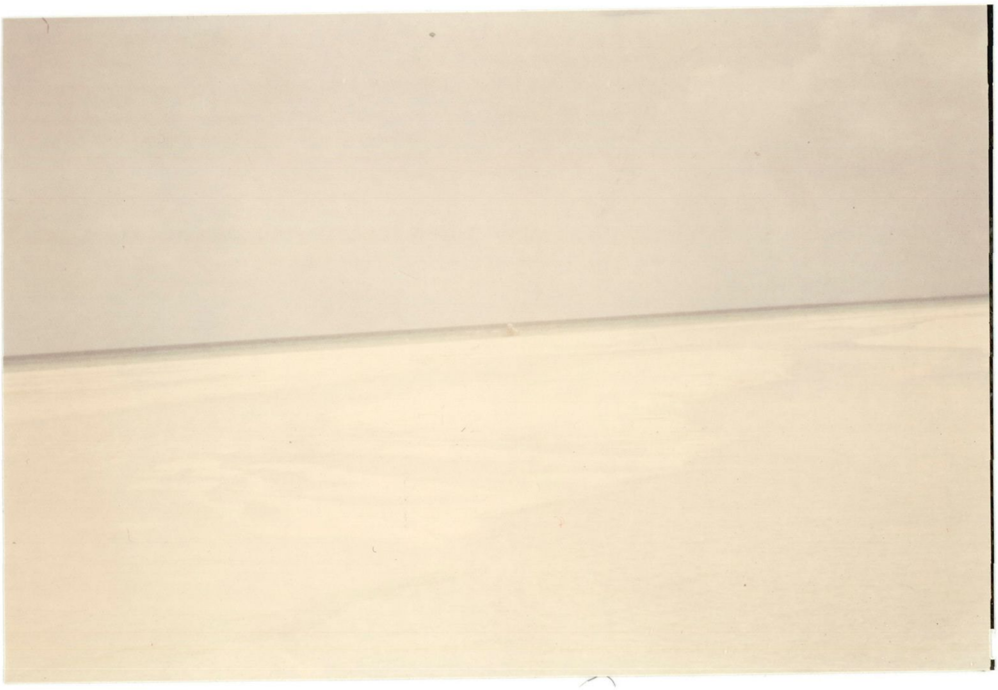


FIG.II.2.0 Oolite shoal near Wood Cay, Eleuthera, Bahamas.

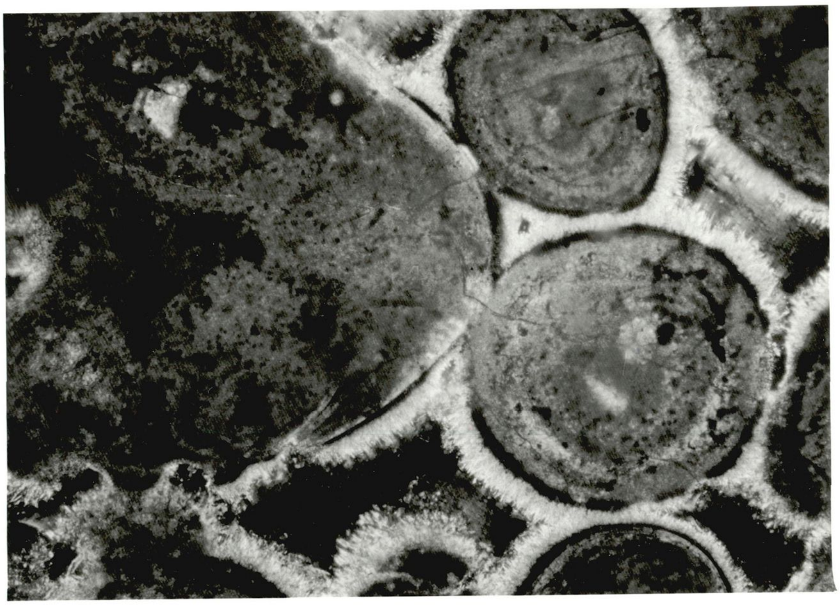


FIG.II.2. Photomicrograph of early diagenetic submarine cementation in Recent oolite.Cement is acicular aragonite. Crossed nicols.
X 75

a) acicular crystals growing toward the center of the boring from its walls and b) acicular crystals radiating outward from the center of the boring (see fig. III.4a). The crystals are larger than those comprising the oriented ooid cortex.

Contemporary sub-marine cementation producing grainstone and packstone crusts and clasts has resulted in widespread generation of surficial oolitic hardgrounds in this area as reported by Ball (1967) and Dravis (1979). The dominant cement is acicular aragonite which occurs as an isopachous rim in a fringe 10 to 30 micron metre thick around each grain (fig.II.2). The well preserved structure of the ooids precludes any suggestion of ooid dissolution as a source of cement; a sea water source is inferred. In addition, Dravis (1979) has reported that other forms of aragonite and high magnesium calcite cement are widespread but subordinate. In particular, he emphasised the contribution of chasmolitic/endolithic algae in binding and cementing ooids by a process of filament calcification.

Almost invariably, widespread cementation occurs in those areas of the intertidal islands peripheral to the sea water margin forming 'rocky' beaches [fig.II.3a]. Sediments in this area are subject to periodic inundation by sea water followed by subaerial exposure. The cement is calcite druse which commonly rims grains in a fringe 10 - 50 micron metre [fig.II.3b]. Ooids show little evidence of alteration either mineralogically or petrographically. The calcite cement is thought to be the result of precipitation through evaporation of films of sea water left adhering to the grains after each retreat of the inundating sea. The calcite cement is reflected in the bulk mineralogy (Calcite, about 16%).

By contrast, the areas of the intertidal islands outside of the beach fronts are made up of uncemented ooid sand. Shallow cores taken to depths of 70cm failed to reveal any evidence of cementation. The sands however, show small scale dissolution commonly in micron metre thick layer around the grain. This lack of cementation is more surprising because the oolite dunes on the windward side of Eleuthera island (fig.II.4a) show evidence of intense and destructive subaerial diagenesis. Here, the ooid grains have undergone varying degrees of alteration, the individual aragonite lamellae having been altered

FIG. II.3a. 'Rocky' beach, Wood Cay, Eleuthera, Bahamas.

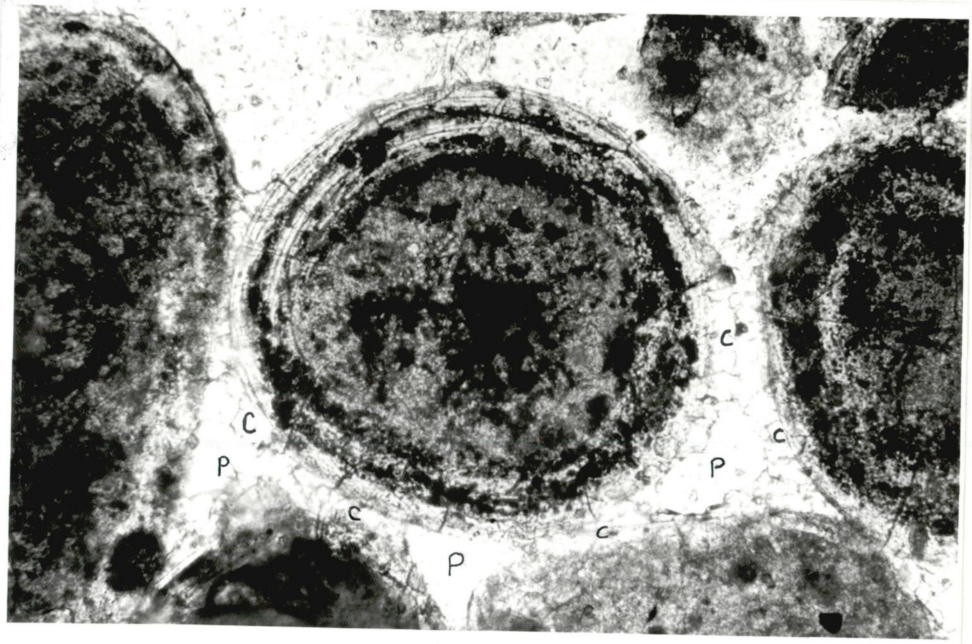


FIG. II.3b. Photomicrograph of early diagenetic cementation in beach oolites. Cement is calcite druse. Plane Polarised light.

X 120

partially or wholly to calcite. A striking feature of these deposits is the near total destruction of primary porosity by blocky calcite cement (fig.II.4b). From the level of alteration of the ooids, the cement is judged to be precipitated from the product of dissolution of parts of the ooids.

The bulk mineralogy of these oolite reflects the inversion of aragonite to calcite under subaerial conditions. Average compositions are 30 - 40% aragonite and 60 - 70% calcite. Any trace of High Mg. calcite would have disappeared.

In his study of diagenesis of oolite, Robinson (1967) measured porosity and permeability values in many Recent and Pleistocene samples. While such knowledge is useful, it is more important to consider the effect of the early diagenetic changes noted in this work on the evolution (with increasing age and depth of burial), of ultimate porosity and permeability patterns in ancient oolite. This approach has been emphasised by Choquette and Pray (1970). Also, Purser (1978) has noted that the basic problem of diagenesis concerns, not the creation of porosity,but rather,its preservation. This is because of the likelihood for the vast bulk of primary porosity to be subsequently destroyed by sparitic cement. For example, measured porosities in Recent unconsolidated oolites range between 35 - 45% (Robinson, 1967; Coogan, 1970). But Cussey and Friedman (1977, fig.4) found that in sections of the Dogger (Middle Jurassic) of France, all of the original pore space has been obliterated; 86% as a result of pressing and squeezing and 14% due to precipitation from the product of dissolution of parts of the rims of the ooid.

It is ,therefore,evident that preservation of porosity is closely dependent on the absence of pressure and creation of pore filling cement. It is in this regard that one appreciates the significance of the examples of early diagenetic lithification encountered in this study. These early cements, while reducing primary porosity establish a rigid grain packing that prevents compaction and consequent pressure solution which leads to the formation of pore destroying cement. In contrast, the uncemented oolites that comprise a large part of each intertidal island would be very susceptible to compaction during burial with resultant pressure

FIG. II.4a. Oolite dune behind Hill Heaven Hotel, Tarpum Bay, Eleuthera, Bahamas.
Note aeolian features.

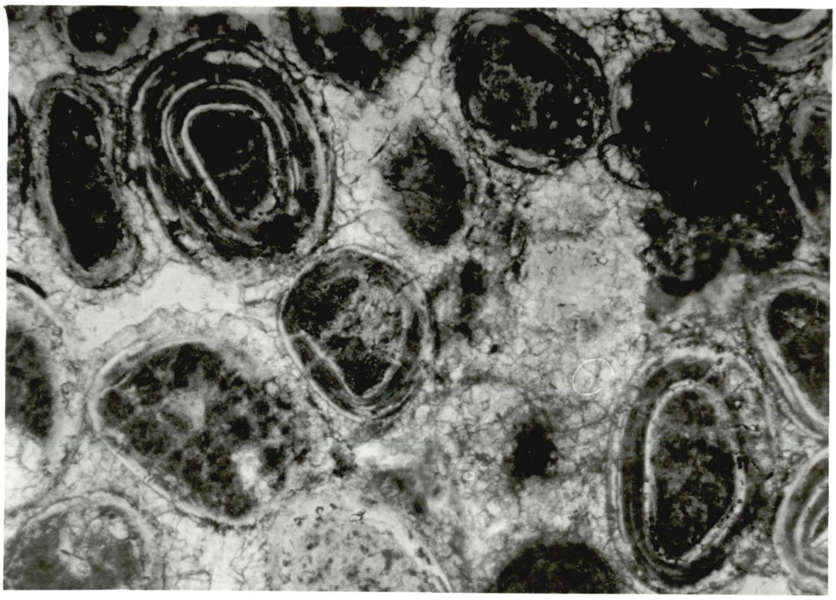


FIG. II.4b. Photomicrograph of subaerial cementation in dune oolites. Cement is blocky calcite. Note near total destruction of porosity. Plane Polarised light

X 100

solution and destruction of porosity.

Purser (1978), from results of studies of early diagenetic fabric within various porous Middle and Upper Jurassic Limestones of the Middle East (Powers, 1962; Dunnington, 1967) and Paris Basin (Purser, 1969, 1975), concluded that early lithification has tended to prevent compaction and the resultant pressure solution.

To buttress his conclusion, Purser (ibid) noted that in most fields where there is a lateral passage from porous to dense limestones, the former has evidence of early diagenetic lithification; on the contrary, the dense limestone lacks any such evidence but, rather, shows a relatively high degree of pressure solution.

As will be demonstrated in a later part of this presentation [Chapter VI] the development of early porosity is also vital to the process of in situ generation and accumulation of petroleum hydrocarbons in oolites.

CHAPTER III

ORIGIN OF OOIDS

> "This stone - - - has a grain altogether admirable, nor have I ever seen or heard of any other stone that has the like."
>
> HOOKE, 1664
> MICROGRAPHY

III. 1 INTRODUCTION

In the introductory chapter, reference was made to the problem of the origin of ooids. Since the controversy is far from being resolved, it is pertinent at this stage to present some views on the subject as they will be relevant to discussions presented later in this thesis.

According to Brown (1914), the first published mention of ooids was by Hooke (1664) who described them in eloquent terms set out in the quotation above. Since then, these somewhat curious deposits have been the subject of a vast but conflicting discussion among geologists. It was, however, the advent of the petroleum industry and the recognition of oolite as host rocks for petroleum which fueled research into their characteristics and origin. While notable progress has been made in elucidating details of their composition and texture, certain mysteries concerning their origin still remain. This rather frustrating state of affairs prompted Cayeux (1935) to declare that 'so large a body of writing should contain so little a body of achievement.' (in French) This view was echoed by Bathurst (1975; p.295) who noted that such contributions were made "by those who had only a passing interest in the origin of these strange little spheroids." Davies et al (1978) called the problem of the origin of ooids 'evergreen'.

The writer's decision to enlist in the campaign to unravel some of the unresolved problems on the origin of ooids was made, almost as an afterthought, while trying to account for the origin of the light hydrocarbons extracted from Recent oolites (see Chapter IV).

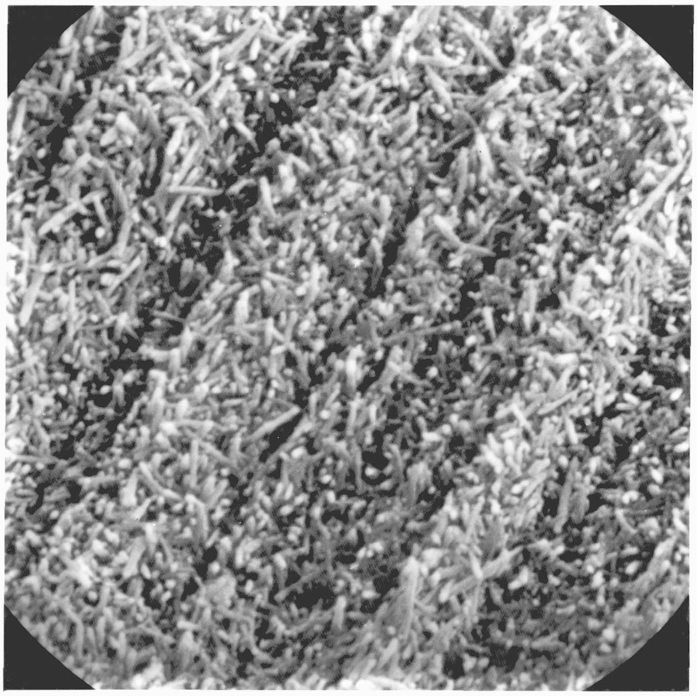


FIG.III.1a Electronmicrograph of the basic structure of an ooid showing alternating lamellae of aragonite needles and organic matter. 1cm = 1 μm

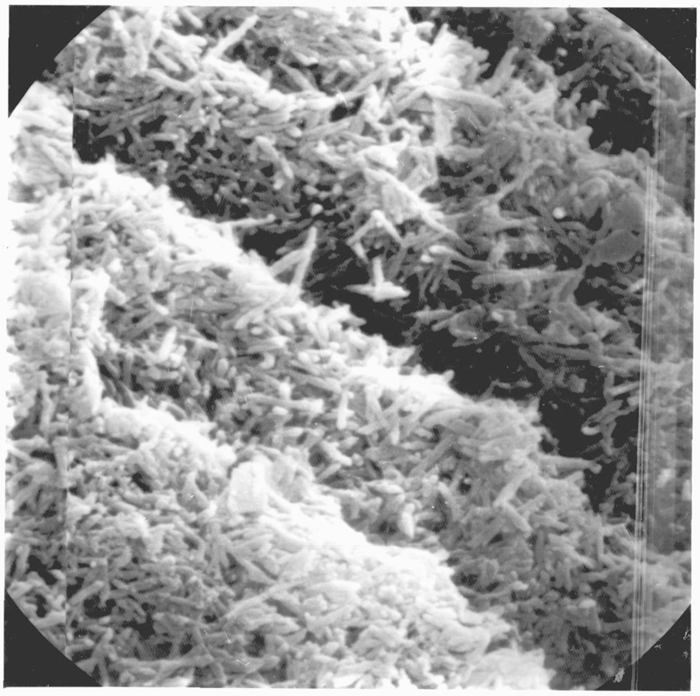


FIG.III.1b Electronmicrograph of the morphology of an ooid showing consecutive aragonite lamellae. 1cm = 1 μm

Briefly stated, the problem of origin of Recent ooids revolves on whether the mechanism of their formation is by mechanical accretion of aragonite crystals which originated elsewhere, or, by direct in situ crystallisation of aragonite. If the accretion, 'snowball', hypothesis of Sorby (1879) is set aside (see Shearman et al, 1970), the other arguments resolve into an organic - inorganic controversy.

The view taken in this paper is the same as that which was advanced by Twenhofoel (1928) and was later supported by Rusnak, (1960), Khale (1974) and Sandberg (1975). It is that ooids can develop under such a considerable range of environments, and in consequence of many different combinations of factors, that it does not seem safe to generalise. It should be stressed, therefore, that the discussion which follows is concerned specifically with marine carbonate oolites of Bahamian type.

III. 2 OOID MORPHOLOGY

Marine ooids are either spheroidal or elipsoidal in shape, the main control being the shape of the nucleus. As measured in thin section, most ooids average 200-500 micron meter in diameter with nuclei of between 100 and 300 micron meter diameter. In the Bahamian ooids the nuclei are commonly peloids, but an assortment of silt to sand sized skeletal and non-skeletal carbonate nuclei also occur. Each nucleus is surrounded by a predominantly multiringed concentric cortex. The cortex is made up of alternating lamellae of carbonate and organic matter, (Shearman, 1970; Mitterer, 1971; Suess & Futterer, 1972; Davies et al, 1978; this work fig. III.1a and b). With the benefit of hindsight afforded by modern very high power electron microscopes, this basic structure of ooids can be deciphered from a lower power photomicrograph.

The carbonate lamellae comprise variable micron thick layers of acicular aragonite crystals, each of which measures 1-3 microns in length and few tenths of a micron in width. It was generally believed from the earlier optical studies of Sorby (1897) and Illing (1954) that the constituent aragonite crystals are tangentially orientated.

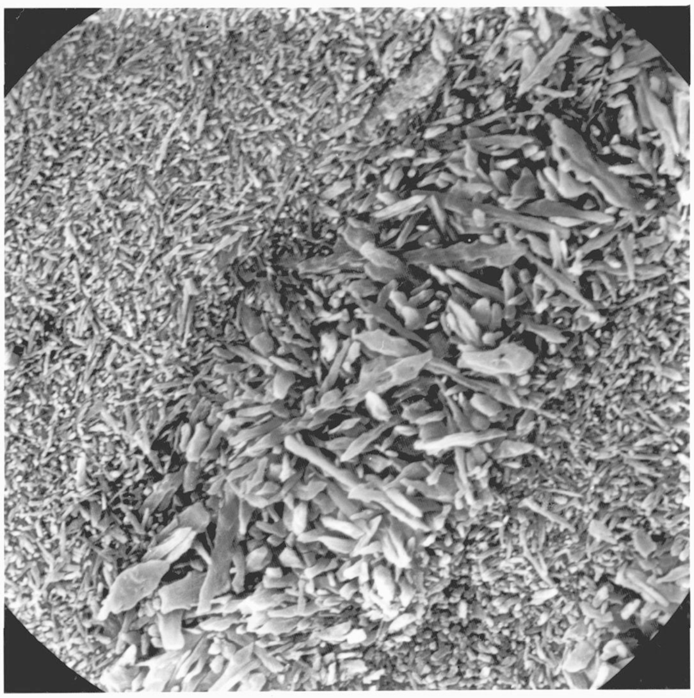


FIG.III.2. Electronmicrograph showing a lamella of randomly disposed aragonite crystals. Note 'platy' habit of crystals compared to the 'needles' of adjacent aragonite lamella. 1cm = 2.27 μm

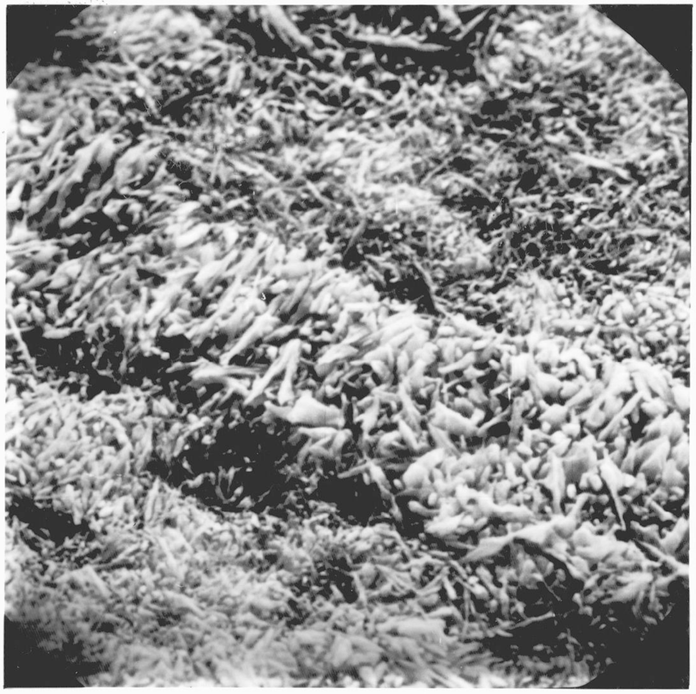


FIG.III.3. Electronmicrograph showing a radially disposed lamella of aragonite needles in contrast to the statistically tangential orientation of needles in adjacent aragonite lamellae. 1cm = 3.125 μm.

However,use of the S.E.M. has revealed that while this might be true for some of the lamellae, the disposition of the needles in others show all gradations from random through tangential to radial (figs. III. 2 and III. 3). This is in consonance with the observations of Fabricus and Klingele (in Suess and Futterer, 1972 p. 135). It has also been noted that although the preferred or dominant habit of the aragonite is as needles, some lamellae are made up entirely of randomly disposed 'platy' crystals (fig.III. 2) similar to those of the aragonite formed by reprecipitation in abandoned algal pits (fig. III 4a and b).

The lamellae of organic matter are well ordered 'membranes' (Ferguson et al, 1978) or mucilaginous material (Newell et al, 1960; Shearman et al, 1970). At various sites on each organic lamella, there are concentrations of dominantly colonial filamentous algae, fungi and bacteria: Newell et al, (1960). These 'dark blebs' are also reported by Purdy (1963b) among others. Earlier, Matthews, (1930) had erroneously interpreted them to be soot particles. The evidence is strong that these organisms were active on the exposed surface of the growing ooid at various stages in its development and they became unwittingly entrapped by the formation of the succeeding carbonate lamellae.

Contrary to general belief, non oriented organic matter is minimal in ooids from active shoal sand environments but could be significant in those ooids taken from the subdued or stabilised sand flats. The view is unanimous that they represent post depositional algal entrants and their role in boring and concomitant micritisation has been emphasised elsewhere [see II.9] by the writer. [see figs III. 4a and III.5].

III. 3 ORIGIN

In accounts of the origin of ooids, a bias has been created in favour of inorganic processes as the specific causative factors. Strengthened by the remarkable and reproducible success attending experiments in oolite formation in which physico-chemical changes in

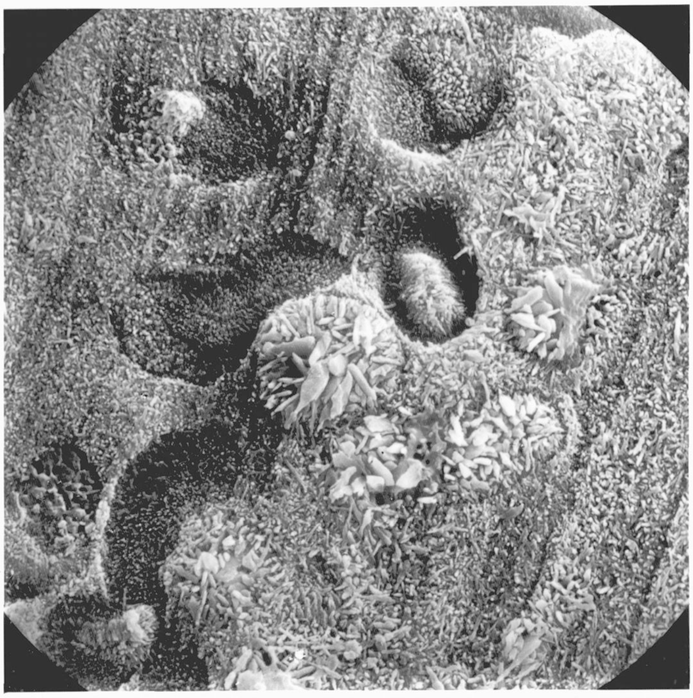


FIG.III.4a. Electron micrograph showing precipitation in abandoned algal bores. 1cm = 3.33 μm

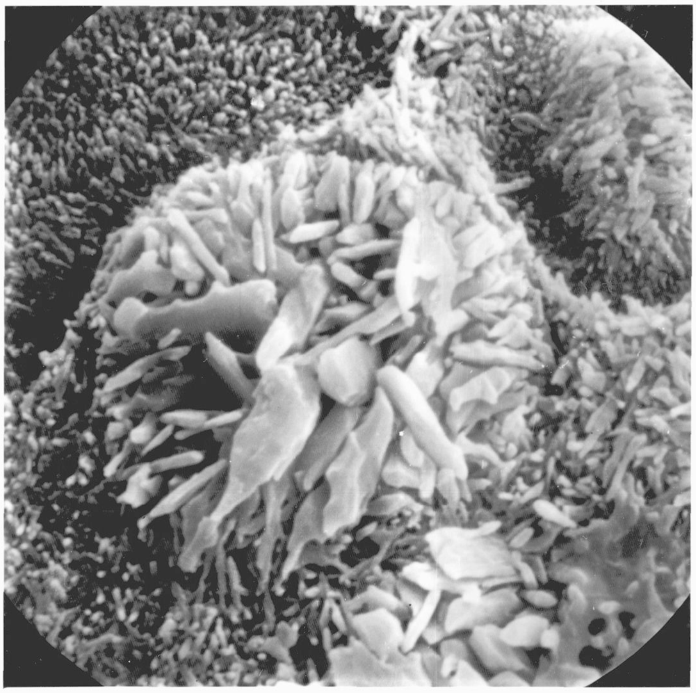


FIG.III.4b. Electron micrograph showing recrystallised aragonite 'plates' in an abandoned algal bore. 1cm =1.06 μm natural and artificial seawater consituted the only methods of treatment (Linck, 1903; Kemp, 1934; Davies et al 1978; and others), the inorganic theory has become too entrenched to permit easy acceptance either of the repeatedly suggested wholesale role of organisms (Rothpletz, 1982; Drew, 1914; Danegard, 1936; Monaghan and Lyte, 1956; Oppenheimer, 1961) or for that matter, the more plausible theory of a contributory role by organic agencies (Shearman et al, 1970; Mitterer, 1971; Suess and Futterer, 1972). In the past (predating the work of Chave, 1965 and Suess, 1968, 1970) the situation was not helped by faulty data and erroneous statements as to the inability of carbonates to adsorb organic matter (Gheman, 1962 p.894) in contradistinction to clays. The general view of the adherents of the inorganic theory has been that organic matter in ooids (when it is admitted to exist) is a passive and accidental component which has no significance in the origin of ooids (Berner, 1971).

Nevertheless,experimental evidence abound to support organic influences in the formation of ooids. Studies of the amino acid content by Mitterer (1968, 1972) and Trichet (1968), the δC 13 data of Deuser and Degens (1969) as well as the revealing Sr^{+2} and F content values in ooids given by Kinsman (1969) and Carpenter (1969) respectively, are suggestive of an origin other than by pure physico-chemical precipitation. After a review of these and other supportive evidence, Milliman (1974, p.50) concluded that 'biochemical processes seem to be important'. Bathurst (1975) in his own assessment of the significance of the above observations, declared that a biologically influenced precipitation of ooids must be considered. Earlier, Black (1933) had urged that both hypotheses are worthy of consideration. In their monumental paper on limits of the natural environment, Baas Becking et al (1960), with reference to similar organic-inorganic controversies, charged workers on such problems " - - - to find a happy mean and to investigate both chemical and biological factors in a given process." (ibid. p.263).

The present account adopts such a concerted approach; it aims to synthesise earlier information and to introduce some fresh

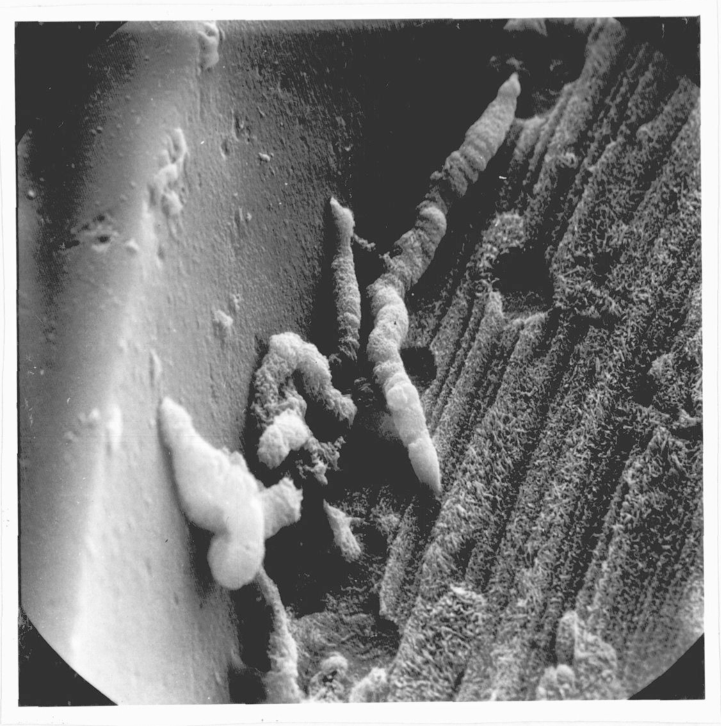


FIG.III.5 Electronmicrograph showing recrystallised algal borings in the peripheral section of an ooid.
1cm = 7.7μm

evidence which will bear on the origin proposed below. An exhaustive review of the different opinions offered is not, however, intended; these have been effectively summarised by Milliman (1974) and Bathurst (1975). The writer will here merely recapitulate those conclusions that are of direct relevance.

III.4 $CaCO_3$ PRECIPITATION

From the various studies on deposition of $CaCO_3$ from sea water, two modes of formation can be defined: a) through organic agencies, and b) through inorganic changes in physico-chemical conditions of the medium. Over shallow water banks which are repeatedly inundated by sea water that is metastable (supersaturated) with respect to $CaCO_3$, the established organic factors are photosynthesis and bacterial decomposition; while the physico-chemical changes result dominantly from variations in temperature and/or extent of agitation. Although any of these factors is in itself competent, under the proper conditions, to cause precipitation of $CaCO_3$ on a large scale, there is nothing materially different in the prerequisite conditions for either mode as to make them mutually exclusive. The probability is that they complement and interact with one another. Indeed, the shoal environments in which oolite deposition occurs are ideal for such 'co-operative' physicochemical and biochemical precipitation (Newell et al, 1960; Sissler: in Cloud, 1962; Dravis 1979).

A detailed account of $CaCO_3$ geochemistry is beyond the scope of this study. It is necessary,however, to recall and comment on the work of Broecker and Takahashi (1966) in the light of new data obtained by the present investigator. The authors tried to obtain material balance information, regarding the $CaCO_3$ precipitation on the Bahama Banks based largely on measurements of the molecular and isotopic composition of the bank waters and precipitates rather than on the physical characteristics of the sediments. Such a quantitative study involving the complex system Co_2 (atmosphere) - sea water -

carbonate sediments had been recognised by Johnston and Williamson (1916) as vital to the resolution of the problem of $CaCO_3$ precipitation.

On the reasoning that any excess CO_2 created by $CaCO_3$ deposition is driven off to the atmosphere and applying material balance calculations, Broecker and Takahashi found that CO_2 escapes from sea water at half the rate at which it is being generated in the water. Convinced of the absence of possible errors in connection with assumptions made in the calculations, they considered the possibility that the remaining CO_2 is permanently fixed by photosynthesis. For this proposal to be valid, the sediments of the Bahama Banks should have an organic carbon content of about 4 per cent. This possibility was dismissed because the organic carbon values of the sediments of the banks, as determined by them, at .27 - .55 wt %, were only about $^1/10$th of those expected. The authors went on to favour an inorganic origin for the sediments of the banks on the basis of a non sequitor argument i.e. that the reaction determined follows a simple second order law. They expressed a reservation on oolites.

However, in 43 Corg. determinations on Recent aragonite muds from the Eleuthera Bank, Bahamas, an average value of about 4 wt.% was recorded (Table III.1). The immediate reaction of the writer, was to try and establish reasons for the great discrepancies in the two sets of results. On examination, it was obvious that the method employed by Broecker and Takahashi for Corg analyses were doomed, as indeed would be all similar determinations, to yield very low and non-representative values.

A 'standard' method for Corg determination involves prior destruction of the carbonate carbon in the sample by acid treatment, discarding the filtrate and directly analysing the washed and dried residue (Trask, 1955; Forsman and Hunt, 1958; Gehman, 1962; Rittenberg et al., 1963; and others). The assumption in discarding the filtrate is that only very minor amounts of organic matter, if any, are solubilised by acid as argued by Guthrie, 1938 and Dancy et al., 1950. But Hunt (1979) has pointed out that this assumption may not be valid for Recent sediments and that considerable error could result if the filtrate is discarded. This is because organic matter in Recent

TABLE III.1 Results of Corg analysis of lime mud from Eleuthera Banks, Bahamas.

SAMPLE NO.	CORG VALUE wt. %
EL-LM-01	4.27
EL-LM-02	3.76
EL-LM-03	3.49
EL-LM-04	4.12
EL-LM-05	4.34
EL-LM-06	4.1
EL-LM-07	3.98
EL-LM-08	3.92
EL-LM-09	4.17
EL-LM-10	3.86
EL-LM-11	3.89
EL-LM-12	4.0
EL-LM-13	4.23
EL-LM-14	4.15
EL-LM-15	5.07
EL-LM-16	4.1
EL-LM-17	4.34
EL-LM-18	3.95
EL-LM-19	4.0
EL-LM-20	4.17
EL-LM-21	4.04
EL-LM-22	4.0
EL-LM-23	3.26
EL-LM-24	3.78
EL-LM-25	4.1
EL-LM-26	4.23
EL-LM-27	3.97
EL-LM-28	4.13
EL-LM-29	4.12
EL-LM-30	4.27
EL-LM-31	4.0
EL-LM-32	3.97
EL-LM-33	3.98
EL-LM-34	4.24
EL-LM-35	2.89
EL-LM-36	4.1
EL-LM-37	4.21
EL-LM-38	4.2
EL-LM-39	3.47
EL-LM-40	3.96
EL-LM-41	4.23
EL-LM-42	5.09
EL-LM-43	4.14

sediments tends to be less complex, less condensed and less tightly bound to the mineral than in rocks. The ease with which some organic substances from Recent sediments can be hydrolysed as against sedimentary rocks has been highlighted by the works of Erdman et al., 1956; Rittenberg et al., 1963; Degens and Reuter, 1964; Hare, 1969. This subject, as it affects modern carbonate sediments, has been critically reviewed by Roberts et al (1973). They found that, depending on the acid strength and length of time of digestion, as much as 44% of the organic carbon in Recent carbonate samples from the Florida Bay is solubilised and lost during the acid treatment. They concluded that previously reported Corg results of analyses in which the acid soluble fraction was discarded should be considered a minimum rather than accurate figures (ibid, p.1159). It is a biochemical cliché that, for example, even the most insoluble proteins are easily dissolved by acid treatment (Haurowitz, 1963, Mitterer, 1972). It is perhaps instructive that Land et al (1979) reported that 67% of the organic matter in Recent oolites from the Baffin Bay, Texas was soluble in 0.1N HCL. Camparative analyses by the writer using 50% HCL and discarding the acid showed a downgrading of results by as much as 71 per cent. In the analyses of Broecker and Takahashi, a greater error was bound to result because an oxidising acid HNO_3 was used for inorganic carbonate dissolution and several washings of the residue with acid and water after discarding the filtrate would have left very little remaining organic matter.

Against the background of the present Corg data, it would appear that photosynthesis could and should indeed account for the excess CO_2 not rationalised by material balance calculations in the experiments of Broecker and Takahasi. Only a few people who have undertaken field studies of the type of environment under discussion can fail to be convinced about the potential and real importance of photosynthetic and allied processes. It is concluded that on a regional scale the prerequisite conditions necessary to $CaCO_3$ precipitation in shallow water, are the co-operative result of both organic and inorganic agencies.

While data from the present work offer new evidence in favour of the above proposal, it must be conceded that the idea is not necessarily original to the writer. Illing (1954) rejected the classification of sediments into 'organic' and 'inorganic' because of the apparent contribution of organic processes in the formation of 'inorganic' deposits. Newell et al (1960, p.493) also underscored such a contribution by noting that "Clearly, however, the physicochemical condition of the water is the result not only of inorganic processes but also of the chemical activities of organisms in the regional as well as the microenvironments." Rusnak (1960) categorically stated the 'obvious' contribution of photosynthesis in bringing about the conditions necessary for the formation of Laguna Madre oolites. The importance of organic processes was alluded to by Cloud (1962 pp.21-22), who observed that at least some of the 'whitings' on the Bahama Banks appear to be increased on local sites of accelerated photoplankton photosynthesis. Wells and Illing (1963) verified this claim from a plankton analysis of the water of the Persian Gulf off Qatar which showed a five to ten fold increase in the diatom population in whitings. They proposed that such blooms, or sudden increases in photoplankton population, with resultant consumption of CO_2 from the water due to photosynthesis, probably provides the mechanism for triggering $CaCO_3$ precipitation. It is noteworthy that the authors added: 'whether the diatoms are the only agents in this trigger mechanism is unknown; it may be that other still smaller and less easily recognised organisms are important.' (ibid.p.434). The significance of this statement will become obvious in a later part of this presentation.

Because of the observed broad chemical similarities in the waters of the Bahama Banks over the oolite and other deposits, the conclusion about the influence of organic contribution is extended to the oolite environment. This has been done despite the $C_{org.}$ values of oolite (1.23 - 4.13 wt.%) which are generally lower than the 4% required by the arguments of Broecker and Takahashi because of the inferred compensating effect of agitation in this environment. It has been stated by other workers (Newell et al, 1960; Dravis, 1979) that the 'sun soaked' and agitated oolite environment is ideal for the combined physiocochemical and biochemical precipitation of $CaCO_3$. Here, the role of organic agencies will not merely be that of contributing on a regional scale to idealic conditions for $CaCO_3$ precipitation but, even more importantly, in localising the process.

The localisation results because it is in the immediate microenvironment surrounding the growing ooid (in suspension) with its concentration of encrusting colonial photosynthetic algae and diatoms together with degrading bacteria and fungi that optimum conditions for precipitation of $CaCO_3$ are achieved. The importance of the immediate microenvironment can hardly be overemphasised with respect to ooid formation. Mitterer (1972, p.1420) underscored this importance by noting that 'in shallow marine sediments, therefore, the microenvironment surrounding a carbonate grain is a complex of inorganic ions and organic molecules interacting to result in isolation of grains or further precipitation, depending on the types of molecules and environmental parameters.' The conclusions of Bathurst (1975, p.305) are similar; that 'there can be no doubt as to the importance of organic processes in modifying locally the chemistry of sea water, especially in microenvironments a few tens or hundreds of microns across - - -'.

This situation reflects the basic tendency for any carbonate particle in the marine environment to be coated by organic matter (Lipman, 1922; Chave, 1965; Shearman and Skipwith, 1965; Meadows and Anderson, 1966, 1968; Suess, 1968). In general, the organic matter which coats grains can be arbitrarily divided into particulate (living and dead) and dissolved organic matter. The dissolved and dead particulate organic matter become attached to grains through demonstrated organo-carbonate associations (Suess, 1970, 1973, Carter and Mitterer, 1978). The living particulate matter (solitary but mostly colonial diatoms and algae) result because of the epilithic habits of these organisms. The algal circumcrusted carbonate grains documented by Wolf (1965) are relevant here. Such organisms in turn provide a vantage substrate and a viable source of nutrient for colonising bacteria and fungi. It is pertinent to recall in this regard, the earlier observations of Lipman (1922). In arguing against the theory of $CaCO_3$ formation by nitrifying bacteria as espoused by Drew (1914), he claimed the absence of nitrifying bacteria and, if so, of nitrification in open sea water but conceded that,'it is remarkable that calcareous sand which is in constant contact with sea water should harbour vigorous nitrifying organisms, whereas the seawater with which it is in equilibrium in the system should not ' (ibid p.502). Lipman expressed difficulty in accounting for this observation but suggested that "small quantities of organic matter covering the sand particles may afford protection for the bacteria.'

Almost invariably, these various organisms in intimate association with the 'passive' organic matter layer coating the carbonate grain, are equipped with mechanisms such as flagellae and other motile extensions of their bodies which serve as floats. In the agitated oolite environment, any silt to sand sized coated grain is a potential nucleus for ooid formation.

III. 5 OOID FORMATION

When a potential nucleus is thrown into suspension by wave or tide action it is kept afloat by the motile parts of the various encrusting organisms which have an interest in maintaining this surface or near surface position. For the photosynthesising algae, light adsorption leading to food manufacture is optimised at this level; also at this level, the activity of the degrading organisms is enhanced. Both of these events disturb the equilibrium probably by changing the pH, Eh, partial pressures, et cetera in the immediate microenvironment around the suspended grain in a medium originally supersaturated with $CaCO_3$; the former (i.e. photosynthetic activity) by diminishing the concentration of HCO_3^-, and the latter (i.e. bacterial decomposition) by increasing the concentration of $CO_3^=$ directly. The net result is the precipitation of $CaCO_3$, immediately peripheral to the layer of organic matter and this would entrap 'as is where is' the organisms whose activities triggered off the precipitation.

Whereas the effect of algal photosynthesis on $CaCO_3$ precipitation is accepted by most workers as is evident from earlier discussion, the efficacy of bacterial decomposition has been in contention since it was formally propounded by Drew (1914). There are those like Cloud (1962) who contest that the principal identifiable bacterial effect is the production of CO_2 and this does not favour $CaCO_3$ precipitation. However, a vast literature exists as to the capacity of bacterial degradation processes to induce $CaCO_3$ precipitation (Kellerman and Smith, 1914; Bavendam, 1932; Lalou, 1957; Oppenheimer, 1961; Berner, 1968; Presley and Kaplan, 1968). More specifically, Purdy (1963) and Berner (1971) have summarised the chemistry of two recognised bacterial processes, ammonia formation and sulphate reduction, in contributing to $CaCO_3$ precipitation. It should be emphasised here, as did Lalou (1957) and Purdy (1963) that the $CaCO_3$ precipitated in this way is not a bacterial physiological product as implied in the lime secretion theory of Rothpletz (1892) but rather, is a bacterially induced chemical precipitate.

Once initiated, precipitation of aragonite needles continues around the organisms and the organic matter which afford vast nucleation sites. Also the new crystals exert a strong influence on the system by offering additional sites for preferred nucleation (Deelman, 1978). Initially, the needles are held together by molecular forces so strong that no other 'cementing' agent is needed (Deelman, 1978). Any orientation adopted by the needles will be such as to maximise these molecular forces against the physical dynamic forces prevalent in the medium at the time of their formation. This may explain the varied orientation of the aragonite crystals in the carbonate lamellae noted by Rusnak (1960); Fabricus and Klingele (in Suess, 1972) ; and the present author (figs. III.1, III.2 and III.3). Along a related line of reasoning, Davies et al (1978) have suggested the effectiveness of turbulence (agitation) in inducing strong grain to grain contact.

Precipitation of lamella of aragonite needles ceases when the water in the microenvironment returns to equilibrium with the surrounding water. From the results of their ingenous experimental work, Davies et al (1978) proposed Mg++ and possibly H^+ poisoning of the carbonate surface, to account for the cessation of each phase of carbonate precipitation. Their account, of course, assumed a passive role for the preceding lamella of organic matter, namely, that of providing preferred sites for nucleation of $CaCO_3$. Even so, the present writer has reservations about this proposal especially in the light of the admission by Davies et al that the Mg++ concentration in their experimental medium far exceeded that in natural environments. Although it is debatable, the effect of Mg++, the writer believes, is in favouring the precipitation of aragonite rather than calcite (Leitmeier, 1910, 1915; Monaghan and Lytle, 1956; Lippman, 1973; Folk, 1974).

Following the formation of the carbonate lamella, the growing ooid, having acquired an 'extra' weight and lost the stabilising effect afforded it by the flagellae and other motile parts of hitherto exposed encrusting micro organisms when it was thrown into suspension, will sink to the bottom; with time, organic material permeates and infills the intercrystal spaces. This explains the 'continuous' organic 'matrix' which is left behind if an ooid in thin section is carefully dissolved in dilute acid and stained with organic dye (Shearman et al, 1970). Subsequently, a layer of organic matter including encrusting micro-organisms forms on the carbonate lamella and if thrown into suspension at this stage, the sequence of events outlined above is repeated. This re-enactment is largely a chance event depending on the likelihood of the developing ooid to be resuspended, because suspension of the ooid is the state that affords opportunity for further growth.

Resuspension depends on one or a combination of the following factors :

a) the burial place of the developing ooid as it sinks after the formation of a carbonate lamella i.e. whether in the shoal or channel, above or below the oolite sand body; this would be related to the hydrodynamic factors in operation at the time of sinking.

b) the weight of the developing ooid relative to the ability of the turbulence of the medium to resuspend it. Is it any wonder that the ooids with very large nuclei generally have fewer oolitic coatings ?

Thus the growth of an ooid could be prematurely aborted or alternatively proceed to 'maturity'; this results in differences in both the extent of development of the cortex as well as the ultimate size of the grain. This is why the distinction by Illing (1954) between real and superficial ooids is unnecessary since the underlying differences are not genetic. Similarly, the attempt by some workers (Matthews, 1930; Deelman, 1978) to interpret the multiringed cortex of ooids in terms of cyclic changes in seawater is incorrect.

When the ooid is no longer able to jump into suspension, rolling and sliding results in the mobile sand areas giving the ooid its polished appearance; in the subdued or stabilised sand areas, the ooid will be subject to boring and consequent micritisation resulting in a mat appearance.

III. 6 SUMMARY OF SCHEME OF OOID FORMATION AND CONCLUSION

If ooid formation is viewed as a sequential event which the writer believes it is, it would be summarised as follows:

a) First a nucleus becomes available on the platform bottom. This could be a relict grain or one of an assortment of silt to sand sized, generally but not necessarily, skeletal and nonskeletal carbonate particle.

b) The nucleus becomes coated with organic matter (both dissolved and particulate) through organo-carbonate reactions. In addition, and 'operationally' more significant, are the various encrusting photosynthetic algae and various degrading bacteria. A lamella of organic matter is formed.

c) The coated nucleus is thrown into suspension by tidal or wave action and is kept afloat at or near the water surface by the motile parts of the organisms; the life activities of these organisms disturb the fragile equilibrium in the immediate micro environment surrounding the grain in a medium already supersaturated with respect to $CaCO_3$. The microenvironment serves as a reaction center for the precipitation of $CaCO_3$, with first, the organic matter layer and then, the newly formed crystals offering vantage nucleation sites. Crystallisation around the grain continues until it is no longer able to attract Ca^{++} and CO_3^{--} ions towards itself i.e., when equilibrium is achieved between the microenvironment and the wider water medium. A carbonate lamella is formed.

d) The developing ooid, having acquired extra weight and lost the buoyancy effects afforded it by the motile parts of encrusting organisms, sinks to the bottom. There, organic matter infills the intercrystal spaces and additionally coats the surface of the aragonite lamella. Meanwhile, encrusting micro-organisms latch on at several sites.

e) Depending on its temporary burial place and/or its weight relative to the intensity of the medium turbulence, the developing ooid may be resuspended for sequences (c) and (d) to be re-enacted or, alternatively, its growth may be prematurely aborted.

f) When the ooid ceases growing for any reason, it is subjected to rolling and sliding in the mobile areas resulting in its polished appearance; if, on the other hand, it ends up in a subdued or stabilised sand area, it acquires a dull appearance due to algal boring, and consequent micritisation.

The above scheme of ooid formation is in consonance with almost all observed morphological features of an ooid. To recapitulate, these are :

a) distinct concentric and alternating lamellae of aragonite needles and organic matter b) the concentration of several colonial algae, bacteria and fungi at about the same level in the organic lamellae c) the seemingly pervading nature of the organic matter upon careful decalcification of the ooid. d) the differences in the extent of development of the ooid cortex both in terms of ultimate size of the ooid and the size of the starting nucleus.

From experimental observations, Davies et al (1978) stated that only about 2% of the life of the developing ooid is spent growing in suspension phase while 95% of the life is spent accreting organic membranes in the subsurface. This corroborates the earlier figures of 5% and 95% respectively estimated by Bathurst (1967b) from field observations in the Brown Cay oolite shoal in the Bahamas. The scheme presented above by the present writer could accordingly be compressed into two stage sequences : (1) A quiet phase (resting and sleeping phases of Davies et al) during which organic matter coats the nucleus or growing ooid;and algae, bacteria and other micro-organisms encrust it - an organic matter lamella is formed; (2) a suspension phase (agitation phase of Davies et al) when the life activities of the micro-organisms disturb the equilibrium of the medium in the micro-environment surrounding the growing ooid resulting in the precipitation of aragonite lamella.

This compressed scheme is largely in line with the reasoning of Milliman (1974, p.49) that 'each (carbonate) lamination may represent one exposure to the precipitating medium, followed by subsequent burial during which algae can aggregate around the ooids surface.'

Repetition of the two stage sequences proposed above is largely a chance event but which generally occurs resulting in a dominantly multiringed cortex of alternating lamellae of concentric aragonite and organic matter.

In conclusion, it should be stated that any account of the origin of ooids should explain its observed morphological features and chemical properties. The contribution of organic agencies highlighted in this presentation is not proposed in opposition to the established physico-chemical influences on $CaCO_3$ precipitation but rather as a complement to them. There is little reason to preclude the formation, under optimum conditions (such as exist in many an experimental precipitating medium), of $CaCO_3$ by strictly inorganic processes but there is also little doubt that,in the less favourable natural environment,the optimum conditions are achieved through a combination of physicochemical and biochemical agencies. The theory of ooid formation which is proposed is in harmony with all the known facts and assumes the regional as well as the micro-environmental significance of biochemical processes in inducing $CaCO_3$ precipitation. It is advocated that such a co-operative view be adopted rather than the present tendency to pigeonhole workers on the problem into 'inorganic' or 'organic' theory adherents. The role of biochemical agencies may be only in changing the physico-chemical conditions such as pH, Eh, partial pressures, et cetera, of the medium to those that favour $CaCO_3$ precipitation as emphasised by Lalou (1957) in his bacterial theory and Newell et al (1960) in their physiocochemical theory of ooid formation but this does not detract from the fact that such contribution is a sine qua non in the formation of marine ooids.

PART 2

ORGANIC GEOCHEMICAL EXPERIMENTS AND RESULTS

CHAPTER IV

OCCURRENCE AND ORIGIN OF LIGHT HYDROCARBONS IN RECENT OOLITES

'Only in our time have we succeeded in discovering, amidst the intricacies of Nature, those routine phenomena long believed unimportant but which in effect bring about the tremendous phenomenon of the origin of oil'.

Vernadskiy, 1924
In La Geochemie

IV. 1 INTRODUCTION

Shortly after the publication of the monumental work of Smith (1952, 1954) who isolated and dated syngenetic hydrocarbons in Recent sediments, it became clear that the problem of the origin of petroleum was far from resolved. This point was highlighted by Sokolov (1959) who stated that the extracts of Smith and follow up investigators(e.g. Stevens et al, 1956) could not be regarded as petroleum since the C_2 - C_{14} hydrocarbons which make up about 50% of many crude oils were not reported. This objection was buttressed by similar observations made by Dunton and Hunt (1962), Erdman, (1962) and others. Meanwhile, the opposing data of Emery and Hoggan (1958) and Veber and Turkeltaub (1958) who had detected measurable C_2+ hydrocarbons in Recent sediments received little more than cursory mention in geological literature. More recent confirmation of light hydrocarbon occurrence in Recent sediments has come from the data of Veber et al (1977), Rumeau and Sourisse (1972), Hunt (1974, 1975, 1978), McIver (1974, 1975), Bernard et al (1978), Whelan (1979); Hunt and Whelan (1979); Kvenvolden et al,(1980) among others. Veber and Maximov (1976) have attributed the failure of some workers to find light hydrocarbons heavier than methane in Recent sediments, to faulty extraction procedure and/or low sensitivity of detectors. The authors added: 'any concentrations of heavy(C_2+) hydrocarbons is not so important as the fact that they are generated regularly during the initial stage of transformation of organic matter.' (ibid p.289).

Although the problem remains controversial, a lot more knowledge has been accumulated and systematised in recent years. The state of this knowledge, particularly as it relates to the present investigations has been summarised in the section on 'Theoretical Framework' [see Section I.3] and there is little merit in repeating the details here.

The light hydrocarbons (also called low molecular weight hydrocarbons) and in particular their saturated members, form a characteristic and important portion of petroleum; again, there is evidence that light hydrocarbons in source beds undergo more pronounced changes with increasing depth of burial (and exposure to higher temperatures) both with respect to yield and composition than higher molecular weight (C_{15}+) hydrocarbons, (Rogers and Koons, 1971; Tissot et al, 1971, Le Tran.1975; Hunt, 1975; Philippi, 1975). These hydrocarbons therefore afford a unique opportunity for a study of the processes of petroleum generation. The upper Carbon number for these hydrocarbons vary according to authors and purpose of investigations but generally include compounds up through and including 10 Carbon atoms.

Due to limitations of the analytical method, that is, the absence in the analytical set up of a mass spectrometer that would have been necessary to distinguish the various isomers of C_5+ hydrocarbons, the light hydrocarbons were defined in this study as C_1 - C_5+ but are understood, particularly in interpretative terms, to include gas and gasoline range hydrocarbons.

IV. 2 GAS EXTRACTION : PREVIOUS TECHNIQUES

There are several methods of recovering light hydrocarbons from rocks and sediments prior to gas chromatographic analysis. Most of these are adaptations of original techniques developed for geochemical prospecting for petroleum. Broadly, the methods resolve into : a) degassing with the aid of elevated temperatures; b) degassing with the aid of vacuum; c) degassing by mechanical or chemical comminution of the rock. These methods can be used alone but are more usually applied in various combinations.

Perhaps the simplest investigative technique involves the analysis of gas that accumulates in the head space of canned cores and has been extensively used in organic geochemical investigations of DSDP samples (McIver, 1971, 1973, 1974; Claypool et al, 1971, 1974; Hunt and Whelan, 1978). Almost identical is the technique of Hachenberg et al (1977) based on the analysis of head space gas which accumulates at room temperature in the sample container. Bayliss (in Hunt, 1973, 1974, 1975) improved the yield of light hydrocarbons in the head space by heating the sample contained in a high speed blender in a water bath at 100°C. Different variations of this technique have found popular use (Snowdon and McCrossan,1973; and others) particularly for investigating Recent sediments.

The principle of degassing by disaggregation of the sample under vacuum, with or without the aid of heat, has led to the construction and use of vacuum motors and vacuum ball mills (Nenadkevich, 1917; Elinson, 1949; Veber et al, 1977; Durand and Espatalie, 1971; Le Tran, 1975; Veber and Maximov, 1976). These devices are invaluable for studying the gas content of cores taken from limestones, dolomites, marls, sandstones et cetera. In a related extraction method utilising the combination effects of heating and grinding, light hydrocarbons are continuously extracted from the sample and collected in a cold trap through the flushing action of an auxilliary gas (Philippi, 1975).

Desorption of rock or sediment is oftentimes accomplished by dissolving it in appropriate acids, either with the aid of heat as in the method of Geoservices (1969); Horvitz (1972); Ferguson (1975) or at room temperature (Thompson et al, 1966). In fact, complete light hydrocarbon extraction is thought possible in some cases only if the calcareous support is disaggregated with acids. The thermovaporisation method of Jonathan et al (1975) is akin to the 'Thermobitumen Survey' method developed in 1951 by V.A. Lobov (in Kartsev et al, 1958) and has special appeal for extracting light hydrocarbons in the C_6+ range.

In the techniques outlined above, the light hydrocarbons are trapped differently and subsequently analysed by gas chromatography. Over the last few years, however, the emphasis in newly developed techniqueshas been to combine the recovery of light hydrocarbons and their gas chromatographic analysis into a single step procedure. In one such method known as hydrogen stripping (Shaefer et al, 1978a, b; Leythauseur et al, 1979) hydrogen functions both as an elution gas stripping the light hydrocarbons from the sample and as carrier gas for the gas chromatographic column; thus any ill effects of fractionation according to molecular type during extraction and transfer procedures are minimised.

The above review of techniques for the investigation of light hydrocarbons in samples, far from being exhaustive, has dealt only with those techniques that have found wide application in one form or another. It would be tedious, if not unnecessary, to review the merits and demerits of each method. It would suffice to discuss them on the basis of the 3 broad divisions outlined at the beginning of this discussion.

Thermally induced desorption techniques are fairly efficient and almost contamination free particularly when effected in a vacuum. There is, however, the risk of overheating which leads to the formation of new gases not previously present in the sample. Therefore, it is widely accepted that heating the sample above 100°C is undesirable but this upper temperature limit is largely arbitrary and it is oftentimes necessary to raise the temperature in order to achieve a more complete desorption, particularly in cases where the gas is known or thought to be adsorbed tightly to mineral and organic matter in the rock.

Apparatus which works only with the aid of a vacuum does not give reliable results in quantitative studies, since it is virtually impossible to attain complete degas$ification and even at that, excessively long time is required for this method. Consequently, vacuum technique is hardly applied alone but has proved effective and reliable in combination with thermal or proven disaggregation procedure.

Rock disaggregation, whether mechanical or chemical, though apparently useful in increasing the amounts of light hydrocarbons evolved, are problem prone. Mechanical pulverisation in mills and motors of steel have been found to produce methane which vitiates the results. This problem can be obviated by the use of brass mills as in the method of Philippi (1975). In addition, this method is a little restrictive since it is not recommended for clays (Kartsev et al 1958).

The short comings of chemical (acid) disintegration of samples are threefold. Perhaps, the least of these is the problem associated with contamination which could be eliminated by careful handling. Secondly, there is a risk, as in thermal methods, of forming reaction products. This was demonstrated by Abell et al (1971) who used deuterated acids (DCl + DF) in extracting gas from Apollo 11 Lunar fines and noted that the Light hydrocarbons detected were mixtures of undeuterated and fully deuterated compounds. Flory et al (1972 p.2096) from the results of their own work on Apollo 12 fines reported that 'it is evident that the major portion (70% or more) of the light hydrocarbons observed result from the acid treatment in agreement with the range of CD_4/CH_4 value reported by others'. Notice of a more extreme influence of acid on light hydrocarbon analysis has come from the work of Neglia et al (1964,p.294) who disclosed that the methane extracted from carbonates by acid attack is on average, more than a thousand times greater than that extracted by gentle heating at 40°C for 2 - 3 hours. The writer thinks, however, that if higher temperatures had been applied, the disparity in results would have been less bizarre.

The third problem related to the use of acids in light hydrocarbon extraction is the known disposition of any unsaturated hydrocarbons in the sample to react with the acid; this would prejudice the composition of the extracted hydrocarbons in favour of the saturated components which could lead to wrong deductions being made.

IV. 3 PRESENT EXTRACTION TECHNIQUE

Since no work had been done before on light hydrocarbon analysis at Imperial College, London, it was necessary, as a first step, for the writer to design and construct an apparatus for the present study. The emphasis was to evolve a desorption method that would be common to the investigation of both ancient and recent sediments.

Considering that the object of investigation was carbonates, acid extraction which theoretically represent the most effective desorption technique and which had been used in related experiments (Thompson,etal 1966; Ferguson, 1975) was attractive but, however, ruled out for reasons already discussed. The idea of substituting EDTA, a milder acid which is preferred for etching carbonates and for other related purposes was considered but was also abandoned because its side effects havenot been properly documented.

An alternative choice was the method of Philippi (1975) whose investigation involved both ancient and recent sediments. In this method, the sample was first ground in a brass mill which was then placed in an oven at 130°C and flushed with pure helium for 2 hours and the effluent collected in a cold nitrogen trap. A custom built apparatus modified after Philippi's set up proved operationally inconvenient but above all yielded inferior results when compared to the method finally adopted - heat desorption into a head space.

This method consists of heating approximately 20gms of sample in a sealed 50cm^3 glass tube at 140°C for 60 minutes. In test measurements using a thermocouple, the effective temperature inside the test tube was about 132°C. Any hydrocarbons are desorbed into the head space containing air. The tube is left to stand for about 30 minutes at room temperature to allow the air-hydrocarbon mixture to equilibriate and the water vapour to condense. The gas is then sampled with a hypodermic syringe through a silicone rubber seal for gas chromatographic analysis.

The choice of desorption temperature was determined from trial experiments. The effect of temperature on the composition of evolved gases was checked by heating duplicate samples of lime mud in an oven at 140^{o}C and in a water bath at 100^{o}C over the same period of time. Subsequent analysis of gas samples from each set of experiments showed no discernible differences both in concentrations and composition.

Desorption for 60 minutes actually amounts to an 'overkill'; the yields of hydrocarbons in ancient and recent sediments peaked at 52 and 43 minutes respectively and remained constant till final time. Experience showed that after 60 minutes, the yields decreased probably due to the effect of leaks around the edges of the seal.

For the ancient samples, crushing was necessary to aid desorption. Trial experiments proved that crushing to about 2mm size fraction offered the best compromise between suspected light hydrocarbon losses during the crushing process and the increased efficiency afforded by smaller grain sizes. In the case of recent sediments, the samples were taken directly out of hermetically sealed containers that had been stored in a deep freezer prior to analysis.

The main virtue of this method is its simplicity; but this attribute ironically has its concomitant problems. Perhaps the most obvious is the desorption efficiency calculated to be about 45% for the ancient sediments and 65% for Recent samples. The calculations for efficiency were performed according to the method of Kartsev et al (1958) as follows : after the first sampling and analysis of the desorbed gas, the sediment sample was cooled in the open air, sealed again and degassed. This process was then repeated and all gas samples were analysed separately. Only 2 re-heats were deemed necessary here because by a third reheat, the gas concentrations, particularly in the recent sediments, were so low as to approach zero reading of the apparatus. The total amounts of hydrocarbons in the 3 desorptions carried out for each sample were taken to be 100% and the initial gas concentration was calculated as a percentage of the total. In Philippi's technique, efficiency was improved by pregrinding the sample and continuously mobilising hydrocarbons produced during the heating by the flushing action of Hydrogen. Bayliss (in Hunt, 1973, 1974, 1975) improved his head space yield by pulverising the sample in a blender prior to heating. But after the failure of earlier complex experimental set ups, it was preferred to keep the apparatus simple.

The next problem was that of contamination. Because the head space in the tube contained air, it would not be possible to investigate other gases like N_2, O_2, CO_2 which are also present in the atmosphere. Happily, such gases were not part of the objective; besides, the fact that the FID (Flame Ionisation Detector) is insensitive to these gases reduced any risk of their adversely affecting the results of hydrocarbon analysis. As for the hydrocarbons, only traces of methane were found in the analysis of laboratory air. A related problem was the possibility of oxidation of desorbed hydrocarbons by the oxygen contained in the air in the head space. This was tested by loading the samples in an atmosphere of nitrogen. The difference in hydrocarbon concentrations was far less than an order of magnitude (ng gas/g sediment).

The effect of leaks around the edges of the seal due to pressure build up inside the tube was a potential source of loss of hydrocarbons that could not be effectively quantified. The dilution effect of air on the hydrocarbons is inevitable with the present technique. No attempts were made to pre-concentrate the gas prior to analysis as in the methods of Hunt (1974) and Whelan (1979). Blank tests with the extraction apparatus showedan almost complete absence of contamination.

IV. 4 GAS ANALYSIS

Light hydrocarbon analysis was carried out on a dual channel Perkin Elmer F.30 Gas chromatograph fitted with a 6' x ⅛" o.d. SS column packed with 80/100 mesh porapak Q and operating isothermally at 130°C. Sample introduction into the gas chromatograph was via a heated precision gas sampling valve with a 2ml volume loop. A column splitter was in use; so effectively only 1ml of gas sample was analysed each time. The carrier gas was N_2 adjusted to a flow of $50cm^3/min$. Air and H_2 flows were pressure controlled at 18lb/sq.in. and 20lb/sq.in. respectively. These conditions allowed the separation of methane, ethene/ethane, propene, propane, isobutane, butene, and n-butane in order of increasing retention times.

Detection was by an FID linked to a wide range amplifier in the external mode. The advantages of the flame ionisation detectors over thermal conductivity detectors have been summarised by Snowdon and McCrossan (1973) and in various gas chromatography handbooks. To recapitulate, these are : a) higher sensitivity for hydrocarbon gases; b) zero response to fixed gases (N_2, O_2, H_2S,CO_2 and water vapour); c) no oxidative destruction of the detector due to air in the samples; and d) wider linear range to cover the possible variations (low and high values of extractable gas). Because the instrument was equipped with a backflush facility, it was possible to switch the C_5+ compounds back to the front of the column to be detected as a single backflush peak.

The FID response for the various compounds was measured via peak areas with a model PE M-2 electronic integrator and their ppb values computed against known standards (manufactured by EDT Research Limited). Each analysis was completed within 14 minutes. Whelan (1979) had used two chromatographs; one for C_1 and the other for C_2 - C_5 analyses claiming that it was not possible to analyse both C_1 and C_2-C_5 hydrocarbons on the same gas sample in a reasonable time because of the appearance of small C_2 - C_5 peaks on the tail of the much larger C_1 peak. No such difficulty was experienced in the present work. The writer would attribute Whelan's problem to the intrinsically low C_2+ hydrocarbons in her samples.

One apparent problem in the present analyses was posed by the inability of the analytical system to discriminate ethene from ethane. Attempts to solve this problem by combining temperature programming with slower carrier gas flow were unfruitful. One possibility is that something in the intrinsic nature of carbonates precludes the formation of ethene. In this respect, it is noteworthy that Thompson et al (1966) found traces of ethene only in some recent carbonate shells. This line of reasoning is not, however, supported by the presence of other alkenes. On the basis of retention time, the C_2 component is listed as ethane but must be understood as probably including minor amounts of ethene.

Despite this problem, the general resolution of the instrument was good. The absolute sensitivity of the system is 1×10^{-11} gg^{-1}; the conditions used here achieved a 1×10^{-9} gg^{-1} sensitivity which was very acceptable for the purpose of this investigation. At this level of detection, the overall accuracy and reproducibility of the method was within 5% for methane and 15% for C_2+ hydrocarbons.

IV. 5 RESULTS AND DISCUSSIONS

The results of C_1 - C_5+ occurrence and distribution in Recent oolites are presented in Appendix III. Since the desorption efficiency was calculated as 65% and considering other within and between effects, that could not be adequately quantified, it must be stressed that the values reported are considered semi-quantitative and should perhaps be multiplied by a factor of 2 when compared to the results of similar investigations. Even then, it must be noted that no two results are comparable except when they have been obtained by the same method. Sokolov et al (1972) have noted that results such as these have the accidental character relative to analytical equipment, of sample taking, et cetera. This point can be better emphasised by noting the differences between the yield and composition of C_1 - C_3 hydrocarbons of Recent oolites obtained by Ferguson (1975) (see Table 1.3) and those from the present investigation (Appendix III). Total C_1 - C_4 saturated hydrocarbon yields of Recent oolites vary between 244 and 1384 ng/g dry sediment or 1.7×10^{-5} and 3.6×10^{-5} per g Corg. A correlation between higher hydrocarbon yields and higher organic content is discernible.

The concentrations (in ng/g dry sediment) of individual hydrocarbons in 208 samples of Recent oolite range from 31 to 76ng of methane; 21 to 46 ng of ethane (probably includes traces of ethene); 27 to 75ng of propene; 108 to 1178ng of propane; 21 to 73 ng i-butane; 26 to 131 ng of butene; 43 to 341 ng of n-butane. The C_5+ compounds were backflushed and integerated as single peaks and range from 744 to 6414 ng. In test experiments, the gas chromatography runs were continued past the emergence of n-butane to gain a rough idea of the distribution of the C_5+ compounds. The results of these runs warrant the definition of C_1 - C_5+ to include gas and gasoline range hydrocarbons.

Among the hydrocarbons heavier than methane, attention is drawn to the presence of considerable amounts of unsaturated hydrocarbons, which indicates at least a partly biochemical nature of the light hydrocarbons.

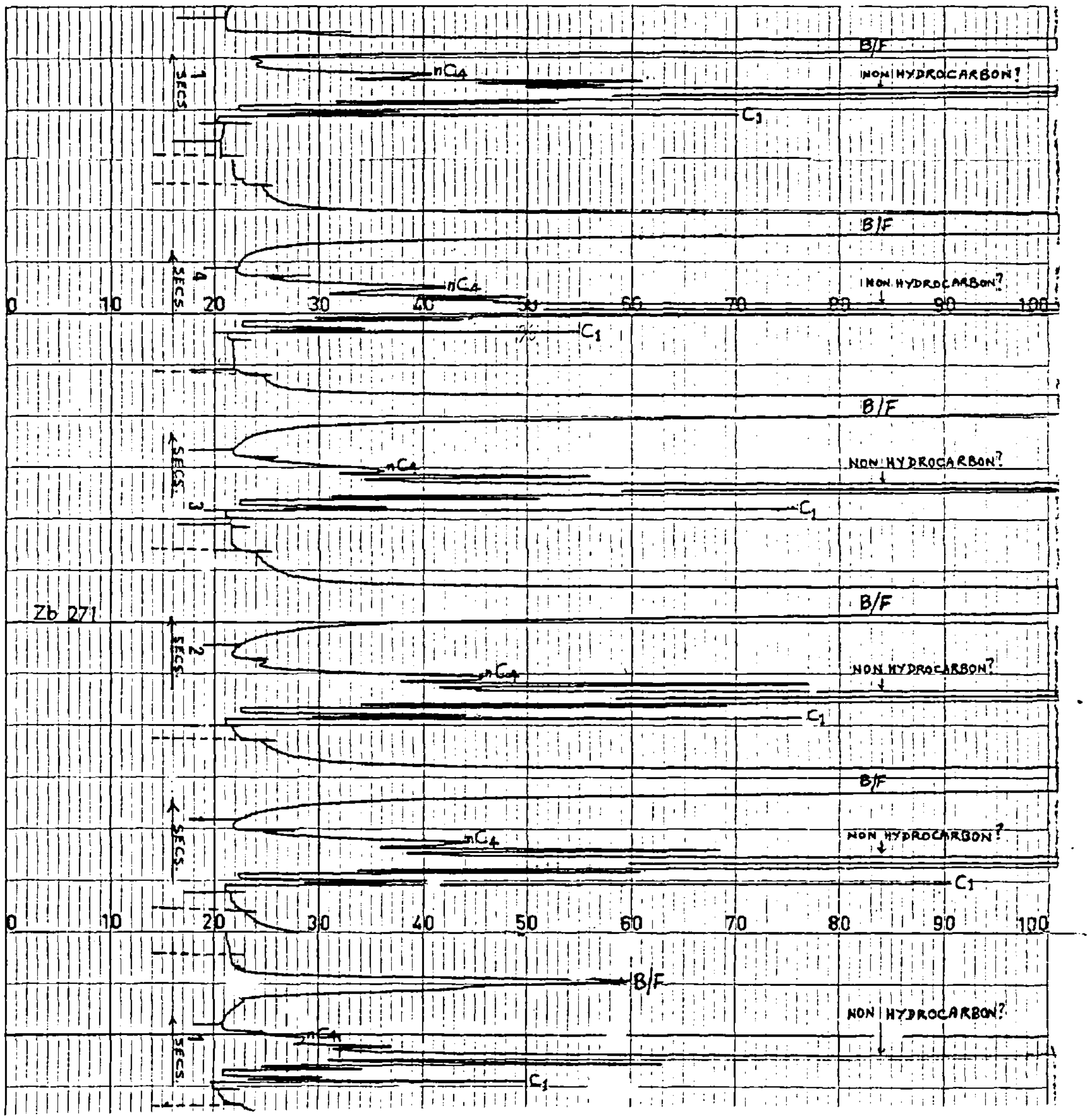
A significant aspect of the gas chromatograms from this study is the occurrence of a massive but unidentified peak retained at 170 seconds (under the conditions of the experiment; see fig.IV.1). This compound which is retained between the propane and butene peaks correlates well with propene and propane values and may suggest that it is a C_3 hydrocarbon possibly cyclopropane or propadiene; but this correlation may be also accidental. Similarly, Abell et al (1971 p.1844) noted the presence of unidentified C_3 and C_4 peaks in their light hydrocarbon analysis of lunar fines. But Thompson et al (1966) who also encountered such 'extraneous peaks' considered them as indicative of the presence of volatile non hydrocarbons. This explanation is preferred by the writer for the unidentified peak in the present experiments.

Another worrying aspect of the results is the inconsistency of the i-butane peak. It is thought that in the majority of cases where it is absent the i-butane is swamped by the massive non hydrocarbon peak referred to above; this inference has been made because, on the basis of retention times, the iso-butane peak closely follows this non hydrocarbon peak. On the other hand, the erratic occurrence of i-butane might be an intrinsic feature of early gas generation as the results of Kvenvolden et al (1980) suggest [see Table I.1]

A very engaging feature of the results is the low methane values as compared to the C_2+ saturated hydrocarbons. This is at variance with most light hydrocarbon results of recent sediments which show a dominantly methane composition with only traces of C_2+ hydrocarbons.

In the past, where relatively low methane values were encountered, it has been attributed to loss of methane during sampling, transportation and storage of sediments prior to desorption and

FIG.IV.1. Selected chromatograms from analysis of gas extracted from Recent oolites.
[see text for GC conditions]
Each run including backflush (B/F) lasts approximately 840 seconds


B/F
NON HYDROCARBON!
nC4
C1
1 SECS
4 SECS
3 SECS
2 SECS
Zb 271
0
10
20
30
40
50
60
70
80
90
100
NON HYDROCARBON?

analysis (Kartsev et al, 1958). This explanation is not, however, tenable in the case of the present results. As has been observed elsewhere [see I.5] the problem of possible light hydrocarbon loss and /or formation was well appreciated at the beginning of the research and appropriate measures were taken to prevent this happening. It would appear that the low methane content is an intrinsic property of the gases contained in oolites.

The low methane values in Recent oolites were not totally unexpected; the first indication of this trend came from the results of preliminary analyses of light hydrocarbons in ancient carbonates (Appendix I). In contrast to the high methane values of various skeletal limestones relative to C_2+ hydrocarbons, it was noted that the oolite (and certain mudstones) had very low methane content against higher C_2+ hydrocarbon values. The available evidence suggests that relative composition of light hydrocarbons is related to the organic precusor for these hydrocarbons and their tendency to ultimately form gas or oil (Thompson et al, 1966; Tichomolova, 1970; Sokolov et al, 1972; Hunt, 1979).

Table IV.1 after Sokolov et al (1972) shows the composition of some typical natural gases from various oil and gas fields. The disparity in the relative concentrations of the C_1 - C_4 components is very striking. In discussing the data of Table IV.1 Sokolov et al defined three predominant compositional trends in natural gases. The first and most familiar type is that in which methane is the main component of the gas (> 98%) and the contribution of hydrocarbons heavier than methane varies between 0.1 and 2%. Some of the largest pools of W.Siberia like Urengoyskoe and Tasovskoe belong to this group. In the second group, typified by the Gashi and Shebelinskoe accumulations, the methane occurs with a considerable admixture of EPB up to 15%. In the third group which comprises gases from the large oil fields like Gnedinzi, EPB concentrations exceed that of methane and in some cases constitute between 80 and 90% of the gas.

It is clear that, even though the gases encountered in this study are early diagenetic products (see Section IV.7) and by implication would undergo further compositional changes (including

TABLE IV.1 THE COMPOSITION OF SOME NATURAL GASES (After Sokolov et al, 1972)

FIELD	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5 - C_6	CO_2	H_2S	N_2
Gas and Gas condensate Fields								
Urengoyskoe	98,5	0,10	traces	traces	-	0,21	-	1,10
Tasovskoe	99,0	0,15	0,003	0,005	0,002	0,30	-	0,50
Gasli (IX layer)	94,7	1,10	0,20	-	-	0,70	0,2	3,10
Shebelinskoe	94,6	3,80	0,60	0,30	-	0,20	-	0,50
Slochteren(Netherlandes)	81,3	2,70	—	0,80	—	0,80	-	14,4
Lacq (France)	73,0	—		3,0	—	8,50	15,0	0,5
Oil Fields								
Romashkino	40,0	19,5	18,0	7,5	4,9	0,1	-	10,0
Tuimazi	38,6	20,2	19,3	6,8	4,1	0,1	-	11,0
Ghedinzi	1,73	20,0	48,65	17,5	5,17	1,25	-	5,70

the hydrogenation of their unsaturated components and dilution by thermally generated light hydrocarbons), they already show the distinct traits of the group 3 gases discussed above. A subsequent survey of petroleum production data in carbonate petroliferous regions like the Middle East revealed that the predominant mode of petroleum occurrence is crude oil. Gas associated with such oil pools bear the characteristics of the group 3 gases. It is concluded,therefore, that the tendency towards the formation of higher C_2+ hydrocarbons is an intrinsic property of the oolitic sediments investigated in the present study.

Although there are slight variations in the relative abundances of the light hydrocarbons in the samples of Recent oolite analysed, a general trend is apparent (excluding isobutane) as follows : methane > ethane <propane > n-butane. At first sight, the relationship whereby ethane concentrations are less than those of propane would seem anomalous; but this is not true. Sokolov et al(1972, p.480) have defined two main types of correlation among C_2H_6, C_3H_8, C_4H_{10}. More often, the trend shown is $CH_4>C_2H_6>C_3H_8>C_4H_{10}$. In other cases, the content of C_3H_8 is higher than C_2H_6. The low order hydrocarbons in oolitic sediment follow this second trend. The experiments of Tichomolova (1970) suggest that the relative abundance of the light hydrocarbons is dependent on the precusor material. For example experiments with stearic acid show that the content of propane in the evolved hydrocarbons is higher than ethane and butane.

Apart from the organic carbon content, the next factor influencing the yield of total hydrocarbons is variations in the composition of sediments analysed. In general, the greater the non skeletal content, the higher the evolved hydrocarbons. So, differences in hydrocarbon yields across the environment exist although values are still within the same order of magnitude; the geochemical implication of such differences is slight. The same conclusion was reached for the little variation in total C_1 - C_4 yields with depth in the short cores taken.

IV. 6 COMPARISON WITH EARLIER RESULTS

It is pertinent, at this stage, to compare the results of the present experiments with the only other known work on light hydrocarbons in Recent oolites reported by Ferguson (1975) (see Table I.3).

In contrast to the present findings, the methane values reported by Ferguson are rather high. The first probability is that his values were influenced by the desorption methods employed, that is, phosphoric acid attack plus heat at 100°C for 30 minutes. The acid would have the effect of biasing the results by up to 70% or more in favour of methane as has been demonstrated by Abell et al (1971), Flory et al (1972) and Funkhouser (1971) in experiments designed, with the aid of deuterated acids, to test the influence of acid desorption on light hydrocarbon investigations. An additional probability is that a lot more methane than was originally present could have been formed by bacterial action during the transportation and storage of samples as no special precautions were taken to prevent this happening. This line of reasoning is supported by the much higher methane values encountered in Recent oolite used in the preliminary experiments of the present study but which had not been treated against further biological activity.

Another difference is the absence of alkenes in the results of Ferguson. It is suggested that the known tendency of acids to preferentially attack unsaturated hydrocarbons would have been responsible for this absence.

There is, however, agreement between the two results on the general compositional relationships of C_2+ hydrocarbons with respect to methane. About this trend, Ferguson commented that the ratio of 2:1:0.6 is abnormal, since results of analysis of gas extracted from recent sediments suggests that methane is dominant with only trace amounts of higher hydrocarbons. He went on to state that "clearly, this result is significant and when the origins of natural gas are considered, may be of some importance" (ibid,p.24).

In concluding this comparison, it must be stated that the verification of the fact of occurrence of light hydrocarbons in Recent oolites afforded by the present study overshadows any little discrepancies between its results and those of Ferguson (1975).

IV. 7 SOURCE OF THE LIGHT HYDROCARBONS IN RECENT OOLITE

In general, there are three main possible explanations for light hydrocarbons found in Recent sediments : a) as a consequence of oil pollution; b) as a result of migration from a lateral or deep seated accumulation either by direct seepage or through diffusion; c) as a product of early diagenetic reactions including some thermal alteration.

The first possibility was discarded because of the considerable admixture of unsaturated hydrocarbons in the extracted gas and their corresponding absence in petroleum. Again, gas chromatographic distribution of the solvent extracts from Recent oolites precludes any such proposition [See V.9.iii].

The second possibility was also discarded partly for reasons given above but including the facts that 1) no known hydrocarbon accumulations exist in this area; none of the wells drilled in adjacent areas has encountered hydrocarbons (Amato, 1978); 2) if the presence of light hydrocarbons is due to migration, it would be expected that the distribution of these hydrocarbons in adjacent sediments should be similar; instead significant differences were found to exist [see Appendix III]; 3) the high values of backflushed C_5+ compounds cannot be accounted for by migration or diffusion; 4) although the relationship is not simple, there is a discernible variation in hydrocarbon yields with organic matter content which is diagnostic of an in situ origin for the gas (Hunt, 1978).

It would appear then that the third possibility - that of the gas being early diagenetic products - would be a preferred explanation. This is elaborated in the discussions that follow.

IV. 8 ORIGIN OF LIGHT HYDROCARBON IN RECENT OOLITES

In the preceding discussions, evidence were adduced that favour an indigenous origin for the light hydrocarbons found in Recent oolite. The obvious source of these hydrocarbons is the organic matter contained in oolites as is borne out by discernible variations of hydrocarbon yields with organic carbon content.

Although the presence of organic matter in marine ooids was first recognised by Rothpletz (1892), comparatively little was known of it since,for the most part, it was considered an accidental component of the oolite. In recent years, however, because of the possible implications of this organic matter on the origin of ooids, a lot more attention has been paid to it. Consequently, it is known that at least 33% of the organic extract from oolite is proteinaceous matter (Mitterer, 1968, 1972; Trichet, 1968). In addition to confirming this finding, Davies et al (1978) have reported the isolation of 25% carbohydrates and 4% lipids from Bahamian oolites.

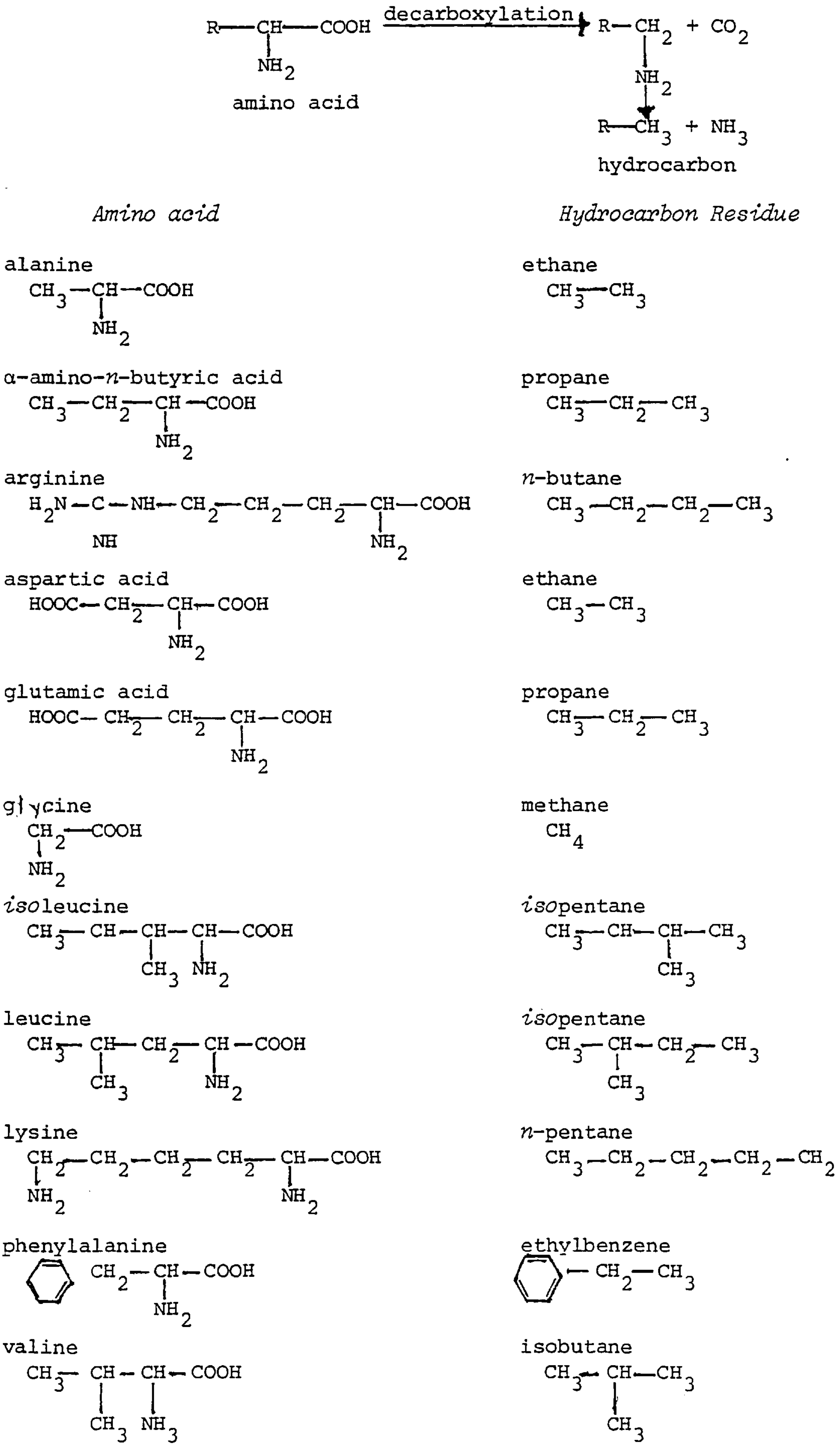
Theoretically, any of these components are capable, on diagenesis, of yielding hydrocarbons. But,because the complex sequence of chemical reactions required to convert carbohydrates is believed to be the most difficult to achieve under sedimentary conditions (Colombo, 1967), only the proteins and lipids will receive considerable discussion as the probable precursors to the light hydrocarbons found in Recent oolites.

The theoretical convertibility of proteins (amino acids) to light petroleum hydrocarbons has been postulated by Erdman (1961; 1967). The mechanism proposed involves decarboxylation and reductive deamination reactions as illustrated at the top end of fig.IV.2. Of the 25 common amino acids, the figure also lists 11 and their corresponding resultant hydrocarbons. According to Erdman, the proposed reactions can account for all aliphatic hydrocarbon isomers with the exception of neopentane which, in any case, is a relatively rare constituent of petroleum.

Despite the brilliance of its conception, Erdman's proposal

FIG.IV.2 A scheme of amino acids as a possible source of low molecular weight hydrocarbons. (after Erdman, 1961)

General reaction -



remained a theoretical possibility until Philippi (1977) published the results of low temperature pyrolysis of common amino acids that lent support to the concept. On the strength of these results, Philippi agreed with Erdman that 'protein derivatives (with their pure hydrocarbon sidechains and a possible contribution by 'non hydrocarbon' sidechains) may be significant source material of the gaseous and of some low molecular weight liquid hydrocarbons of petroleum'. (ibid, p.1085).

In accepting the theoretical validity of the transformation mechanism proposed by Erdman, Philippi expressed reservations about the overall effectiveness of decarboxylation-deamination reactions in nature. He argued instead that high temperature cracking reactions that 'take place raltively deep and are non biological' (p.1085) may be responsible. While this alternative proposal may be valid in accounting for the bulk of low molecular weight hydrocarbons formed during the main phase of oil genesis, there is hardly any doubt that it has little relevance to the origin of early diagenetic hydrocarbons encountered in Recent sediments.

Before the confirmatory experiments of Philippi (1977), Thompson et al (1966) had favoured the dominantly proteinaceous organic matrix of carbonate shells as the precursors of the C_1 - C_5 hydrocarbons which they detected in Recent and fossil shell samples. As a verification of the theoretical conversion mechanism of Erdman (1961), Thompson et al, while admitting of the limitations of their method, compared the characteristic light hydrocarbon distribution in fossil shells with that expected from the conversion to light hydrocarbons of amino acids found in Recent shells based on the data of Hare (1963), Hare and Abelson (1964) and Degens and Love (1965).

Thompson et al (opcit, fig.5) noted certain similarities such as large i-C_5 to n-C_5 ratios and C_2>C_3>i-C_4 relationships and suggested that the conversion mechanism proposed by Erdman may be important in hydrocarbon formation. However, there were also 'obvious dissimilarities' that prompted the authors to declare that 'the overall hydrocarbon-forming process may be rather involved'.

One of the most important reasons, in the view of the writer, for the 'obvious dissimilarities' noted by Thompson et al, is that their calculations assumed that proteins were the only source of low molecular weight hydrocarbons. It is recognised, however, that in nature, this is far from the truth. For example, lipids whose components are structurally similar to naturally occurring hydrocarbons (Meinschein, 1959) are favoured as probably the most important contributors to the formation of petroleum hydrocarbons (Krejci-Graf, 1963; Colombo, 1967). In particular, the role of lipids and especially fatty acids in the formation of aliphatic hydrocarbons has been emphasised by many workers (Craig, 1953; Silverman and Epstein, 1958; Breger, 1960; Cooper and Bray, 1963; Mair, 1964; Eisma and Jurg, 1967; Philippi, 1974). It is known that fatty acids deposited in sediments undergo rapid microbial degradation and resynthesis (Vleet and Quinn, 1979). The importance of these early diagenetic reactions has been clearly demonstrated by several authors (Rhead et al, 1971; Johnson and Calder, 1973; Gaskell et al, 1976; Farrington et al, 1977b).

The possibility of early diagenetic light hydrocarbon formation from lipids is strong. The organic matter in oolite is rich in lipids; in fact the 4% lipid content in oolite reported by Davies et al (1978) would appear to be artificially low. It is suggested that the known early diagenetic reactions of lipids may be responsible for the low values. Abelson (1963) has attributed the low lipid content of recent sediments to the fact of their conversion and incorporation into Kerogen during and immediately after the deposition of the sediments. One important factor in favour of a contribution by fatty acids as precursors for the hydrocarbons found in Recent oolite is the relative concentrations of the individual light hydrocarbons. The distribution is as follows : $C_1 > C_2 < C_3 > 4$. Experiments by Tichomolova (1970) have revealed that such a distribution suggests a derivation of the hydrocarbons from fatty acids.

The presence of low molecular weight alkanes, alkenes and arenes in the range up through seven carbon atoms has been reported both in deep sea sediments (Rogers and Koon, 1971; Claypool et al, 1974;

Hunt, 1974, 1975, 1978; McIver, 1974, 1975; Whelan and Hunt, 1978; Whelan, 1979) and recently in the calcareous surface sediments of the Persian Gulf, Arabian Sea, et cetera (Hunt and Whelan, 1979). On the basis of evidence outlined in the section on 'Theoretical Framework', the various authors believe that, for the most part, these light hydrocarbons are probably in situ products due to a combination of biological and low temperature chemical reactions. Possible precursors to these hydrocarbons mentioned by the various authors include a broad range of lipid and protein derivatives.

Other examples of early diagenetic 'wet' gas formation in Recent sediments have been reported by Veber et al (1977) and Veber and Maximov (1976) Bernard et al (1978), Cooper et al (1979) among others.

The available evidence suggest that the light hydrocarbons encountered in the present experiments are products of biochemical and low temperature chemical reactions.

IV. 9 SCHEME OF LIGHT HYDROCARBON FORMATION

Organic geochemical analyses of Recent ooids reveal that they have sufficient organic matter of the right composition to account for the light hydrocarbons extracted from them. Petrographic observations show an intimate relationship between this organic matter (both dissolved and particulate) and the carbonate mineral. The lamellar and concentric structure of ooids (alternating organic matter and aragonite needles) provides an ideal setting in which microbial and thermochemical diagenesis can occur.

The first set of reactions would be related to the anaerobic degradation of the dissolved and particulate organic matter by the associated bacteria [see Gessey, 1978 figs. 3 and 4 for explicit proof of this process]. It is to be noted that these reactions are a natural succession to the dominantly aerobic decomposition that was operative when the organic matter on the face of the developing ooid was exposed to the sea water medium and which was instrumental to the formation of the successive carbonate lamella that now encloses it.

Although anaerobic reactions had been known for a long time, the microbiology of the process has remained largely unelucidated. Anaerobic degradation is as much an exothermic reaction as aerobic decomposition, the only difference being a matter of scale. Pirt (1978) has summarised both reactions based on a carbohydrate molecule as follows :

Aerobic]

$C_6H_{12}O_6$ + O_2 —— CO_2+ H_2O + dry biomass + heat

Kg 1.00 0.53 0.72 0.60 0.40 1520K cals.

Anaerobic]

$C_6H_{12}O_6$ —— CH_4+ CO_2 + dry biomass + heat

Kg 1.00 0.25 0.69 .056 0.09 K cal.

It is to be expected that these relationships would vary depending on the starting molecule, efficiency of the conversion process, side reactions et cetera.

Evidence of biochemical heating as a result of fermentation has come from controlled experiments utilising Recent core sediments from the Bahama Banks : Sissler (in Cloud, 1962, p.67). A series of temperature measurements following the incubation of the sediments showed a slight increase in temperature (0.2°C after two days at 30°C) of the mud from adiabatic temperature. No increase in temperature occurred in a poisoned control sample.

The established product of microbial degradation is mainly methane although the possibility of some C_2+ hydrocarbons being formed simultaneously by this process, has been documented by various workers (Zobell, 1951; Davis and Squires, 1954; Bokova, 1959; Malyshek, 1962; Weber and Maximov, 1976).

Heat would be one of the by products of this first stage reaction as is evident from the discussion above. Because of the very low thermal conductivity of ooids (determined in our labs to be in the region of 1.7 watts/Meter/°K in SI units; see Table IV.2), the tendency would be towards the conservation rather than dissipation,of

TABLE IV.2 Laboratory Measurements of heat conductivity of Recent Oolites

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                                                       SINGLE DISC ANALYSIS
    DISC       RUN BAR          DEPTH       ERROR      DATE        PAGE    OP.        THICKNESS           VOLTAGES        THRM. RES     CONDUCTIVITY
                             FT.       M.    P.C.                                  INCHES    MM.       V1     V2     V3   MM. OF BAR   C.G.S.    S.I.
LEX-001-A     1    1          -0        0    1.0    18-07-79       3458    SRE      .0390    .9906     60.2   72.4   58.4   1.00683      .53     .222
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                                                    CELL CONDUCTIVITY ANALYSIS
                                                                                                                GEOMETRIC MEAN  MAXWELL MEAN
  SAMPLE   RUN BAR      DEPTH        DATE     PAGE OP. CELL WEIGHT   WEIGHT   WEIGHT GRN. V.F.        VOLTAGES      N.P. CONDUCT. N.P. CONDUCT.
                     FT.      M.                        NO.  DRY     WET 1    WET 2  DEN. FLUID  V1     V2     V3   C.G.S.  S.I.  C.G.S.  S.I.
G.C.14       1   1     0        0 18-07-79 3458 SRE   6  75.474   77.563   77.412 2.88 .376  57.0   95.2   53.9    4.22  1.766   4.02  1.681
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                                                    CELL CONDUCTIVITY ANALYSIS
                                                                                                                GEOMETRIC MEAN  MAXWELL MEAN
  SAMPLE   RUN BAR      DEPTH        DATE     PAGE OP. CELL WEIGHT   WEIGHT   WEIGHT GRN. V.F.        VOLTAGES      N.P. CONDUCT. N.P. CONDUCT.
                     FT.      M.                        NO.  DRY     WET 1    WET 2  DEN. FLUID  V1     V2     V3   C.G.S.  S.I.  C.G.S.  S.I.
G.C.25       1   1     0        0 18-07-79 3458 SRE   7  75.456   77.419   77.308 2.87 .358  60.0   90.1   50.9    4.52  1.892   4.30  1.799
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    *                                               CELL CONDUCTIVITY ANALYSIS
                                                                                                                GEOMETRIC MEAN  MAXWELL MEAN
  SAMPLE   RUN BAR      DEPTH        DATE     PAGE OP. CELL WEIGHT   WEIGHT   WEIGHT GRN. V.F.        VOLTAGES      N.P. CONDUCT. N.P. CONDUCT.
                     FT.      M.                        NO.  DRY     WET 1    WET 2  DEN. FLUID  V1     V2     V3   C.G.S.  S.I.  C.G.S.  S.I.
G.C.26       1   1     0        0 18-07-79 3458 SRE   8  72.293   74.026   73.764 2.47 .269  55.8  102.2   49.6    3.33  1.394   3.03  1.268
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                                                    CELL CONDUCTIVITY ANALYSIS
                                                                                                                GEOMETRIC MEAN  MAXWELL MEAN
  SAMPLE   RUN BAR      DEPTH        DATE     PAGE OP. CELL WEIGHT   WEIGHT   WEIGHT GRN. V.F.        VOLTAGES      N.P. CONDUCT. N.P. CONDUCT.
                     FT.      M.                        NO.  DRY     WET 1    WET 2  DEN. FLUID  V1     V2     V3   C.G.S.  S.I.  C.G.S.  S.I.
G.C.46       1   1     0        0 18-07-79 3458 SRE  29  73.153   75.173   75.083 2.84 .368  57.5   95.5   53.9    4.37  1.827   4.15  1.738
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                                                       SINGLE DISC ANALYSIS
    DISC       RUN BAR          DEPTH       ERROR      DATE        PAGE    OP.        THICKNESS           VOLTAGES        THRM. RES     CONDUCTIVITY
                             FT.       M.    P.C.                                  INCHES    MM.       V1     V2     V3   MM. OF BAR   C.G.S.    S.I.
LEX-001-A     1    1          -0        0    1.0    18-07-79       3458    SRE      .0390    .9906     60.4   72.7   55.7   1.03195      .52     .217
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* Result is probably unrepresentative (J. Wheildon, personal communication.

any heat generated as a consequence of bacterial attack.

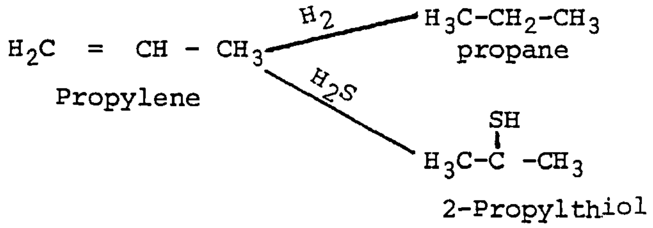
Given the organic geochemical, petrographic and thermal conditions outlined, each ooid could be viewed as a closed unit providing an ideal setting for low temperature chemical diagenesis of the enclosed organic matter, resulting in the formation of largely C_2+ hydrocarbons (including unsaturated hydrocarbons) and perhaps additional methane. The temperatures involved in such reactions have been estimated at under or about 30°C (Hunt and Whelan, 1979) but definitely not above 50°C. These reactions will be probably catalysed by bacteria and/or inorganic catalysts. Trace element analysis of ooids by the Inductively Coupled Plasma technique has revealed the presence of potential catalysts like Ti, Ni, Sr, Mn, V (Tables II.3a and b). Some of these like Cr, Cu, Ni and V are known to be necessary for the life activities of micro-organisms and are mostly inherited from their breakdown products. However, it is pertinent to observe that the results of experiments by Vleet and Quinn (1978) show that reduction reactions in Recent sediments are microbially mediated; no inorganic reduction could be detected.

The lamellar and concentric structure of the ooids with its network of organic matter provides a large and effective internal surface area for the adsorption and retention of the generated hydrocarbons. The capacity of ooids to preserve hydrocarbons in an adsorbed state was demonstrated by Ferguson (1975) following the suggestion, afforded by the earlier works of Suess (1970, 1973), of such a possibility.

The experiments were carried out by connecting tubes containing Recent oolite to a supply of natural gas which was allowed to flow over them for various periods of time. Samples of these runs as well as blanks of original material were desorbed and analysed for contained hydrocarbons. Similar experiments were repeated using precipitated chalk, crushed chalk rock and sandstones. From the results (Table I.3b) Ferguson declared : 'Clearly, the amounts of gas adsorbed by the ooliths is highly significant'.

It is conceivable that this generation - adsorption process will continue through the early diagenetic stage and beyond until the adsorptive capacity of the ooid is satisfied. What follows this stage is the subject of later discussions. (see Chapter VI).

One other probable set of reactions before the termination of the early diagenetic stage is the reduction or polymerisation of unsaturated hydrocarbons to alkanes (Erdman, 1967; Hunt, 1979, p.39). Two possible reduction reactions suggested by Hunt are as follows :



Whereas the presence of H_2S in most Recent sediments is generally accepted, field investigations have not revealed any free H_2 that could take part in the above reaction. For example, Sissler (in Cloud, 1962, p.67) reported large amounts of H_2 (and O_2) from a bacterial culture of a calcareous mud from the Great Bahama Bank. Subsequent on site-investigations by Cloud (1962) failed to detect any free H_2 gas. Sissler suggested that either the bacterially generated gases recombine chemically within the sediments about as quickly as they are formed, or are not generated in sufficient quantity to exceed the absorption capacity of water. The writer would favour the former explanation on the strength of evidence by Hunt and Whelan (1979) that extensive reduction of unsaturated hydrocarbons (and nonhydrocarbons) to paraffins takes place in Recent near surface sediments at temperatures generally below 30°C. More specifically, Hunt (1979, p.153) has stated that hydrogen is produced under widespread conditions, but is immediately utilised for the reduction of nitrogen, sulphur and oxygen compounds.

IV. 10 IMPLICATION OF LIGHT HYDROCARBON OCCURRENCE IN RECENT OOLITE

It is evident from the preceding discussions that the light hydrocarbons extracted from Recent oolites are neither mere biogenic gas nor migrated hydrocarbons but that they are in situ early diagenetic (including thermal) products. According to the arguments detailed in the 'Theoretical Framework' (see Section I.3), the occurrence of such products in Recent sediments is diagnostic of a situation favourable for petroleum hydrocarbon generation. The implication is obvious that with increasing depth of burial and exposure to higher temperatures (and, perhaps, catalytic activity) such sediments would serve a source bed function. It is this possibility that prompted the investigations reported in the following chapter.

CHAPTER V

SOURCE BED CONSIDERATIONS

V.1.
INTRODUCTION

In concluding the discussions of the results of light hydrocarbon occurence in Recent oolite, the suggestion was made that if these sediments contained adequate amounts of organic matter of the right type, they could, upon further burial and exposure to higher temperatures and perhaps, catalysis, generate petroleum.

The objective of this phase of the study was to gather essential supplementary information on the quantity and quality of the organic matter in oolites that would enable the writer to evaluate their petroleum generating potential. The presentation is in two parts; the first deals with the organic content of oolite and its implications while the second part reports on the methods employed for the characterisation of the organic matter and discusses the results. But first, some brief comment is necessary on the correct nomenclature applicable in petroleum source literature.

V.I.1 SOURCE ROCK MISNOMER

So far in this thesis, the term 'source bed' has been used purposely in lieu of 'source rock', an inadequate expression that has found wide usage in organic geochemical literature particularly in the last 25 years or so.

The term 'source bed' is in fact an old one which was used almost exclusively by petroleum geologists since the conception of the source bed theory of petroleum formation about the middle of the last century. But in recent years, with a majority of geochemists advocating the generation and expulsion of petroleum hydrocarbons at depths of burial at which sediments would have become rocks, the term 'source rocks' has been introduced into the literature (Philippi, 1965, 1975; Welte, 1965; Vassoyevich, 1970; Tissot et al, 1971). Ironically, the newer, more commonplace term is too restrictive and less accurate than the original.

TABLE V. 1 DEFINITIONS PERTINENT TO SOURCE BEDS
(after Barker, 1979)

SOURCE BED - A unit of rock that has generated and expelled oil or gas in sufficient quantity to form commercial accumulations. The term "commercial accumulations" is by definition, variable.

LATENT SOURCE BED - A source bed that exists but is as yet concealed or undiscovered. Usually refers to unexplored areas or deep portions of developed basins.

POTENTIAL SOURCE BED - A unit of rock that has the capacity to generate oil or gas in sufficient quantities to form commercial accumulations but has not yet done so because of insufficient thermal maturation.

ACTIVE SOURCE BED - A source bed that is in the process of generating oil or gas.

SPENT SOURCE BED - A source bed that has completed the process of oil or gas generation and expulsion. A source bed may be spent for oil and active for gas.

INACTIVE SOURCE BED - A source bed that was once active but has temporarily stopped generating prior to becoming spent. Usually associated with thermal cooling due to uplift and erosion. Still has some potential left.

LIMITED SOURCE BED - A unit of rock that contains all the prerequisites of a source bed except volume. Commonly refers to thin shale laminations in carbonates or thin coals in continental deposits.

At the centre of the problem is the lack of a credible expulsion mechanism at depths where sediments would have become consolidated, compacted, dewatered and lithified into rock. Again, may petroleum geologists have noted that both empirical data on the habitat of oil accumulation (Pratt, 1947; Weeks, 1961; Hedberg, 1964) as well as researches on recent sediments (Smith, 1954; Emery and Rittenberg, 1952; Kidwell and Hunt, 1958; McIver, 1971, 1974) suggest early generation and migration shortly after burial of sediments.

It would appear that while the problem is far from settled, there is need to revert to the old and more inclusive term covering both source sediment and source rock. 'Source bed' or 'source sequence' or even 'source strata' which avoids the contentious implication of timing for hydrocarbon generation and expulsion is considered more appropriate than 'source rock'. No connotation of thickness is implied by the source bed designation.

V. 2 CATEGORISATION OF SOURCE BEDS

The term 'source beds' has been applied ambiguously in geochemical literature to sedimentary beds in very different stages of hydrocarbon generation and expulsion. Because of the resulting confusion, recent publications have sought to qualify the term to make it more specific for particular discussions.

One of the most comprehensive categorisation of source beds is a modification by Barker (1979) after Dow (1977). Six types are distinguished as follows : a) latent b) potential c) active d) spent e) inactive and f) latent source beds [see Table V.1]

For the purpose of this discussion as indeed for most cases, a broad classification would suffice. This subdivision is based on two related factors that determine the hydrocarbon generating capacity of a sedimentary bed namely, a) the amount and type of organic matter contained in the bed ('organic facies' of Rogers, 1979); b) maturation, which is generally understood as the processes, largely thermochemical, that transform the organic matter into petroleum or petroleum-like substances.

Some sedimentary beds have sufficient organic matter of the right type to generate expellable quantities of petroleum in the future, but are at the present in the ,a) pre-petroleum generating stage; b) generation stage; c) maturation stage or d) preliminary expulsion stage. Such beds are known as potential or immature source beds.

By contrast, other sedimentary deposits have generated and expelled sufficient quantities of petroleum to form commercial reservoir accumulations and are termed effective or mature source beds.

From the light hydrocarbons data of oolites coupled with the age and depth of occurence of these sediments, it is evident that the work in this section was devoted to determining the potential source bed capability of these deposits. This was without prejudice to any 'unexpected' results.

I

V. 3 ORGANIC MATTER IN RECENT OOLITE

The concept of petroleum source beds is rooted in the organic theory of petroleum formation which states that petroleum is a product of organic matter buried with sediments. Almost invariably, all sedimentary beds contain organic matter ranging from disseminated traces in sands and sandstones to the high concentrations of peat and coal beds.

In source bed investigations, the organic matter content of the sample is one of the first parameters to be determined. The results are usually expressed as the percentage carbon/dry weight of sediment after the carbonate carbon has been dissolved away by acid treatment. To compensate for other elements (H,O,N,S) present in organic matter, an organic factor is necessary to translate organic carbon results into statements about total organic matter content. As this factor varies both with workers as well as type of sediments (see Tissot and Welte, 1978 p.430) it is recommended that results of organic matter content should be presented as weight percent organic carbon as long as it is recognised that such an expression is only a representation of the real organic matter content.

The Perkin Elmer 240 Elemental Analyser was used for Organic carbon determination. This equipment accurately determines the carbon content of organic compound by detecting and measuring its combustion product, CO_2. About 3 mg of pulverised (<63 microns) oolite was weighed into purpose made mini platinum boats and treated with 50% HCl to eliminate the inorganic (carbonate) carbon. The solution was evaporated to dryness in an oven at 50°C and the boat containing the residue was introduced into the equipment's furnace maintained at 950°C. Combustion occurs in pure oxygen under static conditions. The combustion product CO_2 is then analysed automatically in a self-integrating, steady-state, thermal conductivity analyser, which eliminates the tedious classical gravimetric analysis weighing of adsorption traps. Results are recorded in a bar graph form, on a 0 - 1 mV recorder.

The results which are presented along with the results of light hydrocarbon analysis (Appendix III) show values of 1.23 - 4.13 wt. %, organic carbon depending on the 'purity' of the samples. The lowest values reflect an increased contribution to the oolite by skeletal debris while the highest values were for those samples containing more than 90% ooids. This contrasts with the correlation of Gehman (1962) who reported lower organic matter (and C_{15}+ hydrocarbon) content with increasing non skeletal composition (ibid,p.887).

As is apparent from the results in Appendix III, the limiting values stated above are more of the exception than the rule, much of the results falling in the range 1.86 - 2.85 wt.%. A confirmation of these results came from a rather unexpected source. As part of the procedure to determine the thermal conductivity of ooids, the grain densities of ooids had been computed; these varied from 2.84 - 2.88 (Table IV.2) revealing a down grading of the results by 2.4 - 3.8 percentage points when compared to the expected density (2.95) were the grain to have been all aragonite.

It was Rothpletz (1892) who first drew attention to the presence of organic matter in oolites. The intimate association of this organic matter with the carbonate mineral in the oolite prompted Rothpletz to propose his algal secretion theory of oolite formation.

Earlier ,Walther (1888, 1891) had, in ascribing a principal role in the formation of oolites to decayed organisms, alluded to the presence of organic matter in oolite. The subsequent identification of various organic material in oolites by other workers formed the basis of support for the organic theory of oolite formation. (Van Tu yl, 1916; Dangeard, 1936; Nesteroff, 1956).

It was, however, Newell et al (1960) that first gave prominence to the quantification of the organic matter in oolite. They reported a dry weight of .13 weight per cent unoxidised organic matter which they likened to the organic slime pelogloea. While this was a significant contribution to knowledge of oolites, it was unfortunate from the view point of this research in that this low value which has been widely quoted by other workders, precluded any chance of investigating a possible source bed role for oolites.

Recent oolites have a high organic content (Shearman et al, 1970; Freidman, 1964; Bathurst, 1975, p.80). The first indication of this comes from a petrographic examination of oolite in thin section which shows a strong brown colour. Since aragonite is colourless, the inference is obvious that it is the contained organic matter that imparts this colour to the oolites. The most useful evaluation of the high organic content of oolite derives from the acid treatment of ooids in thin section. Careful decalcification of the ooids with dilute acid reveals a pervading and complex mass of organic matter (algae, bacteria, fungi etc) which is easily stained by organic dyes (Rothpletz, 1892; Dangeard, 1936; Nesteroff, 1956; Shearman et al, 1970).

On the basis of their visual estimation of organic matter content in oolite which was at odds with the organic content values reported by Newell et al (1960), Shearman et al (1970, p.565) noted that, 'at first sight these low values would appear to belie the importance of organic matter.' Shearman et al tried to rationalise for the low values of Newell et al by invoking the high moisture content of the original mucilage which would mean that any dry weight of this organic matter would represent a substantial underestimation of the true value. Furthermore, Shearman et al explained that by virtue of the low density of the mucilage relative to aragonite (2.95), even small weights could assume considerable significance in terms of volume. The reasoning of Milliman (1974) on the low organic matter values of Newell et al was along similar lines.

While such arguments might still be valid, the verifiable results of the present investigations obviate the need to invoke them in the first place. It is to be noted that the values of 1.23 - 4.13 wt.% organic carbon reported here are in fair agreement with values such as 1.9, 2.5 and 4.7 wt.% organic matter in Recent oolite reported by Milliman (1974,p.46) from the published and unpublished works of several researchers.

The writer has examined the method employed by Dr.W. Bergman who determined the organic matter value reported by Newell et al (1960; see p.491) and concludes that it was bound to yield a very low value. In general, organic carbon values depend, in some measure, on the method of investigation employed (Robinson, 1973; Leventhal et al, 1980). The method adopted by Dr. Bergman in isolating the insoluble material in oolite which he used for the Corg analysis could have resulted in the oxidation of a large part of the organic matter prior to analysis. It is evident that the value obtained by Dr. Bergman represents that fraction of the organic matter in oolite that survived the oxidation process inherent in the isolation procedure. This fact was tacitly admitted by Newell et al (1960) who in their paper reported 0.13 per cent unoxidised organic matter (ibid, p.489). It is noteworthy that the authors, in apparent disregard of this value, went on to state that ' the grains contain much organic matter- - -' (op cit.) Most of the subsequent authors who have quoted this result have, wittingly, or unwittingly, omitted the qualification 'unoxidised' applied by the original authors thereby giving a false impression that the value of 0.13 per cent represented all of the organic matter originally contained in the oolite. Again, Dr. Bergman discarded the filtrate following HCl decomposition of the oolite and 'thoroughly washed [the residue] with HCl and water ---' (ibid,p.491); this is another obvious source of error as has already been highlighted in a related discussion in the chapter on the Origin of OOids. In this regard, it is only pertinent to add that the organic matter in Recent oolite (as in other

Recent sediments) is both acid and base soluble. For example, Land et al (1979) reported that $^2/3$ of the organic matter in Recent Baffin Bay oolite is solubilised by dilute HCl. This is close to the value of 71% acid soluble organic matter in Bahamian oolite obtained by the writer.

V. 4 ORGANIC MATTER CONTENT IN RELATION TO PETROLEUM OCCURENCE IN OOLITE

Organic matter is the basic ingredient in sedimentary beds from which petroleum is formed. A certain amount of organic matter must be present in a sedimentary bed for it to serve a source bed function.

Numerous values of organic carbon content have been suggested as minimum requirement for potential source beds. From the results of numerous researches,and in particular those of Ronov (1958) and Bitterli (1963),based on sediments spanning a variety of geographic and stratigraphic environments, the bare minimum (except for those source beds in a very advanced stage of maturity) is set at about 0.5 wt.% organic carbon. However, such a value can only give an idea about the order of magnitude and nothing more as Welte (1965) rightly observed. The view of Kendrick et al (1978) is similar; that estimates of minimum values would be necessarily arbitrary since the amounts of petroleum generated is dependent on other factors such as the type of organic matter present as well as the expulsion capability of the source bed, which can vary from place to place with the physico-chemical regimen of a basin.

Under the most favourable conditions of conversion, the minimum organic carbon content could be lower than 0.5 wt.%. For example Hunt (1967) and Tissot and Welte (1978) give a value of 0.3 wt. % minimum organic carbon for carbonate and evaporite type sediments. This lower value is thought to be related to a more efficient conversion of organic matter in carbonates. Conversely, some sedimentary beds must contain considerably more organic carbon in order to generate and release hydrocarbons. Schrayer and Zarrella (1963), for instance, reported a 1.5 wt.% minimum organic carbon content for oil source beds based on studies of the Shales of Wyoming.

In general, shales need more organic matter than carbonates to generate the same amount of petroleum. This is because shales almost invariably contain various recycled terrigenous organic matter that yield very little petroleum. Carbonates on the other hand contain high petroleum yielding autochtonous marine organic matter (Hunt, 1979). This is well illustrated by the results of studies by Uspenskii (1949), Petrova et al (1955) Gehman (1962) and Baker (1962). For example, Baker found that the mean hydrocarbon content of both limestones and gray shales from the Cherokee formation was about 100ppm whereas the mean organic carbon content of limestones was 0.19 wt.% as compared to 1.5 wt.% for the shales.

It is evident that the organic carbon contents of oolites (1.23 - 4.13 wt.%) are well above the minimum requirement for a carbonate sedimentary bed to be considered potential source bed for petroleum. But, as has been emphasised in the preceding discussion, organic matter content is not in itself diagnostic of petroleum generating capacity.

II

V. 5 CHARACTERISATION OF THE ORGANIC MATTER IN OOLITE

It is not sufficient to point out the total organic content of sedimentary beds when evaluating their petroleum generating potential because different types of organic matter have different hydrocarbon potentials depending on their chemical composition and structure. The type of organic matter in a sedimentary bed is controlled to a high degree by its depositional environment. In general, aquatic organic matter is more suitable than terrigenous organic matter for petroleum generation.

Equally important in the characterisation of organic matter is the level of maturation which reflects the thermal history of a potential source bed. Fortunately, most of the various optical, physical or chemical methods applied to characterise organic matter give indication of both parameters. As each set of methods has specific merits and limitations, it is advisable to view them as complementary rather than competitive methods (Tissot and Welte, 1978; Hunt, 1979; Leythaeuser et al, 1979; Rogers, 1979). Such a concerted approach was adopted for the present studies.

Sedimentary organic matter is an extremeley complex mixture of many types of compounds; for the sake of convenience in source bed characterisation, it has been defined heretofore as consisting of bitumen and kerogen. The bitumen fraction consists of that part of organic matter which is soluble in common organic solvents, while the kerogen comprises that portion which is insoluble in non-oxidising acids, bases and organic solvents.

V. 6 METHODS BASED ON KEROGEN

The importance of characterisation studies based on Kerogen has been emphasised by several authors (McIver, 1967; Vassoyevich et al, 1970; Tissot et al, 1974; Ishiwatari et al, 1977). Peters et al (1977) have summarised the reasons for this importance; a) Kerogen is of ubiquitous distribution in sediments; b) unless recycled by erosion, it is imobile and probably syngenetic with mineral matrix;
c) it is sensitive to diagenetic effects through a range accompanying most stages in petroleum generation.

The techniques applied in Kerogen studies may involve analysis of the 'whole rock' or separation of the Kerogen from the mineral matrix prior to analysis.

V. 6 i Optical Microscopic Methods

Except in such uncommon sedimentary beds as torbanite and tasmanite, organic matter in sediments occur generally in a disseminated form with very few defined organic remnants. It is almost imperative in the optical study of a majority of presumed source beds to first isolate and concentrate the organic matter.

PROCEDURE:

The first major obstacle in the study of Kerogen is that most effective methods employed to destroy the associated and generally far more abundant inorganic minerals also result in a notable alteration of the general structure of Kerogen (Tissot and Welte, 1978; Hunt, 1979). This is particularly true for recent sediments. Tissot and Welte (1978) recommend the physical methods of separation like the sink-float method based on differences of specific gravity of minerals and organic matter; or the Quass method which utilises the differential wetting of the Kerogen and minerals by two immiscible liquids. These methods and others have been reviewed by Robinson (1969). Although suitable for qualitative studies, physical methods are prone to giving low values in quantitative studies due to incomplete extraction.

The standard method of Kerogen isolation involves the use of HCl to dissolve the carbonate minerals of the sample and HF to destroy the silicious and alumino-silicate minerals (Forsman and Hunt, 1958; McIver, 1967 and others). When pyrite is present, additional treatment is necessary to release the organic matter associated with the mineral and known generally as 'framboids' (Tissot and Welte, 1978). For pure carbonates such as the oolites in this study, HCl decalcification of the rock is usually the only treatment necessary. The Kerogen in such carbonates comprises mostly of small delicate algae, diatoms, fungi and bacteria in addition to amorphous organic matter. Kobluk and Khale (1977) have summarised the methods available for the isolation of such organic matter and favour the use of dilute acid solutions such as 5% acetic acid, 5% Na EDTA and 0.1 - 1N HCl to avoid the vigorous release of gas that might disrupt the delicate structure of the Kerogen.

Following trial experiments, 10% HCL was used in the present experiments and was so thoroughly effective that follow up HF treatment made no difference to the quantity or quality of Kerogen isolated and was therefore considered unnecessary.

Preweighed samples of oolite from mobile sand bars and the intertidal areas were put into separate beakers and thoroughly washed with distilled water. Over a few days, acid was added and decanted many times until there was no reaction on further additions of acid. The insoluble fractions were washed several times with distilled water till the wash water was neutral to pH paper.

Any possible inorganic and in particular, heavy minerals in the insoluble residues were removed by a sink-float method in $ZnBr_2$ solution with specific gravity 2.2. The organic matter floats to the top of the solution and is decanted into a separate container,washed with .1N HCl and centrifuged. This was repeated twice and then was followed by 3 washings with distilled water to remove any trace of acid.

The organic concentrates were then prepared as strewn slides for transmitted light microscopy. Reflected light microscopy was not applicable (see V.6iv).

V. 6ii Type of Kerogen

One of the first objectives in optical microscopy is the identification and description of the Kerogen type. Of relevance here is that part of the organic matter about 1mm or larger although in transmitted light studies, some finer 'amorphous' organic matter, can be identified.

Examination of strewn slides of the organic concentrates in transmitted light reveals that almost invariably the organic matter in oolite comprises dominantly of various solitary, filamentous and colonial algae and other diatoms,et cetera (see figs.V.1 and V.2). Most of the algae belong to the family Cyanophycae (the blue-green algae). In addition, there is an appreciable contribution to the Kerogen by amorphous organic particles. This type of organic matter is frequently termed 'sapropelic' (Tissot and Welte, 1978) and is usually considered as being derived from planktons. However, Tissot and Welte are quick to point out that this is not necessarily true since precipitation or adsorption of dissolved or colloidal organic matter such as humic acids results also in structureless, amorphous organic

TABLE V.2a APPROXIMATE EQUIVALENCE OF VARIOUS TERMS USED IN KEROGEN DESCRIPTION
(After Tissot and Welte, 1978)

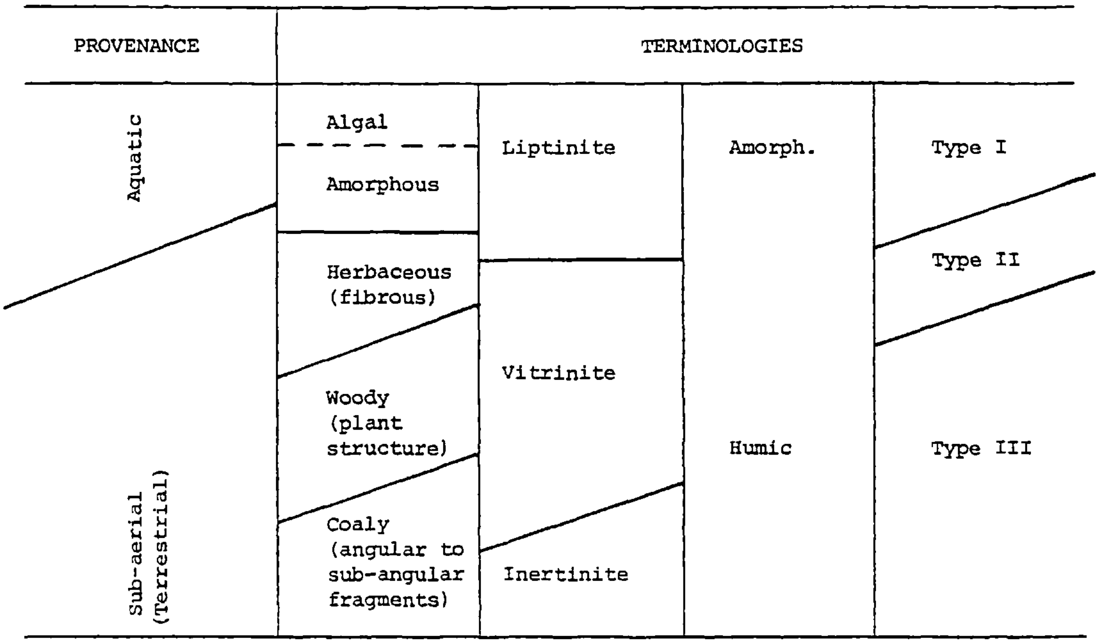


TABLE V.2b CLASSIFICATION OF ORGANIC MATTER IN SEDIMENTARY ROCKS (After Hunt, 1979)

	SAPROPELIC			HUMIC	
KEROGEN (by transmitted light)	Algal	Amorphous	Herbaceous	Woody	Coaly (Inertinite)
COAL		Liptinite (Exinite)		Vitrinite	Inertinite
MACERALS (by reflected light)	Alginite	Amorphous	Sporinite Cutinite Resinite	Telinite Collinite	Fusinite Micrinite Sclerotinite
KEROGEN (by evolutionary pathway)	Types I,II		Type II	Type III	Type III
H/C	1.7-0.3		1.4-0.3	1.0-0.3	0.45-0.3
O/C	0.1-0.02		0.2-0.02	0.4-0.02	0.3-0.02
ORGANIC SOURCE	Marine and lacustrine		Terrestrial	Terrestrial	Terrestrial and recycled
FOSSIL FUELS	Predominately oil Oil shales,boghead and cannel coals		Oil and gas	Predominately gas Humic coals	No oil,trace of gas

matter. Since no other humic organic matter or even spores and pollens are present in the organic concentrate, any herbaceous or woody contribution to the organic matter must be minimal and it is believed that the amorphous organic matter in oolite represent mainly the breakdown products of aquatic organisms. It is noteworthy that the organic residue isolated from sediments taken from adjacent areas contained less than .1% spores and pollens (Traverse and Ginsburg, 1966).

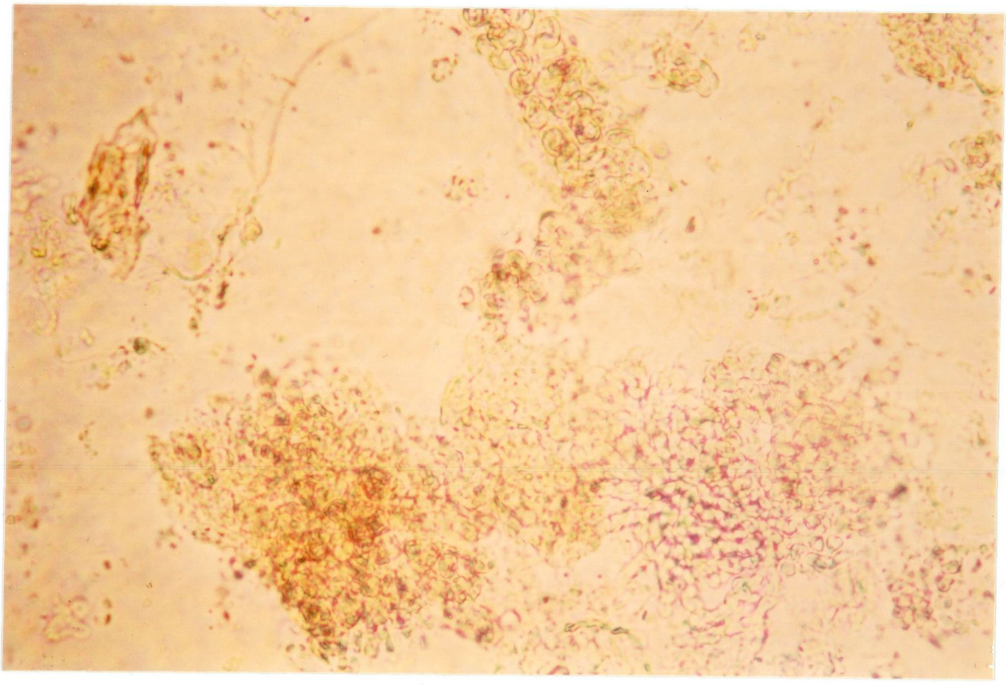
The presence of algae, diatoms, bacteria, fungi,et cetera in oolites is well documented (Rothpletz, 1892; Danegeard, 1936; Nesteroff, 1956; Newell et al, 1960; Purdy, 1963; Shearman et al, 1970; Milliman, 1974; Bathurst, 1975). Because the association of certain endolithic algae with micritisation has been noted by various authors (Purdy, 1968; Shearman et al, 1970; Margolis and Rex, 1971; Golubic, 1975; Kobluk and Risk, 1977a; Harris, 1977), it must be stressed here that while some of the algae found in oolites are post formational entrants, the vast bulk of micro-organisms that make up the Kerogen isolated from oolite in the present study are syngenetic additions (see Chapter III: Origin of Ooids). It is pertinent to reiterate that the oolites macerated for this study were from mobile shoal sands where the influence of postdepositional boring by endolithic algae is virtually nonexistent. The algae that comprise the Kerogen are therefore believed to be 'indigenous'.

The types of organic matter in a sedimentary bed are controlled to a large degree by its depositional environment. In general, aquatic organic matter is more suitable than terrestrial organic matter for petroleum generation. Aquatic organic matter is derived from numerous biotic sources. The principal contributors are believed to be the more abundant life forms such as phytoplankton, algae and bacteria. Other aquatic organisms,both floral and faunal, also may be important depending on the location and depth of sediment deposition. The well illuminated shallow water environment of oolite deposition is an ideally active biochemical and physicochemical environment (Newell et al, 1960; Dravis, 1979) for the synsedimentary accumulation of 'gem' organic matter from the view point of petroleum

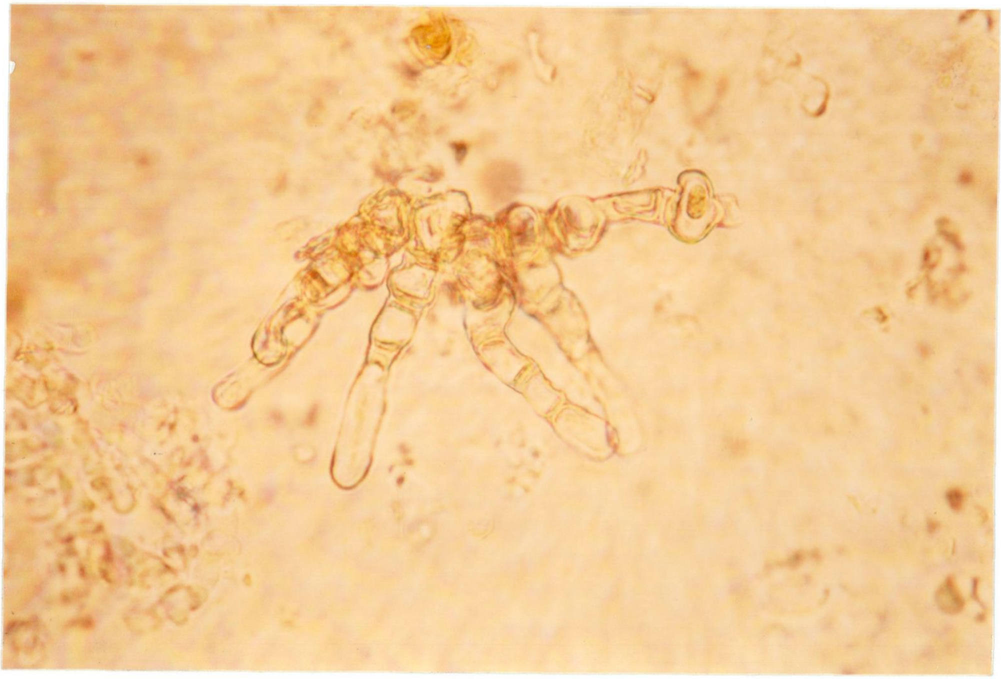
FIGS.V.1. [A,B,C,D] Marine organic matter of algal - amorphous facies (Type 1 Kerogen) extracted from subaqueous Recent oolites of Eleuthera Bank, Bahamas.

Note greenish hue due probably to presence of chlorophyll.

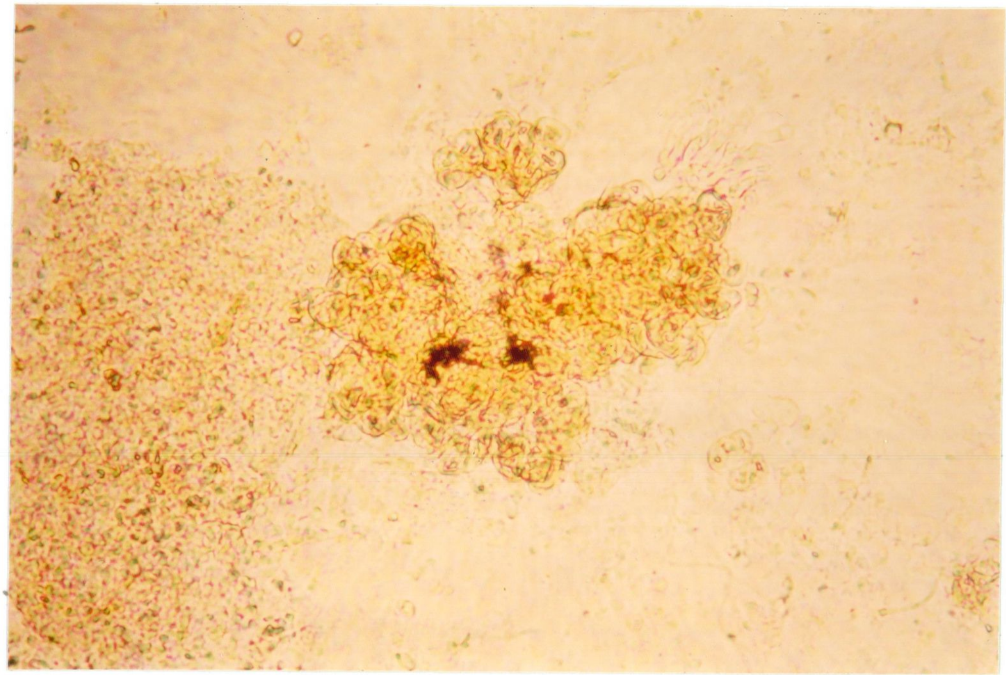
A X 800



B X 200



C X 200



D X 200

generation.

The classification of the organic matter found in sedimentary beds is still in a state of flux. This subject has been discussed by Tissot and Welte (1978) and Hunt (1979) who have attempted to correlate the various terminologies that exist on the subject (Tables V.2a and V.2b respectively). Under any of these schemes, the organic matter isolated from oolites would be described as algal-amorphous organic facies or Type 1 Kerogen or broadly as sapropelic organic matter. Opinion is unanimous that this is the best quality organic matter for petroleum hydrocarbon generation (see Tissot and Welte, 1978; Hunt, 1979). In simulated maturation experiments, Lijmbach (1975) had demonstrated the immense hydrocarbon generating potential of algal and bacterial remains.

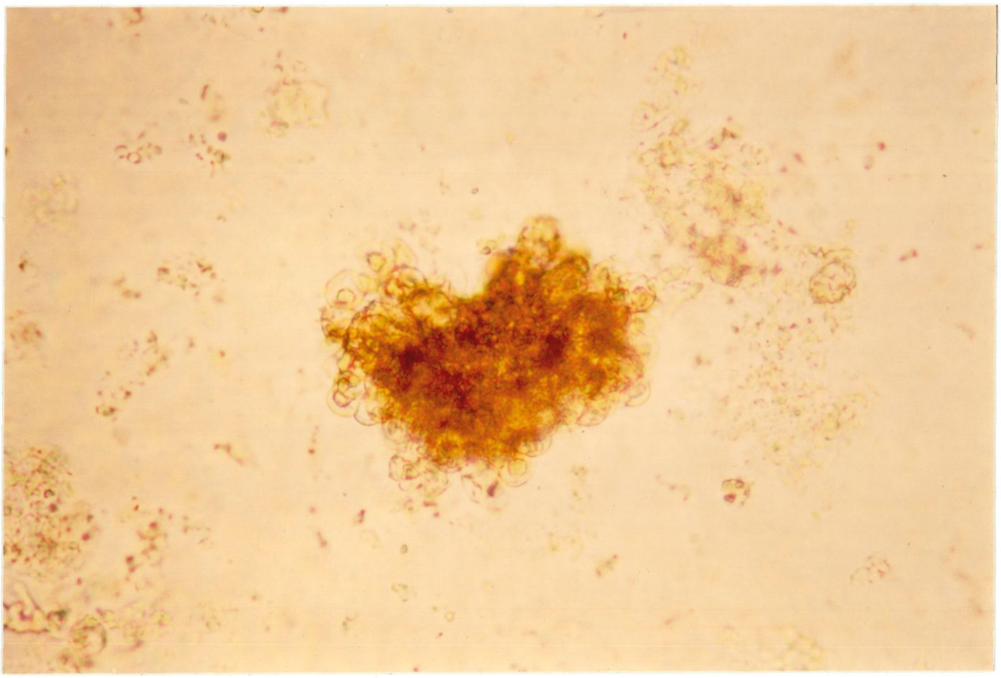
V. 6iii Colour of Kerogen

The continuum of colour changes (generally from yellow through various shades of red and brown to black) recognised by palynologists and organic geochemists as accompanying the transformation of Kerogen to petroleum have been correlated with temperatures extrapolated from known geothermal gradients or measured in boreholes or in short term laboratory experiments and form the basis for the proposal of several 'thermal alteration indices'.

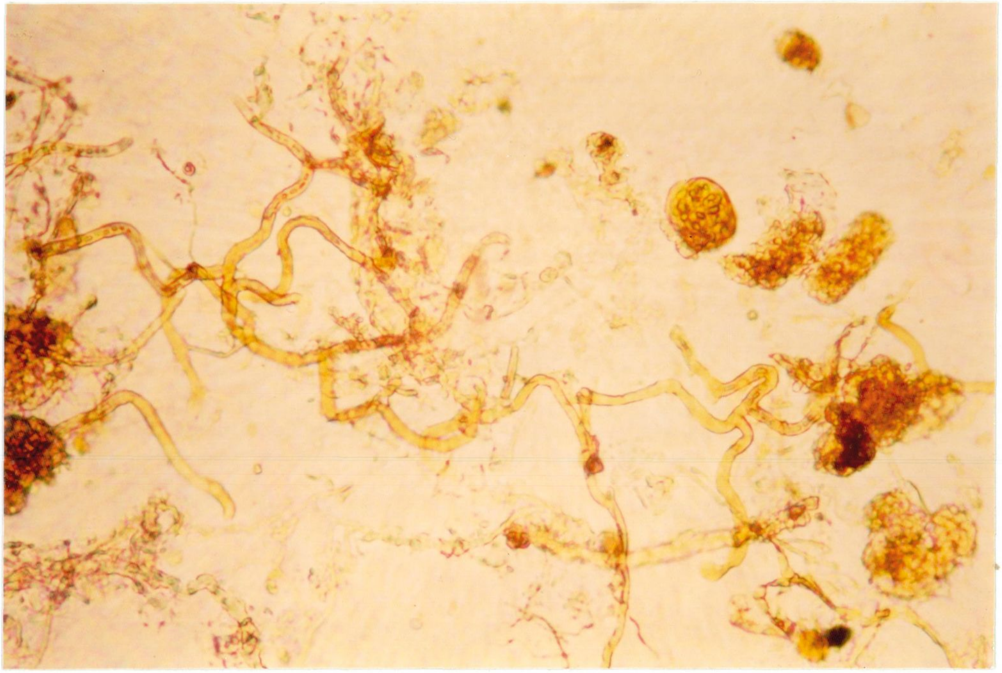
These indices like the 'yellow through brown to black colour scale' of Gutjahr (1966) the 'thermal alteration index' of Staplin (1969), the 'state of preservation index' of Correia (1971) and the 'colour and preservation scale' of Wilson (1971) have found wide application as 'a quick and dirty' (Peters et al, 1977) reference for determining the approximate level of organic maturity and predicting the oil and gas potential of Kerogenous sedimentary beds.

Most thermal alteration indices like those mentioned above are based mainly on Kerogen in the form of recognisable structural organic remains like pollens and spores. Others, as in the work of Peters et al (1977), are based on the more broadly distributed and quantitatively

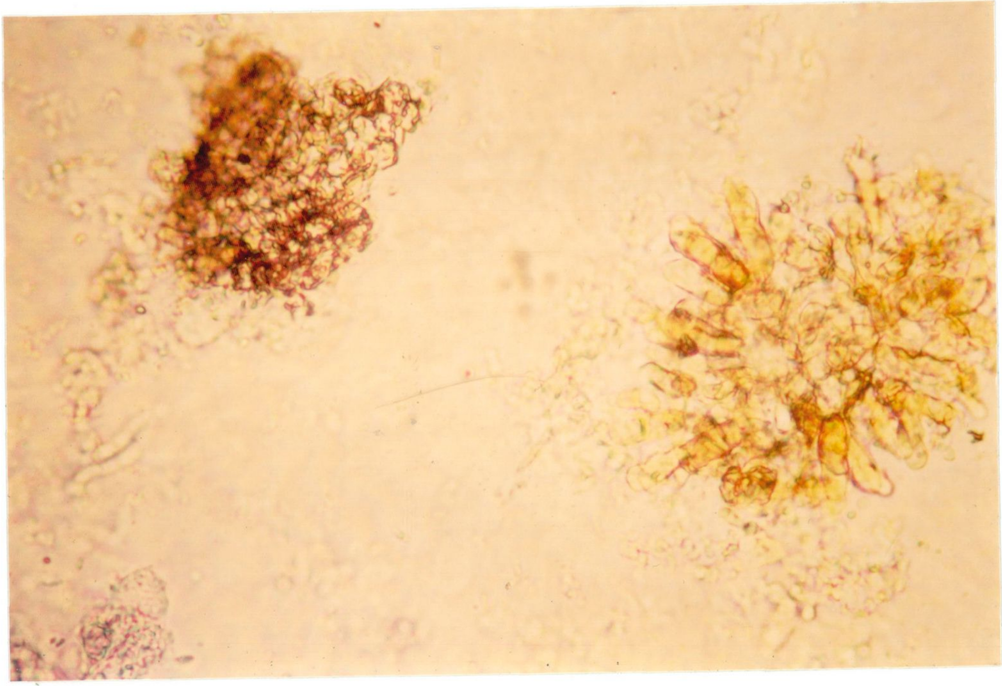
FIG. V.2.[E,F,G,H] Marine organic matter of algal-amorphous facies (Type 1 Kerogen) extracted from subaerially exposed Recent oolites from Wood and Water Cays, Eleuthera, Bahamas. Note that colour hue is darker than that of the organic matter from the stratigraphically equivalent subaqueous oolites.



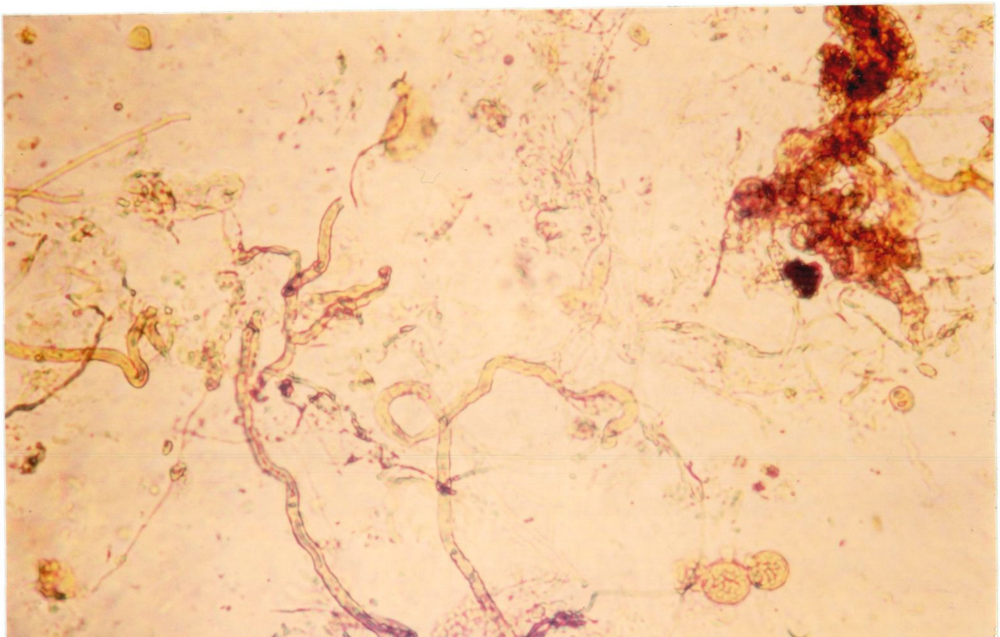
E X 200



F X 200



G X 200



H X 200

more important amorphous fraction of Kerogen and are to be recommended. Generally, the lightest coloured material is used for colour designation assuming it is not a contaminant. Peters et al have summarised the main drawbacks in the application of colour indices. Perhaps, the primary disadvantage is the subjectivity of the colour determination. The use of colour standards such as those of Ridgeway (1912) is recommended as a means of reducing the severity of this problem. Next is the fact of the differential response of Kerogenous material to thermal alteration due to the compositional differences in the starting material as pointed out by Oehler et al (1974). Gutjahr (1966),who perfected the colour technique for subsurface well studies recognised this problem and stated that the technique is valid only if the same type or species of pollen or spore is analysed with depth. Other but less significant sources of error are: a) differences in thickness of the particles which affect the observed colour and b) the possibility of presence of recycled Kerogen.

Of the several colour scales, the Thermal Alteration Index of Staplin (1969) is the most commonly used and was adopted for this study. Opinions on thermal maturity and facies alteration expressed here are based on algae. Although Staplin stated that algae and other phytoplanktons are "less useful as a 'thermometer'", Oehler et al (1974) have demonstrated that palynomorph colour changes as reflected in thermal indices such as Staplin's, and the processes producing these changes, are roughly similar to those observed in the alteration of blue green algae.

On Staplin's scale (Table V.3) the organic matter extracted from all the sub-aqueous oolite samples has a thermal index of 1 (yellow; see fig.V.1); organic matter of oolite from the intertidal islands would have a thermal index of 3 (brown; see fig. V.2). Much of the particulate organic matter show little or no alteration.Whereas the index for the subaqeous oolite which suggests their immaturity is consistent with conclusions reached by other methods, the maturity level indicated by the colour of the subaerially exposed intertidal samples are artificially high and therefore conveys a false impression

TABLE V.3

INTERPRETATIVE SUMMARY : TYPE OF ORGANIC MATTER, DEGREE OF ALTERATION, AND EXPECTED HYDROCARBONS (after Staplin, 1969).

TYPE OF ORGANIC MATTER, MATURED FACIES		ASSOCIATED HYDROCARBONS
a.	Sapropelic, amorphous	wet gas and oil
b.	Plant cuticle, charcoal	Dry gas
c.	Mixture of a. and b.	Wet gas and oil
ORGANIC METAMORPHISM		
a.	Blackening, increase in index of refraction	Wet or dry, depending on thermal alteration index
b.	Pyrobitumen	
c.	Graphite, mineralization	

THERMAL ALTERATION INDEX		ORGANIC MATTER	ASSOCIATED HYDROCARBONS
1.	None	fresh, yellow	Wet or dry
2.	Slight	brownish yellow	Wet or dry
3.	Moderate	brown	Wet or dry
4.	Strong	black	Dry gas
5.	Severe	black, with additional evidence of rock metamorphism	Dry gas to barren

of the thermal history of the sediments. This is a potential pitfall in the interpretation of results based on colour. Hunt (1979) has noted that experience is needed for the interpretation of results from this technique. For example, it is known that recrystallisation in carbonates imparts to their contained organic matter an artificially higher level of maturation than their thermal history would suggest (Hunt, 1979). It is also established that oxidising agencies and weathering cause substantial changes in transcluscency. For the subaerially exposed intertidal oolites of this study,it is thought that a combination of oxidation, recrystallisation and the cumulative effect of direct insolation is responsible for the artificially high maturity index.

If this 'deviant' result is disregarded, the Kerogen in Recent oolites, is judged to be immature. Staplin has stated that where the facies are suitable as in the present case, unaltered to moderately altered organic matter (thermal index 1 to 3) contain free and distillable hydrocarbons i.e. its potential for generating hydrocarbons is high.

V. 6.iv Fluorescence Studies

Fluorescence microscopy which seeks to measure the intensity and colour of fluorescence of Kerogen upon ultraviolet or blue light excitation, has been increasingly applied for the characterisation of the organic particles in sedimentary beds (Teichmuller, 1974; Tissot et al, 1974; Leythaeuser, 1979). In general, fluorescence intensity is high for immature samples and decreases with increasing maturity of the Kerogen.

The fluorescence intensity is one of the most useful parameters in studies where reflectance values are either low and unreliable or cannot be measured as in the present studies because of the largely opaque nature of the Kerogen in reflected light. Fluorescence intensity and reflectance are inversely proportional (Jacob, 1963, in International Committee for Coal Petrology, 1975,p.1).

Fluorescence studies are particularly useful for amorphous liptinitic organic matter (Tissot and Welte, 1978) but cannot be used for Kerogen sample from the supermature (metagenetic) stage (Heroux et al, 1979) since Kerogen is not fluorescent at this level of maturation.

Within the general framework of decreasing fluorescence with increasing maturation level, the fluorescence intensity depends on both the type of organic matter and palynomorph species; measurements carried out on different species of palynomorph or algae can be a source of discrepancy within the same sample. Heroux et al (1979) have also noted that an additional source of variation may be the different methods used in calculating maximum$\lambda$and recommend that spectrofluometry results be carefully standardised to obtain valuable diagnosis.

In the present study, a standard petrologic transmitted light microscope equipped with a source of incident ultraviolet light excitation was used to examine the Kerogen. All the Kerogen samples gave a very strong blue green to green fluorescence which was consistent with expected results for immature Kerogen with a high hydrocarbon generating potential. In the absence of a spectrofluoremeter, no attempt was made to evaluate the observations quantitatively. In addition, oolite in thin section was examined as in the method of Ferguson (1975). The ooids fluoresced to a bright blue green to green colour against the dark background of the mounting medium. In his own observations on thin sections of cemented oolite aimed at accounting for the hydrocarbon yields of the oolite, Ferguson noted that ' --- ooliths fluoresced (blue green to green) against the calcite matrix (blue), indicating that --- the hydrocarbon gas were resident in the ooliths'. He went on to report that,'in general, the ooliths showed fluorescence proportional to the amounts of hydrocarbons present' (ibid, p.22).

Since the present investigations were largely qualitative, a discussion of limiting fluorescence intensity values and their variations with Kerogen as related to the onset of hydrocarbon generation by thermal degradation of Kerogen has been deliberately omitted. The interested reader is referred to the excellent presentation by Leytheauseur et al (1979, p.5).

V. 7 CHEMICAL ANALYSIS OF KEROGEN

Elemental analysis of the Kerogen is one of the basic chemical methods employed in characterising the organic matter in sediments. This study requires a preliminary elimination of the mineral fraction and concentration of the Kerogen. This step has been already described in the section on Optical Microscopy (V.6.1).

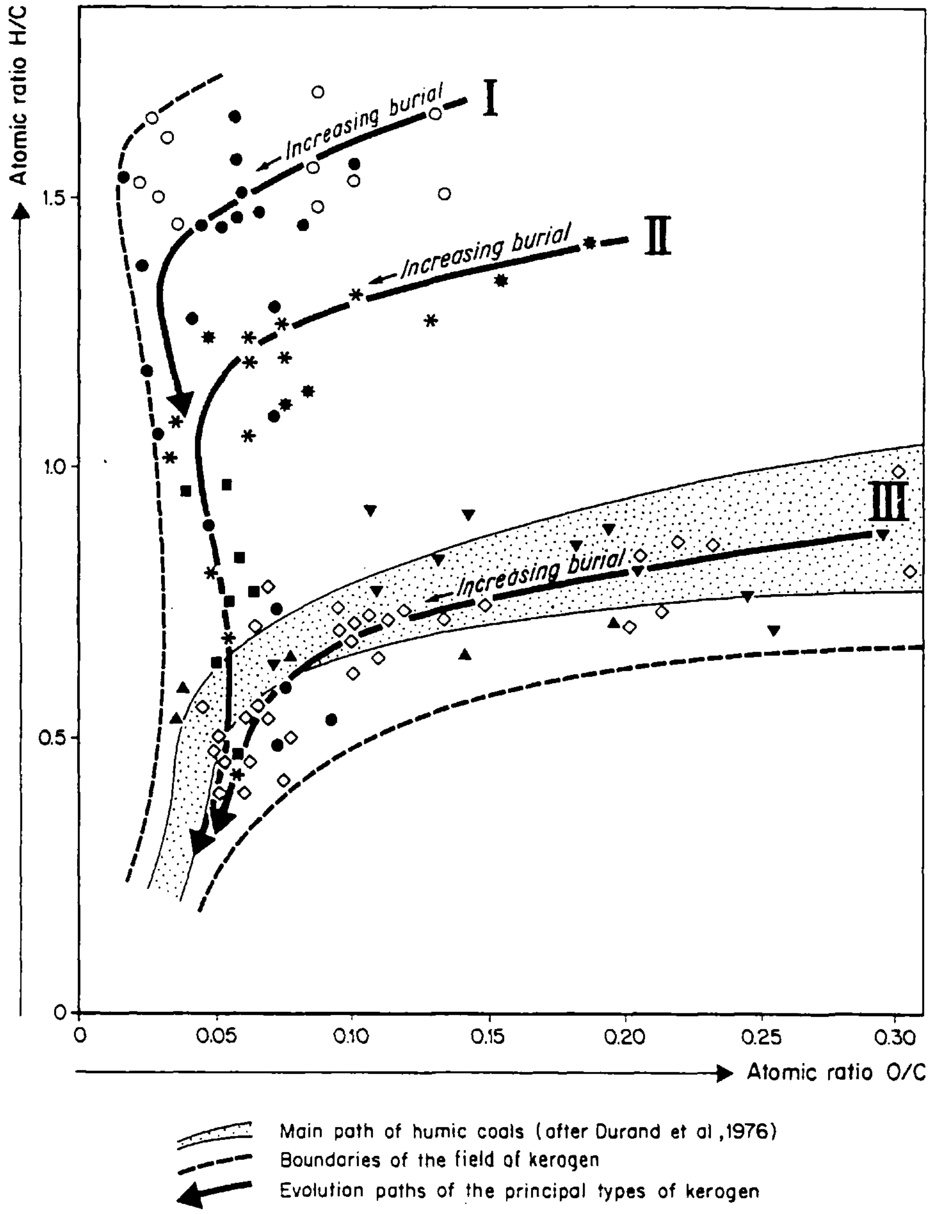
The concentrated Kerogen was dried overnight to a constant weight in an oven at 50°C. The dried Kerogen was analysed for C, H, N composition using the Perkin Elmer 240 Elemental Analyser. The results, in weight percent, for the elements were used to calculate the relevant atomic ratios [Table V.4]. Unfortunately, the instrument was not equipped to measure O which is one of the objectives of such analysis. This omission is not prejudicial to the conclusions reached in this study; the O/C ratio is not by itself diagnostic whereas the H/C ratio is. This is because the key to the type and quantity of hydrocarbons eventually generated is the hydrogen content of the Kerogen (McIver, 1967; Laplante, 1974; Harwood, 1977, Hunt, 1979).

The factors controlling the composition of a Kerogen appear to be the environment of deposition and source of the organic material, as well as the extent of maturation the material has experienced.

The global composition of the three major elements (C,H,O) is shown in fig.V.3 (after Tissot and Welte, 1978). This figure, which is a graph of atomic H/C against O/C ratios, is the basis of Kerogen classification (Forsman, 1963; McIver, 1967; Welte, 1969; Durand et al, 1972; Tissot et al, 1974; Laplante, 1974). But as has been implied above, in experiments such as the present study where O cannot be measured, the H (wt.percent) and the Atomic H/C values provide valid basis for Kerogen classification. On the criterion of hydrogen content (wt %) oil-generating Kerogens usually have 6 percent or more of hydrogen, gas generating Kerogen 3-5 percent, and nongenerating Kerogen less than 3 percent, (Hunt, 1979,p.344). Based on H/C (Atomic) values, Type I Kerogen has a high initial ratio of 1.5 or more; H/C values for Type II Kerogen are close to those for I while Type III Kerogens have

TABLE V. 4 ELEMENTAL COMPOSITION OF KEROGEN ISOLATED FROM RECENT OOLITE

	LOCATION	EVOLUTION STAGE	WEIGHT % C	H	N	ATOMIC $^{H}/C$
1	El-P-101-b	Early Diagenetic	44.5	6.2	10.4	1.7
2	106-b	" "	44	6.8	11.1	1.8
3	108-b	" "	44.2	6.5	10.6	1.8
4	109-a	" "	43.8	6.4	8.5	1.8
5	110-a	" "	44	6.4	8.4	1.7
6	112-a	" "	43.8	6.5	8.2	1.8
7	116-a	" "	44.1	6.5	9.1	1.8
8	118-a	" "	44.3	6.8	10.4	1.8
9	El-Q-201-a	" "	43.7	6.5	8.5	1.8
10	203-a	" "	44.2	6.1	9.3	1.7
11	206-b	" "	44.3	6.4	10.3	1.7
12	208-a	" "	45	6.8	11.4	1.8
13	211-b	" "	43.8	6.5	10.6	1.8
14	214-a	" "	44.2	6.5	10.1	1.8
15	217-a	" "	44.3	6.8	11.2	1.8
16	218-b	" "	43.8	6.4	8.6	1.8
17	El-R-301-b	" "	45	6.6	9.4	1.8
18	305-a	" "	44.4	6.8	10.6	1.8
19	310-a	" "	44.6	6.4	10.3	1.7
20	311-a	" "	44.2	6.4	9.8	1.7
21	312-a	" "	44	6.8	9.3	1.8
22	314-a	" "	46	6.1	8.7	1.7
23	314-a	" "	45	6.5	8.2	1.7
24	317-a	" "	46	6.3	8.5	1.7
25	El-S-401-a	" "	44.1	6.5	10.3	1.8
26	404-b	" "	43.8	6.5	9.2	1.8
27	406-a	" "	44	6.8	10.1	1.8
28	411-a	" "	44.3	6.4	9.3	1.7
29	413-b	" "	44.2	6.1	9.2	1.7
30	416-b	" "	44	6.5	10.4	1.8
31	418-b	" "	43.6	6.5	10.2	1.8
32	420-a	" "	44.1	6.6	9.8	1.8
33	El-T-501-a	" "	43.8	6.4	10.3	1.8
34	502-a	" "	44.3	6.8	10.4	1.8
35	508-a	" "	45	6.2	9.7	1.7
36	510-a	" "	44.5	6.7	9.3	1.8
37	512-a	" "	43.7	6.3	8.9	1.7
38	514-b	" "	44.2	6.5	8.7	1.8
39	520-b	" "	45.1	6.3	9.2	1.7
40	524-a	" "	44.4	6.4	10.2	1.7



Type	Age and /or formation	Basin, country	
I	Green River shales (Paleocene - Eocene)	Uinta, Utah, U.S.A.	●
	Algal kerogens (Botryococcus, etc...). Various oil shales		○
II	Lower Toarcian shales	Paris, France; W. Germany	*
	Silurian shales	Sahara, Algeria and Libya	■
	Various oil shales		✱
III	Upper Cretaceous	Douala, Cameroon	◇
	Lower Mannville shales	Alberta, Canada	▲
	Lower Mannville shales (Mc Iver, 1967)	Alberta, Canada	▼

FIG. V.3. PRINCIPAL TYPES AND EVOLUTION PATHS OF KEROGEN (from Tissot and Welte, 1978) ratios generally less than 1.

From the elemental analysis, the Kerogen isolated from Recent oolites is the oil generating Type I. The carbon content of 43-46% is low and indicates little or no carbonisation. In general, carbonisation increases with depth of burial (temperature) and age of sediment and is reflected by higher C (wt.%) content. This relationship is vividly illustrated in fig.V.4 after Laplante (1974) which also shows the variations of H and O with depth of burial. The obvious implication of the low carbon content of the Kerogen from oolites is that of a low thermal history for these sediments; that is, the contained organic matter is immature.

Before concluding this discussion, it is pertinent to mention the only other known data on the elemental analysis of organic residue isolated from Recent oolite. Bergman (in Newell et al, 1960; p.491) reported 52.42% C and 6.44% H. While his H values are very close to those obtained in this study, the C values are slightly higher. The reason for this is not clear. One suggestion is that the harsh isolation procedure adopted by Bergman could be responsible for the higher carbonisation level reported.

Another feature of the results of the present study worthy of particular comment is the high N content of the Kerogen. This depicts a high proteinaceous content as is evident from biochemical analysis of oolite (Mitterer, 1968; 1971; 1972; Trichet, 1968; Davies et al, 1978). It also depicts the immaturity of the Kerogen since it is known that the nitrogenous compounds in Kerogen, in general, undergo rapid diagenesis even at shallow depths; there is a progressive loss of the Nitrogen of peptidic bonds and functional groups accompanied by a decrease of hydrolysable nitrogen and also of the N/C ratio, (Bordovskiy, 1965; Brown et al, 1972; Kemp et al, 1972; Huc and Durand, 1974). The remaining nitrogen in Kerogen generally amounts to 2 to 3% by weight and may be essentially engaged in heterocyclic condensed structures. (Tissot and Welte, 1978).

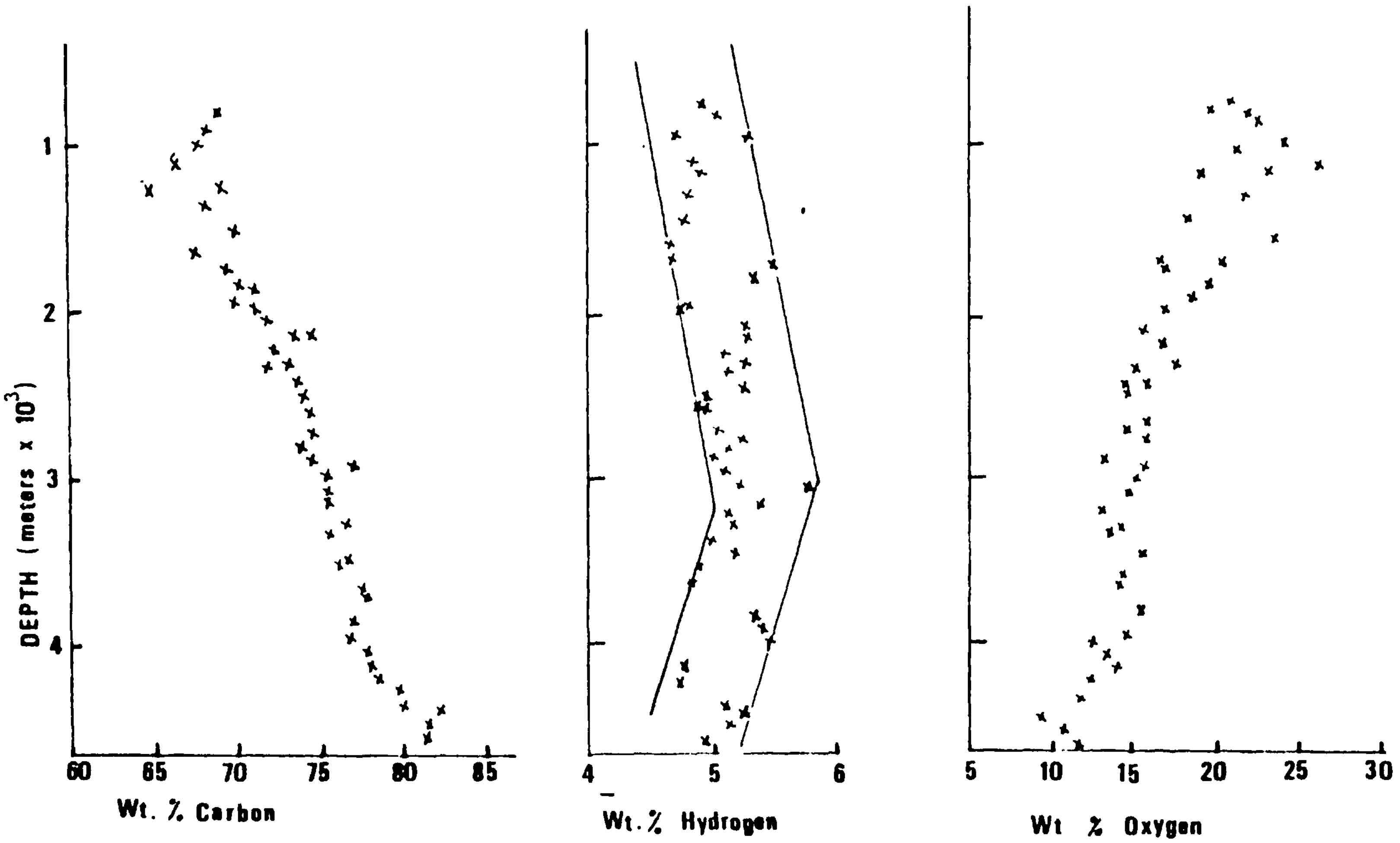


FIG. V.4 CARBONISATION OF KEROGEN WITH DEPTH
SOUTH PECAN LAKE FIELD, LOUISIANA, U.S.A. (after La Plante, 1974)

V. 8 PYROLYSIS TECHNIQUE

'Pyrolysis is probably the best routine tool for determining type and maturation of organic matter at the same time' (Tissot and Welte, 1978, p.464). Several variations of this technique have been developed by various workers (Bordenave, 1970; Gransch and Eisma, 1970; Baker, 1974a; Tissot et al, 1974; Claypool and Reed, 1976; Leventhal, 1976; Espatalie,et al 1977).The basis of the various pyrolysis methods is that petroleum generating process can be simulated by heating presumed source bed samples in an inert atmosphere. In general, experimental temperatures considerably higher than those involved in petroleum generating reactions are necessary so that appreciable reaction can occur in a reasonably short time.

An added virtue of most pyrolysis methods is that they offer a semi-quantitative evaluation of the genetic potential and transformation ratio. Organic matter of a source bed can be classified into 2 broad categories, a 'reactive' and an 'inert' parts both of which occur in varying proportions depending upon the type of organic matter. The reactive part represents that fraction of the TOC which upon further burial will be converted into petroleum. This has been termed 'useful carbon' by Tissot,Deroo et al (1978) and is pyrolysis degradable. The inert part, on the other hand, remains essentially unaffected by temperatures consequent upon burial and has been referred to as 'dead carbon' (Hood and Castano, 1974), a term which the writer dislikes.

The dead carbon is thought to have a dual origin (Leythaeuser et al, 1979). Part of it is original and inherited from Kerogen precursor material as inertite particles e.g. air borne transported charcoal; the other and by far more dominant part originates as a by-product of petroleum generating reactions and is termed 'Residual or Fixed Carbon', a term preferred by many workers and used in a sense synonymous with the 'dead carbon' of Hood and Castano.

For the present study, the pyrolysis method of Gransch and Eisma (1970) which compares the total organic carbon CT or TOC with the residual carbon CR or FC was used. This ratio, CR/CT or FC/TOC is known as the carbon ratio. A development from an original technique in Coal chemistry (Hilt, 1873; White, 1915; Thom, 1934), it was initially proposed by the authors as a quick and inexpensive method to evaluate the degree of thermal maturity of a presumed source bed sample but was later to be used also in characterising the Kerogen type. This ratio has since been used widely and the experimental procedure has been automated by LeTran and Van der Weide (1969).

V. 8. i Carbon Ratio (CR/CT) OR (FC/TOC)

CT or TOC values were determined as described in section V.3. CR or FC was determined on whole rock sample as in the original procedure of Gransch and Eisma after pyrolysis for 1½ hours at 900°C in a current (40cm^3/min) of N_2 except that the samples were not pre-extracted with solvent. This is believed not to affect the results adversely. Barker (1974) briefly reviewed the possible effect of this omission and concluded that the influence of bitumen on results is negligible for Recent sediments. This is borne out by the very low bitumen ratios of Recent oolite (see section V.9.ii).

The influence of the mineral matrix of the sample on CR/CT ratios has received comment by some workers. In their original discussion, Gransch and Eisma (1970), estimated the influence of the inorganic matter to be of the order of 0.05 and indicated that, though slight, this influence should be taken into account. Subsequent workers (Barker, 1974; Souron et al, 1977) were of the opinion that this influence is very minimal and that it is not necessary to isolate the Kerogen for most pyrolysis experiments. Recently Espatalie et al (1980) have revived the debate about the effect of the mineral matrix. Their experimental results show that any influence is confined largely to shales or clayey sediments and especially montmorillonite and illite bearing sediments but non existent or negligible for carbonate facies such as the oolites in this investigation. The experimental results of Horsfield and Douglas (1980) are similar.

In brief, the pyrolysis causes thermal cracking of the Kerogen

TABLE V. 5 RESULTS OF PYROLYSIS OF SELECTED RECENT OOLITE 'WHOLEROCK' SAMPLES

	SAMPLE LOCATION	CT OR TOC	% Wt.LOSS ON PYROLYSIS AT 900°C	CR OR FC	$^{CR}/_{CT}$ or $^{FC}/_{TOC}$
1	El-P-101-b	1.86	43.6	0.32	.2
2	106-b	1.6	44.8	0.22	.1
3	108-b	3.0	44.4	0.38	.2
4	109-a	2.89	44.2	0.57	.2
5	110-a	2.72	44	0.48	.2
6	112-a	2.35	43.8	0.45	.2
7	116-a	2.44	44	0.54	.2
8	118-a	2.7	44.7	0.41	.2
9	El-Q-201-a	1.87	44.3	0.37	.2
10	203-a	2.4	43.5	0.48	.2
11	206-b	1.23	44.6	0.12	.1
12	208-a	2.44	43.7	0.56	.2
13	211-b	2.51	45.1	0.5	.2
14	214-a	1.7	43.6	0.39	.2
15	217-a	1.86	42.6	0.24	.1
16	218-b	1.52	43.8	0.27	.2
17	El-R-301-b	1.56	43.6	0.32	.2
18	305-a	2.6	42.7	0.56	.2
19	310-a	3.24	42.5	0.36	.1
20	311-a	2.89	45.8	0.46	.2
21	312-a	3.18	43.9	0.45	.1
22	314-a	2.56	44.1	0.41	.2
23	317-a	2.2	44	0.38	.2
24	320-a	2.41	43.4	0.43	.2
25	El-S-401-a	2.37	44.6	0.55	.2
26	404-b	2.36	44	0.43	.2
27	406-a	1.92	43.5	0.46	.2
28	411-a	2.72	44.5	0.31	.1
29	413-b	2.56	43.4	0.4	.2
30	416-b	2.58	44.2	0.53	.2
31	418-b	2.37	44.5	0.41	.2
32	420-a	2.63	42.4	0.5	.2
33	El-T-501-a	1.85	43.2	0.34	.2
34	502-a	2.0	38.5	0.35	.1
35	508-a	2.43	44.3	0.28	.1
36	510-a	2.33	43.6	0.51	.2
37	512-b	1.98	42.9	0.49	.2
38	514-b	2.12	44.2	0.4	.2
39	520-b	2.47	44.8	0.4	.2
40	524-a	2.63	44	0.34	.1

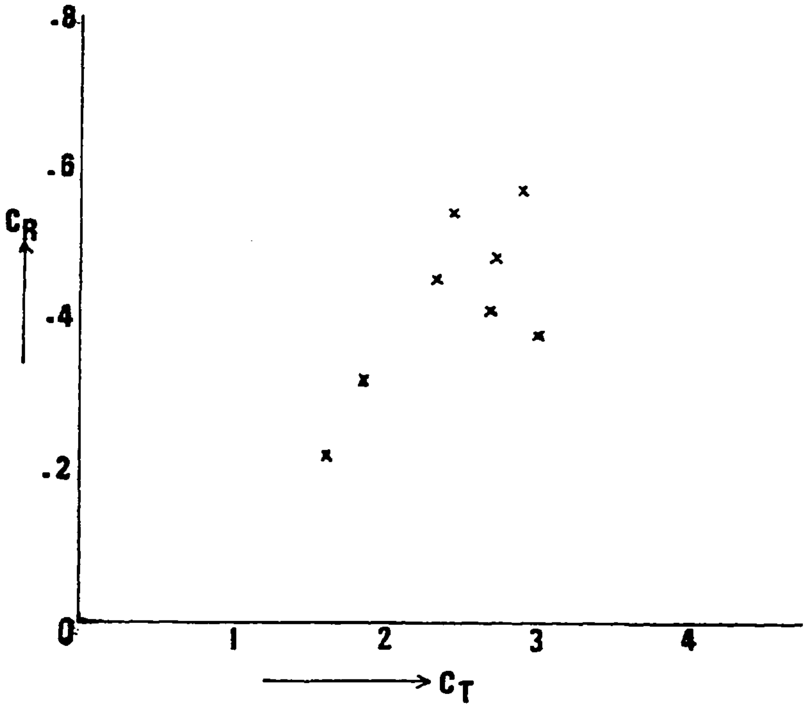
in the sample. The 'useful carbon' of the Kerogen is converted into hydrocarbons and volatilised and flushed out by the stream of N_2 leaving behind a graphitic residue (CR). The initial sample (< 1gm) is weighed before and after pyrolysis and the percentage weight loss determined as in standard thermo-gravimetric analysis. The percentage weight loss is necessary for normalising the weight of sample (about 2-5mg) analysed for CR. The value of CR was determined and expressed as a percentage of the whole rock sample as in CT determination.

The results of the present investigation are presented in Table V.5 and expressed in fig.V.5.

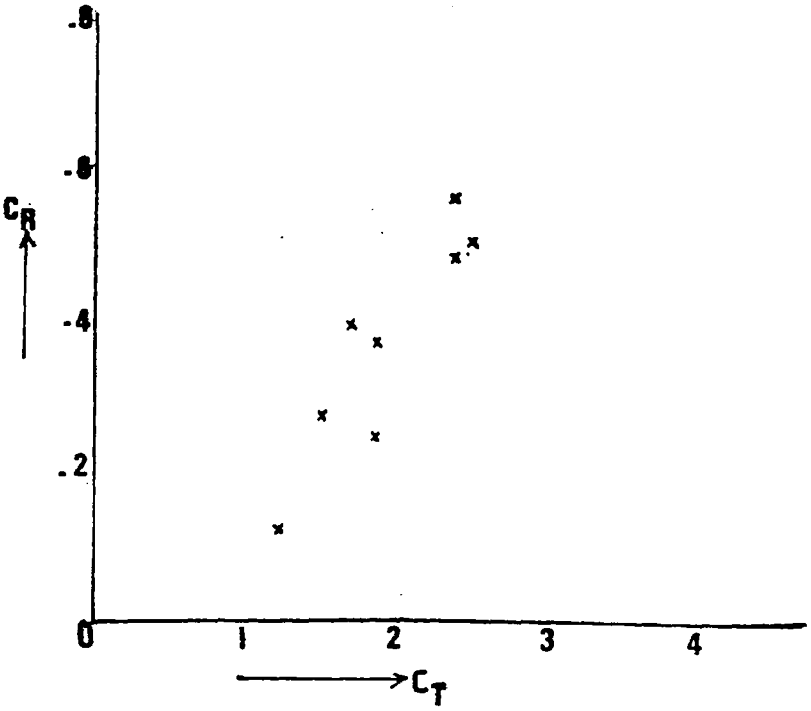
In the method used, the amount of volatile or useful carbon CT-CR is roughly equal to the 'S_2' peak of the Rockeval method of Espatalie et al (1977) and is a good indication of the hydrocarbon generating potential of the samples.

If a Kerogen contains a large proportion of reactive carbon, the CR/CT ratio is low and it is said to be immature. Conversely, a greater proportion of residual carbon i.e. higher CR/CT ratio means the Kerogen has probably generated and expelled hydrocarbons and is indicative of thermal maturity. Under this scheme, the Recent oolites in this experiment are thermally immature. CR/CT values do not only give an indication of thermal maturity but also of the predominant type of organic matter and by implication,its hydrocarbon generating potential. In their original paper, Gransch and Eisma (1970) proposed some limiting values. If the CR/CT ratio is below 0.6, it indicates organic matter favourable to the generation of hydrocarbons. On the other hand, if samples of various sediment layer of one section are compared, the unfavourable organic matter can be distinguished by their high CR/CT ratios (0.6-0.8). The most recent support of this concept has come from Heroux et al (1979) who found that Kerogen types I and II will give CR/CT ratios lower than 0.4 to 0.5 for Recent Kerogen whereas a Type III Kerogen of the same stratigraphic age will have CR/CT ratios in the range of 0.6 to 0.7. Based on these limiting values, the Kerogen of the Recent oolite, though thermally immature, is judged to have a very high hydrocarbon generating potential.

FIG.V.5 CR/CT PLOTS FROM PYROLYSIS OF RECENT OOLITES FROM THE BAHAMAS

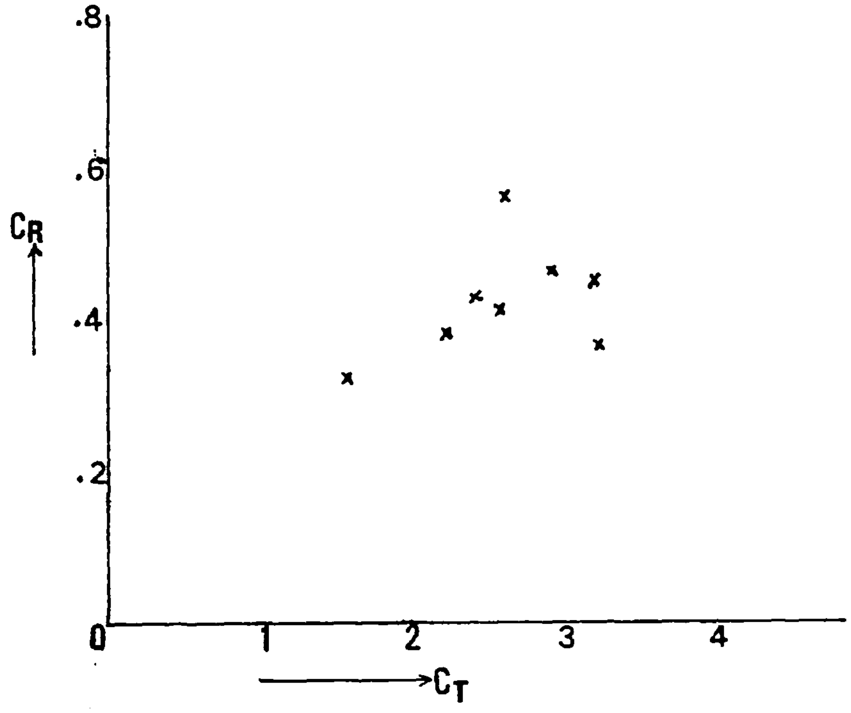


Selected Samples from traverse P

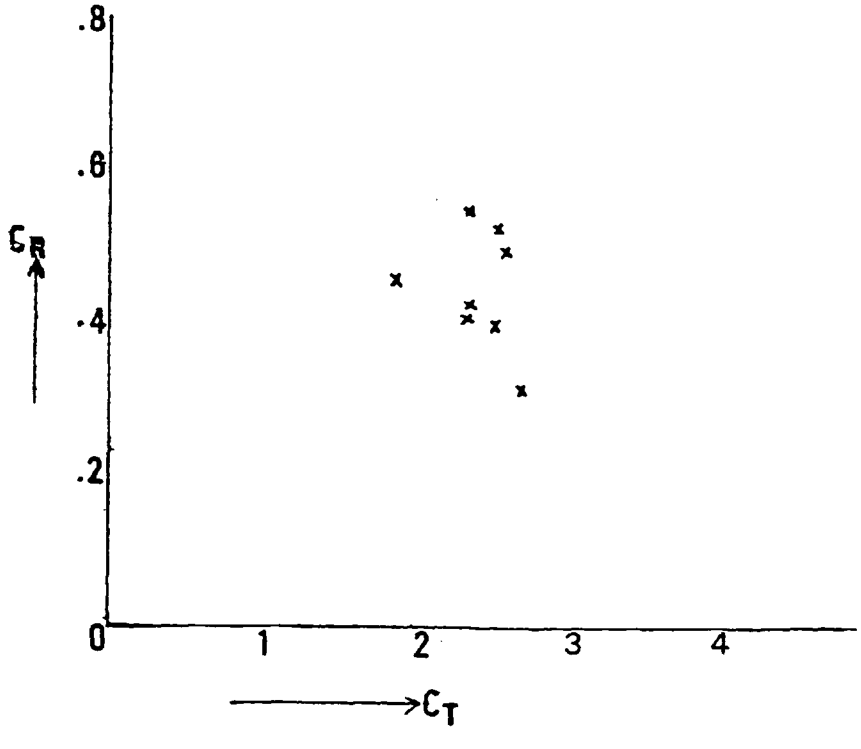


Selected Samples from traverse Q

FIG.V.5 contd.

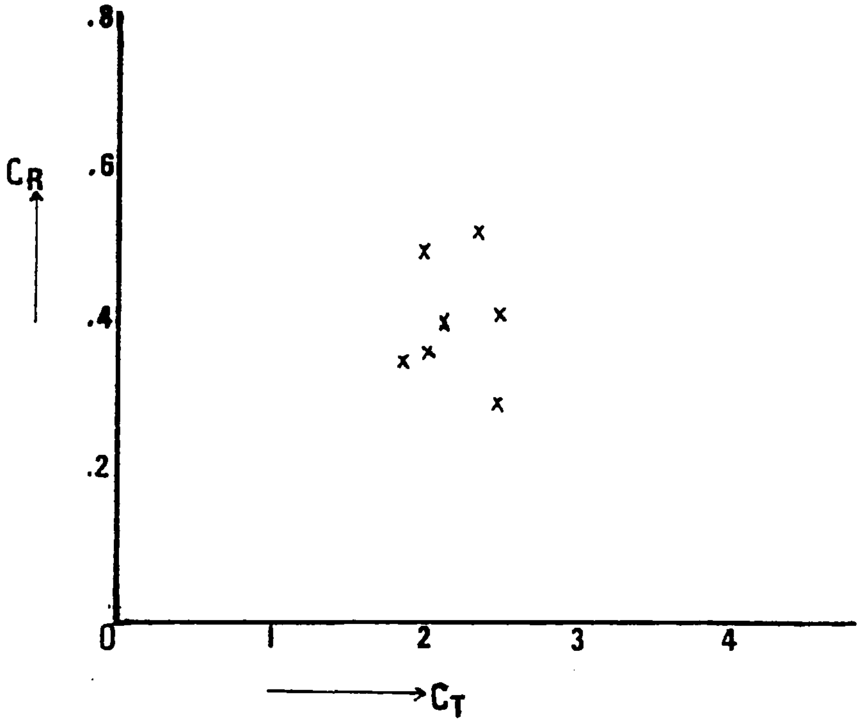


Selected Samples from traverse R



Selected Samples from traverse S

FIG.V.5 contd.



Selected Samples from traverse T

The usefulness of CR/CT values in indicating Kerogen types is, ironically, its major drawback as a maturation index particularly in a hole spanning different Kerogen types. For example the change of sedimentation from one bed containing a more aliphatic Kerogen (Type I or II) to another bed containing a more aromatic type is also marked by an increase in the CR/CT ratio which can be erroneously interpreted as an increase in maturation level. Tissot and Welte (1978) and Hunt (1979) are quick to point out this attendant ambiguity since, for instance, high CR/CT ratios may correspond either to mature source bed sample or relatively immature sediments containing aromatic rich Kerogen. This limitation has prevented the CR/CT ratio becoming the effective characterisation tool it was hoped to be.

However, it must be added that in relatively simple situations where samples are of the same lithologic type and from the same stratigraphic level, the CR/CT ratio is a reliable indicator of both the maturity and type of contained organic matter.

V. 9 CHARACTERISATION OF ORGANIC MATTER BASED ON BITUMEN

Certain parameters used in the characterisation (type and level of maturation) of organic matter are based on the solvent extractable fraction termed bitumen. Among these are a) the ratio of total organic extract (TOE) to the total organic carbon (TOC); b) the composition of this extract as determined by successive elution of saturates, aromatics and resins on a chromatographic column generally after desulphurisation and precipitation of asphaltenes; c) the gas chromatographic pattern of total alkanes (CPI or OEP).

Parameters a) and c) were employed in this study while b) was omitted for technical reasons (see Section V.9.ii).

V. 9.i Bitumen Extraction

It is obvious that the first and crucial step of this analytical technique is to isolate the bitumen. For this, the solvent methods are the more popular and most effective; other methods like the ultrasonic probe extraction introduced as more convenient alternatives have been beset with problems of contamination and have been dropped (Hunt, 1979).

Of the two solvent methods available, that is, Soxhlet and Reflux extractions, experience at the Source'Rock'Laboratories at Imperial College, London, has shown that the soxhlet method offered the most balanced compromise between the ideals of convenience, efficiency of extraction and reproducibility. The average extract yield by this method was found to be 9% higher than the reflux method (Kinghorn - unpublished research).

The selection of a most suitable solvent has always been a major problem in extraction experiments. Central to this problem is the observation by Murphy (1969) that the compounds removed from a specimen are largely determined by the polarity of the extracting solvent. Carbon tetrachloride ($CHCl_4$) was one of the earliest solvents used (Trask, 1942). Its successors like chloroform ($CHCl_3$) and trichloroethane (CH_3 CCl_3) still find restricted use.

In the early 1950's, a triple mixture of benzene-methanol-acetone which had the distinct advantage of removing the organic compounds in the presence of much larger amounts of water and at temperatures below 100°C, was introduced by Hunt and Meinert (1954). Smith (1954) used this mixture in his extraction experiments. Stevens et al (1956), on the other hand excluded acetone from the mixture for their own work. Brenneman and Smith (1958) evaluated the effectiveness of forty different individual solvents and combinations and advocated the use of a mixed benzene, methanol and acetone. But Bonnet (Unpublished Ph.D Thesis, 1958) noted the very low yield of Stevens et al, compared to that of Smith for samples from the same location (Grand Isle, Louisiana) and considered the possibility that acetone condensation contributed to the higher yields of Smith. To resolve the problem, Bonnet performed dual extractions on certain sediments to compare the yields given by an acetone-free solvent with that given by a mixture containing acetone. He found that, in general, a somewhat larger extract was obtained with the benzene-methanol mixture.

As a result of later investigations by other workers, acetone has been excluded from solvent mixtures because it tended to add polymers and other impurities to the bitumen extract (Hunt, 1979). There are, however, researchers like Ferguson (1962) who believe that mixed solvents remove excessive amounts of non-hydrocarbon material which tend to interfere with the chromatographic separation of the extract. Despite such objections, benzene-methanol mixtures have found almost universal application in solvent extractions. Consequently, a Benzene-Methanol azeotrope mixture was used in the present study.

Preweighed samples of oolite were washed in slightly acidified distilled water to get rid of any external organic coatings, then dried at room temperature and pulverised (< 63 microns) in small portions in a TEMA mill. Each sample was completely homogenised, dried overnight at 50°C and a weighed aliquot (about 200gm) was transferred to a prewashed 60 X 175mm size cellulose thimble in which a spiral of filter paper had been placed. In test experiments, it was discovered that packing the sample around a filter paper spiral prevents the solvent from channelling down one side of the thimble and improved considerably the efficiency of the extraction (Kinghorn - personal communication).

Each sample was soxhlet extracted for 22 hours with an azeotropic mixture of approximately 60% benzene and 40% methanol (boiling point, 58.5°C). All solvents were re-distilled prior to use and extractions using thimbles only showed no detectable C_{15}+ residues. Following extraction, the solvent was fractionally distilled through a column packed with glass fenske helices to reduce 1.5 litres of solvent to a small bulk. The latter is transferred to a little container and evaporated to dryness at 50°C in an oven equipped with an air extractor. It is believed that this procedure reduces to a minimum potential losses of the more volatile compounds associated with other methods used to concentrate the extracts.

The amount of extract (TOE) is weighed and the result expressed as a percentage of the weight of the aliquot used.

In concluding this discussion on solvents used for bitumen extraction, it is pertinent to point out that because of the preoccupation of many research laboratories with issues of safety, the use of benzene in solvent extractions is being gradually phased out; as a result, the chlorinated solvents are, again, finding increasing use.

V. 9.ii Abundance of Bitumen (TOE/TOC)

The abundance of bitumen may either be expressed as bitumen ratio or as hydrocarbon ratio (Tissot and Welte, 1978). The former parameter is used here; it is the ratio, expressed in percent of the total organic extract (TOE) over the total organic carbon (TOC) and permits the evaluation of a sample 'yield' (Heroux et al, 1979). This 'yield' is very weak for immature organic matter. In such cases, the 'yield' is equivalent to the transformation ratio of Tissot and Welte (1978). It starts increasing at the threshold of the 'oil window' and then decreases again in the metagenic stage.

Four extractions were carried out on 3 Recent and 1 ancient oolite samples before the experiments had to be aborted due to a breakdown of the degreasing plant which made further work impracticable. The results are presented in Table V.6. The values of 560-640 ppm are at least twice those (220ppm and 200ppm respectively) reported from Recent oolites by Bergman (in Newell et al, 1960 p.491) and Ali-Zade and Shoikhet (1967, p.526). This is thought to be related to the enhanced effectiveness (up to 75%: Kinghorn, Unpublished research) of the extraction technique employed in the present study.

The two results (for cores E and G) with asterisks are corrected values. It was discovered, following a visual examination that these extracts had, not only a greenish hue due probably to chlorophyll, but also, salt crystals. The presence of these salt crystals explained the artificially high initial values of these two extracts (.14 and .11wt.% respectively). Because of the known

TABLE V.6

EXTRACTABLE ORGANIC MATTER (BITUMEN) IN CARBONATE OOLITE

SAMPLE NO.	LOCATION	AGE	BITUMEN CONTENT (TOE)	TOC	BITUMEN RATIO TOE/TOC
Core E	Beach sand (10 - 20cm) Eleuthera	Recent	* .064 wt.% or 640ppm	2.85 wt.%	.02
Core G	Shoal sand (15 - 30cm) Eleuthera	Recent	* .061 wt.% or 610ppm	2.36 wt.%	.02
Core I	Wood Cay (20 - 30cm) Eleuthera	Recent	.055 wt.% or 560ppm	1.87 wt.%	.03
KO 19	Outcrop Kirklington, Oxfordshire	Ancient	+ .063 wt.% or 630ppm	.78 wt.%	.08

* Corrected Values

\+ Artificially low due to probable effects of weathering

*+ See text (Section V.9.ii) for comments

solubility of inorganic salts in extraction solvents, this problem had been anticipated.

The salt crystals were eliminated by slightly modifying the technique of recovering the solvent using a separating funnel. The solvent extract was recovered with about 3mls of water in a glass vial, sealed with a cork wrapped in aluminium foil and allowed to stand at - 25°C for approximately one hour. At this temperature, the solubility of NaCl in solvent was found to be below the limits of detection. With the brine frozen, the solvent was easily recovered and concentrated in the usual way. The weights of these two extracts were found to be of the same order of magnitude as the other extract from the stratigraphically equivalent Wood Cay sample.

In absolute terms, the values of organic extracts from Recent oolites are quite high compared to extracts from other Recent sediments (see Smith, 1954; Stevens et al, 1956; Bonnet, 1958). Given the high organic matter content of Recent oolites, this is hardly surprising. Nevertheless, the high extract values would appear to be indicative of some degree of chemical transformation already taking place in these Recent oolites. In fact Ali-Zade and Shoikhet (1967) who found that between 26.1% and 30.9% of the bitumen extracted from Recent oolites were 'oils', argued that this proved that bitumen transformation in the direction of oil formation was operative within these Recent deposits. While it is admitted that the soluble organic extracts from Recent oolites may not be mere 'inherited' products from the marine organisms within the ooids, any extensive transformation is not supported by the low bitumen ratios of 20 to 30 mg/g of total organic carbon obtained in this study. There are some limitations in using the bitumen ratio to determine the stage of maturation of a source bed since it is also a function of the Kerogen type and the geothermal gradient occuring in the basin. Tissot et al (1978) took a useful step in eliminating the influence of Kerogen type by comparing the hydrocarbons used for hydrocarbon ratio determinations, to the pryolysis degradeable organic carbon rather than the TOC. Even then, short range migrations might alter the amount of bitumen present in a sedimentary bed.

In view of the uniformity of the samples investigated and, by corollary , their contained organic matter, plus the indigenous origin of the extract from oolites, the problems discussed above have little bearing on the results from this work.

The 'yield' from the one ancient oolite sample extracted for comparison is about the same order of magnitude as those of the Recent sediments. The value is considered anomalously low, given the age of the sample (Jurassic). Again, this was not totally unexpected. The sample was taken from a surface outcrop and despite attempts to remove suspected weathered portions with a diamond saw before crushing for extraction, it is thought that the low result is due to the effect of weathering. Studies by Leythaeuser (1973) and by Clayton and Swetland (1978) on the effects of weathering on organic matter in rocks showed that $C_{15}+$ hydrocarbons and total bitumen losses of about 50 per cent can occur in outcrops down to depths of 3 metres. An additional factor might be that lack of burial and/or destructive diagenesis resulted in a lower transformation ratio than the age of the rock would suggest.

V. 9.iii The Gas Chromatographic pattern of Alkanes [CPI]

The progressive change in the distribution of long-chain n-alkanes typified by a decrease in the odd-even ratio of these alkanes in going from recent sediments to ancient rocks to crude oil, is the basis of the Carbon Preference Index. Proposed by Bray and Evans (1961), it is probably the most discussed of the methods based on the chemical composition of bitumen. Its verification in several sedimentary basins by various authors has resulted in many expressions of this ratio (Philippi, 1965; Albretch, 1970; Scalan and Smith, 1970; Nixon, 1973; Tissot et al, 1977).

The first step in obtaining the gas chromatographic pattern of n-alkanes from which CPI is calculated, is the fractionation of the solvent extract into alkanes, aromatics and asphaltene fractions.

Of the methods available for fractionation, most workers advocate column adsorption chromatography (Smith, 1954; Baker, 1962;

Hunt, 1974). Urea adduction techniques have also been successfully applied for this purpose (Zimmers-Cheid et al, 1950; Evans et al, 1957; Meinschein and Kenny, 1957; Murquart et al, 1968) as have been methods based on molecular sieves (see Gibbs, 1970). In recent years, separation by thin layer chromatography has become popular.

Kinghorn (unpublished research) has studied these methods in demonstration experiments and identified two broad problems common to all of them: a) the degree of separation may be limited; b) losses are associated with the separation which cannot be quantified. These problems were also recognised by Hunt (1979, p.451) who stated that such separations are not quantitative and advised that periodic monitoring, during separation of extracts, by mass spectometry is necessary to ensure that separations are adequate for the problem being studied.

In the study of recent sediments, the problems outlined above are compounded by the generally low bitumen yields. To obviate the need for separation of extract prior to analysis, Kinghorn recommends the gas chromatographic analysis of 'whole extract' dissolved in an effective eluting solvent like chromatographic grade benzene. A standard alkane mixture of known composition can then be used for identifying the individual alkanes on the basis of their elution times. In test experiments, non separation of the extract was found not to affect in any obvious way, the results sought. An added advantage of this method is that the extract is available 'intact' for follow up experiments like elemental analysis, et cetera.

This alternative procedure was pointed out to the author by Dr. R. R. F. Kinghorn (personal communication, 1979) following the shutdown of the extraction laboratory for technical and safety reasons and was applied to obtain the results presented here.

A Perkin Elmer F.30 Gas Chromatograph equipped with a 12m x 1mm o.d. glass column (Si oil ov-1 SCOT stationary phase). Column conditions for the analysis were: initial 140°C temperature programmed at 3°/minute to 268°C, using helium (10 psi) as carrier gas. The analysis was carried out under stringent dilution/injection/instrument sensitivity conditions. The ratios were calculated, via peak areas determined on an attached electronic integerator (model PE M-2), using the formula of Hunt (1974) as follows :

$$\mathrm{CPI} = \frac{\dfrac{C_{25} + C_{27} + C_{29} + C_{31}}{C_{26} + C_{28} + C_{30} + C_{32}} + \dfrac{C_{25} + C_{27} + C_{29} + C_{31}}{C_{24} + C_{26} + C_{28} + C_{30}}}{2}$$

The chromatograms and results are presented in fig. V.6.

The CPI, in its various formulations,has found wide application in source bed evaluation. According to Bray and Evans (1961), CPI values range from 2.5 to 5.3 for recent muds, from o.98 to 2.3 for sedimentary rocks, and from 0.92 to 1.13 for crude oils. This change occurs because the transformation of organic matter to petroleum adds paraffins with an odd/even ratio of 1, thereby reducing the CPI ratio as the sediments become more mature. Under this scheme, the extracts in the present experiment [ratios, 1.1 - 1.3] would appear to have the consistency of crude oil although the chromatographic pattern suggests otherwise; herein lies one of the limitations to the universal applicability of the CPI. This and other limitations of its use, have been effectively summarised by Tissot and Welte (1978)and Hunt (1979).

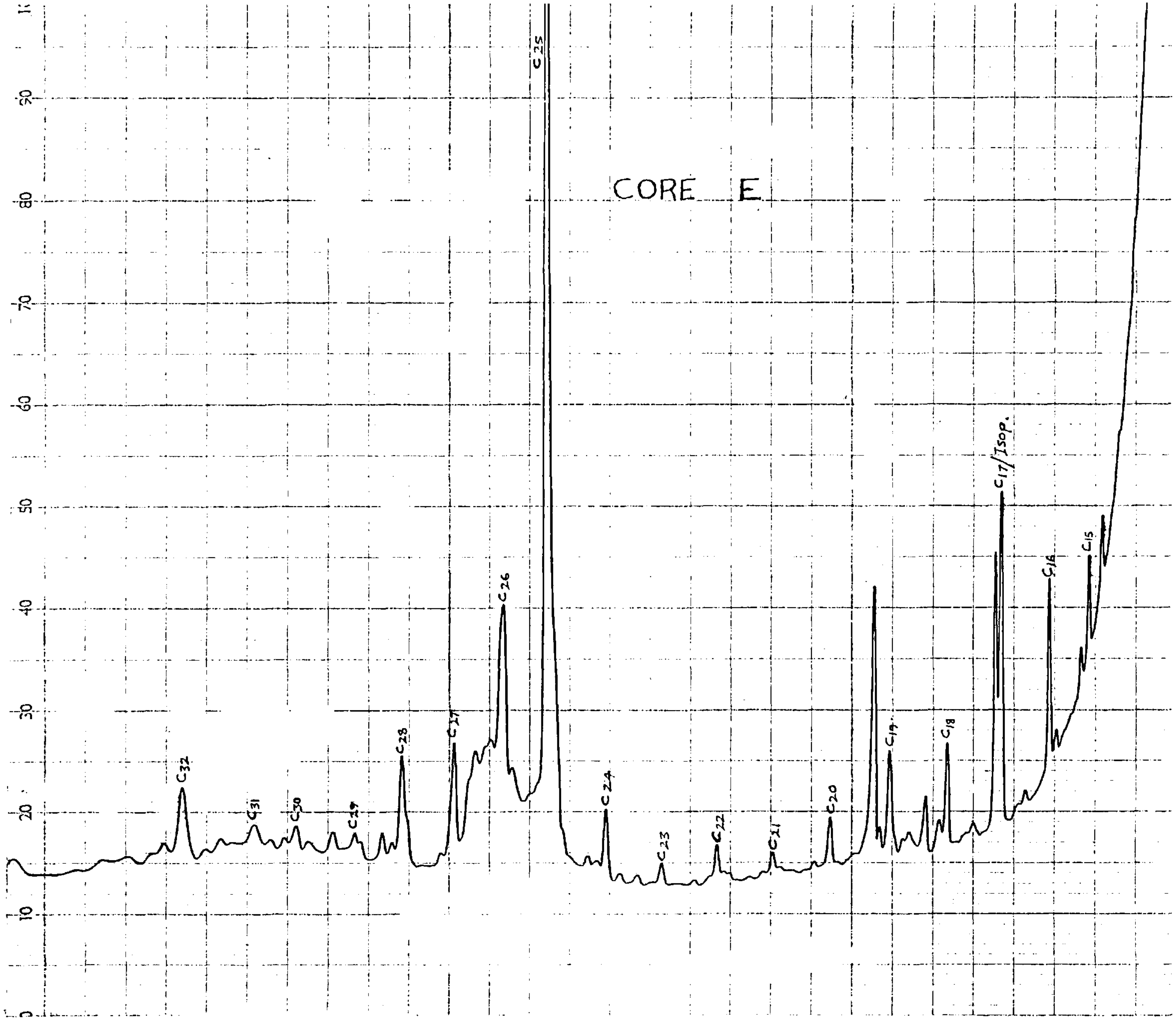
Of relevance to the present results is the recognition that CPI values are influenced by differences in the type of organic matter. For example, sediments whose organic content is composed of only or dominantly marine organisms (phytoplanktons, bacteria, et cetera) will have a CPI near 1 both for immature surface sediments and at all depths (Tissot and Welte, 1978, p.462; Hunt, 1979, p.302). The reason is that, unlike terrestrial organic matter, marine organisms synthesise odd-carbon chains only in the low molecular weight range but show little odd or sometimes, even predominance,in the C_{24} - C_{33} range. Many carbonate and evaporite type sediments containing mostly autochtonous marine organic matter exhibit this trend (Brooks, 1970; Powel and McKirdy, 1973; Tissot and Welte, 1975; Dembicki et al, 1975). It is in this light that the CPI values for the extracts from these Recent oolites should be viewed. No opinion is offered on the CPI result of the one ancient sample analysed for comparison because, as has been pointed out, weathering effects would be expected to have altered the intrinsic distribution of its contained hydrocarbons.

When, as in the present extracts, the CPI is not diagnostic, the n-alkane distribution pattern is useful in its own right for a visual interpretation of the source and maturity of the extract. Clark and Blumer (1970) have noted two principal sources that contribute hydrocarbons to the marine environment: a) Fossil fuels either through pollution or seepage b) recent organisms.

The absence of several carbon numbers [see fig. V.6] in the present extract precludes the first source. Besides, the distribution bears a striking resemblance to several published results of hydrocarbons extracted from microscopic algae and bacteria (see Clark and Blumer, 1970; Gelpi et al, 1970; Schneider et al, 1970; Blumer et al, 1971; Youngblood et al, 1973). This similarity suggests little dilution of the inherited bitumen by thermally generated hydrocarbons; it would appear that large parts of the extracts comprise of geochemical fossils (according to the terminology of Tissot and Welte, 1978). These compounds represent a first source of hydrocarbons in the subsurface. The bulk of other data, indicate that with deeper burial and heat, both this bitumen and the Kerogen will be transformed to petroleum.

FIG.V.6. Gas chromatograms of analysis of bitumen 'whole extracts', revealing the alkane composition of oolites.
[see text for GC conditions]

Core E = Recent Beach oolite
Core G = Recent Shoal oolite
Core I = Recent Wood Cay oolite
Kirk KO19 = Ancient Kirklington oolite


CORE E
C_{25}
C_{26}
C_{27}
C_{28}
C_{29}
C_{30}
C_{31}
C_{32}
C_{24}
C_{23}
C_{22}
C_{21}
C_{20}
C_{19}
C_{18}
C_{17}/Isop.
C_{16}
C_{15}
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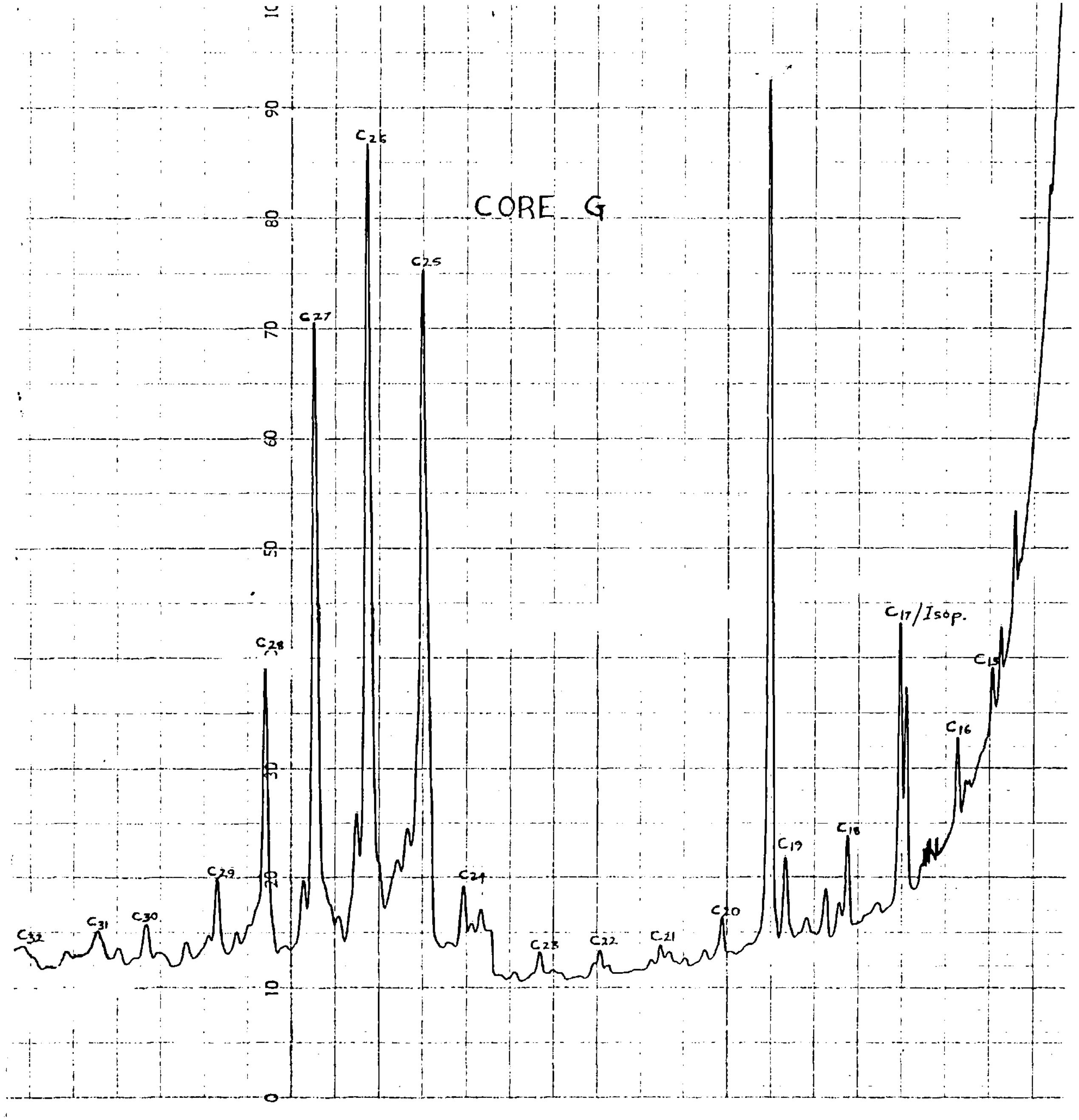
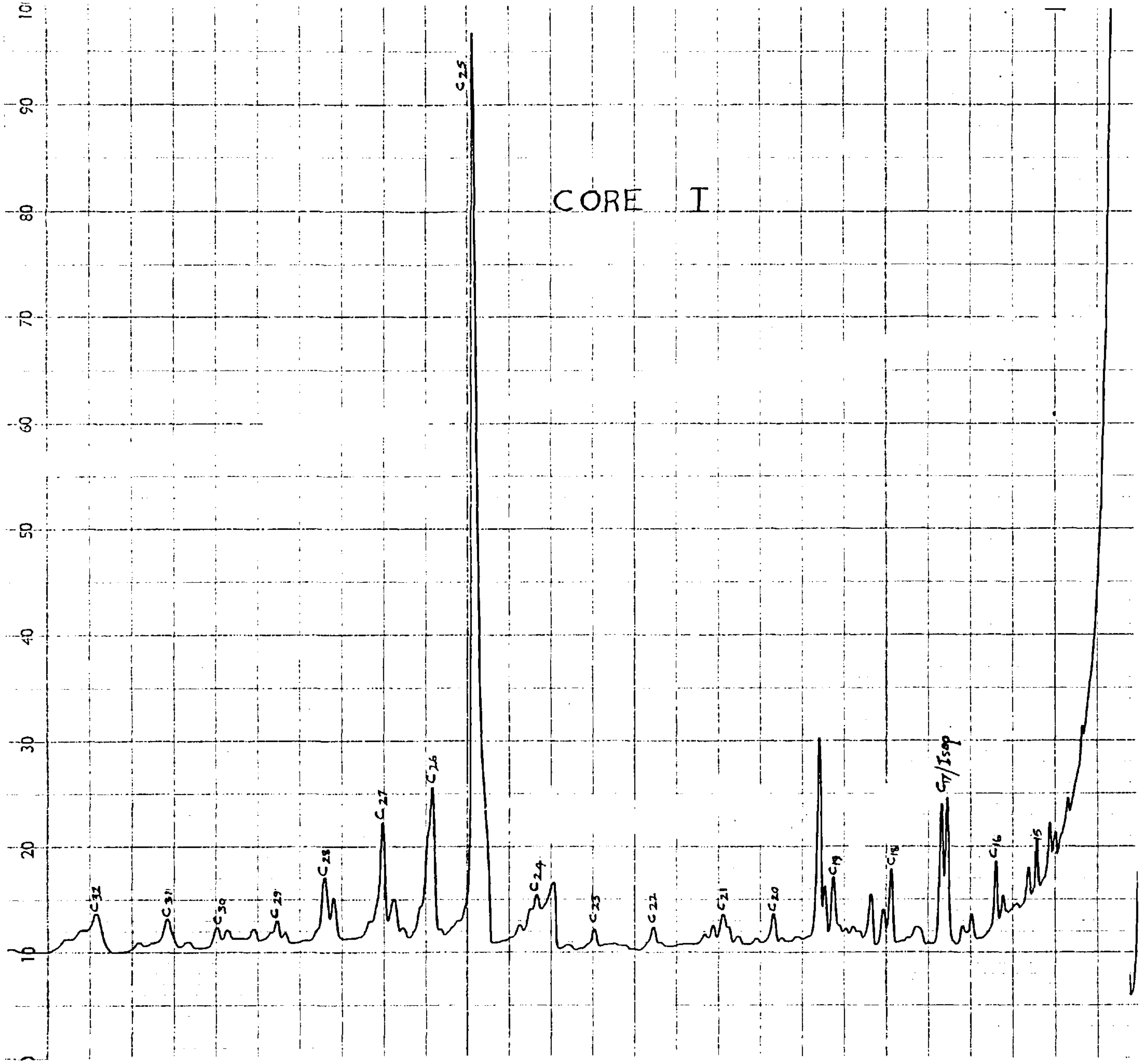
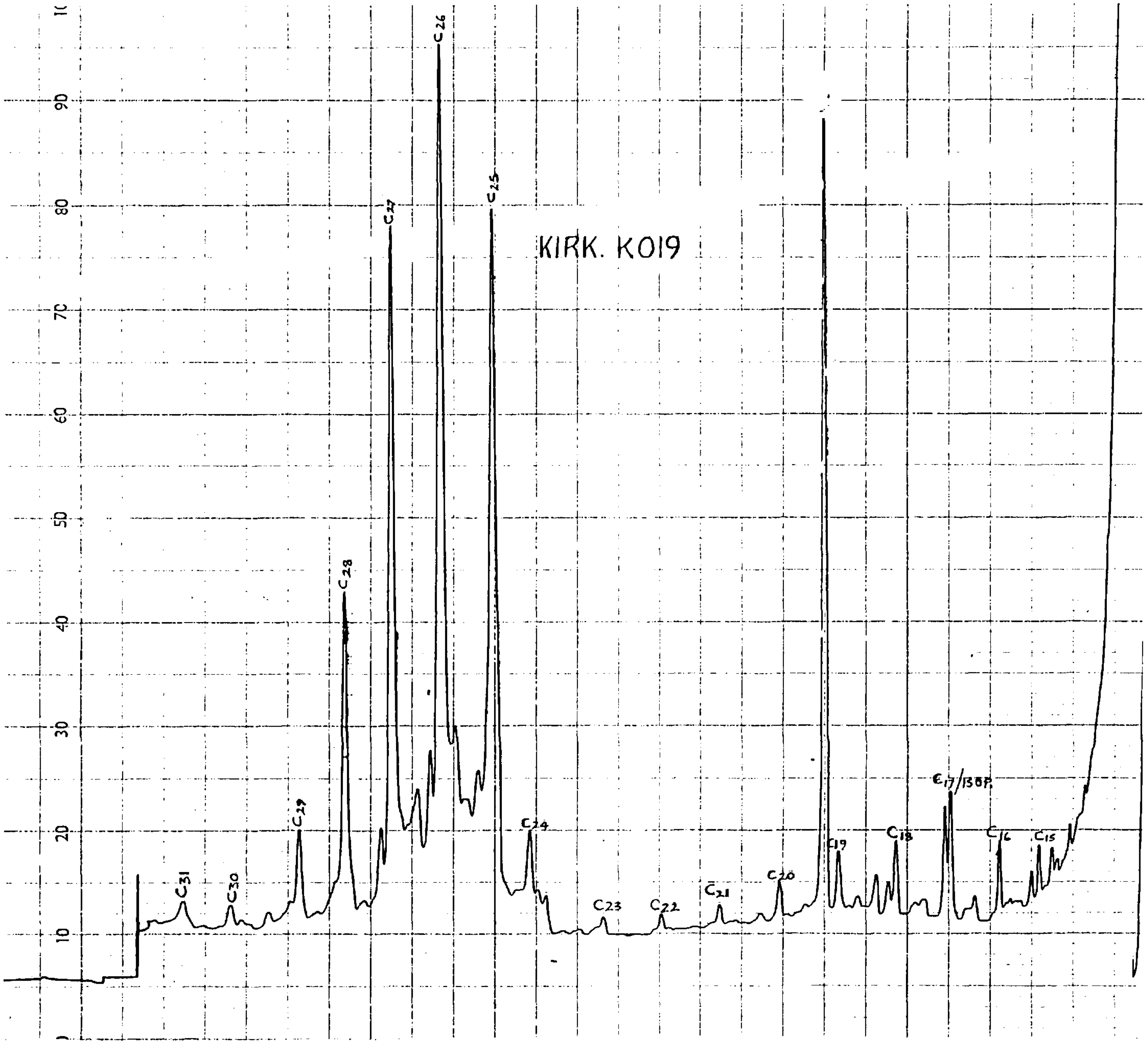
60
50
40
30
20
10
0


CORE G
C32
C31
C30
C29
C28
C27
C26
C25
C24
C23
C22
C21
C20
C19
C18
C17/Isop.
C16
C15
0
10
20
30
40
50
60
70
80
90
10


CORE I
100
90
80
70
60
50
40
30
20
10
0
C32
C31
C30
C29
C28
C27
C26
C25
C24
C23
C22
C21
C20
C19
C18
C17/Isop
C16
15


KIRK. K019
10
20
30
40
50
60
70
80
90
C31
C30
C29
C28
C27
C26
C25
C24
C23
C22
C21
C20
C19
C18
C17/ISOP.
C16
C15

PART 3

INTERPRETATIVE DISCUSSIONS

CHAPTER VI

IN SITU ORIGIN OF PETROLEUM IN OOLITES

'It cannot be denied that there is a real distinction between ideas about the objective world which are deduced from phenomena by experiment, or verified by experiment, and ideas which are not ---.'

L. T. More
Isaac Newton, A Biography

VI. 1 INTRODUCTION

In part 2 of this Thesis, the results of several techniques employed in the study of the organic fraction of Recent oolites revealed that these sediments have abundant organic matter of the right type to generate commercially significant amounts of hydrocarbons and could be considered potential source deposits. However, this organic matter has undergone very little transformation, mostly biochemical although some slight low temperature chemical reactions may have occurred. At this early stage of evolution towards petroleum formation, such potential source deposits are termed, 'immature'.

The oolites investigated are 'juvenile' (457 ± 76 to 1516 ± 86 yrs.), mainly surface sediments (0 - 70 cm) which have a low temperature history (30°C, interstitial water summer temperature). The implication is that if, over a sufficient interval of time, these deposits become buried deeply enough to expose them to temperatures above the threshold of petroleum generation, they have the capacity to serve as effective source beds, generating petroleum principally of the crude oil type.

This conclusion is promising. Ancient oolites which occur repeatedly in the stratigraphic record are familiar host rocks for petroleum. The excellent reservoir characteristics of these productive oolites have been invoked to explain the vast volumes of their contained oil as well as their notably superior productivity. In general, the oolites are thought to have no source function.

Nevertheless, over the years, geologists working in carbonate petroliferous provinces have 'reluctantly' reached the conclusion that the petroleum found in many oolitic host rocks is indigenous in origin (Henson, 1951; Baker and Henson, 1952; Steineke et al, 1958; Aramco staff, 1959; Owen, 1964). The evidence on which this opinion is based, though 'overwhelming', is for the most part circumstantial,being dependent on field lithologic associations. The data from the present work, however, afford experimental verification of the inferred indigenous origin of the petroleum stored in oolites.

Is it possible that the reportedly large volumes of petroleum accumulation and superior productivity of oolites are related, not only to their excellent reservoir characteristics, but also to the fact of in situ generation of their hydrocarbons which eliminates a 'wasteful' primary migration process ? As part of the attempt to answer this question,it is instructive to, a) conceive of a scheme for petroleum generation and accumulation in oolites and b) to test its validity by a selected case study in nature. Consequently, the presentation is in two parts.

I

VI. 2 THE THERMOCHEMICAL GENERATION OF PETROLEUM

To provide the background to the first part of the discussion, it is necessary to first review briefly the general concept of the thermochemical generation of petroleum.

The evolution of organic matter in sediments towards petroleum is generally conceived of as occurring in three main and continuous stages. According to the terminology of Tissot et al (1974), these are : a) Diagenesis; b) Catagenesis; c) Metagenesis. These correspond respectively to the Protocatagenesis, Mesocatagenesis and Apocatagenesis of Vassoyevich et al (1970). A general scheme of hydrocarbon formation as a function of burial of the source sediments is presented in figure VI.1.

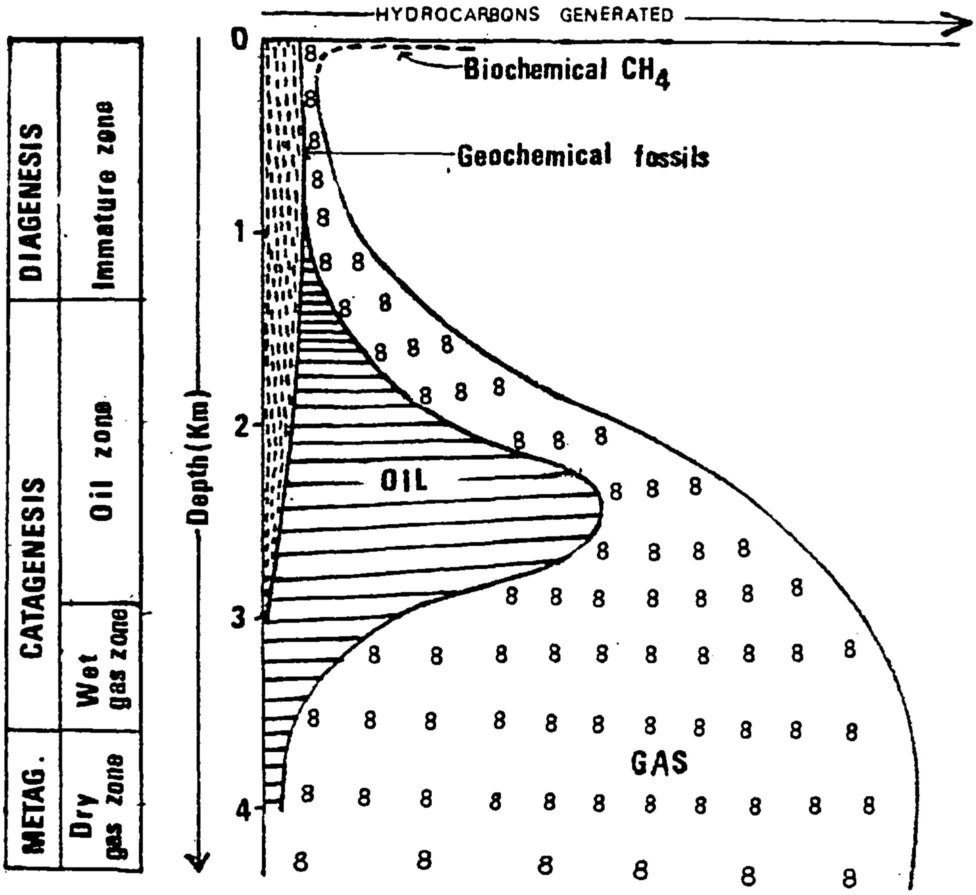


FIG. VI.1. General scheme of petroleum formation with increasing depth of burial of source beds (after Tissot and Welte, 1978)

VI. 2 i Diagenesis

Diagenesis begins in recently deposited sediments where microbial activity is one of the main agents of transformation. During the early stages of burial, petroleum compounds are not formed in significant quantities except, perhaps, for biogenic methane. It has been estimated that only about 9 per cent of the hydrocarbons up to 40 carbon atoms which occur in sedimentary rocks are formed in the diagenetic stage. (Hunt, 1977a). Most of this is in the C_{15}+ range and comprises mainly simple paraffin, naphthene, and aromatic structures 'inherited' from living organisms with minor modification.

Chemical reactions during diagenesis include: a) hydrogen disproportionation; b) decarboxylation and reduction; c) elimination and reduction; d) dimerisation; e) dehydration and reduction; f) deamination, decarboxylation and reduction; g) deformylation; and h) β-carbon dealkylation and reduction.

Of particular interest in this discussion is the presumed absence of light hydrocarbons in the diagenetic stage which has been cited generally as a criterion to draw rigid dividing lines between protopetroleum, which is the main product of diagenesis and the ultimately formed petroleum (eg.Dunton and Hunt, 1962; Erdman, 1962). Recent researches including this study, however, have revealed the presence in Recent and shallow sediments of light hydrocarbons that are believed to be products of diagenetic biochemical and low temperature chemical reactions (see Section I.3 and Chapter IV). Hunt (1979),has reviewed the data and concluded that such occurrence indicates that 'some of the reactions leading to light hydrocarbons are initiated in the diagenetic stage'(ibid, p.117). A case is made here for the inclusion of this fact of some light hydrocarbon formation during diagenesis in accounts of the general scheme of petroleum formation. The temperature range for diagenetic reactions is 0-50°C. It should be noted that, as a result of diagenesis, the bulk of the organic matter undergoes changes that render it more inert to strong acids and bases and is generally termed kerogen.

VI. 2.ii Catagenesis

Thermal degradation of Kerogen as a result of increasing temperature during burial in a sedimentary basin, is responsible for the generation of most hydrocarbons necessary for an exploitable petroleum accumulation. This is accomplished principally by a type of chemical reaction known as thermocracking but supplemented by thermocatalytically generated hydrocarbons, the relative quantities varying from one source-bed to another.

The cracking reactions almost always proceed by the breaking of carbon to carbon bonds either through homolytic (free radical reaction) or heterolytic cleavage. Other types of interatomic bonds especially carbon-hydrogen bonds are either broken or formed during oil-generating process, but these reactions become important only after carbon-carbon cracking has started.

For any chemical reaction, there is a minimum amount of heat energy, called the activation energy, which must be supplied to the reacting molecules before they can undergo reaction. From theoretical, experimental and empirical data, it has been established that a minimum temperature of about 50°C is required for organic matter to generate commercially significant hydrocarbons during geologic time. Erdman (1975) has correctly emphasised that a reaction temperature for the initiation of thermochemical oil and gas generation does not exist. However, petroleum geologists still adopt this concept as practically useful, for mathematical modelling of the process of petroleum generation.

In general, time and temperature are inter-related (Philippi 1965; Welte, 1967; Bordenave, 1967); that is, the younger the sediments, the higher the temperatures required to provide peak hydrocarbon generation. Theoretically, the temperatures required for oil generation in young sediments could be offset somewhat by increased reaction rate if active catalysts were present. The depths at which oil-generation reactions are initiated in a given sedimentary basin depend on a number of factors but largely, on the local geothermal gradient. The temperatures for catagenic reactions are thought to be between 50 and

200°C.

VI. 2.iii Matagenesis

The last stage in the evolution of organic matter into petroleum is reached only at great depths and normally at sediment temperatures greater than 250°C and possibly, great pressures. In this stage, hardly any more hydrocarbons are produced from the organic matter except, perhaps, for methane.

Much of the reactions now involve the cracking of the oils formed in the catagenic stage and their conversion to gas (ultimately, methane). Hence methane and graphite are the two thermodynamically stable end products of the thermochemical reactions which convert organic matter into petroleum.

VI. 3 A SCHEME FOR IN SITU GENERATION AND ACCUMULATION OF HYDROCARBONS IN OOLITES

Petrographic and organic geochemical analyses reveal that each ooid contains organic matter (and associated micro-organisms) in intimate contact with the finely crystalline aragonite that constitute the ooid, thus setting up a closed system in which microbial, and ultimately, thermal transformation of the organic matter can occur.

To achieve brevity without loss of clarity, it is proposed to advance this scheme for in situ generation and accumulation of hydrocarbons in oolites along the lines of the preceding discussion on thermochemical generation of petroleum.

VI. 3.i Diagenetic Stage

Exothermic anaerobic degradation of the algal and dissolved organic matter by associated bacteria provides the trigger mechanism for hydrocarbon generation forming methane but with the possibility of some C_2+ hydrocarbons being formed. Because of the low thermal conductivity of the ooids (determined to be in the region of 1.7 Watts/Metre/^{o}K) the tendency would be towards the conservation rather than dissipation of any heat generated. Evidence of biochemical heating as a by-product of microbial activity has been discussed in Section IV.9. This heating induces low temperature (about 30^{o}C but less than 50^{o}C : Whelan, 1979) reactions probably catalysed by bacteria and inorganic catalysts, resulting in the preliminary formation of C_2+ hydrocarbons.

The simultaneous biologic and low temperature chemical reactions would explain the saturated and unsaturated light hydrocarbons encountered in this study. Any hydrocarbons generated will be adsorbed by the organic matter in the ooids. The capacity of ooids to adsorb petroleum hydrocarbons has been demonstrated by Ferguson (1975) (see Section I.4). Active reduction processes operating at shallow depths will convert some of the unsaturated hydrocarbons to saturated members (Hunt and Whelan, 1979).

It must be stressed that at this stage, only very minor amounts of hydrocarbons are formed and these make very little contribution to the commercial petroleum accumulation found in oolites. But geochemically, the formation of light hydrocarbons at this stage indicates that, given adequate conditions of burial and temperature, the sediments would generate exploitable hydrocarbons (Hunt, 1979).

VI. 3.ii Catagenic Stage

With increasing burial, the organic matter within the ooids, each of which is conceived of as a closed environment, would strive to attain equilibrium with the newly imposed and rapidly changing external conditions of temperature (and pressure ?). This effort results in the generation of more hydrocarbons which would be adsorbed by the residual organic matter.

At this stage, any contribution by biologic processes is virtually nil and the reactions are mainly thermochemical, probably supplemented by thermocatalytic reactions fueled by inorganic catalysts known to be present in ooids (see Section II.4). In the continuing stage of thermochemical generation, the bacteria and other micro-organisms would progressively die from the accompanying 'heat wave' and contribute their biomass to the organic matter stock, thereby ensuring continuity of the hydrocarbon generating process. Lijmbach (1975 p.361) has found that degrading micro-organisms contribute substantially to the organic source material for petroleum formation.

The generation - adsorption of hydrocarbons continues till the adsorptive capacity of the ooids is exceeded. The hydrocarbons would migrate along the continuous Kerogen networks of the ooids into the pore spaces if they are available (Erdman, 1964; McAuliffe, 1978). Thermodynamically, this migration will favour increased generation of hydrocarbons within the ooids. The availability of pore space is vital to the fulfilment of hydrocarbon accumulation to form petroleum. Its role here is not merely passive; it serves to impel the migration of hydrocarbons from the ooids which in turn stimulates further generation of hydrocarbons.

It is in this respect that the evidence of early diagenetic cementation encountered in this study and outlined in Section II.9 are important. It has already been noted that although in such cases of early cementation some loss of porosity (about 10%) results, its role in the preservation of ultimate porosity cannot be overemphasised. This is termed constructive diagenesis (after the terminology of Alexanderson, 1972) and ensures that, by the time the adsorptive capacity of the ooids is exceeded, and the hydrocarbons are ready to migrate the short distance, some pore space is available. The entry of the hydrocarbons into the pore space will in turn contribute to the preservation of porosity (Wilson, 1977; Purser, 1978).

Apparently, it is also important that migration into the pore space takes place at a time subsequent to the deposition of sealing beds. In this respect, the synchronous deposition of anhydrite or other evaporite type sediments with oolites is a factor favouring accumulation of generated hydrocarbons. Once in the pore space, hydrocarbons would collect in the highest part of the structure by gravitative adjustment. This involves neither the introduction of fluids into the 'reservoir' nor loss of fluids from it. (Howard, 1934; p.375).

By contrast, if for any reasons such as initial or later destructive diagenesis the porosity of the oolite becomes destroyed before the generation and/or migration of hydrocarbons from the ooids, any further reactions involving the organic matter within the ooids will be effectively aborted. Is it any wonder that those oolites that have had their porosities destroyed not only do not bear hydrocarbons (which is obvious !) but also show little transformation of their contained organic matter (see Section V.9).

VI. 3.iii Metagenic Stage

With increasing temperatures greater than 250°C hardly any more hydrocarbons are generated in significant amounts from the organic matter within the ooids. Reactions during this stage are confined largely to the cracking of oil formed in the catagenic phase. Such cracking reactions are thought to have been operative in those cases where oolitic reservoirs are found to bear mainly gaseous hydrocarbons since, by the facts of their formation, oil should be the normal products.

VI. 3.iv Conclusion

It is evident from the preceding discussion that the diagenetic pathway of an ooid accumulation, that is, constructive vis-a-vis destructive diagenesis, is crucial to the fulfilment or failure of the scheme of in situ generation presented here; given a favourable diagenesis, then the synchronous deposition of potentially sealing beds becomes a second determining factor.

It is pertinent to note that although the above scheme of the in situ origin of oolitic carbonate petroleum can be used in many cases to explain the occurrence of oil and gas in oolites, the writer does not regard the scheme as universally applicable. For example, there are cases of petroleum production from leached oolites. Here the ooids, due to unfavourable diagenesis have been leached out leaving voids, which are separated by undissolved matrix and cementing material (Levorsen, 1967; Ginsburg, 1957; Friedman; 1964; Robinson, 1967). This type of porosity has been called 'oomoldic' porosity and rocks having this porosity often are good petroleum reservoirs.

It is obvious that in such cases, their contained hydrocarbons could not have originated in situ. 'Leached oolites' are normally associated with extensive carrier beds and some source facies are identifiable locally. 'Leached oolite' reservoirs have been described by Biederman (1966) who called them 'an oil finders key' (ibid, p.174).

II

VI. 4 IN SITU FORMATION OF PETROLEUM IN OOLITES : A CASE STUDY

For an unequivocal discussion of an oolite reservoir productive of petroleum generated in situ, it would be necessary to describe in some detail those formations both underlying and overlying, or lateral to, the formation of interest which, because of thier hydrocarbon content in the general region, might perhaps be supposed to have been the original source of the petroleum now found in the oolites. Such an account would be too detailed than space would permit. The need arises, therefore, for the selection of an example which allows the least number of alternative possibilities. This was the guiding principle behind the choice of the prolific Arab Formation (Upper Jurassic) of Saudi Arabia as a case study(see fig.VI.2).

Table VI.1 shows the stratigraphic position of the Arab Formation which is composed of four carbonate members ('A', 'B', 'C'

TABLE VI.1

STRATIGRAPHIC SEQUENCE FOR SAUDI ARABIA SHOWING POSITION OF THE ARAB FORMATION (after Steineke et al, 1958)

ROCK UNITS	MAIN ROCK TYPES	THICKNESS (TYPE SECTION)	AGE
Hofuf formation	Sandy marl and limestone; local quartz gravel at base	95m	Miocene or Pliocene
Dam formation	Shale, marl and limestone, with chert	90m	Probably Middle Miocene
Hadrukh formations	Sandstone,shale, marl & chert	84m	? Miocene
Unconformity			
Dammam formation	Limestone,dolomite,clay and marl	28m	Lower and Middle Eocene
Rus formation	Anhydrite,marl,shale and limestone	56m	Lower Eocene
Umm er Radhuma formation	Mainly limestone and dolomite	About 229m	Paleocene and Lower Eocene
Aruma formation	Limestone,with dolomite and shale	144m	Late Upper Cretaceous (Campanian? and Maestrichtian)
Unconformity			
Wasia formation	Sandstone and shale with subordinate limestone	42m	Early Upper Cretaceous (Cenomanian)
Unconformity			
Biyadh sandstone	Sandstone, with shale	About 270m	Lower Cretaceous
Buwaib formation	Limestone,with subordinate shale and sandstone	34m	Lower Cretaceous
Unconformity			
Yamama formation	Calcarenite and fine-grained limestone	58m	Lower Cretaceous (Neocomian)
Sulaly limestone	Limestone,with a basal calcarenite unit	About 180m	Lower Cretaceous?
Disconformity			
Riyadh group			
Hith anhydrite	Anhydrite	71m	Probably Upper Jurassic
Arab formation	Limestone,dolomite and anhydrite	127m	Late Upper Jurassic
Jubaila limestone	Limestone	About 110m	Upper Jurassic(Kimmeridgian)
Hanifa formation	Limestone	101m	Upper Jurassic(?Oxfordian)
Tuwaiq Mountain Limestone	Limestone,mainly coral-bearing	215	Upper Jurassic(Callovian)
Unconformity			
Dhruma formation	Limestone,and shale	383m	Middle Jurassic (Bajocian-Bathonian)
Marrat formation	Limestone,dolomite and red shale	111m	Lower Jurassic(Toarcian)
Unconformity			
Minjur sandstone	Sandstone, with vari-colored shale	315m	Triassic or Jurassic
Jilh formation	Sandstone,shale and limestone	About 326m	Middle Triassic
Sudair shale	Mainly red shale	116m	Permian or Triassic
Khuff limestone	Limestone,with shale and marl	235m	Permian(Probably Upper)
Unconformity			
Basement complex			

and 'D' from top to bottom) which alternate with synchronous anhydrite members. The Arab Formation is directly underlain by the dense impermeable limestones of the Upper Jubaila and overlain by the thick and persistent Hith Anhydrite. Oil production comes from porous beds of oolite (some dolomitised) in 'A', 'B', 'C' and 'D', wedged within the thick and persistent anhydrite units except for 'D' which is underlain, not by anhydrite but by dense and tight limestones. Laterally, the productive oolitesoccur as porous belts between the evaporitic sediments to the west and dense impermeable limestones to the east. More detailed accounts of the stratigraphy of the Arab Formation have been given by Henson (1951) Baker and Henson (1952), Steineke et al (1958), Aramco Staff (1959), Powers (1962) and Billo (1979). Of this formation, Hedberg (1964,p.1789) wrote: 'Thus the Arab producing zones are nearly closed systems surrounded by sealing beds of either anhydrite or dense limestones.'

It is this 'closed'nature of the Arab 'reservoirs' that compelled earlier workers to propose, against the geological thinking of their day, that the oil in these beds is of indigenous origin. Henson (1951) was the first, to state unequivocally, the in situ origin of the petroleum deposits of the Arab Formation. On the formation of the oil, Henson stated: 'Since fossils are often scarce in these deposits, the author believes that certain algae may have played their part in the formation of oil and oolite' (ibid. p.1928). Baker and Henson (1952) reviewed the geological conditions of oil occurrence in the Middle East and concluded that the oil of the Arab Zone is indigenous to the rocks in which it is now stored.

Steineke et al (1958, p.1327) who noted that, 'the area of maximum calcarenite (oolite) development in [the Arab Zone] is likewise that of the largest oil accumulation' proposed an in situ origin for the oil arguing that the rocks of the individual members cannot be eliminated as source even when they are coarse grained facies. Aramco Staff (1959) also noted that, 'high oil productivity goes in general with calcarenites' (p.445) and expressed the belief 'that the oil originated in the rocks in which it is now found' (p.452). They, however, added a suggestion, without further clarification, that 'the

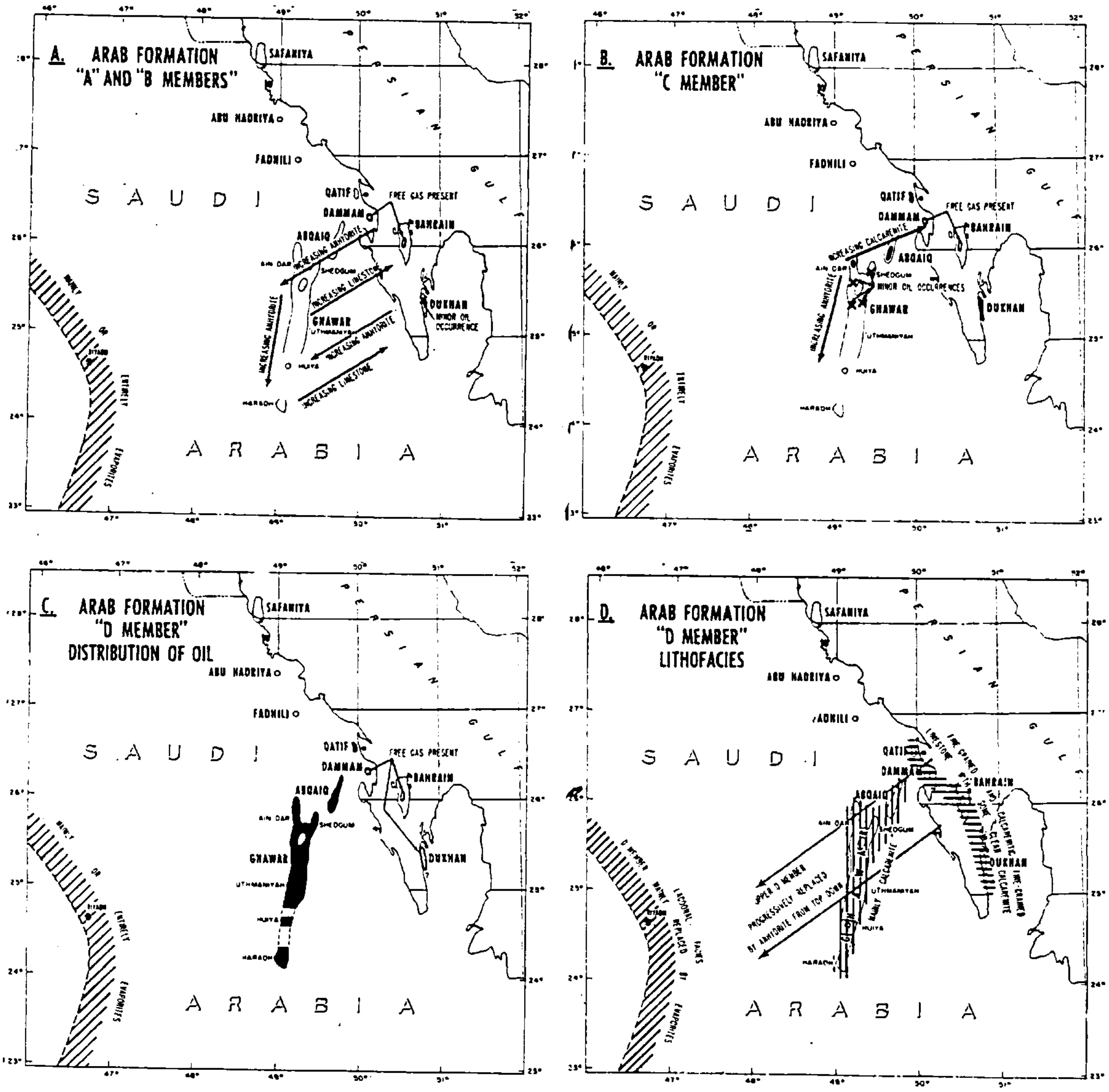


Fig. VI .2 DISTRIBUTION OF OIL AND LITHOFACIES OF THE ARAB FORMATION, SAUDI ARABIA (from STEINEKE ET AL., 1958) volume of oil forces an assumption of substantial lateral migration' (loc.cit.).

Commenting on the Arab producing zones, Hedberg (1964 p.1789) stated: 'It seems unavoidable that the oil of the three Upper Zones ['A' - 'C'] must have originated in these thin zones between anhydrites, to some extent perhaps in the reservoir rocks themselves; but more probably in the carbonate muds which are intercalated with them and replace them to the east.' Following the same line of reasoning, he allowed for some likely contribution of oil to the Arab 'D' from the dense tight limestones to the east of 'D' and underlying it.

It is evident from the preceding discussions that, but for some likely contribution of oil to the Arab 'D' from the Upper Jubaila (see later discussions) the stratigraphic position of the Arab Formation as well as the basic lithologic associations within it, prove as untenable any assumption of vertical movement of hydrocarbons either from other formations,or from one member to the other. This improbability leaves a choice of either lateral migration or in situ generation and accumulation of hydrocarbons to explain the origin of the oil in the porous oolite beds of the Arab Formation.

To propose a lateral migration of hydrocarbons would be to suggest the now dense impermeable (lithographic) limestones which replace the oolites to the east as the source of the hydrocarbons, since opinion is unanimous that the evaporitic sediments to the west have no source bed function. On dense limestones, like those to the east of the oolites, Dunnington (1958; p.1203) observed: 'Source potentialities are seen in these postulated basinal sediments ---' (ibid p.1203). More recently Meyerhoff and Hatten (1974), concluded from studies of two carbonate areas - one in Mexico (EL - Abra Limestone) and the other in Florida (Sunniland Limestone) - that basinal, lithographic and sublithographic pelagic - microfossil-bearing Limestones comprise one set of limestones in which organic materials may be buried and from which oil and gas may be generated. Several other geologists have suggested that petroleum can be generated in many types of carbonate facies deposited under euxinic conditions favourable to the preservation of organic matter (Trask, 1928;

Hedberg, 1964; Veber and Gorskaya, 1965; Owen, 1964; Hunt, 1967; Alizade and Shoikhet, 1967; Ginsburg, 1980).

Theoretically, therefore, it seems plausible to propose the now dense and tight limestones to the east of the porous oolites and underlying the Arab 'D' as the source of the oil in the Arab zones. Implicit in such a proposal, is a tacit suggestion of a very early generation and migration of petroleum hydrocarbons probably in the first few meters of burial, when the carbonate muds, which ultimately formed the dense limestones, were still compactible. Although the processes of hydrocarbon migration are not well understood, many authorities on the subject are agreed that solution migration (that is, migration of hydrocarbons with formation fluids) may be a far more prevalent mechanism (Hodgson et al, 1964; Magara, 1968, 1973, 1976a; Tissot and Welte, 1978, p.298; Hunt, 1979,pp.221-231). The history of early lithification of carbonate muds is, however, well known through the studies of Ginsburg (1957), Weller (1959), Zankel (1969), Freidman (1975), Sayles and Manheim (1975) among others.

While evidence of early migration of hydrocarbons could be cited (Kidwell and Hunt, 1958; Gealy and Davies, 1969; McIver, 1973, 1974, 1975), the consensus of opinion, is that such phenomenon is not responsible for commercial petroleum accumulations since the bulk of petroleum hydrocarbons are formed through thermochemical reactions at considerable depths of burial of sediments (Sokolov et al., 1963; Philippi, 1965, 1975; Vassoyevich, 1970; Tissot et al, 1974). Presumably, also, sufficient time must be allowed for, in order that, potential sealing beds may be deposited. Therefore, a major drawback to the proposal of the dense tight limestones as the source of or contributory to the hydrocarbons stored in the oolites, is the lack of a credible expulsion mechanism at depths of hydrocarbon generation when, by and large, the hitherto carbonate muds would have been dewatered and lithified into dense impermeable limestones.

Hedberg (1964), Owen (1964) and Hunt (1967), among others, have stated that any hydrocarbons generated in such muds after consolidation will become 'locked up' in the progressively condensing carbonate matrix. The generation of hydrocarbons in cemented carbonates so tight that there is essentially no fluid transmission has been cited as a major cause of abnormal pressures in carbonate reservoirs (Tissot and Welte, 1978 p.264 - 268; Hunt, 1979, p.249). When such dense and tight limestones are penetrated by the drilling bit they are found to contain globules of oil (Weeks and Alexander, 1942; Owen, 1964). This, is both a confirmation of the ability of these limestones to generate hydrocarbons as well as their inability to expel them.

It is known that, where such otherwise impermeable beds are sufficiently fractured or have acquired other secondary porosity through diagenetic changes, and are not anhydritic, they can form reservoirs [source-reservoirs, senu stricto] in their own right. Illing et al (1967) have cited as examples, the famous Asmari Limestone (Oligocene - Miocene) and the lime-mudstones and wackestones of the Bangestan Limestones (Mid Cretaceous) which are intrinsically so tight and dense that it would be impossible to produce their contained hydrocarbons but which have become important 'reservoirs' because of their very extensive network of joints and fractures as well as dolomitisation.

Tissot and Welte (1978), following an earlier suggestion by Hedberg (1964), have asserted that hydrocarbon phase migration through microfissures which does not demand water for hydrocarbon movement, provides a plausible migration mechanism for the oil and gas generated in dense carbonate beds. These authors, however, concede that 'the distances covered by [such] primary migration mechanism are in the order of metres or tens of metres' (ibid, p.298). Hunt (1979, p.236) expressed an identical view. It is clear that little credence can be given to such a migration mechanism to justify a proposal of 'substantial' migration across the thousands of metres of dense impervious limestones, that replace the oolites of the Arab Zone to the east. Any contribution to the oil in the oolites from the east or from the equally dense and tight limestones of the Upper Jubaila formation, would be very minimal and restricted to areas of the dense carbonates peripheral to the porous oolites. It is pertinent in this regard to recall the conclusions of Steineke et al (1958) that no evidence has been detected to show that jointing plays any role in the accumulation of petroleum in this area (p.1327).

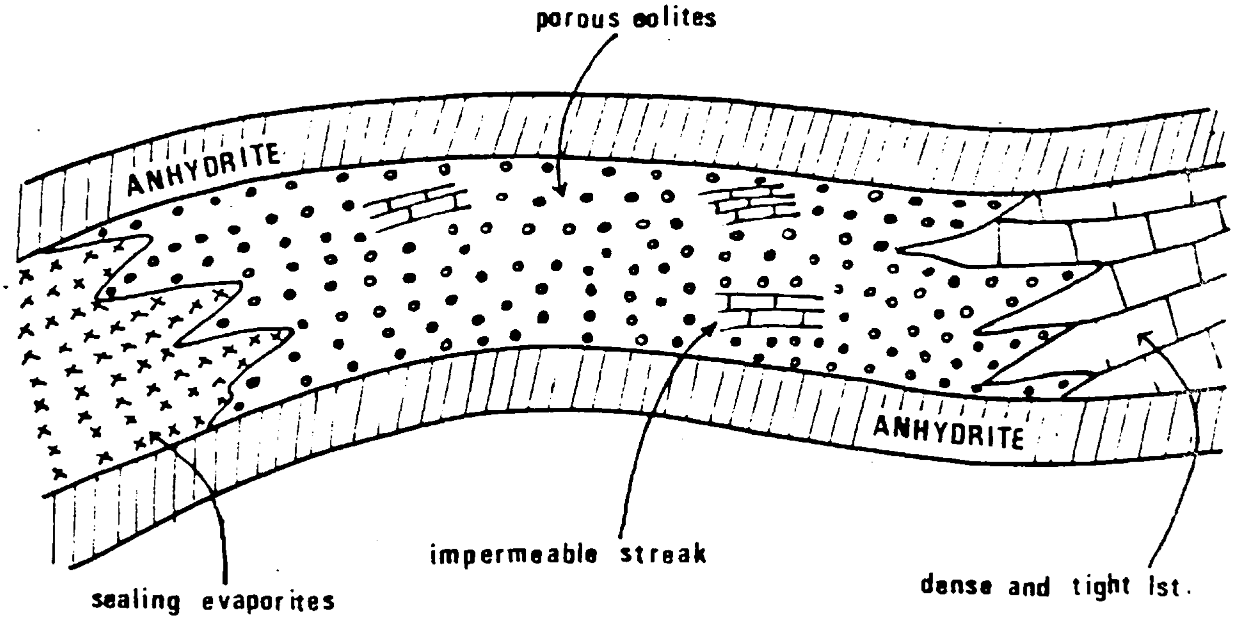
From the foregoing, it is imperative that one looks to the Arab Zone oolites and oolitic rocks (some dolomitised) themselves for the source as well as the present reservoirs of their contained hydrocarbons. Admittedly, in the light of present geologic thought on the origin of petroleum, oolites and oolitic deposits are generally regarded as the most unfavourable source beds of petroleum. Yet, all available evidence (experimental and from literature survey) assembled in this study, indicate that petroleum in very large volumes are indigenous in oolites.

One of the main objections to the concept of in situ generation of petroleum in coarse grained sediments such as oolites is the likelihood that circulation of fluids in the sediments immediately after deposition could have caused oxidation and dissipation of any original organic matter present in the deposits. This argument assumes that the organic matter in oolites and other coarse grained carbonate facies is contained in the pore spaces. Although algal filaments are present in pore spaces and cement sediments through algal calcification (Purdy, 1963a, Golubic et al, 1975; Kobluk and Risk, 1977; Dravis, 1979), it is known from the results of several researches that the bulk of organic matter in oolites is contained within the individual ooids where it is in intimate contact and continuity with the $CaCO_3$ crystals forming the ooids. Such organic matter would therefore be 'safe' from any oxidative influences of the environment. Furthermore, the scheme of ooid formation presented in this study (Chapter III) suggests that the marine organic matter entrapped within ooids is relatively 'fresh' (unaltered) before the onset of microbial and, subsequently, thermal reactions.

Given the capacity of oolites to generate hydrocarbons, it is obvious that the role of the dense impermeable facies that replace the oolites to the east and which underlie the Arab 'D', would be that of providing an effective permeability barrier to the hydrocarbons generated within the oolites; this is an example of a stratigraphic

WEST ← → EAST

A. UPPER ARAB ('A'-'C') RESERVOIRS



B. ARAB 'D' RESERVOIR

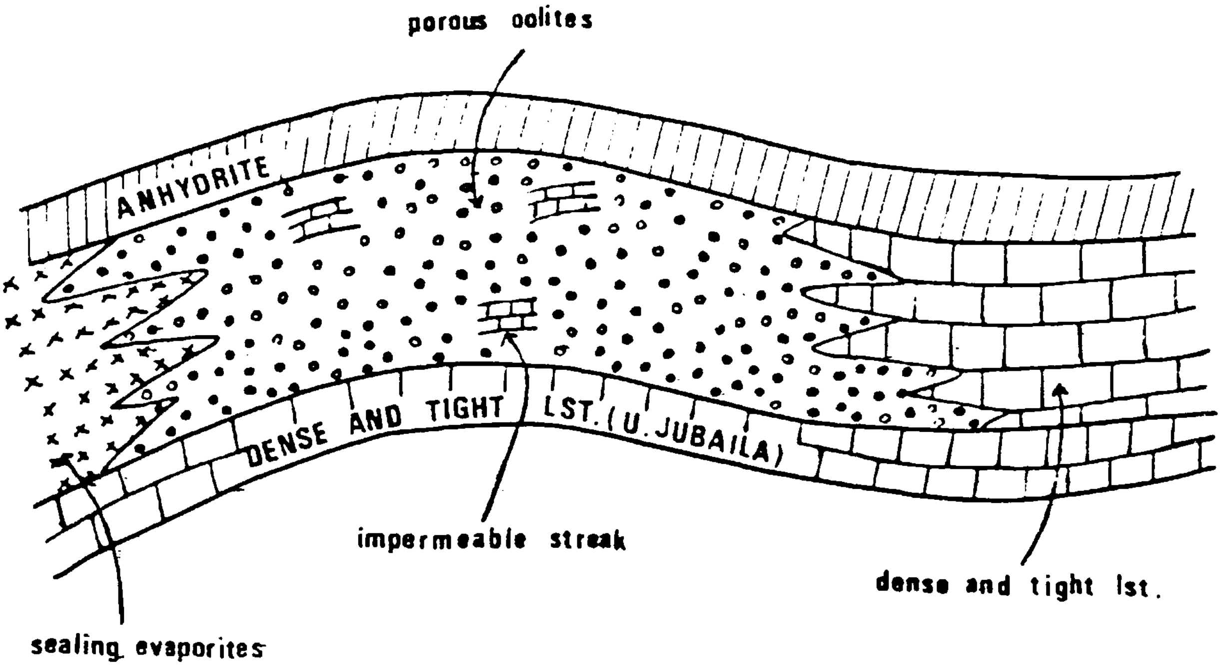


FIG.VI.3A & B SCHEMATIC REPRESENTATION OF STRATIGRAPHIC TRAP MECHANISM IN THE ARAB RESERVOIRS trap. Fig.VI.3 is a schematic representation of this kind of trap. Illing et al (1967, p.497) have stated that, 'stratigraphic traps are likely to exist where clean sands pass laterally into more muddy carbonates as on the flanks of pelletoid and oolite shoals.'

The most obvious objection to the theory of indigenous origin of petroleum in oolites presented in this discussion is that the quantities of oil contained in the oolite reservoirs are so great that it is difficult to conceive of an origin for the petroleum to the exclusion of the adjacent potential source beds. The explanation is simple. The writer believes that the in situ generation of petroleum in oolites which precludes an extensive and inefficient migration process affords another explanation for the great volumes of oil stored in oolites and for their notably superior productivity.

Although the exact processes of primary migration remain 'so elusive, so mysterious, so controversial and of course so frustrating' (Roberts and Cordell, 1980), one thing is known for sure, namely, that in petroliferous provinces where there are distinct source and reservoir beds, hydrocarbon migration is a 'wasteful' process (Hunt and Jamieson, 1956; Philippi, 1956; Hunt, 1961). One of the best illustrations of this fact has come from the data of Hunt (1961). From a study of the Frontier Formation (cretaceous) in the south-west section of the Powder River Basin in Wyoming, Hunt calculated that the volume of hydrocarbons remaining in the Frontier source shales is nine times greater than the volume accumulated in Frontier reservoirs. When the calculations were extended vertically through the entire Cretaceous section of the area, the quantity of oil expelled from the source beds appear to be an even smaller fraction of the total oil formed. Table VI.2 presents estimates of the volume of oil in all Cretaceous sediments in the Wyoming part of this Basin. The data indicate that the oil expelled from presumed source beds into their associated reservoirs is less than 5 percent. While such results should be seen as broadly qualitative rather than quantitatively accurate, they show that petroleum expulsion from source beds is a very inefficient process.

Several factors affect the efficiency of the expulsion process. These include: a) the age of the source bed; b) the hydrocarbon adsorption capacity of the source sediments; c) the thickness and

TABLE VI. 2 ESTIMATED VOLUME OF HYDROCARBONS IN RESERVOIR AND NON-RESERVOIR ROCK OF THE CRETACEOUS FORMATIONS OF THE POWDER RIVER BASIN IN WYOMING (TOTAL AREA APPROXIMATELY 15,000 miles^2) (after Hunt, 1961)

FORMATION	AVERAGE SHALE THICKNESS (ft)	ESTIMATED OIL IN SHALE (BARRELS)	ESTIMATED OIL IN RESERVOIR SANDS (BARRELS)
Pierre-Steel	3100	74×10^9	520×10^6
Niobrara	450	85×10^9	2×10^6
Frontier-Carlile	750	27×10^9	3000×10^6
Mowry	250	4.25×10^9	0
Thermopolis-Skull Creek	150	4.25×10^9	400×10^6
Dakota-Fuson-Lakota	50	$.15 \times 10^9$	2680×10^6
TOTAL	4750	196×10^9	6602×10^6
Ratio of	$\frac{\text{oil in shale}}{\text{oil in reservoir}}$	$\frac{196 \times 10^9}{6.6 \times 10^9} = \frac{30}{1}$	

homogeneity of the source sequence; d) permeability; e) amount of water in the source bed available for desorbing and dewatering; included here would be the presence of hydrated clays; e) the presence of migration pathways in and adjacent to the source strata; f) the proximity of carrier beds and reservoirs to dispose of expelled fluid; g) pressure differential between source bed and surroundings; et cetera. There is reason to believe that higher efficiencies than those suggested by the data of Hunt are possible under optimum conditions but even so, the best estimates available (such as 20 percent efficiency in the Los Angeles Basin: Philippi, 1965; Jones, 1980) confirm that by far a greater proportion of oil generated is left behind in the source bed after primary migration.

It is therefore evident that under the scheme of in situ generation and accumulation of hydrocarbons in oolites presented here, the waste inherent in the expulsion process operative in Shale-Sandstone sequences would be eliminated; this would explain the exceptionally rich petroleum accumulation in oolite reservoirs (and, for that matter, in most inherently porous carbonate rocks: see Chapter VII). Is it any wonder then, that areas of maximum oolite development in the Arab zones are also those of the largest oil accumulations ?

CHAPTER VII

THE ORIGIN OF PETROLEUM IN CARBONATE ROCKS

> 'The entire history of the discovery and exploitation of petroleum has been full of surprises --- but when required to believe that limestones --- make one of the great oil rocks of our geological scale, it is hard to prevent our surprise from passing into incredulity.'
>
> Orton, 1888
> In:Ohio Geological Survey,Report 6.

VII. 1 INTRODUCTION

Carbonate rocks are hosts to at least 40% of the world's petroleum although they represent only about 16 percent of the sediments of the basins of the continents and continental shelves compared to about 50 percent for clay shales (Weeks, 1958). In relative terms, therefore, carbonates are the most important sedimentary lithology, from the viewpoint of petroleum occurrence. Yet the origin of their contained hydrocarbons remains largely speculative since very little published data exist on this important subject (Momper, 1975).

It has often been assumed that petroleum does not originate in carbonate sediments (Owen, 1964; Hunt, 1967). Shales are regarded by the overwhelming majority of petroleum geologists as the basic, perhaps the only, source facies for petroleum (Snider, 1934; Andreev et al, 1968; Dott and Reynolds, 1969). However in a number of petroliferous regions like the Middle East, there are practically no shales which can be regarded as the source for the petroleum contained in the carbonate rocks. Besides, the impervious nature of the rocks surrounding many carbonate reservoirs, makes it unlikely that oil migrated into them in the same way as it is believed to have entered sandstones. Despite these convincing evidence, only grudging acceptance is made of the possibility of the formation of petroleum in limestones.

Even those authors (eg. Hedberg, 1964; Hunt, 1967) who admit of a restricted source bed role for carbonates tend in general to 'single' out the fine grained carbonate facies and in particular those with some considerable clay content (marly beds) as the most prospective source candidates. However, as the results of the present investigations show, even coarse grained facies like oolites have the capacity to have generated their contained hydrocarbons. The data of Thompson and Creath (1966), Veber and Gorskaya (1965) and Ali-Zade and Shoikhet (1967) among others, have demonstrated this possibility for other coarse grained shelly carbonates.

Nevertheless, a large number of contemporary geologists still exclude carbonate sediments from petroleum source beds. Many of those who strenuously object to the idea of carbonates as effective source beds offer as their reasons, a) the lean organic matter content of carbonate rocks; b) the lack of an effective, or for that matter any, hydrocarbon expulsion mechanism.

It is proposed in this chapter, to examine these objections; in addition, a third related and important factor, that of the convertibility of organic matter to petroleum under the physico-chemical conditions prevalent in carbonate sedimentary environments, will be considered. On the principle of the present as a key to the past,much of the discussion is based on evidence from Recent sediments.

VII. 2 ORGANIC MATTER CONTENT OF CARBONATES

Organic matter is the basic ingredient in sedimentary beds from which petroleum is formed. Almost invariably, all sedimentary beds contain organic matter, ranging from disseminated traces in sandstones to the high concentrations of peat and coal beds. As part of this study, sediment samples of a wide variety of textural types were collected from Recent carbonate environments of the Bahamas and Florida Keys. The samples were analysed for organic carbon content according to the method described in Section V.3.

Table VII.1 presents the results of the analyses. The consistently high organic carbon values (0.98 - 18.69 wt.%) are particularly striking and are far in excess of the 0.3 weight percent minimum organic carbon requirement for carbonate facies to be considered potential source beds. Gehman (1962) who carried out a rather

TABLE VII.1 SHOWING ORGANIC CARBON VALUES FOR CARBONATE SEDIMENTS OF A WIDE TEXTURAL VARIETY FROM THE FLORIDA KEYS AND BAHAMAS.

FLORIDA KEYS

SAMPLE NO	BROAD LITHOLOGIC DESCRIPTION	CORG VALUES (WT.%)
FL-RAS-01	Fine-Coarse grained Reef Associated Sands	1.93
-02	Fine-Coarse grained Reef Associated Sands	1.7
-03	Fine-Coarse grained Reef Associated Sands	2.21
-04	Fine-Coarse grained Reef Associated Sands	1.76
-05	Fine-Coarse grained Reef Associated Sands	1.84
-06	Fine-Coarse grained Reef Associated Sands	1.96
FL-BS- 11	Skeletal (shelly) Bank Sediments	.98
- 12	Skeletal (shelly) Bank Sediments	1.54
- 13	Skeletal (shelly) Bank Sediments	1.96
- 14	Skeletal (shelly) Bank Sediments	1.6
- 15	Skeletal (shelly) Bank Sediments	1.72
- 16	Skeletal (shelly) Bank Sediments	1.63
FL-SM- 21	Gray, slightly argillaceous shoal mud	3.97
- 22	Gray, slightly argillaceous shoal mud	4.15
- 23	Gray, slightly argillaceous shoal mud	3.07
- 24	Gray, slightly argillaceous shoal mud	3.76
- 25	Gray, slightly argillaceous shaol mud	4.24
- 26	Gray, slightly argillaceous shoal mud	2.85
FL-LM- 31	Dark gray (slightly argillaceous)'Lake' mud	3.63
- 32	Dark gray (slightly argillaceous)'Lake' mud	4.29
- 33	Dark gray (slightly argillaceous)'Lake' mud	3.47
- 34	Dark gray (slightly argillaceous)'Lake' mud	3.67
- 35	Dark gray (slightly argillaceous)'Lake' mud	2.89
- 36	Dark gray (slightly argillaceous)'Lake' mud	4.13
FL-GHM-41	Dark gray silty grass held mud	5.23
-42	Dark gray silty grass held mud	2.97
-43	Dark gray silty grass held mud	3.73
-44	Dark gray silty grass held mud	4.19
-45	Dark gray silty grass held mud	3.86
-46	Dark gray silty grass held mud	3.9

TABLE VII.1 contd/...

SAMPLE NO.	BROAD LITHOLOGIC DESCRIPTION	CORG VALUES (WT.%)
FL-AS-51	Algal scum (from Crane Key)	16.2
-52	Algal scum (from Crane Key)	17.34
-53	Algal scum (from Crane Key)	18.69
-54	Algal scum (from Crane Key)	17.94
-55	Algal scum (from Crane Key)	16.8
-56	Algal scum (from Crane Key)	17.83
ELEUTHERA BANK		
EL-SS-01	Med.-Coarse grained shelly skeletal sands	1.7
-02	Med.-Coarse grained shelly skeletal sands	1.9
-03	Med.-Coarse grained shelly skeletal sands	1.42
-04	Med.-Coarse grained shelly skeletal sands	2.32
-05	Med.-Coarse grained shelly skeletal sands	1.86
-06	Med.-Coarse grained shelly skeletal sands	1.76
EL-CS-11	Coarse grained coralgal sands	1.1
-12	Coarse grained coralgal sands	1.3
-13	Coarse grained coralgal sands	1.97
-14	Coarse grained coralgal sands	1.8
-15	Coarse grained coralgal sands	1.72
-16	Coarse grained coralgal sands	1.0
EL-LM-21	Pelletal lime mud	4.04
-22	Pelletal lime mud	4.0
-23	Pelletal lime mud	3.26
-24	Pelletal lime mud	3.78
-25	Pelletal lime mud	4.1
-26	Pelletal lime mud	4.23
EL-CRS-31	Coral Reef Stalk	3.42
-32	Coral Reef Stalk	4.2
-33	Coral Reef Stalk	2.83
-34	Coral Reef Stalk	2.9
-35	Coral Reef Stalk	3.4
-36	Coral Reef Stalk	4.24

comprehensive study of organic matter in ancient and modern limestones reported that unconsolidated lime sediments contain an average of 3 percent organic matter and almost always contain more than 1 percent. There is a fair agreement between the two sets of results although the present values would appear in general to be higher than those reported by Gehman. This slight disparity is attributed to the different methods of analysis employed. This subject, as it affects Corg. results in Recent carbonate sediments,has been discussed by the writer in Section III.2 and it will be repetitive to detail the arguments here. Briefly stated, the generally lower results of Gehman would have resulted from the adverse effects of using strong acids (6 N HCl) for destroying the carbonate carbon and/or filtering the dissolved sample, discarding the filtrate and washing the residue prior to analysis (Roberts et al, 1973; Hunt, 1979). In a critical review of methods employed in Corg. determinations in Recent sediments, Roberts et al (1973, p.1159) concluded that previously reported results obtained through precedures similar to that of Gehman, 'should be considered as minimum values rather than accurate figures.' The Corg. results published by Roberts et al on Florida Keys sediments which ranged from 1.58 (for fine to coarse-grained shell debris) to 3.47 weight percent are more consistent with values recorded in this study for sediments from the same area.

It would appear that, in general, Recent carbonate sediments contain organic matter in as high or even greater proportions as those reported for Recent shales (clays). Also the proportion of organic matter generally increases as the mean grain size decreases for carbonate sediments as in terrigenous facies (Scholl, 1960; Veber et al, 1960; Gehman, 1962). For example, Veber and Gorskaya, 1965 have published values of between 1.64 (calcareous sands) to 5.19 (carbonate mud) weight percent organic matter from their analyses of Recent carbonate sediments from the Kenderli Gulf; the authors stated that compared to Recent terrigenous sediments, the absolute amounts of organic matter in Recent carbonates may be relatively high. The conclusion of Ali-Zade and Shoikhet (1967) was identical; they noted that in the Recent sediments of the Caspian Sea, the content of Corg is greater in carbonate facies (3wt.% and more) than in terrigenous sediments (about 2wt.%)

These results are hardly surprising; it is in fact a sedimentological cliché that carbonate grains in the marine environment are readily coated with organic matter, both living and dead, particulate and dissolved (Lipman, 1922; Chave, 1965). It follows that the natural association of carbonate sediments with environments of high organic productivity should favour the high organic carbon values found in these deposits. Shimkus and Trimonis (1974), for example, observed a good correlation between large amounts of organic matter and high concentrations of $CaCO_3$ in Black Sea sediments.

However, in contrast to Recent sediments, the organic carbon content of ancient carbonates are consistently much lower than the Corg content in ancient shales (Hunt, 1961; Gehman, 1962; Baker, 1962; Tissot and Welte, 1978). Weeks (in Gehman, 1962,p.895) sought to explain this disparity by invoking aeration and oxidation in the shallow water depositional environment of carbonates; but as Gehman (ibid, p.896) pointed out: 'Because we find so much organic matter in Recent lime sediments, it is difficult to explain the lack of organic matter in ancient limestones by their relatively shallow aerated environment of deposition.' While oxidising conditions characterise certain coarse grained carbonate facies (as indeed, coarse terrigenous facies), carbonate sediments, in general, also form reducing conditions. Romm (1956: in Veber and Gorskaya, 1965) concluded from a study of various Recent sediment facies that more negative Eh, higher ratios of Fe(ll) to Fe (lll) and so on tend to go with higher carbonate content. Based on the ratios of Fe(ll) to Fe(lll) and S reduced to S sulphate, Alizade and Shoikhet (1967) also confirmed the deeper reduction of the carbonate sediments on the eastern coast of the South Caspian Sea as compared to the chiefly terrigenous deposits of the basin. Measurements made during the present study revealed that the majority of Recent carbonate facies have a negative Eh and smell strongly of H_2S, which in itself is indicative of reducing conditions. Lindbloom and Upton (1961) have noted 'the extreme reducing conditions and the high H_2S content associated with carbonate muds. They found that carbonate muds from Florida Bay and the Gulf of Batabano had an average Eh of -200 mV compared to positive Eh for some Orinoco Delta clays. The high content of Sulphur in crude oils from carbonate reservoirs attest, in part, to the high reducing conditions that were operative in the sediments. The fact of euxinic conditions in carbonate mud environments has been noted by several authors. (Hedberg, 1964; Mayerhoff and Hatten, 1974; and others).

The author believes that the answer to the lower Corg content of ancient carbonates as compared with ancient shales lies in the convertibility of the organic matter in carbonates; this subject matter is treated as part of the following discussion on the type and convertibility of organic matter in carbonates.

VII. 3 TYPE AND CONVERTIBILITY OF ORGANIC MATTER IN CARBONATES

Sedimentary organic matter is derived from numerous biotic sources. In general, aquatic organic matter is more suitable than terrestrial organic material for petroleum generation. This is because the amount and type of hydrocarbons that an organic matter can generate is mainly a function of its hydrogen content and terrestrial organic matter contains, on the average, only about one half as much hydrogen as aquatic organic matter.

Carbonate facies are formed and deposited in aquatic environments. Because of this basic association, the organic matter in carbonates would be aquatic organic matter. The principal contributors are believed to be the more abundant subaqueous life forms such as phytoplankton$ and algae. Other aquatic organisms, both floral and faunal also may be important, depending on the location and depth of sediment deposition. In near shore carbonate environments, some terrestrial organic matter contribution is possible. Theoretically, therefore, carbonates contain the best organic matter from the view point of petroleum hydrocarbon generation. By corollary, the convertibility of such organic matter into petroleum hydrocarbons would be very high. It is pertinent, therefore, to consider the results of measurements of the transformation of organic matter in carbonates made by various authors.

The transformation of organic matter begins at the earlier stages of sediment diagenesis; most probably, it is mainly of a biochemical nature at this stage although evidence is emerging to suggest that low temperature ($<50^{o}C$) reactions may also take place (see Section I.3). Results of studies of bitumens from Recent sediments give exceptionally valuable evidence on trends in the conversion of organic matter in carbonates. Particularly illuminating data have come from the researches of Veber and Gorskaya (1965) and Ali-Zade and Shoikhet (1967) who analysed the bitumen contents of Recent carbonate sediments and analagous argillaceous facies from locations stretching from the Caspian Sea through the Indian Ocean and Cuba to the shelf off Australia and New Zealand. Their results are presented here as Tables VII.2 and VII.3 respectively. Separate results of hydrocarbon analysis of Recent sediments are shown in Table VII.4.

It is remarkable that the carbonates equal or exceed the terrigenous facies as regards total bitumen content. Earlier, Hunt (1961) and Gehman (1962, p.891), had come to a similar conclusion from a comparative study of Recent carbonate and clay sediments. More significant from the viewpoint of petroleum generating reactions is the phenomenon of reduction of these bitumens in the direction of petroleum formation as expressed by the high proportions of oils and hydrocarbons in the bitumens and which apparently is as intense (or even greater) in carbonates as it is in terrigenous deposits. Veber and Gorskaya (ibid) and Ali-Zade and Shoikhet (ibid) also found that the hydrocarbons in the bitumens of these Recent sediments, not only have a similar origin, but are also genetically related to the hydrocarbons of petroleum bitumens (see, for example, Table 8 of Veber and Gorskaya, 1965). The implication of the results is that, under adequate conditions of burial and temperature, the Recent bitumens will proceed along the paths of maturation to form petroleum.

On the strength of the preceding observations, both

TABLE VII.2

DISTRIBUTION OF BITUMEN (INCLUDING BITUMEN COMPOSITION) IN RECENT SEDIMENTS

(after Veber and Gorskaya, 1965)

Specimen	Depth, m	Terrigenous part*, %	Bitumens A + C in dry weight of sediment, %	Benzene fraction, %	Bitumen coefficient, %	Composition of benzene part of bitumen A + C					Components of benzene part of bitumen A + C, %			
						C,%	H,%	S,%	O + N,%	C/H	Oil	Benzene tars	A-b tars	Asphalt and asphaltic acids
1	5	19.3	0.129	87.5	8.2	66.2	10.5	1.4	21.9	6.3	27.2	10.0	11.7	51.1
2	6	15.9	0.502	82.3	9.6	64.9	9.6	3.1	22.4	6.8	21.0	9.3	17.5	52.5
3	1	14.8	1.160	92.2	20.9	74.2	9.5	3.2	13.1	7.6	25.0	12.2	13.9	48.9
4	0.3	57.6	0.092	64.1	9.0	72.1	10.3		13.9	7.0	25.5	22.7	16.8	35.0
5	56	95.3	0.088	84.5	15.4	72.8	10.6	0.8	15.8	6.9	50.3	19.2	15.8	14.7
6	140	26.8	0.028	88.3	5.1	71.5			17.1	6.7	31.3	23.3	18.2	27.4
7	120-125	0.7-2.1	0.014	82.6	8.0	75.0	11.1	0.7	13.2	6.8	37.7	29.6	15.6	17.1
8	4000	35.6	0.027	76.6	5.3	64.5	9.1	0.5	25.9	7.2	31.1	17.7	10.8	40.4

* Dry residue after decalcification.

1) Calcareous sand, Mean diameter (Md) = 0.23 mm, Kenderli Gulf;
2) Calcareous mud, Mean diameter (Md) = 0.033mm, Kenderli Gulf;
3) Calcareous sand, Mean diameter (Md) = 0.056mm, Cuba;
4) Terrigenous sand (for comparison), Mean diameter (Md) = 0.145mm, shore of Caspian;
5) Terrigenous (sandy-silt) mud, Mean diameter (Md) = 0.086mm, Kergelen Island;
6) Calcareous sand, Mean diameter (Md) = 0.3mm, Kergelen Island;
7) Coarse carbonate rubble (mean of 3 analyses), shelf to south of New Zealand and Australia;
8) Deep-water foraminiferal mud (mean of four analyses), Indian Ocean.

TABLE VII.3

DISTRIBUTION OF BITUMEN COMPONENTS IN THE UPPER HORIZONS OF SEDIMENTS

from the Caspian Sea (After Ali-Zade and Shoikhet, 1967)

NOS OF STATIONS	SEA DEPTH (m)	HORIZON OF SEDIMENT (cm)	TYPE OF SEDIMENT	COMPONENT COMPOSITION OF BITUMEN, %				
				OILS	BENZENE	ALCOHOL-BENZENE RESINS	ASPHALTENES	ASPHALTOGENIC ACIDS
			CARBONATE SEDIMENTS OF THE EASTERN SLOPE					
25	6	0-25	Pelitomorphic mud	20.6	10.3	27.3	15.8	26.0
27	8	0-10	Coarse-grained sandy mud	30.9	2.5	30.9	11.8	23.9
14	14	0-10	Sandy mud	13.9	4.9	53.2	16.5	12.2
15	18	0-10	Sandy mud	13.8	1.6	50.0	51.8	32.8
26[a]	22	0-15	Muddy sand	11.7	10.6	48.3	17.9	11.5
19 + 28	32-38	0-5	Shelly-oolitic sand	26.1	1.9	51.4	3.1	17.5
28	38	5-10	Sandy mud	16.0	13.3	36.3	10.6	23.8
18	45	0-20	Pelitomorphic mud	11.7	1.8	51.0	10.0	26.0
20	65	0-20	Pelitomorphic mud	12.8	4.3	43.3	13.5	26.1
			TERRIGENOUS SEDIMENTS OF THE WESTERN SLOPE					
4	78	0-20	Argillaceous mud	14.2	5.2	56.6	4.2	19.8
7	120	0-30	Argillaceous mud	10.2	5.0	36.2	16.2	32.4
3	140	0-30	Argillaceous mud	19.4	1.3	38.0	8.9	32.4
1	170	4-30	Argillaceous mud	29.8	6.1	35.2	19.7	9.2
2	240	0-30	Argillaceous mud	18.9	1.3	32.2	15.6	32.0

TABLE VII.4

HYDROCARBON CONTENT IN SEDIMENTS OF CASPIAN SEA

(after Ali-Zade and Shoikhet, 1967)

Facies	Type of Sediment	Number of Samples	Hydrocarbon content in sediment,% (variation range)	% of the sum of hydrocarbons	
				Naphthenic-methanoic	Aromatic
	CARBONATE SEDIMENTS				
of the bay	pelitomorphic mud	1	0.0388	86.1	13.9
the same	sandy mud	1	0.0285	84.8	15.2
of the littoral shallow-water zone	coarse-grained sandy mud	2	0.0056,0.0129	88.7	7.1
near the bay				92.9	11.3
of the open shelf (sub-littoral zone)	shelly-oolitic sand	2	0.0045	75.0	25.0
the same	muddy sand	1	0.025	93.2	6.8
the same	sandy mud	4	0.0020-0.0130	77.1-94.4	5.6-22.9
the same	mud	3	0.0010-0.0044	70.0-93.2	6.8-30.0
of the outer shelf	pelitomorphic mud	7	0.0020-0.0047	83.7-94.5	5.5-16.3
	TERRIGENOUS SEDIMENTS				
of the sub-littoral zone	sandy mud	2	0.0073-0.0152	93.2	6.8
the same	mud	2	0.0055-0.0090	84.8-91.5	8.5-15.2
the same	argillaceous mud	4	0.0041-0.0170	81.8	18.2
of the continental slope	the same	12	0.0069-0.0680	83.2-89.3	10.7-16.8

Veber and Gorskaya (ibid) and Ali-Zade and Shoikhet (ibid) claimed independently that their data confirmed that geologically more ancient carbonate rocks may be syngenetically oil-bearing. It was part of the objective of this study to experimentally verify this possibility. The technique employed for this was Pyrolysis. 60 samples were analysed for Total Organic Carbon (CT) and for Residual Carbon (CT) (Table VII.5 and fig.VII.1). The theory and procedure of this technique have been discussed in section V.6. In this method, CT-CR is approximately equal to 'S_2' in the Rock-e-val method of Espatalie et al (1977). Applying this consideration, it is obvious that a very great proportion of the organic matter in carbonates is pyrolysis degradable. This fraction is called 'useful carbon' and represents that portion of the organic matter which would be transformed during petroleum generating reactions. Correspondingly the CR/CT ratios are very low. The indication is that the contained organic carbon would convert more readily and more completely to hydrocarbons given adequate physico-chemical conditions. The present results confer added validity to the concept of syngenetic petroleum formation in carbonate rocks.

One of the earliest pyrolysis experiments on Recent carbonate sediments as a clue to the origin of the petroleum in carbonate rocks, was performed by Trask (1928). He found that on distillation, modern carbonate sediments from Lake Macaraibo, Pamlco Sound, Florida Bay, and the Gulf of Batabano in Cuba, yielded up to 2.5 gallons of oil per ton (that is, about 1 percent by weight). Trask declared: 'the fact that one percent of the total weight of these sediments can be caused to become volatile and condense to a liquid oil is very significant and indicates that such beds are potential future source beds ----' (ibid, p557). He concluded: 'Consequently, the evidence indicates that limestones may be source beds of oil' (loc.cit.).

In the light of the demonstrated potential of Recent carbonate sediments to generate hydrocarbons, it is pertinent at this juncture to recall the subject of low organic matter, but high hydrocarbon content,of ancient carbonates vis-a-vis shales , which

TABLE VII.5 RESULTS OF PYROLYSIS OF RECENT CARBONATE SEDIMENTS

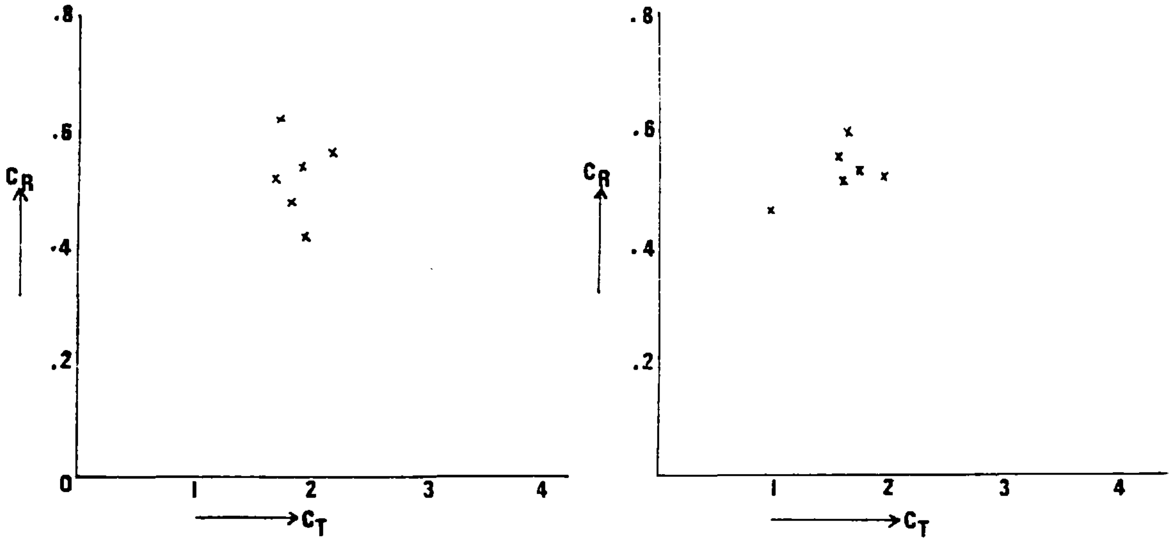
SAMPLE NO.	CT	WT.% LOSS ON PYROLYSIS	CR	CR/CT
FL-RAS-01	1.93	34.6	.54	.3
-02	1.7	35.2	.52	.3
-03	2.21	34.8	.56	.3
-04	1.76	34.5	.62	.4
-05	1.84	35.7	.48	.3
-06	1.96	36.0	.42	.2
FL-BS- 11	.98	33.6	.46	.5
- 12	1.54	34.2	.55	.4
- 13	1.96	36.1	.52	.3
- 14	1.6	34.7	.51	.3
- 15	1.72	35.6	.53	.3
- 16	1.63	34.3	.6	.4
FL-SM- 21	3.97	42.7	.28	.1
- 22	4.15	43.2	.26	.1
- 23	3.07	42.5	.3	.1
- 24	3.76	41.8	.27	.1
- 25	4.24	43.5	.34	.1
- 26	2.85	42.6	.32	.1
FL-LM- 31	3.63	44.3	.26	.1
- 32	4.29	43.7	.29	.1
- 33	3.47	42.8	.36	.1
- 34	3.67	43.2	.24	.1
- 35	2.89	44.0	.32	.1
- 36	4.13	43.7	.37	.1
FL-GHM-41	5.23	43.2	.24	.1
-42	2.97	44.2	.2	.1
-43	3.73	45.1	.22	.1
-44	4.19	44	.26	.1
-45	3.86	43.1	.21	.1
-46	3.9	42.0	.32	.1

TABLE VII.5 contd/....

SAMPLE NO.	CT	WT.% LOSS ON PYROLYSIS	CR	CR/CT
FL-AS- 51	16.2	63.8	.15	<.1
- 52	17.34	62.1	.19	<.1
- 53	18.69	64.0	.21	<.1
- 54	17.94	63.6	.22	<.1
- 55	16.8	62.8	.18	<.1
- 56	17.83	65.2	.14	<.1
EL-SS- 01	1.7	31.3	.54	.3
- 02	1.9	33.6	.47	.2
- 03	1.42	32.1	.43	.3
- 04	2.32	33.4	.5	.2
- 05	1.86	32.8	.52	.3
- 06	1.76	33.2	.54	.3
EL-CS- 11	2.1	34.1	.49	.2
- 12	2.3	33.6	.61	.3
- 13	1.97	32.9	.58	.3
- 14	1.8	33.3	.55	.3
- 15	1.72	34.6	.43	.3
- 16	2.0	33.4	.47	.3
EL-LM- 21	4.04	44.3	.23	.1
- 22	4.0	45.0	.3	.1
- 23	3.26	44.1	.34	.1
- 24	3.78	43.6	.33	.1
- 25	4.1	44.2	.36	.1
- 26	4.23	43.8	.41	.1
EL-CRS-31	3.42	42.4	.48	.1
-32	4.2	44.3	.52	.1
-33	2.83	45.2	.51	.2
-34	2.9	44.8	.48	.2
-35	3.4	43.6	.43	.2
-36	4.24	44.2	.47	.1

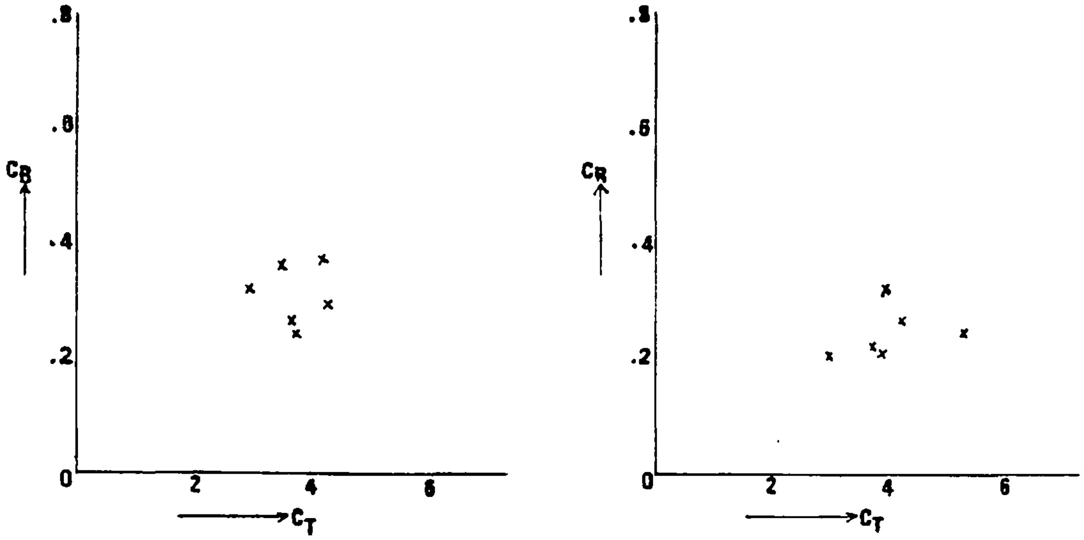
FIG.VII.1 $^{CR}/CT$ PLOTS FROM PYROLYSIS OF RECENT CARBONATE SEDIMENTS FROM FLORIDA AND THE BAHAMAS

A. FLORIDA KEYS SEDIMENTS



Samples FL-RAS-01→ 06

Samples FL-BS-11 → 16

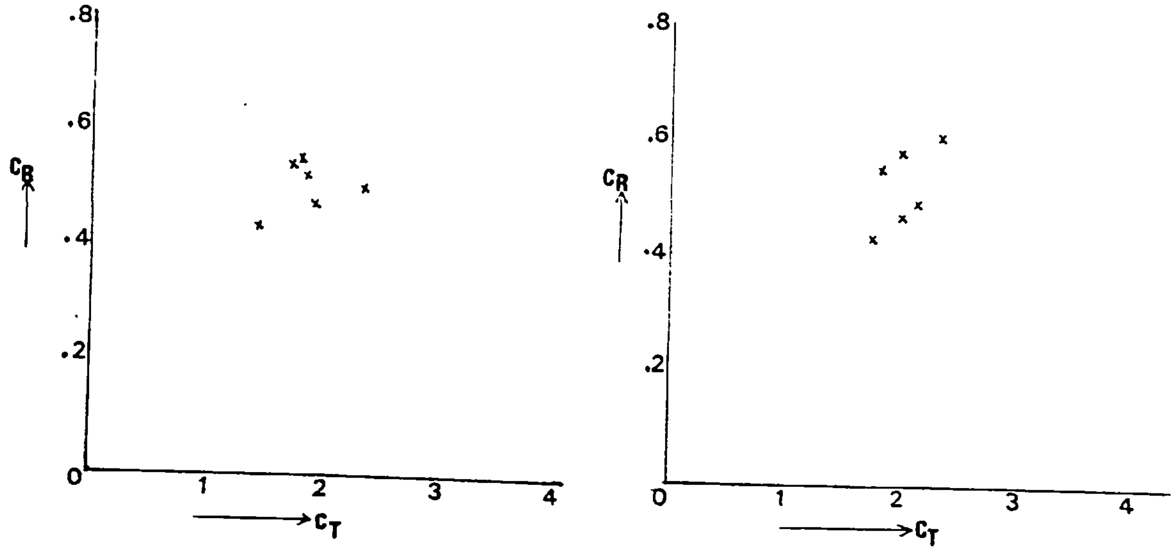


Samples FL-LM-31 → 36

Samples FL-GHM-41 → 46

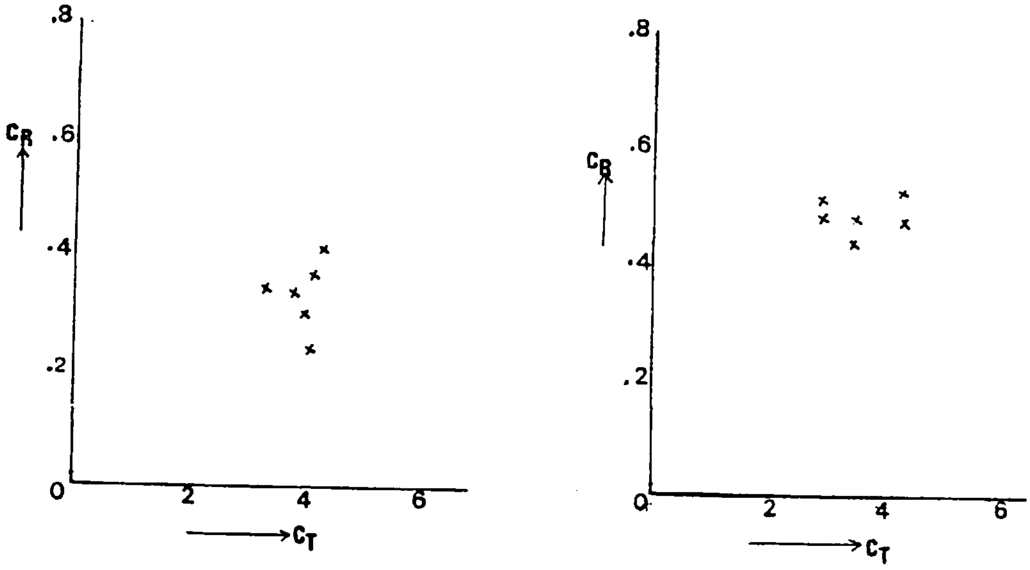
FIG. VII.1 contd.

B. ELEUTHERA BANK SEDIMENTS



Samples EL-SS-01 → 06

Samples EL-CS-11 → 16



Samples EL-LM-21 → 26

Samples EL-CRS-31 → 36

was touched upon in the preceding section (VII.2), but deferred for later discussion in this section.

From independent researches, Hunt (1961), Baker (1962) and Gehman (1962) noted that in contrast to Recent sediments, ancient limestones have much less organic matter but higher hydrocarbon content when compared to ancient shales. Earlier, similar data had been presented by Upsenskïi(1949) and Petrova et al (1955). Table VII.6 (after Hunt, 1961) emphasises this fact. The mean hydrocarbon content of ancient limestones was 340ppm whereas shales contained 300 ppm against organic matter values of .29 and 2.1 weight percent respectively. In discussing his own data, Gehman (ibid) posed two questions : a) why do ancient limestones have so much less total organic matter than Recent sediments of identical textural type ? b) why does the organic matter of ancient limestones contain such a high proportion of hydrocarbons compared to that of ancient shales ?

In answer to the first question, Gehman suggested that the lack of adsorptive capacity of carbonate minerals (in contradistinction to clay minerals) would render the organic matter in carbonates more susceptible to leaching by meteoric waters in situations where clays would retain their organic matter. Gehman published the results of adsoprtion experiments comparing clay and carbonate minerals. According to his data (fig.VII.2), carbonates show essentially no adsorption, compared to the high capacity shown by clays. Gehman concluded: 'The measured difference in adsorptive power suggests that limestones may lose their organic matter because they cannot hold it; shales on the other hand, retain their organic matter because it is tightly adsorbed and protected from chemical attack and leaching (ibid.p894). This argument has been repeated by many workers (eg. Hunt, 1967). However, the data and interpretation of Gehman have been invalidated by the experimental results of Suess (1968), Chave and Suess (1970), Suess (1970, 1973), Mitterer and Carter (1977), Carter and Mitterer (1978), Carter (1978) which demonstrate that organo-carbonate association is as effective and prevalent a phenomenon as organo-clay reactions.

TABLE VII.6 DISTRIBUTION OF HYDROCARBONS AND TOTAL ORGANIC MATTER IN SHALES AND CARBONATES (after Hunt, 1961)

HYDROCARBONS			TOTAL ORGANIC MATTER		
RANGE OF HC (p.p.m.)	DISTRIBUTION AS % OF TOTAL		RANGE OF OM AS % OF ROCK	DISTRIBUTION AS % OF TOTAL	
	SHALES	CARBONATES		SHALES	CARBONATES
0-3.1	0.0	0.0	0.00-0.031	0.1	0.5
3.1-6.2	0.3	0.4	0.031-0.062	0.7	14.9
6.2-12.5	3.0	4.3	0.062-0.125	1.5	21.9
12.5-25	10.3	10.3	0.125-0.25	3.9	32.0
25-50	20.0	14.9	0.25-0.50	11.1	19.9
50-100	19.4	18.9	0.50-1.0	22.0	7.1
100-200	19.3	16.7	1.0-2.0	35.3	2.3
200-400	11.8	18.5	2.0-4.0	16.6	1.3
400-800	6.4	7.5	4.0-8.0	5.2	0.3
800-1600	5.2	5.0	8.0-16.0	1.8	0.0
1600-3200	2.5	2.1	16.0-32.0	1.6	0.0
3200-6400	1.5	0.7	32.0-64.0	0.1	0.0
6400-12800	0.0	0.7			
No. of samples	791	281		791	397
Logarithmic mean	103 p.p.m.	112 p.p.m.		1.2%	0.17%
Arithmetic mean	300 p.p.m.	340 p.p.m.		2.1%	0.29%

Concerning his second question on the abundance of hydrocarbons in limestones compared to shales, Gehman (1962) suggested: 'One possibility, of course, is that more hydrocarbons are generated by chemical reaction in limestones than in shales' (ibid, p.894). As an alternative, he suggested that the effects of leaching would result in relative enrichment of hydrocarbons but the merit of this argument is contradicted by the data of Suess (1968) and others cited above.

The writer believes that both questions posed by Gehman can be answered by invoking the greater convertibility of the organic matter contained in carbonate facies. Given adequate thermal energy supply, the convertibility of organic matter to oil depends on the availability of hydrogen atoms and the molecular structures of the organic compounds. As has been emphasised elsewhere (section VII.2), opinion is unanimous that the aquatic organic matter normally associated with carbonates and in particular, marine organic remains of phytoplanktons, algae, et cetera appear to have the highest convertibility factor. By contrast, terrestrial organic matter have the lowest convertibility factor primarily because of their relatively low hydrogen content and richness in lignin and carbohydrates neither of which contributes significantly to oil-forming processes. From a study of average compositions of organic matter in different facies, Ali-Zade and Shoikhet (1967, p.525) observed that the main peculiarities distinguishing carbonate sediments from terrigenous ones are a higher content of easily hydrolysed components and the corresponding decrease in the amount of insoluble organic residue. The observations of Taguchi (1975) were similar.

Another relevant consideration in the convertibility of organic matter is the presence or absence of recycled organic matter in a sedimentary bed. Such reworked material is essentially spent when it is deposited and will generally not take part in hydrocarbon generating reactions. Carbonates contain autochtonous aquatic material but little or no reworked material; therefore their organic matter would apparently convert more readily and more completely than organic matter in shales which generally have higher recycled organic

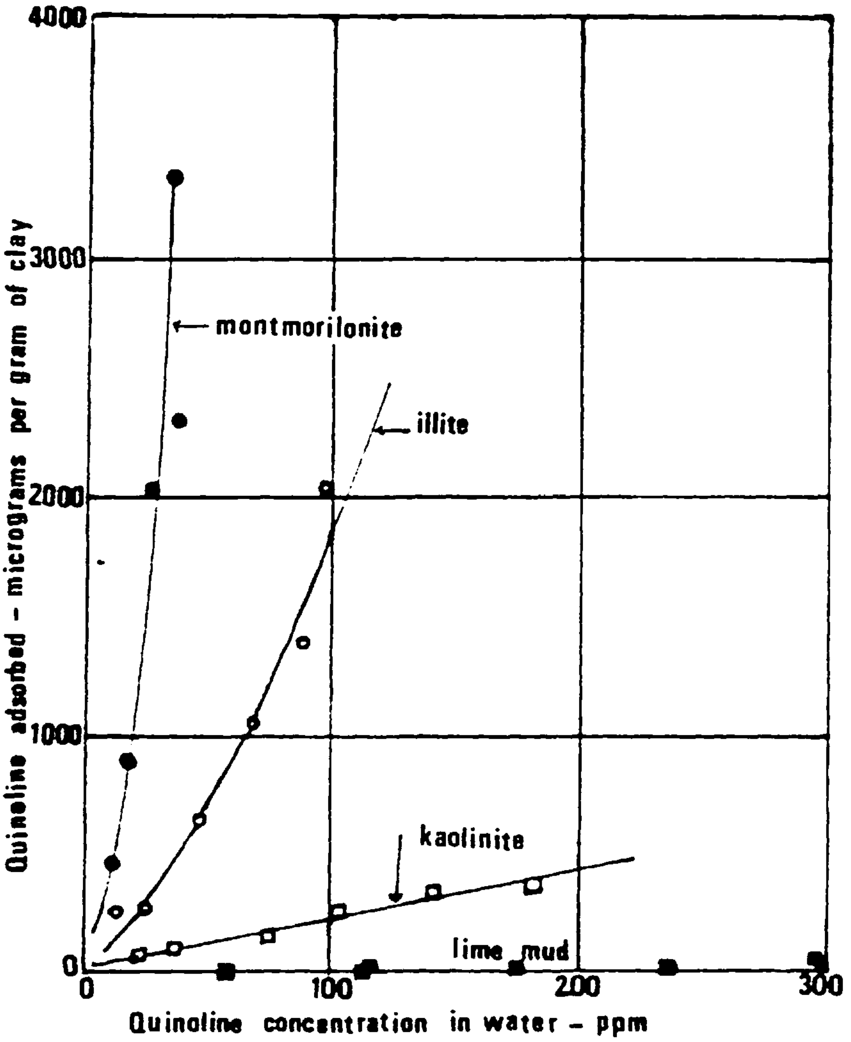


FIG. VII.2 ADSORPTION OF QUINOLINE BY CLAY MINERALS AND LIME MUD (after Gehman, 1962) materials. For many ancient sedimentary rocks in basins where the geothermal gradient and geologic time are deemed to have been adequate to have allowed for the generation and expulsion of petroleum hydrocarbons, the organic matter content in such rocks represents residual organic matter sensu stricto. It is obvious that ancient limestones which have generated (and expelled) hydrocarbons will have very little residual organic matter whereas shales would have higher residual organic matter due to the higher initial content of recycled materials. For example, in a separate research, the writer found that paralic shale samples from the Niger Delta petroliferous province, after pyrolysis, contained residual carbon of up to 1.7 wt. percent even though their CR/CT ratios were high (.6 - .8) and the shales deemed to have generated and expelled hydrocarbons which are now found in the contigous sandstone reservoirs (Lambert - Aikhionbare and Ibe, 1980). A subsequent microscopic examination of the organic residue after maceration showed it contained appreciable reworked terrigenous organic material including coaly particles. In contrast, presumed carbonate source beds had residual carbon values of less than or about .1 wt. percent (Analyses file: Source Rock laboratory, Imperial College). As many authors have cautioned, failure to identify and allow for recycled material in shales may result in a non-source bed being misinterpreted as a potential or effective source bed (Philippi, 1965; Tissot and Welte, 1978). The reverse is also true, namely, failure to recognise that organic matter in carbonates converts more completely to hydrocarbons could result in the rejection of a carbonate source bed because of its very low residual organic content.

One further point deserves mention here. Several authors have tended to associate the presence of clay minerals in sedimentary beds with greater efficiency of conversion of their contained organic matter to petroleum hydrocarbons. Although the role of clays in organic matter transformation has been questioned (Sokolov, 1948; Hoering and Abelson, 1963) particularly in the presence of formation water (see Hunt, 1979, p.129), there is experimental evidence to demonstrate their efficacy in the generation of hydrocarbons from organic matter (Frost, 1945; Brooks, 1948, 1952; Weiss, 1963; Jurg and Eisma, 1964, Goldstein (in Press); Eisma et al, 1967. Consequently, the absence of clays in pure carbonates has been used as one argument against the capacity of such carbonates to generate petroleum. It should, however, be recognised that even pure carbonates contain a number of trace elements that would serve the function of catalysts in lieu of clay minerals (Andreev, 1956; Shimoyama and Johns, 1972 ; Hunt, 1979; this work, see section II.4) Also, organic catalysts in Recent carbonates may be more important than has been recognised (Vleet and Quinn, 1978) particularly in the early stages of organic matter transformation. Besides, the possibility of a catalytic role for carbonate minerals has been indicated by the results of Valitov (1974).

VII. 4 A PETROLEUM EXPULSION MECHANISM IN CARBONATES ?

At a glance, the apparent lack of an effective expulsion mechanism would appear to be the most serious and relevant of all the objections to the concept of carbonates as effective source beds. Although the processes of petroleum migration from source beds into reservoir rocks are not entirely clear, it is generally held that migration with formation fluids during late compaction is the dominant mechanism (Hodgson, 1964; Magara, 1968, 1973, 1976a; Tissot and Welte, 1978; Hunt, 1979). In later stages of compaction, the release of water associated with the transformation of clay minerals provides a boost to fluid migration. It is clear from previous arguments that the history of early lithification in most carbonate sediments and the general absence of clays in pure carbonates precludes the operation, in carbonates, of this dominant mode of hydrocarbon migration.

In fractured reservoirs which occur mostly in tectonised belts, the fractures have been invoked as major avenues of migration of oil and gas from some deep lying source beds (Lees, 1933, 1934, 1938; Lees and Richardson, 1940; Dunnington, 1958). While there is little question about the theoretical possibility of this proposal, there are grave objections to the theory and an alternative view point is that the oil in these fractured limestones is also indigenous (Richardson, 1924; Howard, 1934; Thomas, 1950; Weeks, 1950, 1958) and that the fractures only provided low pressure centres for the 'gathering' of the oil generated within such reservoirs. On one of the better known examples of a fractured reservoir, the Asmari Limestone, Richardson (1924,p.276) stressed; 'If it is a matter of evidence of association, the indigenous theory of the origin of oil in the Asmari Limestone has much more in its favour'. Migration of hydrocarbons through microfissures formed by abnormal pressures has been proposed by Tissot and Welte (1978) as a viable mechanism in dense impermeable limestones. This proposal has been found untenable in a discussion in Section VI.5 and it will be repetitive to detail the arguments here.

It would appear, therefore, that in the majority of cases, the usual migration mechanisms cannot operate in carbonates. The implication is that, even with the demonstrated capacity to generate hydrocarbons, carbonates cannot become source beds since they cannot expel their generated hydrocarbons. This objection is valid only if petroleum generation and accumulation in carbonates are conceived of along the lines of the model operative in shale - sandstone sequences where there are separate source beds and reservoir formations. However, it is evident from preceding discussions that not only are petroleum forming materials deposited at the same time and place with inorganic carbonate minerals, but that conditions are usually adequate for their ultimate conversion to petroleum. Given this capacity of carbonates to generate their own hydrocarbons, it is not necessary to propose an external source for their contained hydrocarbons; it would appear that accumulation of hydrocarbons would also result in those carbonate facies in which primary porosity has been preserved. In other cases where carbonate facies undergo early lithification, development of secondary porosity through fracturing, solution or recrystalisation would create free space favourable to the accumulation of hydrocarbons in these otherwise impermeable facies (Illing et al, 1967; Andreev et al, 1968).

In such instances, migration of hydrocarbons need occur only from other sections within the same bed in which it is generated to 'gather' in the newly formed porosity.

CHAPTER VIII

SUMMARY AND CONCLUSIONS

'To live comfortably with Science, it is necessary to live with a dynamically changing system of concepts. It is necessary to live with enough conservatism to resist the easy abandonment of concepts, but enough flexibility to be able, when necessary, to switch rather than fight.'

Walter Orr Roberts, 1967
'Science, a wellspring of our discontent.'

VIII. 1- BACKGROUND TO PRESENT STUDY

The light hydrocarbons, and in particular the saturated members up through 5 carbon atoms, form the bulk of natural gas and a minor but characteristic fraction of crude oils. Of these hydrocarbons, only the lowest member, methane, has been recognised as a natural product of microbial degradation. The geochemical significance of light hydrocarbons (C_2+) lies in the fact that, unlike the C_{15}+ compounds, these hydrocarbons have not been reported as constituent of living organisms or as metabolic products and are practically absent in Recent and shallow sediments. According to the present state of geochemical knowledge, the occurrence of C_2+ light hydrocarbons in recent and shallow sediments is diagnostic of either migration or diffusion of hydrocarbons from a petroleum accumulation at depth or possibly, the onset of thermal diagenesis of the organic matter in the sediments. The former is the basis of geochemical exploration for petroleum.

Following a detailed mathematical and statistical treatment of geochemical exploration data acquired over the Locton Natural gas reservoir by the British Gas Corporation, Ferguson (1975) established a strong correlation between the content of carbonate,and in particular oolites,in the analysed samples and higher concentrations of light hydrocarbons detected. This factor led to doubts about the validity of the anomaly maps prepared from the data. From results of comparative analysis of analagous samples from Weardale, an area underlain by granites (thus ruling out migration from depth), Ferguson concluded that the source of the hydrocarbons was the carbonates contained in the samples. To account for the origin of the hydrocarbons, Ferguson extracted and analysed light hydrocarbons from Recent oolites and oolitic sediments collected from the United Arab Emirates, Arabian Gulf. The relative concentrations of methane, ethane and Propane (2:1:0.6) was rather unexpected and prompted Ferguson to declare that, 'Clearly this result is significant and when the origins of petroleum are considered, may be of some importance' (ibid, p.24).

VIII. 2 SUMMARY OF RESULTS AND DISCUSSIONS

In the present study, over 200 Recent carbonate oolites were analysed by a different technique for content and composition of light hydrocarbons (C_1 - C_5+). The concentrations (in ng gas/g dry sediment) of individual hydrocarbons range from 31 to 76 methane, 21 to 46 ethane (probably includes traces of ethene), 27 to 75 propene, 108 to 1178 propane, 21 - 73 i-butane, 26 - 131 butene, 43 to 341 n-butane. The C_5+ compounds were backflushed and integrated as single peaks and range from 744 to 6414. Total C_1-C_4 saturated hydrocarbons vary between 1.7×10^{-5} and 3.6×10^{-5} g.perg. of organic carbon. Based on their characteristics, the hydrocarbons were judged not to be mere biogenic or migrated gas but rather, authigenic products of early diagenetic biochemical and low temperature chemical reactions. Among the arguments cited in favour of this inference are the following:

a) the C_2+ saturated hydrocarbons exceed methane content;

b) there are differences in the amounts and distribution of C_1-C_5+ hydrocarbons present in the oolites and those in the sedimentary carbonate facies adjacent to the oolites;

c) the considerable admixture of unsaturated hydrocarbons;

d) the high values of backflushed C_5+ compounds

e) no known hydrocarbon accumulations exist in this area; none of the wells drilled in adjacent locations encountered petroleum (Amato, 1978)

f) although the relationship is not simple, there is a discernible variation in hydrocarbon yields with organic carbon content.

The implication of the results of the light hydrocarbon analysis is that with increasing depth of burial and exposure to higher temperatures, the sediments would serve as petroleum source beds. For this inference to be correct, the oolites must contain adequate organic matter of the right kind to generate commercially significant hydrocarbons. Organic carbon analyses of the oolites showed values of 1.23 - 4.13 wt. percent which are well above the 0.3 wt. percent minimum requirement for carbonate sediments (0.5 wt. percent for clastic facies) to be considered potential source beds for petroleum. Standard physical and chemical techniques were applied to characterise both the bitumen and Kerogen fractions of the organic matter. The results revealed that, although immature, the organic matter is of algal-amorphous facies, indicating a very high potential for generating petroleum hydrocarbons.

This conclusion is promising; over the years, many petroleum geologists have suggested that the petroleum in oolites is indigenous to the rocks in which it is now found (Henson, 1951; Baker and Henson, 1952; Steineke et al, 1958; Aramco Staff, 1959; Hedberg, 1964; Owen, 1964). The arguments adduced in favour of this proposal have been largely circumstantial, based for the most part on field lithologic associations in the areas of petroleum occurrence. The results of the present study afford experimental support to hitherto inferential evidence. A scheme for in situ generation and accumulation of petroleum hydrocarbons in oolites has been advanced and as a test of its validity, a case study in nature was undertaken. The prolific Arab formation of Saudi Arabia which produces oil from 'closed' oolitic beds was selected for this purpose because it offers the least number of alternative solutions. The outcome of that study was supportive of the concept of the indigenous origin of their contained hydrocarbons.

The most obvious objection to such a theory is that the quantities of petroleum stored in carbonate 'reservoirs' are so great that it is very difficult to preclude at least some contribution from an extraneous source. It is suggested however, that the in situ formation of petroleum in oolites which obviates an extensive and wasteful primary migration process, affords another explanation for the exceptionally rich petroleum accumulations in such inherently porous carbonates. It is admitted that in the present geological thinking, oolites are known as excellent reservoirs with no source bed role. Even those authors who admit of a limited source bed function for carbonates seek, in general, to distinguish between effective source beds like the fine grained carbonate facies and porosity providers like oolites and reefs. The demonstration, in this study, of a probable source bed role for oolites is therefore considered significant to the whole problem of the origin of the petroleum found in carbonate rocks.

As part of the objective of this research several samples of a wide textural variety collected from the Recent carbonate environments of the Bahamas and Florida Keys were analysed for organic carbon content. The results which showed values between 0.98 and 18.69 weight percent pointed to the need to investigate their petroleum source potential. Pyrolysis of these samples revealed that their organic matter was highly degradable (that is, the content of useful carbon is high) and therefore possess excellent potential for hydrocarbon generation.

Many of those who strenuously object to the idea of pure carbonates as source beds offer as their reasons; a) the lean organic content of carbonate rocks; b) the absence of clay minerals necessary to catalyse the conversion of organic matter to petroleum; and c) the lack of any effective migration mechanism.

These objections have been examined against the background of the organic carbon data and pyrolysis results. It was argued that the organic matter in ancient carbonate rocks represents residual organic carbon sensu stricto; since Recent carbonate sediments are found to have as much or even greater organic matter compared to Recent shales, the low residual organic matter content of ancient carbonates reflects the general absence of recycled materials in the dominantly autochtonous organic matter of carbonates and, by corollary, its higher convertibility to petroleum hydrocarbons. Although the catalytic action of clay minerals in the conversion of organic molecules has been demonstrated by several workers, it has been suggested that in pure carbonates, the role of catalysts is fulfilled by the various elements like V, Cr, Ti, Sr, Al, Fe, Cu which are present in trace amounts. These trace elements are associated either with the organic matter in carbonates or 'inherited' as impurities from the precipitating medium. Besides, indication of a possible catalytic role for carbonate minerals has come from the work of Valitov (1974).

As for the lack of an effective hydrocarbon expulsion mechanism, such an objection could only apply if petroleum accumulation in carbonates is conceived of along the lines of the model operative in shale - sandstone sequences where there are separate source and reservoir beds. However, given the capacity of carbonates to generate hydrocarbons, it is reasonable to propose that accumulation of these hydrocarbons would result in those carbonates with porosity, whether primary or secondary. Many unproductive impermeable limestones are impregnated with oil which is both a confirmation of their ability to generate petroleum and their inability to expel it without the development of porosity. The suggestion has often been made that certain properties of oil produced from carbonates, like their high sulphur and Nitrogen contents, are genetic and in some way suggestive of an indigenous origin for the oil.

VIII. 3 CONCLUSIONS

One of the 'lingering' problems of petroleum geology is the origin of the petroleum stored in carbonate rocks. At the hub of the problem is the preponderant view among the overwhelming majority of investigators that shales are the basic, perhaps the only, existing source for petroleum. However, a serious difficulty in admitting such a universal source facies is the fact of the occurrence of petroleum in carbonates in a number of regions, like the Middle East, where it is impossible to find shale beds which can be regarded as source for the petroleum.

Almost since the inception of the organic theory of petroleum formation, the possibility of the formation of petroleum in carbonates has been repeatedly suggested. The evidence adduced in support of this proposal, though overwhelming have, for the most part, been deduced from field stratigraphic relationships in petroliferous carbonate provinces (Hunt, 1863; Orton, 1888; Richardson, 1924; Hedberg, 193 ; Adams, 1934; Howard, 1934; Muir, 1934; Thomas, 1950; Baker and Henson, 1952; Steineke et al, 1958; Aramco Staff, 1959; Hedberg, 1964; Owen, 1964; Hunt, 1967 among others). But experimental evidence have also been advanced in support of this concept (Trask, 1928; Uspenskii, 1949; Putsillo, 1951; Andreev, 1955; Petrova, 1955; Hunt, 1961; Gehman, 1962; Baker, 1962; Veber et al, 1960; Veber and Gorskaya, 1965; Ali-Zade and Shoikhet, 1967 and others).

Nevertheless, only grudging acceptance is made of the <u>possibility</u> of carbonates as source beds for petroleum. The present investigations were undertaken in the hope of contributing to the rather limited knowledge about the effectiveness of 'pure' carbonates as source beds. Attention was directed at Recent carbonate sediments on the principle of the present as a key to the past. The choice of oolites as a starting material was appropriate because oolites are familiar host rocks for petroleum but are thought to have no source bed role; yet in a majority of cases, field lithologic associations in oolite 'reservoirs' admit of no other suggestion than an indigenous origin of their oil.

The study of light hydrocarbons from oolites was essentially exploratory in nature. The results, however, were indicative of the need to further investigate the potential of the sediments to generate hydrocarbons. Subsequent physical and chemical analyses in furtherance of this possibility proved that, in many cases, oolites are also the source for their contained petroleum. To the knowledge of the writer, the results of this study represent the first experimental verification of a possibility that has been started by various authors. The scheme for in situ generation and accumulation of petroleum hydrocarbons presented in Chapter 6 represents only a rough scheme or first approximation, needing perhaps, further refinement; but as an initial statement on this subject, it is hoped that it would provide a vantage platform for more profound study of the mechanism of petroleum formation in oolites.

The accumulation of huge quantities of 'gem' organic matter in carbonate sedimentary environments is an undisputed geological fact. Investigation of Recent carbonate facies of a wide textural variety revealed that carbonates, in general, possess the capacity to generate petroleum hydrocarbons. The inference is obvious that in those carbonates that possess adequate porosity, accumulation of the generated hydrocarbons would also result to form petroleum. In many petroleum bearing carbonates, the petroleum forming materials were deposited at the same time and place as the reservoir material; therefore there are no distinct source and reservoir beds but rather integerated source-reservoir beds. Neither is it necessary to account for the migration of hydrocarbons except within the beds that now bear them.

For many years, petroleum geologists have sought the reasons for the notably superior petroleum accumulations in carbonate petroliferous provinces like the Middle East. This puzzle was emphasised more recently by Murris (1980, p.617) who wrote: 'The question remains as to why the Middle East is such an exceptionally rich habitat. Source rocks are not exceptionally thick or rich --- Reservoirs --- are not a class apart --- seals are not unusually thick or abundant.' It is proposed here, that the answer to such questions lies in the in situ origin of their contained hydrocarbons which precludes an extensive and 'wasteful' primary migration process. The need is therefore urgent to further subject this concept to fundamental tests to prove its validity. The writer would wish to impress upon others who may investigate this intriguing problem, the importance of selecting 'pure' carbonates for analyses; this is because, many hybrid sediments (argillaceous limestones and calcareous shales) 'appear both chemically and geologically to be source beds' (Hunt, 1967; p.235). It is also urged that conclusions reached through experimental studies be supported by case studies in nature because, in the final analysis, the questions on the origin of petroleum are primarily a geological problem and it is not sufficient to point out chemical possibilities that cannot be reconciled with geological evidence (Krejci-Graf, 1963; Colombo, 1967).

Considering the reluctance of many contemporary petroleum geologists to accept the concept of the indigenous origin of petroleum in carbonates, the idea had surprisingly early origins. Earliest statements in this regard came from T. Sterry Hunt, beginning in 1861 and based on his observations from petroleum bearing carbonates in Ontario, Canada and Ohio, U.S.A. Initial opposition to the concept grew out of Hunt's insistence on the correctness of an adjunct theory, namely, that of limestones as universal source beds for petroleum. Hunt's problem was underscored by Peckam (1884) who, in reviewing the hypotheses on the origin of petroleum postulated in those days, pointed out that, 'for the most part, the opinions expressed may be said to be provincial --- and from these limited observations, generalisations are made to include all the varied conditions under which, bitumen occurs in different parts of the world' (ibid.,p.37).

It must be stressed, therefore, that although the conclusions reached from the present study on the mode of petroleum formation in carbonates are in accord with the known structural and stratigraphic habitat of the vast majority of petroleum accumulations in carbonate rocks, the concept of the indigenous origin of petroleum is not proposed as a universal theory applicable to all cases of hydrocarbon occurrence in carbonates. Despite this reservation, the writer believes, that the proposals advanced in this thesis would prove an important cornerstone, if not the foundation, to the ultimate elucidation of the problem of the origin of the petroleum stored in carbonate rocks.

APPENDIX 1

APPENDIX 1. RESULTS OF ANALYSES OF LIGHT HYDROCARBONS (C_1-C_5+) EXTRACTED FROM VARIOUS ANCIENT (CARBONIFEROUS AND JURASSIC) CARBONATE ROCKS

SAMPLE NO	GROSS CHARACTERISTICS AND LOCATION	AGE	HYDROCARBONS x 10^{-9} g/g dry rk.					CORG Wt.%
			C_1	C_2	C_3	C_4	B/F	
Db/S/601	Dark Skeletal packstone (Somerset,Derbyshire)	Visean	336	28	61	21	N/I	.26
Db/S/602	" "	"	279	64	46	26	69	.34
Db/S/603	" "	"	240	57	36	32	11	.3
Db/S/607	" "	"	224	49	34	29	N/I	.32
Db/S/610	" "	"	219	50	34	32	50	.3
Db/S/613	" "	"	246	58	55	53	57	.29
Ox/B/201	Light coloured mudstone (Bladon Quarry,Oxfordshire)	Middle Bathonian	30	10	43	26	36	.19
Ox/B/206	" "	"	29	13	36	23	NI	
Ox/B/209	" "	"	34	11	39	18	NI	.13
Ox/B/210	" "	"	43	17	55	15	43	.16
Ox/B/211	" "	"	51	23	76	34	39	.14
Ox/B/213	" "	"	33	16	29	46	51	.13
Ls/O/503	Skeletal oolitic packstone (Lincolnshire Limestone) (Wollaston,Northamptonshire)	Lower Bajocian	20	7	56	3	50	.23
Ls/O/505	" "	"	40	19	36	21	62	.19
Ls/O/508	" "	"	37	15	29	23	NI	.24
Ls/O/513	" "	"	43	13	27	35	59	.2
Ls/O/516	" "	"	28	17	25	23	48	.31
Ls/O/519	" "	"	39	13	25	31	56	.17
Ls/O/521	" "	"	23	11	38	29	43	.19
Fr/C/001	Coarse grained skeletal packstone (Chatillon Sur Mer,France)	Bathonian	768	49	104	62	114	.08
Fr/C/002	" "	"	625	36	32	18	15	.06
Fr/C/003	" "	"	810	50	57	34	55	.09
Fr/C/005	" "	"	852	53	57	45	NI	.06
Fr/C/006	" "	"	659	48	69	37	NI	.10
Fr/C/007	" "	"	731	54	63	39	41	.08
Yk/G/701	Dark med.grained skeletal grainstone (Greenhow Mine,Yorkshire)	Visean	59	8	42	403	127	.17
Yk/G/702	" "	"	48	15	42	627	79	.23
Yk/G/705	" "	"	50	14	29	186	74	.25
Yk/G/706	" "	"	20	7	77	428	256	.18
Yk/G/708	" "	"	26	12	25	417	144	.27
Yk/G/714	" "	"	23	4	12	298	42	.22

SAMPLE NO	GROSS CHARACTERISTICS AND LOCATION	AGE	HYDROCARBONS x 10^{-9} g/g dry rk.					CORG Wt.%
			C_1	C_2	C_3	C_4	B/F	
Yk/I/801	Procelainous mudstone (Ingleton, Yorkshire)	Visean	65	23	256	656	1072	.11
Yk/I/803	" "	"	69	23	189	453	488	.13
Yk/I/804	" "	"	65	41	182	576	593	.17
Yk/I/805	" "	"	71	39	221	598	632	.14
Yk/I/807	" "	"	67	25	193	472	501	.16
Yk/I/813	" "	"	63	21	264	618	807	.11
Fr/L/101	Rose coloured mudstone with bird's eye structure (Laize-France)	Bajocian	65	12	16	24	50	.06
FR/L/103	" "	"	53	15	11	19	49	.1
FR/L/104	" "	"	66	19	17	21	43	.09
FR/L/105	" "	"	49	17	23	19	47	.13
FR/L/109	" "	"	51	15	13	11	34	.14
FR/L/111	" "	"	49	19	21	17	45	.1
Ox/K/301	Fine grained oolitic pelletal grainstone (Kirklington, Oxfordshire)	Bathonian	20	12	64	116	177	.78
Ox/K/303	" "	"	18	11	70	132	188	.65
Ox/K/306	" "	"	23	14	59	97	126	.72
Ox/K/307	" "	"	26	11	63	89	138	.59
Ox/K/310	" "	"	24	17	49	103	147	.63
Ox/K/316	" "	"	31	15	71	94	109	.54
Ox/K/401	Dark medium grained oolitic grainstone (Kirklington, Oxfordshire)	Bathonian	26	52	98	133	201	.37
Ox/K/403	" "	"	21	36	55	69	86	.28
Ox/K/404	" "	"	28	49	104	113	192	.42
Ox/K/405	" "	"	31	41	97	139	146	.38
Ox/K/407	" "	"	29	56	107	142	187	.31
Ox/K/412	" "	"	33	63	118	163	218	.29
Nb/G/901	Fine grained foraminiferal limestones (Great Limestone) (Ireshopesburn, Northumberland)	Namurian	371	99	151	112	306	.40
Nb/G/902	" "	"	360	89	74	57	66	.38
Nb/G/903	" "	"	292	72	58	45	11	.36
Nb/G/906	" "	"	281	73	61	48	41	.33
Nb/G/910	" "	"	327	82	86	59	127	.33
Nb/G/913	" "	"	392	96	73	67	55	.34

SAMPLE NO	GROSS CHARACTERISTICS AND LOCATION	AGE	HYDROCARBONS X 10^{-9} g/g dry rk.					CORG Wt.%
			C_1	C_2	C_3	C_4	B/F	
Fr/Ch/050	Fine grained oolitic grainstone (Chamont, France)	Bathonian	58	26	78	143	189	.63
Fr/Ch/051	" "	"	61	36	69	127	134	.74
Fr/Ch/052	" "	"	54	29	98	71	121	.64
Fr/Ch/053	" "	"	57	23	101	123	93	.67
Fr/Ch/054	" "	"	73	34	79	115	163	.76
Fr/Ch/055	" "	"	59	29	84	76	107	.78
Nb/LL/950	Dark coloured carbonaceous mudstone(Little Limestone) Cowhill,Northumberland	Namurian	459	170	165	82	318	.35
Nb/LL/952	" "	"	411	103	110	70	145	.29
Nb/LL/953	" "	"	371	95	83	62	111	.26
Nb/LL/954	" "	"	351	88	90	54	75	.24
Nb/LL/958	" "	"	292	73	64	38	53	.28
Nb/LL/961	" "	"	325	79	61	42	68	.31

APPENDIX II

APPENDIX II

Approximate field measurements for Waters (Surface and Interstitial) along traverse P (0920 - 1240 hrs, 21st June 1979)

	P101		P102		P103		P104		P105		P106		P107		P108		P109		P110	
	*S	+I	S	I	S	I	S	I	S	I	S	I	S	I	S	I	S	I	S	I
Depth in m	-	1.2	-	1.4	-	3	-	2.4	-	1.3	-	-	-	2.8	-	4.1	-	1.2	-	2.9
T° C	28.5	29	28.2	29	28.2	29.2	28.3	28.9	28.4	29.2	-	30.4	28	29	28.2	28.3	28.5	29	28.1	28.9
pH	8.2	8.18	8.2	8.2	8.2	8.1	8.18	8.16	8.2	8.18	-	8.2	8.2	8.15	8.1	8.0	8.2	8.15	8.1	7.9
Eh (+ m volts) corrected	383	365	392	371	385	345	402	387	416	402	-	486	369	347	348	343	442	399	394	352
Salinity °/oo	36	36	35.8	35.9	35	35.8	35.7	36	36	36.2	-	-	35.8	36.1	36.0	36.2	36	36	35.9	36.1

	P111		P112		P113		P114		P115		P116		P117		P118		P119	
	S	I	S	I	S	I	S	I	S	I	S	I	S	I	S	I	S	I
Depth in m	-	1.4	-	1.2	-	2.2	-	1.8	-	1.6	-	2.1	-	3.3	-	1.8	-	1.6
T° C	28.5	29	28.2	28.3	28.5	28.2	27.9	28.2	28.1	28.3	27.8	28.3	28	28.1	28.2	28.3	28.1	28.5
pH	8.2	8.18	8.2	8.15	8.1	7.95	8.2	8.2	8.1	8.0	8.18	8.15	8.1	7.9	8.2	8.2	8.1	8.15
Eh (+m volts) corrected	407	396	452	403	385	372	441	369	423	381	392	343	357	331	405	387	396	386
Salinity °/oo	36.1	3.63	35.9	36	35.7	36	36.1	36.2	35.9	36.1	36.3	36.2	36.1	35.9	35.7	36.1	36	36.1

* S = Surface Water

\+ I = Interstitial Water

APPENDIX II contd

Approximate field measurements for waters (Surface and Interstitial) along traverse Q (1410 - 1750 hrs, 21st June, 1979)

	Q201		Q202		Q203		Q204		Q205		Q206		Q207		Q208		Q209		Q210	
	S	I	S	I	S	I	S	I	S	I	S	I	S	I	S	I	S	I	S	I
Depth in m	-	.8	-	1.4	-	2.9	-	1.2	-	1.6	-	-	-	2.4	-	2.8	-	.6	-	.8
T^{o} C	29.3	29.5	29.7	30	30.1	30.2	30	30	30.5	30.2	-	31	30.4	30.5	30	30.1	29.9	31	30	31
pH	8.1	8.0	8.15	8.1	8.0	7.9	8.1	8.05	8.2	8.06	-	8.2	8.1	7.9	8.0	7.85	8.1	8.15	8.2	8.15
Eh(+ m volts) corrected	423	405	414	393	387	345	413	398	378	401	-	478	439	397	402	343	430	398	437	389
Salinity ^{o}/oo	37	37.4	36.9	37.5	37	38	37.1	37.3	37.2	37.8	-	-	37	37.6	36.9	37.8	37.1	37.4	36.8	37

	Q211		Q212		Q213		Q214		Q215		Q216		Q217		Q218		Q219	
	S	I	S	I	S	I	S	I	S	I	S	I	S	I	S	I	S	I
Depth in m	-	1.9	-	.7	-	.6	-	.6	-	.4	-	.6	-	.4	-	.8	-	.4
T^{o} C	30	30.1	30.2	31	31	31.2	30	31.3	31	31	30.1	30.8	31	31.2	30	30.3	30	30.1
pH	8.0	7.95	8.0	8.0	8.1	8.15	8.1	8.0	8.1	8.05	7.9	8.0	8.1	8.0	8.1	8.15	8.1	8.0
Eh (+ m volts) corrected	415	346	423	417	397	412	423	389	443	413	412	387	420	402	392	387	413	395
Salinity ^{o}/oo	37	36.8	36.9	37	37.2	37.4	36.8	36.9	37	37.1	36.8	37	37	36.9	37.1	37.4	36.9	37.6

APPENDIX II contd

Approximate Field measurements for waters (Surface and Interstitial) along traverse R (0910-1255 hrs, 22nd June, 1979)

	R301		R302		R303		R304		R305		R306		R307		R308		R309		R310		R311		R312	
	S	I	S	I	S	I	S	I	S	I	S	I	S	I	S	I	S	I	S	I	S	I	S	I
Depth in m	-	1.4	-	.8	-	1.6	-	1.2	-	2.0	-	.9	-	1.5	-	.7	-	.6	-	2.5	-	.6	-	.6
T° C	31.5	31	31.2	31.5	31	31.8	31	31.5	31.2	32	30.9	31	31.3	31.5	31.8	32	31.6	31.8	32	31.7	31.2	31.8	32	32.1
pH	8.0	7.9	8.05	8.0	8.0	7.9	7.95	7.9	8.0	7.85	8.0	8.1	8.0	7.95	8.05	7.95	8.0	8.0	8.1	7.8	8.0	7.95	7.95	7.9
Eh(+ m volts) corrected	364	345	371	373	347	323	381	402	374	335	367	358	378	331	381	342	365	347	377	314	369	349	371	363
Salinity °/oo	37.9	38	37.8	38	38	38.2	37.8	38	38.2	38.1	38	37.9	37.8	38	38	38.1	38	38.2	37.9	38.1	38	38.2	38.1	38.3

	R313		R314		R315		R316		R317		R318		R319		R320		R321	
	S	I	S	I	S	I	S	I	S	I	S	I	S	I	S	I	S	I
Depth in m	-	.6	-	.4	-	1.2	-	.9	-	.8	-	1.2	-	1.6	-	2.0	-	1.4
T° C	30.8	31.2	31	31.5	31	31	31.8	32	31.2	31.5	31	31.2	31.7	31.8	31.1	31.4	31	31.7
pH	8.0	8.1	8.0	8.0	8.1	7.92	7.95	8.0	8.0	7.9	7.95	7.8	8.1	7.93	8.0	8.0	8.1	7.9
Eh(+ m volts) corrected	369	351	363	368	370	343	358	361	381	346	362	329	374	348	381	349	361	342
Salinity °/oo	38.1	38.3	38.2	38.2	37.9	38	38.1	38.2	38.1	38.3	38.1	38.5	37.9	38.2	38.1	38.2	38.1	38.3

APPENDIX II contd

Approximate field measurements for waters (Surface and Interstitial) along traverse S (1345-1735 hrs, 22nd June, 1979)

	S401		S402		S403		S404		S405		S406		S407		S408		S409		S410	
	S	I	S	I	S	I	S	I	S	I	S	I	S	I	S	I	S	I	S	I
Depth in m	-	1.4	-	1.2	-	.8	-	1.8	-	.9	-	-	-	2.2	-	-	-	2.0	-	.75
T° C	27.5	27.9	27.8	28	28	28.1	28.2	28.7	28.9	29.2	-	30.6	30.4	30.2	-	30.8	31	30.7	30.9	31
pH	8.2	8.15	8.2	8.2	8.2	8.18	8.16	8.04	8.18	8.12	-	8.0	8.1	7.9	-	8.0	8.0	7.95	8.1	8.0
Eh(+ m volts) corrected	357	343	367	361	373	349	401	423	394	374	-	456	379	363	-	425	394	379	401	398
Salinity °/oo	35.9	36	36	36	36.1	36.3	36	35.8	36	36.1	-	-	35.9	36.1	-	-	36.3	36.5	36.4	36.7

	S411		S412		S413		S414		S415		S416		S417		S418		S419		S420	
	S	I	S	I	S	I	S	I	S	I	S	I	S	I	S	I	S	I	S	I
Depth in m	-	2.3	-	.6	-	.84	-	.6	-	1.0	-	1.1	-	1.2	-	1.4	-	1.6	-	1.6
T° C	31.2	31.7	32	31.7	31.3	30.8	31	31.6	31.1	31.9	32	31.6	31.7	31.4	31.6	31.9	31.2	31.7	31.8	31.9
pH	7.95	7.9	8.0	8.1	8.0	7.92	8.0	7.95	8.1	8.05	8.0	7.94	7.95	8.0	7.95	7.85	8.0	8.1	8.0	7.9
Eh(+m volts) corrected	443	427	412	378	375	383	393	345	373	357	383	359	373	415	379	358	369	349	373	401
Salinity °/oo	36.5	36,7	36.8	37	37.1	37.3	37.5	37.7	37.5	38	38	38.1	38.1	38.2	37.9	38	38	38.2	38.1	38.2

APPENDIX II contd

Approximate field measurements for waters (Surface and Interstitial) along travers T(0940-1520hrs, 23rd June 1979)

	T501		T502		T503		T504		T505		T506		T507		T508	
	S	I	S	I	S	I	S	I	S	I	S	I	S	I	S	I
Depth in m	-	1.4	-	1.2	-	.9	-	1.6	-	.86	-	1.24	-	2.0	-	.8
T° C	27	27.5	27.5	27.8	27.9	28	28	28.1	27.9	28.1	28.2	28.4	28.1	27.9	28.2	28.5
pH	8.2	8.1	8.18	8.2	8.2	8.2	8.16	8.2	8.12	8.16	8.1	8.0	8.1	8.05	8.0	7.95
Eh(+ m volts) corrected	395	347	376	349	385	356	401	420	443	412	402	394	387	356	378	345
Salinity°/oo	36	36.1	36.2	36	36.3	36.2	35.9	36.2	36.1	36.3	36.5	36.1	36.5	36.7	35.9	36.1

	T509		T510		T511		T512		T513		T514		T515		T516	
	S	I	S	I	S	I	S	I	S	I	S	I	S	I	S	I
Depth in m	-	1.2	-	1.1	-	2.3	-	1.2	-	1.1	-	2.2	-	.9	-	.8
T° C	28.7	29	28.6	28.9	29	29.2	29.1	28.7	29.2	29.5	29.3	29.5	28.7	29	29.1	30
pH	8.1	8.0	8.2	7.9	8.0	8.1	8.05	7.98	8.0	7.95	7.9	8.1	8.0	8.0	7.95	8.0
Eh(+ m volts) corrected	390	401	403	387	417	419	413	388	393	367	424	426	391	377	407	396
Salinity °/oo	36	36	36.1	36	36.5	36.7	37	36.7	37.1	37.3	37.2	37.1	37.5	37.6	37.8	38

	T517		T518		T519		T520		T521		T522		T523		T524		T525	
	S	I	S	I	S	I	S	I	S	I	S	I	S	I	S	I	S	I
Depth in m	-	2.4	-	.85	-	2.0	-	1.8	-	1.6	-	1.4	-	1.2	-	1.1	-	1.2
T° C	29.5	30	30	29.7	30	30.5	30.3	31	31	31	31	29	31	31.2	30.9	31	30	31
pH	7.95	8.0	8.1	7.95	8.0	7.95	7.9	7.8	8.0	8.0	7.95	7.9	7.9	7.85	8.0	7.88	7.97	8.0
Eh(+ m volts) corrected	398	401	378	345	356	338	364	371	371	357	357	342	356	339	341	343	372	343
Salinity°/oo	38	38.1	37.9	38	38	38.2	38	37.9	37.6	38.1	38	38	38.1	38.3	38.2	38	38.1	38.15

APPENDIX III

APPENDIX III

ANALYSES OF C_1 - C_5+HYDROCARBONS FROM RECENT OOLITES.

Table shows : a) C_1 - C_5+ hydrocarbons in ng gas/g dry sediment

b) Corg values in wt.percent

c) Total C_1 - C_4 saturated hydrocarbons/gm of Organic matter

SAMPLES FROM TRAVERSE P

SAMPLE NUMBER	CH_4	C_2H_6	C_3H_6	C_3H_8	iC_4H_{10}	C_4H_8	nC_4H_{10}	B/Flush C_5+	Corg wt.%	Total C_1-C_4 Sat/gm Corg
E1-P-101-a	42	24	34	299	-	75	148	2054	2.22	2.3×10^{-5}
b	47	23	37	259	-	73	127	2132	1.86	2.4×10^{-5}
E1-P-102-a	52	28	42	335	69	116	281	2541	2.8	3.1×10^{-5}
b	49	31	43	287	-	121	248	2283	2.4	2.6×10^{-5}
E1-P-103-a	58	33	47	338	-	57	46	2938	2.12	2.2×10^{-5}
b	53	31	39	297	47	101	97	3172	2.28	2.3×10^{-5}
E1-P-104-a	59	37	58	483	39	103	121	3526	2.6	2.8×10^{-5}
b	62	39	61	252	53	106	215	3739	2.36	2.6×10^{-5}
E1-P-105-a	69	35	59	474	-	101	119	3472	2.52	2.8×10^{-5}
b	54	28	53	289	-	96	124	3582	2.2	2.3×10^{-5}
E1-P-106-a	37	25	31	121	-	65	48	2610	1.36	1.7×10^{-5}
b	37	29	32	181	-	79	53	2728	1.6	1.9×10^{-5}
E1-P-107-a	73	21	47	388	-	108	121	4609	2.4	2.5×10^{-5}
b	68	35	42	301	37	112	124	3933	2.36	2.4×10^{-5}
E1-P-108-a	61	41	62	1178	-	128	341	5029	3.56	4.6×10^{-5}
b	72	39	67	532	63	140	243	6170	3.0	3.1×10^{-5}
E1-P-109-a	59	24	37	512	48	92	140	5628	2.84	3.1×10^{-5}
b	63	29	41	471	-	107	123	3987	2.68	2.6×10^{-5}
E1-P-110-a	78	47	59	401	-	97	214	5721	2.72	2.7×10^{-5}
b	78	39	60	387	-	113	97	5286	2.41	2.5×10^{-5}
E1-P-111-a	56	31	47	361	56	79	115	3431	2.54	2.9×10^{-5}
b	47	28	39	206	27	103	98	2944	1.83	2.2×10^{-5}
E1-P-112-a	65	31	43	273	35	97	123	4568	2.35	2.5×10^{-5}
b	59	28	37	258	63	111	103	3998	2.18	2.3×10^{-5}
E1-P-113-a	59	45	53	313	-	121	141	4619	2.34	2.4×10^{-5}
b	61	43	61	389	-	109	97	4865	2.44	2.4×10^{-5}
E1-P-114-a	58	23	41	215	-	91	47	2869	1.76	1.9×10^{-5}
b	53	21	39	241	46	87	103	3892	2.07	2.2×10^{-5}
E1-P-115-a	49	23	37	205	-	101	73	2157	1.72	2.0×10^{-5}
b	51	27	43	234	29	67	121	3552	2.0	2.3×10^{-5}

SAMPLE NUMBER	CH_4	C_2H_6	C_3H_6	C_3H_8	iC_4H_8	C_4H_8	nC_4H_{10}	B/Flush C_5+	Corg wt.%	Total C_1-C_4 Sat/gm Corg
E1-P-116-a	63	39	57	385	46	115	123	3563	2.44	2.7×10^{-5}
b	71	43	53	472	-	109	245	4707	2.92	2.9×10^{-5}
E1-P-117-a	74	38	49	478	-	75	198	5019	2.85	2.8×10^{-5}
b	69	41	56	381	74	103	121	3526	2.66	2.6×10^{-5}
E1-P-118-a	73	39	62	1020	-	106	252	5712	3.76	3.7×10^{-5}
b	71	41	59	438	-	57	146	4938	2.7	2.6×10^{-5}
E1-P-119-a	64	43	61	483	-	131	197	3896	2.64	2.6×10^{-5}
b	67	37	51	287	-	120	184	4178	2.36	2.4×10^{-5}

SAMPLES FROM TRAVERSE Q

E1-Q-201-a	42	44	86	238	-	61	37	2077	1.87	1.9×10^{-5}
b	54	39	67	298	29	72	45	2562	2.03	2.3×10^{-5}
E1-Q-202-a	49	33	59	213	38	28	114	1359	1.92	2.3×10^{-5}
b	51	29	46	224	41	58	71	2174	2.0	2.0×10^{-5}
E1-Q-203-a	43	28	34	296	-	75	149	2080	2.4	2.5×10^{-5}
b	57	31	49	243	-	86	123	2719	1.9	2.0×10^{-5}
E1-Q-204-a	56	43	73	314	-	65	47	3517	2.18	2.1×10^{-5}
b	59	39	68	394	37	103	109	3786	2.53	2.5×10^{-5}
E1-Q-205-a	61	42	62	1178	-	130	342	4039	4.13	3.9×10^{-5}
b	65	46	51	473	-	123	94	3861	2.56	2.6×10^{-5}
E1-Q-206-a	43	25	32	108	21	56	47	1926	1.42	1.7×10^{-5}
b	39	21	29	109	-	44	51	1465	1.23	1.7×10^{-5}
E1-Q-207-a	65	44	69	416	-	65	46	3647	2.34	2.4×10^{-5}
b	58	38	41	398	-	57	96	3184	2.4	2.5×10^{-5}
E1-Q-208-a	71	36	58	375	39	101	119	3474	2.44	2.6×10^{-5}
b	68	41	53	436	48	97	131	4017	3.08	2.4×10^{-5}
E1-Q-209-a	74	39	62	1004	55	104	248	5628	3.26	4.2×10^{-5}
b	62	45	51	487	61	88	164	4381	2.85	2.9×10^{-5}
E1-Q-210-a	68	43	67	428	34	57	46	3938	2.4	2.6×10^{-5}
b	68	41	59	394	-	75	54	3781	2.24	2.5×10^{-5}
E1-Q-211-a	71	41	38	1129	-	-	65	6414	3.36	3.9×10^{-5}
b	67	43	51	497	33	69	37	4388	2.51	2.7×10^{-5}
E1-Q-212-a	60	25	33	290	-	16	15	3121	1.98	2.0×10^{-5}
b	63	39	47	318	-	39	45	2891	2.07	2.2×10^{-5}

SAMPLE NUMBER	CH_4	C_2H_6	C_3H_6	C_3H_8	iC_4H_{10}	C_4H_8	nC_4H_{10}	B/Flush C_5+	Corg wt.%	Total C_1-C_4 Sat/gm Corg
E1-Q-213-a	59	26	31	468	34	29	76	3952	2.41	2.8×10^{-5}
b	48	31	39	286	-	66	97	3340	2.08	2.2×10^{-5}
E1-Q-214-a	51	23	30	254	29	9	21	2899	1.7	2.2×10^{-5}
b	54	34	43	189	47	68	89	3156	1.9	2.2×10^{-5}
E1-Q-215-a	61	27	32	275	-	15	20	2995	1.59	2.4×10^{-5}
b	68	41	54	298	58	78	51	4233	2.25	2.3×10^{-5}
E1-Q-216-a	53	29	42	334	-	117	66	3640	2.00	1.9×10^{-5}
b	51	33	54	293	-	102	95	3187	2.03	2.3×10^{-5}
E1-Q-217-a	48	23	37	289	-	93	31	2894	1.86	2.1×10^{-5}
b	45	31	39	215	32	46	98	2386	1.6	2.3×10^{-5}
E1-Q-218-a	49	31	43	273	64	102	92	2769	1.8	2.5×10^{-5}
b	37	29	43	198	-	93	37	2185	1.52	2.0×10^{-5}
E1-Q-219-a	43	25	36	195	-	77	51	2050	1.60	2.0×10^{-5}
b	45	29	31	217	-	64	93	2163	1.8	2.1×10^{-5}

SAMPLES FROM TRAVERSE R

E1-R-301-a	31	15	43	152	17	29	35	744	1.36	1.8×10^{-5}
b	37	23	27	198	18	23	47	1980	1.56	2.0×10^{-5}
E1-R-302-a	45	26	35	239	-	80	54	2145	1.6	2.3×10^{-5}
b	51	31	40	217	-	63	41	1761	1.45	2.0×10^{-5}
E1-R-303-a	66	46	70	251	-	67	98	2207	1.8	2.6×10^{-5}
b	56	34	44	293	-	93	103	2590	2.1	2.3×10^{-5}
E1-R-304-a	71	37	61	483	67	106	122	4615	2.78	2.8×10^{-5}
b	65	43	53	416	35	97	130	4168	2.56	2.7×10^{-5}
E1-R-305-a	69	44	67	436	-	60	148	3874	2.6	2.7×10^{-5}
b	71	39	59	397	67	84	101	3168	2.52	2.7×10^{-5}
E1-R-306-a	67	42	75	421	48	66	119	3645	2.8	2.5×10^{-5}
b	58	37	61	439	-	58	79	3487	2.4	2.5×10^{-5}
E1-R-307-a	63	39	64	465	49	97	124	3896	2.72	2.7×10^{-5}
b	73	45	59	483	-	103	195	4035	2.85	2.8×10^{-5}
E1-R-308-a	76	41	64	1011	-	105	256	5669	3.78	3.6×10^{-5}
b	71	40	53	495	38	86	103	3918	2.74	2.7×10^{-5}
E1-R-309-a	73	41	59	398	41	97	239	4893	2.92	2.7×10^{-5}
b	51	33	63	319	63	77	89	2987	2.23	2.5×10^{-5}
E1-R-310-a	77	51	61	679	34	55	165	6895	3.24	3.1×10^{-5}
b	73	49	59	317	43	64	49	4183	2.34	2.3×10^{-5}
E1-R-311-a	58	45	67	565	-	17	107	3926	2.89	2.9×10^{-5}
b	59	39	51	473	-	39	73	4398	2.42	2.7×10^{-5}

SAMPLE NUMBER	CH_4	C_2H_6	C_3H_6	C_3H_8	iC_4H_{10}	C_4H_8	nC_4H_{10}	B/Flush C_5+	Corg. wt.%	Total C_1-C_4 Sat/gm Corg
E1-R-312-a	74	48	72	667	-	51	162	6724	3.18	3.0×10^{-5}
b	61	37	46	485	29	78	107	6183	2.51	2.9×10^{-5}
E1-R-313-a	51	45	69	345	35	61	20	3900	2.21	2.2×10^{-5}
b	71	43	51	397	-	83	102	4532	2.47	2.5×10^{-5}
E1-R-314-a	73	43	65	433	-	79	147	4289	2.56	2.7×10^{-5}
b	57	38	53	384	27	87	93	3788	2.37	2.5×10^{-5}
E1-R-315-a	75	48	61	589	-	103	214	6387	3.0	3.1×10^{-5}
b	57	32	49	391	-	67	88	4970	2.24	2.5×10^{-5}
E1-R-316-a	52	39	58	259	-	95	89	4278	1.97	2.2×10^{-5}
b	65	41	69	316	-	78	110	3981	2.18	2.4×10^{-5}
E1-R-317-a	69	45	63	274	-	86	107	4385	2.2	2.3×10^{-5}
b	63	38	41	347	61	77	100	4298	2.36	2.6×10^{-5}
E1-R-318-a	67	38	58	497	-	106	77	4877	2.5	2.7×10^{-5}
b	61	33	50	367	54	78	129	4156	2.4	2.7×10^{-5}
E1-R-319-a	64	41	57	312	-	83	98	4233	2.21	2.3×10^{-5}
b	62	37	48	293	-	65	93	3984	2.18	2.2×10^{-5}
E1-R-320-a	59	34	45	424	-	38	124	3891	2.41	2.7×10^{-5}
b	61	43	57	318	65	78	93	4135	2.21	2.6×10^{-5}
E1-R-321-a	54	31	41	392	-	71	87	3985	2.3	2.5×10^{-5}
b	55	39	40	287	-	93	103	4230	2.1	2.3×10^{-5}

SAMPLES FROM TRAVERSE S

E1-S-401-a	57	27	49	348	63	31	138	3913	2.37	2.7×10^{-5}
b	51	31	65	398	39	66	86	4017	2.31	2.6×10^{-5}
E1-S-402-a	53	25	39	287	-	57	119	3189	2.1	2.3×10^{-5}
b	57	29	43	418	-	59	191	4079	2.53	2.8×10^{-5}
E1-S-403-a	51	31	37	368	-	79	123	3457	2.32	2.5×10^{-5}
b	41	34	44	307	-	37	85	3115	2.03	2.3×10^{-5}
E1-S-404-a	54	39	49	398	-	119	125	3287	2.4	2.6×10^{-5}
b	62	37	57	385	-	50	101	3165	2.36	2.5×10^{-5}
E1-S-405-a	55	32	42	352	33	29	154	3872	2.41	2.6×10^{-5}
b	51	29	39	317	-	63	87	2893	2.1	2.3×10^{-5}
E1-S-406-a	33	21	25	218	-	59	97	2191	1.92	1.9×10^{-5}
b	34	23	29	206	-	61	77	2614	1.78	1.9×10^{-5}
E1-S-407-a	56	37	49	397	63	107	176	4560	2.63	2.8×10^{-5}
b	59	30	43	297	-	61	83	3995	2.14	2.2×10^{-5}
E1-S-408-a	31	23	34	189	-	103	49	2156	1.6	1.8×10^{-5}
b	37	29	41	191	-	73	85	2967	1.8	1.9×10^{-5}
E1-S-409-a	63	39	57	418	-	99	103	3987	2.34	2.7×10^{-5}
b	63	37	51	398	39	60	93	3956	2.46	2.6×10^{-5}
E1-S-410-a	65	29	41	391	-	96	114	4042	2.31	2.6×10^{-5}
b	68	34	47	419	26	73	102	2865	2.42	2.7×10^{-5}

SAMPLE NUMBER	CH_4	C_2H_6	C_3H_6	C_3H_8	iC_4H_{10}	C_4H_8	nC_4H_{10}	B/Flush C5+	Corg. wt.%	Total C_1-C_4 Sat/gm Corg
El-S-411-a	65	39	67	514	-	47	135	4150	2.72	2.8×10^{-5}
b	63	41	55	398	53	71	98	4268	2.4	2.7×10^{-5}
El-S-412-a	67	44	61	441	39	69	123	3561	2.56	2.8×10^{-5}
b	65	43	49	405	43	78	100	3166	2.47	2.7×10^{-5}
El-S-413-a	69	41	63	321	-	48	87	3992	2.21	2.3×10^{-5}
b	71	43	58	425	63	75	93	4033	2.56	2.7×10^{-5}
El-S-414-a	70	39	61	507	-	63	79	3875	2.48	2.8×10^{-5}
b	69	37	71	453	46	57	81	3615	2.53	2.7×10^{-5}
El-S-415-a	73	44	69	479	-	46	109	3291	2.51	2.8×10^{-5}
b	63	39	57	381	-	67	93	4106	2.3	2.5×10^{-5}
El-S-416-a	72	42	63	517	-	78	149	4980	2.65	2.9×10^{-5}
b	68	42	65	470	37	86	106	4087	2.58	2.8×10^{-5}
El-S-417-a	71	39	58	498	-	52	98	4187	2.54	2.8×10^{-5}
b	60	41	47	386	39	67	91	3678	2.4	2.6×10^{-5}
El-S-418-a	71	41	61	425	35	93	147	4245	2.6	2.8×10^{-5}
b	65	37	53	391	-	87	107	3918	2.37	2.5×10^{-5}
El-S-419-a	73	35	67	476	-	101	98	4784	2.47	2.8×10^{-5}
b	59	29	63	395	-	96	47	3193	2.27	2.3×10^{-5}
El-S-420-a	73	46	68	512	-	103	124	5187	2.63	2.9×10^{-5}
b	69	41	55	418	-	93	131	4981	2.41	2.7×10^{-5}

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El-T-501-a	48	29	41	235	-	26	43	1575	1.85	1.9×10^{-5}
b	53	31	39	297	54	47	86	2098	2.17	2.4×10^{-5}
El-T-502-a	50	32	42	305	-	26	45	2271	2.0	2.2×10^{-5}
b	49	29	39	356	-	63	97	3029	2.21	2.4×10^{-5}
El-T-503-a	52	29	47	387	-	85	39	2877	2.18	2.3×10^{-5}
b	52	33	57	377	-	47	83	3192	2.25	2.4×10^{-5}
El-T-504-a	49	31	47	324	38	56	73	2890	2.2	2.3×10^{-5}
b	47	34	35	298	-	65	97	2567	2.12	2.2×10^{-5}
El-T-505-a	51	29	43	337	-	93	68	3138	2.22	2.2×10^{-5}
b	57	35	51	348	35	67	78	3093	2.3	2.4×10^{-5}
El-T-506-a	54	33	39	379	-	101	76	3461	2.28	2.4×10^{-5}
b	49	30	53	397	36	96	109	3188	2.37	2.6×10^{-5}
El-T-507-a	55	27	43	369	-	73	110	3580	2.3	2.5×10^{-5}
b	53	29	40	319	34	68	99	3871	2.1	2.1×10^{-5}
El-T-508-a	57	31	51	431	31	95	87	3492	2.43	2.6×10^{-5}
b	50	31	39	410	-	47	89	3105	2.36	2.5×10^{-5}
El-T-509-a	56	31	47	398	36	101	79	3684	2.38	2.5×10^{-5}
b	53	29	41	307	31	58	77	3078	2.21	2.2×10^{-5}

SAMPLE NUMBER	CH_4	C_2H_6	C_3H_6	C_3H_8	iC_4H_{10}	C_4H_8	nC_4H_{10}	B/Flush C_5+	Corg wt.%	Total C_1-C_4 Sat/gm Corg
El-T-510-a	59	33	49	324	39	87	103	3324	2.33	2.4×10^{-5}
b	41	27	43	291	-	73	107	3115	2.08	2.2×10^{-5}
El-T-511-a	59	30	43	318	-	102	95	2898	2.17	2.3×10^{-5}
b	59	40	47	385	-	91	78	3860	2.32	2.4×10^{-5}
El-T-512-a	60	29	57	423	-	97	86	3979	2.60	2.3×10^{-5}
b	47	34	43	281	-	63	74	2917	1.98	2.2×10^{-5}
El-T-513-a	58	27	41	390	-	91	67	3811	2.29	2.4×10^{-5}
b	50	35	39	305	54	67	103	3980	2.31	2.4×10^{-5}
El-T-514-a	61	39	56	398	49	85	128	4230	2.47	2.7×10^{-5}
b	58	33	51	318	-	71	48	2965	2.12	2.2×10^{-5}
El-T-515-a	63	41	57	425	-	101	132	4562	2.51	2.6×10^{-5}
b	63	39	53	409	-	83	59	4078	2.46	2.5×10^{-5}
El-T-516-a	63	39	54	413	-	98	105	4309	2.37	2.6×10^{-5}
b	57	31	49	318	33	101	81	3097	2.28	2.3×10^{-5}
El-T-517-a	65	41	61	387	-	103	75	3917	2.34	2.4×10^{-5}
b	60	39	53	391	43	93	107	3717	2.43	2.6×10^{-5}
El-T-518-a	65	39	53	419	68	97	129	4276	2.57	2.8×10^{-5}
b	59	37	43	389	-	104	51	3861	2.23	2.4×10^{-5}
El-T-519-a	64	40	62	405	-	87	76	4287	2.36	2.5×10^{-5}
b	67	45	57	421	54	69	87	3915	2.51	2.7×10^{-5}
El-T-520-a	63	37	57	397	36	93	68	4180	2.38	2.5×10^{-5}
b	63	35	51	386	73	71	102	4923	2.47	2.7×10^{-5}
El-T-521-a	67	29	49	341	59	107	85	4787	2.28	2.5×10^{-5}
b	64	35	53	307	-	100	69	4019	2.14	2.2×10^{-5}
El-T-522-a	67	33	61	418	-	97	123	4835	2.42	2.6×10^{-5}
b	67	32	59	397	37	53	83	4561	2.36	2.6×10^{-5}
El-T-523-a	69	39	58	478	-	103	107	4305	2.51	2.8×10^{-5}
b	55	28	49	391	43	79	102	3196	2.37	2.6×10^{-5}
El-T-524-a	71	41	63	481	-	98	137	4692	2.63	2.8×10^{-5}
b	73	41	61	470	58	105	77	4352	2.65	2.8×10^{-5}
El-T-525-a	69	43	57	425	-	101	133	4765	2.59	2.6×10^{-5}
b	71	40	63	397	-	121	146	4266	2.41	2.7×10^{-5}

CORE E : BEACH, WATER CAY

Depth <u>cm</u>										
0	42	31	39	339	-	61	87	2096	2.2	2.3×10^{-5}
10	55	34	41	421	34	64	98	3568	2.41	2.7×10^{-5}
20	57	33	43	338	-	56	127	3880	2.34	2.4×10^{-5}
30	54	31	47	375	-	101	119	3472	2.32	2.4×10^{-5}
40	61	37	49	473	-	104	148	4654	2.51	2.9×10^{-5}
50	55	34	45	468	41	53	84	3997	2.43	2.8×10^{-5}
60	63	41	53	399	38	117	79	4276	2.37	2.6×10^{-5}
70	65	39	47	507	47	93	106	4563	2.61	2.9×10^{-5}

CORE G: BAR SANDS

Depth cm	CH_4	C_2H_6	C_3H_6	C_3H_8	iC_4H_{10}	C_4H_8	nC_4H_{10}	B/Flush C_5+	Corg wt.%	Total C_1-C_4 Sat/gm Corg
0	54	33	43	281	39	68	89	3145	2.16	2.3×10^{-5}
10	51	31	44	266	-	49	73	2996	1.98	2.1×10^{-5}
20	56	34	39	307	-	83	101	3272	2.2	2.3×10^{-5}
30	55	37	47	348	-	78	143	3185	2.32	2.5×10^{-5}
40	63	41	51	284	27	47	97	3418	2.18	2.3×10^{-5}
50	61	41	49	417	34	87	172	3829	2.93	2.5×10^{-5}
60	57	43	45	296	-	104	78	3417	2.8	1.7×10^{-5}
70	63	39	41	323	37	97	69	4715	3.22	2.4×10^{-5}

CORE K : STABILISED SAND FLATS

Depth cm										
0	59	42	49	383	38	67	195	3566	2.56	2.8×10^{-5}
10	47	39	51	224	47	89	103	2817	1.97	2.3×10^{-5}
20	61	41	54	280	-	91	107	3316	2.28	2.6×10^{-5}
30	57	37	48	317	34	64	134	3777	2.89	2.0×10^{-5}
40	63	45	57	408	-	76	109	4977	2.38	1.6×10^{-5}
50	65	41	59	398	-	84	117	3523	2.35	2.6×10^{-5}
60	61	39	57	385	-	101	123	3890	2.8	2.2×10^{-5}
70	63	44	53	419	-	121	107	4173	3.02	2.3×10^{-5}

CORE I : CENTRE WOOD CAY

Depth cm										
0	32	15	27	184	29	46	57	1034	1.66	1.9×10^{-5}
10	34	19	33	197	23	63	47	1733	1.59	1.9×10^{-5}
20	37	22	29	212	-	56	79	1572	1.72	2.0×10^{-5}
30	34	20	31	209	34	37	62	1887	1.8	2.0×10^{-5}
40	39	23	27	243	-	45	97	2317	1.98	2.0×10^{-5}
50	41	26	33	205	-	67	73	2781	1.7	2.0×10^{-5}
60	44	31	31	187	-	59	75	2919	1.86	1.8×10^{-5}
70	42	31	29	147	35	63	87	2685	1.7	2.0×10^{-5}

APPENDIX III contd...

RESULTS OF COMPARATIVE ANALYSES OF SELECTED SEDIMENTS ADJACENT TO THE OOLITE FACIES, ELEUTHERA BANKS

SAMPLE NO.	CH_4	C_2H_6	C_3H_6	C_3H_8	iC_3H_{10}	C_4H_8	nC_4H_{10}	B/F C_5+	Corg wt.%	C_1-C_4 Sat/g Corg
1. LIME MUD FACIES										
EL-LM-21	108	30	23	28	14	12	8	126	4.04	4.7×10^{-6}
EL-LM-22	110	34	21	29	-	13	9	143	4.0	4.6×10^{-6}
EL-LM-23	116	37	19	24	15	15	11	135	3.26	6.2×10^{-6}
EL-LM-24	121	37	17	24	14	13	7	121	3.78	5.4×10^{-6}
EL-LM-25	113	31	13	24	-	9	11	141	4.1	4.4×10^{-6}
EL-LM-26	111	29	17	21	13	11	8	127	4.23	4.3×10^{-6}
2. SKELETAL CARBONATE SANDS										
EL-SS-01	37	8	5	4	-	2	4	11	1.7	3.1×10^{-6}
EL-SS-02	43	7	6	3	-	5	3	14	1.9	2.9×10^{-6}
EL-SS-03	53	9	7	15	3	2	5	7	1.42	5.9×10^{-6}
EL-SS-04	39	11	5	4	-	3	2	9	2.32	2.2×10^{-6}
EL-SS-05	37	8	6	5	-	4	3	13	1.86	2.8×10^{-6}
EL-SS-06	34	7	5	13	-	3	4	11	1.76	3.3×10^{-6}
3. COARSE GRAINED CORALGAL SANDS										
EL-CS-11	29	13	9	11	-	7	3	18	1.1	5.1×10^{-6}
EL-CS-12	31	11	9	6	-	4	3	21	1.3	3.9×10^{-6}
EL-CS-13	34	16	12	8	-	6	5	26	1.97	3.2×10^{-6}
EL-CS-14	26	12	7	6	4	5	3	19	1.8	2.8×10^{-6}
EL-CS-15	35	14	13	4	6	7	2	24	1.72	3.5×10^{-6}
EL-CS-16	27	9	6	4	-	8	4	22	1.0	4.4×10^{-6}

REFERENCES

REFERENCES

ABELL, P.I., CADOGAN, P.H. EGLINTON, G., MAXWELL, J.R. and PILLINGER,C.J., 1971. Survey of lunar carbon compounds 1. The presence of indigenous gases and hydrolysable carbon compounds in Apollo 11 and 12 samples. Proc.2nd Lunar Sc.conf.Geochim.Cosmochim.Acta Suppl. 2, 1843 - 1863.

ABELSON, P.H., 1963. Organic geochemistry and the formation of petroleum. In Proc. 6th World Pet.Congr.Frankfurt/ Maine 1. Hamburg: Verein Zur Forderung Des 6. Welt-Erdol-Kongresses, 397 - 407.

ABELSON P.H., HOERRING, T.C. and PARKER, P.L., 1964. Fatty acids in sedimentary rocks. In Colombo, U and Hobson, G.D., eds. Advances in Organic Geochemistry 1962. London: Pergamon Press, 169 - 174.

ADAMS, J.E., 1934. Origin, migration, and accumulation of petroleum in limestone reservoirs in the Western United States and Canada. In Wrather, W.E. and Lahee, F.H., eds. Problems of petroleum geology Tulsa, Okla.: Am.Assoc.Petrol.Geol., 347 - 363.

ALBRETCH, P. 1970. Etude de constituants organiques des series sedimentaires de Logbaba et de Messel. Transformations diagénétiques. Université de Strasbourg, Memoires du Service de la Carte Geologique d'Alsace et de Lorraine. 32, 119p.

ALEXANDERSSON, T., 1972. Micritisation of carbonate particles: processes of precipitation and dissolution in modern shallow-marine sediments. Bull.Geol.Inst.Univ. Uppsala, N.S.3, 201 - 236.

ALI-ZADE, A.A. and SHOIKHET, P.A. 1967. Geological-geochemical conditions of the transformation of organic matter in the sediments of the Caspian Sea. 7th World Petroleum Cong.,Mexico 2 London: Elsevier Pub.Co., 517 - 533

AMATO, F.L., 1978. Petroleum developments in South America, Central America, Mexico and Caribbean Area in 1977. Am. Assoc.Petrol.Geol.Bull. 62, 2044 - 2110.

ANDREEV, P.F., 1956. Cited in Transformation of Petroleum in Nature by Andreev, P.F., Bogomolov, A.I., Pobryanskii,A.F., Kartsev, A.A., 1968. English transl.Intern.Series Monographs in Earth Sciences 29. Oxford: Pergamon Press, 25.

ANDREEV, P.F., BOGOMOLOV, A.I., DOBRYANSKII, A.F. and KARTSEV, A.F., 1968. Transformation of petroleum in nature. English transl.Intern.Series Monographs in Earth Sciences, 29 Oxford: Pergamon Press. 466p.

ANDRICHUK, J.M., 1958. Mississipian Madison stratigraphy and sedimentation in Wyoming and southern Montana. In Weeks, L.G.ed. Habitat of Oil. A Symposium. Tuba, Okla. Am.Assoc.Petrol.Geol., 225 - 267.

ARABIAN AMERICAN OIL COMPANY STAFF, 1959. Ghawar oil field, Saudi Arabia. Am.Assoc.Petroleum Geologists Bull. 43, 434 - 454.

BAAS BECKING, L.G.M., KAPLAN, I.R., and MORE, D., 1960. Limits of the natural environment in terms of pH and oxidation-reduction potentials. Jour.Geol.68, 243 - 284.

BAKER, D.R., 1962. Organic geochemistry of Cherokee Group in southeastern Kansas and northeastern Oklahoma. Am.Assoc.Petrol.Geol.Bull.46, 1621 - 1642.

BAKER, N.E. and HENSON, F.R.S., 1952. Geological conditions of oil occurrence in Middle East oil fields. Am.Assoc. Petrol.Geol. Bull.36, 1885 - 1901

BALL, M.M., 1967. Carbonate sand bodies of south Florida and the Bahamas. Jour.Sed.Petrology 37, 556 - 591.

BARKER, C., 1974a. Pyrolysis techniques for source-rock evaluation. Am.Assoc.Petrol.Geol. Bull.58, 2349 - 2361.

BARKER, C., 1979. Organic geochemistry in petroleum exploration. Am.Assoc.Petrol.Geol.Course note series 10, 159p.

BATHURST, R.G.C., 1966. Boring algae, micrite envelopes and lithification of molluscan biosparites, Geol.Jour. 5, 15 - 32.

BATHURST, R.G.C., 1967b. Depth indicators in sedimentary carbonates. Marine Geol. 5, 447 - 471.

BATHURST, R.G.C., 1975. Carbonate sediments and their diagenesis. 2nd ed. Developments in Sedimentology, 12. Amsterdam: Elsevier Pub. Co., 620p.

BAVENDAM, W., 1932. Die mikrobiologische Kalkfallung in der tropischen Sec. Arch.Mikrobiol. 3, 205 - 276.

BERGMANN,W., 1960. Letter dated September 24, 1959. In Newell, N.D., Purdy, E.G., Imbrie, J., 1960. Bahamian Oolitic Sand.Jour.Geol. 68, 481 -497.

BERGMANN, W. and LESTER, D., 1940. Coral-Reefs and the formation of petroleum. Science 92, 452 - 53.

BERNARD, B.B., BROOKS, J.M. and SACKETT, W.M., 1978. Light hydrocarbons in recent Texas continental shelf and slope sediments. J.Geophys.Res.83, 4053 - 4061.

BERNER, R.A., 1968. Calcium carbonate concretion formed by the decomposition of organic matter. Science 159, 195 - 197.

BERNER, R.A., 1971. Principles of Chemical Sedimentology. New York: Mcgraw-Hill, 240p.

BIEDERMAN, E.W., Jr., 1966. Leached oolites - oil finders' key. World Oil, July, 174.

BILLO, S.M., 1980. Future petroleum resources seen great in Saudi Arabia. Oil and Gas Journal, Jan.1, 1979, 97 - 102.

BITTERLI, P., 1963. Aspects of the genesis of bituminous rock sequences. Geologie en Mijnbouw, 42, 183 - 201.

BLACK, M., 1933. The precipitation of calcium carbonate on the Great Bahama Bank. Geol.Mag. 70, 455 - 466.

BLACK, M., 1938 (rev.). HATCH, F.H., AND RASTELL, R.H. The petrology of the sedimentary rocks. 3rd ed. London.

BLATT, H., MIDDLETON, G. and MURRAY, R., 1972. Origin of Sedimentary Rocks. Englewood Cliffs, New Jersey: Prentice - Hall Inc., 634 p.

BLUMER, M., GUILLARD, R.R.L. and CHASE, T. 1971. Hydrocarbons of marine phytoplankton. Mar.Biol. 8, 183 - 189.

BOKOVA, E.N., 1959. Formation of heavy gaseous hydrocarbons during anaerobic decomposition of organic matter. Petroleum Geology. 3, 8 - 13.

BONNETT, B., 1958. Organic matter in fine-grained rocks, and its relation to the origin of petroleum. Unpublished Ph.D. Thesis, University of London.

BORDENAVE, M., 1967. Organic genesis of petroleum, part 2. From burial of sediments to migration of hydrocarbons. Sci. Progr. Nature (Paris) 3392, 451 - 458.

BORDENAVE, M., COMBAZ, A. and GIRAUD, A., 1970. Influence de l'origine de matières organiques et de leur degre d'evolution sur les produits de pyrolyse du Kerogène. In Hobson, G.D. and Speers, G.C.(eds.), Advances in organic geochemistry, 1966. Pergamon Press, London, 389 - 405.

BORDOVSKIY, O.K., 1965. Accumulation and transformation of organic substance in marine sediments. Mar.Geol. 3, 1 - 114.

BRAY, E.E. and EVANS, E.D., 1961. Distribution of n-paraffins as a clue to recognition of source beds. Geochim. Cosmochim. Acta 22, 2 - 15.

BREGER, I.A., 1960. Diagenesis of metabolites and a discussion of the origin of petroleum hydrocarbons. Geochim. Cosmochim. Acta 19, 297 - 308.

BRENNEMAN, M.C. and SMITH, P.V. Jr., 1958. The Chemical relationships between crude oils and their source rocks. In. Weeks, L.G. (ed.), Habitat of Oil: A symposium Am.Assoc. Petrol. Geol., 818 - 849.

BROECKER, W.S. and TAKAHASHI, T., 1966. Calcium carbonate precipitation on the Bahama Banks. J. Geophys. Res. 71, 1575 - 1602.

BROOKS, B.T., 1948. Active-surface catalysts in formation of petroleum. Am.Assoc.Petrol.Geol.Bull. 32, 2269 - 2286.

BROOKS, B.T., 1952. Evidence of catalytic action in petroleum formation Ind. and Eng. Chem. 44, 2570 - 2577.

BROOKS, J.D., 1970. The use of coals as indicators of the occurrence of oil and gas. Aust.Pet. Expl.Assoc.Jour. 10, 35 - 50.

BROWN, T.C., 1914. Origin of oolites and the oolitic texture in rocks. Bull.Geol.Soc. America XXV, 745 - 780.

BROWN, F.S., Baedecker, M.J. NISSENBAUM, A., KAPLAN, I.R., 1972. Early diagenesis in a reducing fjord, Saanich Inlet, British Colombia - III. Changes in organic constituents of sediment. Geochim. Cosmochim. Acta 36, 1185 - 1203.

CARPENTER, R., 1969. Factors controlling the marine geochemistry of fluorine. Geochim.Cosmochim. Acta 33, 1153 - 1167.

CARTER, P.W., 1978. Adsorption of amino acid-containing organic matter by calcite and quartz. Geochim. Cosmochim. Acta 42, 1239 - 1242.

CARTER, P.W. and MITTERER, R.M., 1978. Amino acid composition of organic matter. Geochim. Cosmochim. Acta 42, 1231 - 1238.

CAYEUX, L., 1935. Les Roches Sédimentaires de France; Roches Carbonatées. Paris: Mason. 463p.

CHAVE, K.E., 1965. Carbonates: association with organic matter in surface seawater. Science 148, 1723 - 1724.

CHOQUETTE, P.W. and PRAY, L.C., 1970. Geological nomenclature and classification of porosity in sedimentary carbonates. Am.Assoc.Petroleum Geologists Bull. 54, 207 - 250.

CLARK, R.C. Jr. and BLUMER, M., 1967. Distribution of n-paraffins in marine organisms and sediment. Limnol. and Oceanogr. 12, 79 - 87.

CLARK, F.W. and WHEELER, W.C., 1922. The inorganic constituents of marine invertebrates. U.S.Geol.Surv.Paper 124. Washington D.C.: U.S. Govt. Printing Office, 62p.

CLAYPOOL, G.E. and PRESLEY, B.J.and KAPLIN,I.R.,1971.Gas analyses in sediment samples from legs 10, 11, 13, 14, 15, 18 and 19. In Craeger, J.S., Scholl, D.W., et al, 1973. Initial Reports of the Deep Sea Drilling Project 19. Washington D.C.: U.S. Govt. Printing Office, 879 - 884.

CLAYPOOL, G.E. and PRESLEY, B.J. and KAPLAN, I.R., 1974. The origin and distribution of methane in marine sediments. In Kaplan I.R.,ed., Natural Gases in Marine sediments. New York: Plenum Press, 99 - 139.

CLAYPOOL, G.E. and REED, P.R., 1976. Thermal-analysis technique for source rock evaluation: Quantitative estimate of organic richness and effects of lithologic variation. Am.Assoc.Petrol.Geol. Bull.60, 608 - 626.

CLAYTON, J.L. and SWETLAND, P.J., 1978. Subaerial weathering of sedimentary organic matter. Geochim. Cosmochim. Acta 42, 305 - 312.

CLOUD Jr., P.E., 1962a. Environment of calcium carbonate deposition west of Andros Island, Bahamas. U.S. Geol.Surv. Prof. papers, 350, 1-138.

CLOUD, Jr. P.E., 1962b. Behaviour of calcium carbonate in sea water. Geochim. Cosmochim. Acta. 26, 867 - 884.

COLOMBO, U., 1967. Origin and evolution of petroleum. In Nagy, B and Colombo, U., eds. Fundamental aspects of petroleum geochemistry. Amsterdam: Elsevier Pub.Co., 331-369.

COOGAN, A.H., 1970. Measurements of compaction in oolitic grainstone. J.Sed.Petrology. 40, 921 - 929.

COOPER, J.E. and BRAY, E.E., 1963. A postulated role of fatty acids in petroleum formation. Geochim. Cosmochim. Acta 27, 1113 - 1127.

COOPER, A.K., SCHOLL, D.W., MARLOW, M.S., CHILDS, J.R., REDDEN, G.D. KVENVOLDEN, K.A. and SEVENSON, A.J. 1979. Hydrocarbon potential of Aleutian Basin, Bering Sea. Am.Assoc.Petrol. Geol. 63, 2070 - 2087.

CORREIA, M., 1971. Diagenesis of sporopollenim and other comparable organic substances: application to hydrocarbon research. In J. Brooks, et al., eds., Sporopollenin. New York: Academic Press, 569 - 620.

CRAIG, H., 1953. The geochemistry of the stable carbon isotapes. Geochim.Cosmochim. Acta 3, 52 - 92.

CUSSEY, R. and FRIEDMAN, G.M., 1977. Patterns of porosity and cement in ooid reservoirs in Dogger (Mid.Jurassic) Am.Assoc.Petrol.Geol.Bull.61, 511 - 518.

DANCY, T.E. and GIEDROYE, V., 1950. Further researches on the determination of the chemical composition of oil shales.Jour.Inst.Petroleum 36, 593 - 602.

DANGEARD, L., 1936. Étude des calcaires par coloration et decalcification. Bull.Soc.géol.France, 6th ser. 6, 237 - 245.

DAVIES, P.J., BUBUELA, B. and FERGUSON, J., 1978. Formation of ooids. Sedimentology 28, 703 - 730.

DAVIS, J.B. and SQUIRES, R.M., 1954. Detection of microbially produced gaseous hydrocarbons other than methane. Science 119, 381 - 382.

DEELMAN, J.C., 1978. Experimental ooids and grapestones: Carbonate aggregate and their origin. Jour.Sed.Petrology 48, 503 - 512.

DEGENS, E.T., CHILLINGAR, G.V. and PIERCE, W.D., 1964. On the origin of petroleum inside freshwater carbonate concretions of Miocene age. In Colombo, U and Hobson, G.D. eds., Advances in organic geochemistry, 1962. New York: Mac-millian press, 149 - 164.

DEGENS, E.T. and LOVE, S.,1965. Comparative studies of amino acids in shell structures of Gyraulus trochiformus, Stahl, from the Tertiary of Steinheim, Germany. Nature, 205, 876 - 878.

DEGENS, E.T. and REUTER, J.H., 1964. Analytical techniques in the field of Organic Geochemistry. In Colombo, U and Hobson, G.D., eds. Advances in Organic Geochemistry 1962. Oxford: Pergamon Press, 377 - 402.

DEMBICKI, Jr. H., MEINSCHEIN, W.G. and HATTON, D.E., 1975. Possible ecological and environmental significance of the predominance of even-carbon number C_{20} - C_{30} n-alkanes. Geochim.Cosmochim.Acta 39, 203 - 208.

DEUSER, W.G., and DEGENS, E.T., 1969. O^{18}/O^{16} and C^{14}/C^{12} ratios of fossils from the hot brine deep area of the central Red Sea. In: Degens, E.T. and Ross, D.A., eds. Hot brines and recent heavy metal deposits in the Red Sea. Berlin: Springler-Verlag, 336 - 347.

DOTT Jr., R.H. and REYNOLDS, M.J., eds., 1969. Source book for Petroleum Geology. Mem.5. Tulsa Okla: Am.Assoc. Petrol.Geol. 471p.

DRAVIS, J., 1979. Rapid and widespread generation of Recent oolitic hardgrounds on a high energy Bahamian platform, Eleuthera Bank, Bahamas. Jour. Sed. Petrology. 49, 195 - 208.

DREW, G.H., 1914. On the precipitation of calcium carbonate in the sea by marine bacteria, and on the action of denitrifying bacteria in tropical and temperate seas. Papers Tortugas Lab.; Carnegie Inst. Wash. Publ. 182, 7 - 45.

DUNNINGTON, H.V., 1958. Generation, migration, accumulation and dissipation of oil in northern Iraq. In Weeks,L.G., eds. Habitat of Oil: At symposium. Tulsa Okla: Am.Assoc.Petrol.Geol., 1194 - 1251.

DUNNINGTON, H.V., 1967. Stratigraphical distribution of oil fields in the Iraq-Iran-Arabia basin. Jour.Inst.Pet. 53, 129 - 161.

DUNTON, M.L. and HUNT, J.M. 1962. Distribution of low-molecular-weight hydrocarbons in Recent and ancient sediments. Am.Assoc. Petroleum Geologists Bull.46, 2246 - 2248.

DURAND, B. and ESPITALIÉ, J., 1972. Formation et evolution des hydrocarbures des C_1 a C_{15} et des gaz permanents dans les argiles du Toarcien du Bassin de Paris. In Gaertner, H.R. and Wehner, H., eds. Advances in Organic Geochemistry 1971. Oxford:Pergamon Press, 455 - 468.

DURAND, B., ESPITALIÉ, J., NICAISE, G. and COMBAZ, A., 1972. Etude de la matière organique insoluble (Kérogène) de argile du Toarcien du Bassin: 1, Etude par les procédés optiques, analyse élementaire, étude en microscopie et diffraction electroniques. Rev.Inst.Fr.Pétr. 27, 865 - 884.

EARDLEY, A.J., 1938. Sediments of Great Salt Lake, Utah. Am.Assoc. Petroleum Geologist Bull.22, 1305 - 1411.

EISMA, E. and JURG, J.W., 1967. Fundamental aspects of the diagenesis of organic matter and the formation of hydrocarbons. 7th World Pet.Congr.Mexico 2, 61 -72.

ELINSON, M.M., 1949. Toward the question of the method of study of the gas content of the rocks (in Russian).Izv.Nauk SSSR, Otdel. Tekh. Nauk, 2.

EMERY, K.O. and HOGGAN, D., 1958. Gases in Marine sediments. Am.Assoc. Petroleum Geologists Bull. 42, 2174 - 2188.

EMERY, K.O. and RITTENBERG, S.C., 1952. Early diagenesis of California Basin sediments in relation to origin of oil. Am.Assoc. Petroleum Geologists Bull. 36, 735 - 806.

ERDMAN, J.G. 1961. Some chemical aspects of petroleum genesis as related to the problem of source bed recognition. Geochim. Cosmochim. Acta 22, 16 - 36.

ERDMAN, J.G., 1962. Cited in Dunton, M.L. and Hunt, J.M., 1962. Distribution of low molecular-weight hydrocarbons in Recent and Ancient sediments. Am.Assoc. petroleum Geologists Bull. 46, 2246-2248.

ERDMAN, J.G., 1964. Geochemistry of the high molecular weight non-hydrocarbon fraction of petroleum. In Colombo, U and Hobson, G.D.,eds. Advances in Organic Geochemistry 1962. Oxford:Pergamon Press, 215-238.

ERDMAN, J.G.,1967. Geochemical origins of the low molecular weight hydrocarbon constituents of petroleum and natural gas. In Proc. 7th World Pet. Cong. Mexico 2. London: Elsevier Pub.Co., 13 - 24.

ERDMAN, J.G., MARLETT, E.M. and HANSON, W.E., 1956. Survival of amino acids in marine sediments. Science 124, 1026.

ESPITALIE, J., LA PORTE, J.L., MADEC, L., MARQUIS, F., LEPLAT, P., PAULET, J. and BONTEFEU. 1977. Method rapide de caracterisation des roches meres de leur potentiel petrolier et de leur degre d'evolution. Rev. de l'Inst.Francais Petrol.32, 23 - 42.

ESPITALIE, J., MADEC, M. and TISSOT, B., 1980. Role of mineral matrix in Kerogen pyrolysis: Influence on petroleum generation and migration. Am.Assoc. Pet.Geol.Bull. 64, 59 - 66.

EVANS, C.R., 1975. Panel Discussion. In Proc. 9th World Pet.Congr. Tokyo 2. Essex, England: Applied Science Pub.Co., 199 - 205.

EVANS, E.D., KENNY, G.S., MEINSCHEIN, W.G. and BRAY, E.E., 1957. Distribution of n-paraffins and separation of saturated hydrocarbons from recent marine sediments. Anal.Chem.29, 1858-61.

FABRICIUS, F. and KLINGELE, H., 1970. Cited in Suess, E. and Futterer,D., 1972. Aragonitic Ooids: Experimental precipitation from seawater in the presence of humic acid. Sedimentology 19, 129 - 139.

FAGERSTROM, J.A., 1967. Development, Flotation, and mud crusts - neglected factors in sedimentology. Jour.Sed. Petrology 37, 73 - 79.

FARRINGTON, J.W., HENDRICHS, S.M. and ANDERSON, R., 1977b. Fatty acids and Pb-210 geochronology of a sediment core from Buzzards Bay, Massachusetts. Geochim.Cosmochim. Acta 41, 289 - 296.

FEDYNSKY, V.V., KARUS, E.V. and POLSHKOV, M.K., 1975. Geophysical and geochemical surface surveys for detection of oil and gas pools. In Proc. 9th World Petrol. Congr. 3. Essex, Egland: Applied Science Pub.Ltd., 279 - 288.

FERGUSON, W.S., 1962. Analytical problems in determining hydrocarbons in sediments. Am.Assoc.Petrol.Geol.Bull.46, 1613-1620.

FERGUSON, J. 1973a. A statistical study of geochemical data from the Locton area. Report for British Gas Corporation 15p.

FERGUSON, J. 1973b. A statistical study of further geochemical data from the Locton area. Report for British Gas Corporation. 10 p.

FERGUSON, J. 1973c. A statistical study of Geochemical data from Weardale, Co.Durham. Report for British Gas Corporation 6 p.

FERGUSON, J., 1974. Stratigraphic Geochemical survey, Lokton, 1974. Report for British Gas Corporation. 16 p.

FERGUSON, J., 1975. A report on Hydrocarbon Geochemical prospecting. Report for British Gas Corporation. 35 p.

FLORY, D.A., WIKSTROM, S., GUPTA, S., GILBERT, J.M. and ORO, J., 1972. Analysis of organogenic compounds in Apollo 11, 12 and 14 samples. Proc. 3rd Lunar Science Conf. Houston. Geochim.Cosmochim. Acta, 2091 - 2108.

FOLK, R.L., 1974. The natural history of crystalline calcium carbonate: Effect of magnesium content and salinity. Jour.Sed. Petrology 44, 40-53.

FORSMAN, J.P. and HUNT, J.M., 1958. Insoluble organic matter (Kerogen) in sedimentary rocks of marine origin. In Weeks, L.G. ed. Habitat of Oil: A symposium Tulsa, Okla: Am.Assoc.Petrol.Geol., 747 - 778.

FRIEDMAN, G.M., 1959. Identification of carbonate minerals by staining methods. Jour.Sed.Petrology 29, 87 - 97.

FRIEDMAN, G.M., 1964. Early diagenesis and lithification in carbonate sediments. Jour.Sed.Petrology 34, 777 - 813.

FRIEDMAN, G.M., 1975. The making and unmaking of limestones or the downs and ups of porosity. Jour.Sed.Petrology 45, 379 - 398.

FRISHMAN, S.A., 1969. Geochemistry of Oolites, Baffin Bay, Texas. Unpublished Masters Thesis, University of Texas at Austin, 82 p.

FROST, A.V., 1945. The role of clays in the formation of petroleum in the crust. Progress in Chemistry 14, 1 - 20.

FUNKHOUSER, J., JESSBERGER, E., MULLER, O. and ZAHRINGER, J., 1971. Active and inert gases in Apollo 12 and 11 samples released by crushing at room temperature and by heating at low temperature. Proc.2nd Lunar Sci. Conf. Geochim.Cosmochim. Acta Suppl.2, 1381 - 1396.

GASKELL, S.J., RHEAD, M. M., BROOKS, P.W. and EGLINTON, G., 1976. Diagenesis of oleic acid in an estuarine sediment. Chem.Geol.17, 319 - 324.

GEALY, E. L. and DAVIES, T.A., 1969. The Deep Sea Drilling Project. Geotimes 14, 10.

GEHMAN Jr., H. M., 1962. Organic matter in limestones. Geochim. Cosmochim. Acta 26, 885 - 897.

GELPI, E., SCHNEIDER, H., MANN, J. and ORO, J., 1970. Hydrocarbons of geochemical prospecting or oil and gas using reference horizons. J. Geochem.Explor.2, 1 - 9.

GEOSERVICES LTD., 1969. Gas map: a new method of surface prospection. Paris: Technical Pub.

GESSEY, G.G., MUTCH, R., COSTERTON, J.W. and GREEN, R.B., 1978. Sessile bacteria: An important component of the microbial population in small mountain streams. Limnol. Oceanogr. 23, 1214 - 1223.

GIBBS, G.W., 1970. Collection and storage of samples in organic geochemistry. Geochim. Cosmochim. Acta 34, 629 - 630.

GIBSON, H.S., 1948. The production of oil from the fields of south western Iran. Jour.Inst.Petroleum 34, 374 - 398.

GINSBURG, R.N., 1957. Early diagenesis and lithification of shallow-water carbonate sediments in south Florida. In: LeBlanc, R.J. and Breeding, J.G. eds. Regional Aspects of Carbonate Deposition. Soc. Econ. Paleontologists Mineralogists, Spec. 5, 80 - 99.

GINSBURG, R.N., and SCHLAGER, W., 1980. Carbonates. Geotimes, 25, 15 - 16.

GOLDSTEIN, T.P. In Press. Geocatalytic reactions in the formation of oil. Am.Assoc.Petrol.Geol.Bull.

GOLUBIC, S., PERKINS, R. and LUKAS, K.J., 1975. Boring micro-organisms and microborings in carbonate substrates. In Frey, R.W. ed. The Study of Trace Fossils. New York: Springer Verlag.Inc., 229 - 260.

GRANSCH, J.A. and EISMA, E., 1970. Characterisation of the insoluble organic matter of sediments by pyrolysis. In Hobson, G.D. and Speers, G.C. eds. Advances in Organic Geochemistry, 1966. Oxford:Pergamon Press, 407 - 426.

GUTHRIE, R. 1938. Studies of certain properties of oil shale and shale oil. U.S. Bur.Mines.Bull. 415, 159 p.

GUTJAHR, C.C.M., 1966. Carbonisation measurements of pollen grains and spores and their application. Leidse Geol. Mededelingen 38, 1 - 29.

HACHENBERG and others, 1977. Gas chromatographic Headspace Analysis. London: Heyden and Son.

HARE, P.E., 1963. Amino acids in the proteins from aragonite and calcite in the shells of Mytilus Californianus. Science 139, 216 - 217.

HARE, P.E., 1969. Geochemistry of peptides and amino acids. In Eglinton, G. and Murphy, T.J. eds. Organic geochemistry: Methods and results. New York: Springler-Verlag, pp. 438 - 463.

HARE, P.E. and ABELSON, P.H., 1964. Proteins in mollusk shells. Carnegie Inst. Washington Yearbook 53, 267 - 270.

HAUROWITZ, F., 1963. The Chemistry and Functions of Proteins. London: Academic Press, 455p.

HARRIS, P.M., 1977. Sedimentology of the Joulters Cays ooid sand shoal, Great Bahama Bank. Unpublished Ph.D. thesis, Univ. Miami, Coral Gables, Fla. 492 p.

HARRIS, P.M., 1979. Comparison of endolith floras from Holocene - Pleistocene (Bahama-Florida) ooids. Geology V, 216 - 220.

HARWOOD, R.J., 1977. Oil and gas generation by laboratory pyrolysis of Kerogen. Am.Assoc.Petrol.Geol.Bull. 61, 2082 - 2102.

HEDBERG, H.D., 1931. Cretaceous limestone as petroleum source rock in northwestern Venezuela. Am.Assoc.Petrol.Geol.Bull. 15, 229 - 246.

HEDBERG, H.D., 1964. Geologic aspects of origin of petroleum. Am.Assoc. Petrol.Geol.Bull.48, 1755 - 1803.

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

HENSON, F.R.S., 1951. Observations on the geology and petroleum occurrences of the Middle East. In Proc.3rd World Pet.Congr.Hague 1. Leiden: E.J. Brill, 118 - 140.

HEROUX, Y., CHAGNON, A. and BERTRAND, R., 1979. Compilation and correlation of Major Thermal Maturation Indicators. Am.Assoc.Petrol.Geol.Bull.63, 2128 - 2144.

HILT, C., 1873. Die Bezie hungen zwischen der Zusa mmensetzung und den technischen Eigenschaften der Steinkohle. Sitzber Aochener Bezirksvereinigung VDI 4.

HODGSON, G.W., HITCHON, B. and TAGACHI, K., 1964. The water and hydrocarbon cycles in the formation of oil accumulation. In Miyake, Yand Koyamer, T.eds. Recent researches in the fields of the Hydrosphere, Atmosphere and Nuclear Geochemistry. Tokyo: Maruzen, 217 - 242.

HOERING, T.C. and ABELSON, P.H., 1963. Hydrocarbons from Kerogen Carnegie Inst. Washington Year Book 66, 510 - 515.

HOOD, A. and CASTANO, J.R., 1974. Organic metamorphism. Its relationship to petroleum generation and application to studies of authigenic minerals. United Nations ESCAP CCOP [Committee for Co-ordination of Joint Prospecting for Mineral Resources in Asia Offshore Areas] Technical Bull. 8, 85 - 118.

HOOKE, R., 1664. Micrography, or some physiological descriptions of minute bodies made by magnifying glasses, with observations and inquiries thereupon. Nov.23 1664. Cited in Brown, T.C.,1914.Bull.Geol.Soc. America XXV, 745.

HORSFIELD, B. and DOUGLAS, A.G., 1980. The influence of minerals on the pyrolysis of Kerogens. Geochim.Cosmochim. Acta 44, 1119 - 1131.

HORVITZ, L., 1939. On geochemical prospecting. Geophysics 4, 210 - 225.

HORVITZ, L., 1972. Vegetation and geochemical prospecting for petroleum. Am.Assoc.Petrol.Geol.Bull.56, 925 - 940.

HORVITZ, L., 1980. Near surface evidence of hydrocarbon movement from Depth. In Roberts III, R.H. and Cordell, R.J. eds. Problems of petroleum migration. Am.Assoc.Petrol. Geol.Studies in Geology 10,241 - 269.

HOWARD, W.V., 1934. Accumulation of oil and gas in limestone. In Wrather, W.E. and Lahee, F.H. eds. Problems of Petroleum Geology Tulsa Okla: Am.Assoc.Petrol.Geol., 365-376.

HUC, A.Y. and DURAND, B.M., 1974. Etude des acides humiques et de l'humine des sédiments récents considerés comme precurseurs des Kérogénes. In Tissot, B. and Bienner, F., eds. Advances in Organic Geochemistry 1973.Paris:Technip.,53 - 72.

HUNT, J.M., 1961. Distribution of hydrocarbons in sedimentary rocks. Geochim.Cosmochim.Acta 22, 37 - 49.

HUNT, J.M., 1967. The origin of petroleum in carbonate rocks. In Chillingar, G.V., Bissel, H.J. and Fairbridge, R.W. eds. Carbonate Rocks. New York:Elsevier Pub.Co., 225 - 251.

HUNT, J.M., 1974. Organic geochemistry of the marine environment. In Tissot, B. and Bienner, F. eds. Advances in Organic Geochemistry 1973. Paris: Technip, 593 - 604.

HUNT, J.M., 1975. Origin of gasoline range alkanes in the deep sea. Nature 254, 411 - 413.

HUNT, J.M., 1977a.Distribution of carbon as hydrocarbons and asphaltic compounds in sedimentary rocks. Am.Assoc.Petrol. Geol.Bull. 61, 100 - 104.

HUNT, J.M., 1978. Light hydrocarbons in Holes 361 and 364, Leg 4. Supplement; Initial Reports of the Deep Sea Drilling Project 40, Washington, D.C.: U.S. Government Printing Office, 649 - 650.

HUNT, J.M., 1979. Petroleum Geochemistry and Geology. San Francisco: Freeman and Co. 617 p.

HUNT, J.M. and JAMIESON, G.W., 1956. Oil and organic matter in source rocks of marine origin. Am.Assoc.Petrol.Geol.Bull. 40, 477 - 488.

HUNT, J.M. and MEINERT, R.N., 1954. Petroleum prospecting. U.S. Patent 2. 854.396. Patent Trademark Office, Washington D.C. 20231.

HUNT, J.M. and WHELAN, J.K., 1979. Volatile organic compounds in Quatenary sediments. Organic Geochemistry 1, 219 - 224.

HUNT, T.S., 1861. Notes on the history of petroleum or rock oil. Canadian Natur. and Geol. 6, 241 - 255.

HUNT, T.S., 1863. Report on the geology of Canada. In Canadian Geol. Surv.Rept: Progress to 1863. Canadian Geol.Surv. 983 p.

ILLING, L.V., 1954. Bahamian calareous sands. Am.Assoc.Petrol.Geol. Bull.38, 1 - 95.

ILLING, L.V., WOOD, G.V. and FULLER, J.G. C.M., 1967. Reservoir Rocks and Stratigraphic Traps in Non-reef Carbonates. In Proceedings 7th World Pet. Congress 2. London: Elsevier Pub. Co., 487 - 500.

ISHIWATARI R., ISHIWATARI, M., ROHRBACK, B.G. and KAPLAN, I.R., 1977. Thermal alteration experiments on organic matter from recent marine sediments in relation to petroleum genesis. Geochim. Cosmochim. Acta 41, 815 - 828.

JACOB, H., 1963. In International Handbook of Coal Petrology. International Committee for Coal Petrology, 1963. Suppl.2nd ed. 1972, 1975. Paris: 1975. Centre National de la Reserche Scientifique.

JOHNSTON, J. and WILLIAMSON, E.D., 1916. The role of inorganic agencies in the deposition of calcium carbonate.Jour. Geol.24, 729 - 750.

JOHNSON, R.W. and CALDER, J.A., 1973. Early diagenesis of fatty acids and hydrocarbons in a salt marsh environment. Geochim.Cosmochim. Acta 37, 1943 - 1955.

JONATHAN, D., L"HOTE, G. and DU ROUCHET, J., 1975. Analyse geochimique des hydrocarbures legers par thermovaporisation. Rev.Inst.Fr.Pet.30, 65 - 88.

JONES, R.S., 1980. 1980. Some mass balance and geological constrainsts on migration mechanisms. In Roberts, W.H. and Cordell, R.J., eds. Problems of Petroleum Migration. Tulsa, Okla: Am.Assoc.Petrol.Geol. Studies in Geology 10,47 - 68.

JURG, J.W. and EISMA, E., 1964. Petroleum hydrocarbons: Generation from fatty acids. Science 144, 1451.

KAPLAN, I.R. and RITTENBERG, S.C., 1963. Basin sedimentation and diagenesis. In The Sea 3. Interscience Publ. New York. John Wiley and Sons.Inc., 583 - 613.

KARTSEV, A.A., TABASARANSKII, Z.A., SUBBOTA, M.I. and MOGILEVSKII, G.A., 1958. Geochemical Methods of Prospecting and Exploration for Petroleum and Natural Gas. English Transl. Witherspoon, P.A. and William, D., 1959. California: UCLA Press. 347p.

KARTSEV, A.A., VASSOYEVICH, N.B., GEODEKIAN, A.A., NERUCHEV, S.G., SOKOLOV, V.A., 1971. The principal stage in the formation of petroleum. In Proc. 8th World Pet.Congr., Moscow 2, Applied Science Pub.Co.,3 - 11.

KELLERMAN, K.F. and SMITH, N.R., 1914. Bacterial precipitation of calcium carbonate. J.Wash.Acad.Sci.4, 400 - 402.

KEMP, A.H., 1934. Artificial oolites from spray from ammonia-cooling tower of ice plant, Seymour, Texas. Jour.Sed. Petrology, 4, 139 - 140.

KEMP, A.L. and MUDROCHOVA, A., 1972. Distribution and forms of nitrogen in a Lake Ontario sediment core. Limnol.Oceanogr. 17, 855 - 867.

KENDRICK, J.W., HOOD,A. and CASTANO, J.R., 1978. Petroleum-generating potential of sediments from the eastern Mediterranean and Black Seas. In Ross, D.A., Neprochnov, Y.P., et al., 1978. Initial Reports of the Deep Sea Drilling Project 42. Washington, D.C.: U.S. Govt. Printing Office, 483 - 488.

KHALE, C.F., 1974. Ooids from Great Salt Lake, Utah, as an analogue for the genesis and diagenesis of ooids in marine limestones. J.Fed.Petrology. 44, 30 - 39.

KIDWELL, A.L. and HUNT, J.M., 1958. Migration of oil in Recent sediments of Pedernales, Venezuela. In Weeks, L.G. ed. Habitat of Oil: A symposium. Tulsa, Okla.: Am.Assoc.Petrol.Geol. pp. 790 - 817.

KINGHORN, R.R.F. Unpublished. In Gill, W.D., Ala, M.A., and Kinghorn, R.R.F., Experimental methods of studying organic matter in potential source rocks. (Unpublished Research).

KINSMAN, D.J.J., 1969. Interpretation of Sr^{+2} concentrations in carbonate minerals and rocks. Jour.Sed.Petrology 39, 486 - 508.

KOBLUK, D.R. and KHALE, C.F., Bibliography of the endolithic (boring) algae and fungi and related geologic processes. Bull. Canadian.Petrol.Geol. 25, 208 - 223.

KOBLUK, D.R. and RISK, M.J., 1977a. Calcification of exposed filaments of endolithic algae, micrite envelope formation and sediment production. Jour.Sed.Petrology 47, 517 - 528.

KREJCI-GRAF, K., 1963. Origin of Oil. Geophys.Prospecting 11, 244 - 275.

KVENVOLDEN, K.A. and REDDEN, G.R., 1978. Hydrocarbon gas in sediment from the shelf; slope and basin of the Bering Sea. Geochim.Cosmochim. Acta 44, 1145 - 1150.

LALOU, C., 1957. Studies on bacterial precipitation of carbonates in sea water. Jour.Sed.Petrology 27, 190 - 195.

LAMBERT-AIKHIONBARE, D. and IBE, A.C., 1980. The Agbada shales as major source beds of the Niger Delta petroliferous province. In Proc. 16th Nigerian Mining and Geosciences Society Conf., Lagos Apr.14 - 18, 1980 (Abst).

LAND, L.S., BEHRENS, E.W. and FRISHMAN, S.A., 1979. The ooids of Baffin Bay, Texas. Journ. Sed.Petrology 49, 1269 - 1278.

LAPLANTE, R.E., 1974. Hydrocarbon generation in Gulf Coast Tertiary sediments. Am.Assoc.Petrol.Geol.Bull. 58, 1281 - 1289.

LAUBMEYER, G., 1933. A new geophysical prospecting method, especially for deposits of hydrocarbons. Petroleum 29, 1 - 4.

LEES, G.M., 1933. The reservoir rocks of Persian oil fields. Am.Assoc. Petrol.Geol.Bull. 17, 229 - 240.

LEES, G.M., 1934. Source rocks of Persian oil. Proc. 1st. World Pet. Cong. London 1. London: Congress Office publ., 3 - 5.

LEES, G.M., 1938. Geology of the oil field belt of Iran and Iraq. In The Science of Petroleum. Oxford: University Press, 140 - 148.

LEES, G.M. and RICHARDSON, F.D.S., 1940. The Geology of the Oilfield belt of southwest Iran and Iraq. Geol.Mag. 77, 227 - 251.

LEITMEIER, J., 1910. Zur Kenntnis der Carbonate, Die Dimorphie des Kohlensauren Kalkes. I.Teil. Neues Jahrb.Mineral., Heft 1, 49 - 74.

LEITMEIER, H., 1915. Zur Kenntnis de Carbonate.II. Teil: Neues Jahrb. Mineral., Beilageband 40, 655 - 700.

LE TRAN, K., 1975. Analyse et étude des hydrocarbures gazeux occlus.dan la sediments. Exemples d'application à l'exploration pétrolière. Bull.Cent.Rech.Pau.9, 223 - 243.

LE TRAN, K. and VAN DER WEIDE, B.M., 1969. Determination automatique du degré de carbonisation de las matière organique de roches. Bull.Centre Rech.Pau-SNPA 3, 449 - 453.

LEVENTHAL, J.S., 1976. Stepwise pyrolysis - gas chromatography of Kerogen in sedimentary rocks.Chem.Geol. 18, 5 - 20.

LEVENTHAL, J.S. and SHAW, V.E., 1980. Organic matter in Appalachian Devonian Black Shale:1. Comparison of techniques to measure organic carbon.II. Short range organic carbon content variations. Jour.Sed.Petrology 50, 77 - 82.

LEVORSEN, A.I., 1967. Geology of Petroleum. 2nd ed. San Fransisco: W.H. Freeman and Co.

LEYTHAEUSER, D., 1973. Effects of weathering on organic matter in shales. Geochim.Cosmochim. Acta. 37, 113 - 120.

LEYTHAEUSER, D., SCHAEFER, R.G. and WEINER, B., 1979a. Generation of low molecular weight hydrocarbons from organic matter in source beds as a function of temperature and facies. Chem.Geol.25, 95 - 108.

LEYTHAEUSER, D., HAGEMANN, H.W., HOLLERBACH, A., and SCHAEFER, R.G., 1979b. Hydrocarbon generation in source beds as a function of type and maturation of their organic matter: A mass balance approach. Preprint 10th World Pet.Congr. Bucharest PD1. London: Heyden and Son, 11 p.

LIJMBACH, G.M., 1975. On the origin of petroleum. In Proc. 9th World Pet. Congr.2. London: Applied Science Publ. Co., 357 - 369.

LINCK, G., 1903. Die Bildung de oolithe und Rogensteine.Neues. Jahrb. Mineral., Geol. Paläontol. 16, 495 - 513.

LINDBLOOM, G.P. and LUPTON, M.D., 1961. Microbial aspects of organic geochemistry. Develop. Ind.Microbiol.2, 9 - 22.

LINK, T.A., 1950. Theory of transgressive and regressive reef (bioherm) development and origin of oil. Am.Assoc.Petrol. Geol.Bull. 34, 263 - 294.

LIPMAN, C.B., 1922. Does nitrification occur in Sea water ? Science 56, 501 - 503.

LIPPMAN, F., 1973. Sedimentary Carbonate Minerals. Berlin: Springer-Verlag, 228 p.

LOBOV, V.A., 1951. Cited in Kartsev et al, 1959. Geochemical methods of prospecting and exploration for petroleum and natural gas. Eng.Transl. California: UCLA press.

LONG, G., NEGLIA,S. and FAVRETTO, L., 1964. Geochemical contribution to research for the reconstruction of the palaeogeography of a sedimentary basin. In Colombo, U and Hobson, G.D., eds. Advances in Organic Geochemistry. Oxford: Pergamon Press, 239 - 260.

LOUIS, M. 1964. Sur le pouvoir rotatoire des hydrocarbures contenus dans les roches sedimentaires anciennes. Paris: C.R. Acad. Sci. 259, 1889 - 1890.

MAGARA, K., 1968. Compaction and migration of fluids in Miocene mudstone, Nagoaka plain, Japan. Am.Assoc. Petrol.Geol.Bull.52, 2466 - 2501.

MAGARA, K., 1975. Re-evaluation of montmorillonite dehydration as cause of abnormal pressure and hydrocarbon migration. Am. Assoc.Petrol.Geol.Bull.59, 292 - 302.

MAGARA, K., 1976. Water expulsion from clastic sediments during compaction directions and volumes. Am.Assoc.Petrol.Geol.Bull. 60, 543 - 553.

MAIR, B.J., 1964. Terpenoids, fatty acids and alcohols as source materials for petroleum hydrocarbons. Geochim. Cosmochim.Acta 28, 1303 - 1321.

MALYSHEK, V.T., SHOKHET, P.A., GASANOV, M.V. AND SAL'MIEV, S.K., 1962. The biogenic formation of the higher gaseous hydrocarbons in bottom sediments. Izv. Akad.Nauk Azerbaidzhanian SSR, Ser. Geolog. - Geograf. Nauk i Nefti 1, 63 - 72.

MARGOLIS, S. and REX, R.W., 1971. Endolithic algae and micrite envelope formation in Bahamian oolites as revealed by Scanning electron microscopy. Geol.Soc.Am.Bull. 82, 843 - 852.

MARQUART, J.R., DELLOW, G.B. and GREITAS, E.R., 1968. Determination of normal paraffins in petroleum heavy distillates by urea adduction and gas chromatography. Anal. Chem. 40, 1653 - 1657.

MARTIN, E.L. and GINSBURG, R.N., 1965. Radiocarbon ages of oolitic sands on Great Bahama Bank. Proc. 6th Intern.Conf. Radiocarbon Tritium Dating, Pullman, Washington, 705 - 719.

MATTHEWS, A.A., 1930. Origin and growth of Great Salt Lake ooliths. Jour.Geol.38, 633 - 642.

MAYERHOFF, A.A. and HATTEN, C.W., 1974. Bahama Salient of North America: Tectonic framework, Stratigraphy and Petroleum Potential. Am.Assoc. Petrol.Geol.Bull.58, 1201 - 1239.

McAULIFFE, C.D., 1978. Chemical and physical constraints on petroleum migration with emphasis of hydrocarbon solubilities in water. In Physical and Chemical constraints on petroleum migration 2. Notes for Am.Assoc.Petrol. Geol.short course, Oklahoma City, April 9, 1978.

McCROSSAN, R.G., BALL, N.L. and SNOWDON, L.R., 1972. An evaluation of surface geochemical prospecting for petroleum, Olds-Caroline, Alberta. Geol. Surv.Canada. Paper 71 - 31, 101 p.

McIVER, R.D., 1967. Composition of Kerogen - clue to its role in the origin of petroleum. In Proc. 7th World Pet.Cong. Mexico 2. London: Elsevier Pub.Co., 26 - 36.

McIVER, R.D., 1971. Evidence of migration of hydrocarbons in Pleistocene sediments of the Shatsky Plateau, Western Pacific. In Fisher, A.G., Heezen et al., Initial Reports of the Deep Sea Drilling Project VI Washington, D.C.: U.S. Govt. Printing Office, 1327 - 1329.

McIVER, R.D., 1973. Geochemical significance of gas and gasoline - range hydrocarbons and other organic matter in a Miocene sample from Leg 13, Site 134. In Ryan, et al., Initial Reports of the Deep Sea Drilling Project XIII. Washington D.C.: U.S. Govt. Printing Office, 813 - 816.

McIVER, R.D., 1974. Evidence of migrating liquid hydrocarbons in Deep Sea Drilling Project cores. Am.Assoc.Petrol.Geol. Bull. 58, 1263 - 1271.

McIVER, R.D., 1975. Hydrocarbon Occurrences from Joides, Deep Sea Drilling Project. In Proc. 9th World Pet.Congr. Tokyo 2. Essex, England: Applied Publ.Co., 269 - 280.

MEADOWS, P.S. and ANDERSON, J.G., 1966. Micro-organisms attached to marine and freshwater sand grains. Nature 212, 1059 - 1060.

MEADOWS, P.S. and ANDERSON, J.G., 1968. Micro-organisms attached to marine sand grains. J. Marine Biol.Assoc.U.K. 48, 161 - 175.

MEINSCHEIN, W.G., 1959. Origin of Petroleum. Am.Assoc.Petrol.Geol.Bull. 43, 925 - 943.

MEINSCHEIN, W.G. and KENNY, G.S., 1957. Analyses of a chromatographic fraction of organic extracts of soil. Anal.Chem. 29, 1153 - 1161.

MILLIMAN, J.D., 1974. Marine Carbonates. New York. Springler-Verlag. 375 p.

MITTERER, R.M., 1968. Amino acid composition of organic matrix in calcareous oolites. Science 162, 1498 - 1499.

MITTERER, R.M., 1971a. Influence of natural organic matter on $CaCO_3$ precipitation. In Bricker, O.P., ed. Carbonate sediments. Baltimore: John Hopkins: University Press, 252 - 258.

MITTERER, R.M., 1972. Biogeochemistry of aragonite mud and oolites. Geochim. Cosmochim. Acta 36, 1407 - 1422.

MITTERER, R.M. and CARTER, P.W., 1977. Some analytical and experimental data on organic-carbonate interaction. Proc.3rd Intern.Coral Reef Symposium. University of Miami, Florida, 541 - 547.

MOMPER, J.A..1975. Panel Discussion. In Proc.9th World Pet.Congr. Tokyo 2. Essex London:Applied Science Pub.Co.,199-205.

MONAGHAN, P.H. and LYTLE, M.A., 1956. The origin of calcareous oolites. Jour.Sed.Petrology 26, 111 - 118.

MOORE, L.T., 1962. Isaac Newton, a biography. New York: Dover Publ. Inc.

MUIR, J.M., 1934. Limestone reservoir rocks in the mexican oil fields. In Wrather, W.E. and Lahee, F.H., eds. Problems of petroleum geology. Tulsa, Okla: Am.Assoc.petrol. Geol., 377 - 398.

MURPHY, M.T.J., 1969. Analytical methods. In Eglinton, G. and Murphy, M.T.J., eds. Organic Geochemistry. London: Longmans, 74 - 86.

MURRIS, R.J., 1980. Middle East: Stratigraphic evolution and oil habitat. Am.Assoc. Petrol. Geol.Bull. 64, 597 - 618.

NEGLIA, S. and FAVRETTA, L. 1964. Study of an analytical method for the execution of surface geochemical prospecting for petroleum and natural gas. In Colombo, U and Hobson, G.D., eds. Advances in Organic Geochemistry, 1962. Oxford: Pergamon Press, 285 - 296.

NENADKEVICH, K.A., 1917. On the content of H_2S in limestones and dolomites. Izv.Ross.Akad.nauk. Petrograd., 1037 - 1040.

NESTEROFF, W.D., 1956. De l'origine des oolithes. Compt.Rend. 242, 1047 - 1049.

NEWELL, N.D., PURDY, E.G. and IMBRIE, J., 1960. Bahamian oolitic sand. Jour.Geol. 68, 481 - 497.

NIXON, R.P., 1973. Oil source beds in Cretaceous Mowry shales of northwest interior United States. Am.Assoc.Petrol.Geol. Bull. 57, 136 - 161.

OEHLER, J.H., AIZENSHTAT, A. and SCHOPF, J.W., 1974. Thermal alteration of blue-green algae and blue-green algal chlorophyll. Am.Assoc.Pet.Geol.Bull. 58, 124 - 132.

OPPENHEIMER, C.H., 1960. Bacterial activity in sediments of shallow marine bays. Geochim.Cosmochim.Acta 19, 244 -260.

OPPENHEIMER, C.H., 1961. Note on the formation of spherical aragonite bodies in the presence of bacteria from the Bahama Bank. Geochim. Cosmochim. Acta 23, 295 - 296.

OPPENHEIMER, C.H. and KORNICKER, L., 1958. Effect of microbial production of hydrogen sulphide and carbon dioxide on the pH of recent sediments. Publ.Inst.Marine Sci.Univ.Texas 5, 5 - 15.

ORTON, E., 1888. The Trenton limestone as a source of oil and gas in Ohio. Ohio Geol.Surv.Rept.6, 101 - 310.

OWEN, E.W., 1964. Petroleum in Carbonate rocks. Am.Assoc.Petrol.Geol. Bull.48, 1727 - 1730.

PANEL DISCUSSION, 1975. Time and temperature relations affecting the origin, expulsion and preservation of oil and gas. In Proc. 9th World Petr.Congr.Tokyo 2. Essex, England: Applied Science Publ. Co., 199 - 205.

PENTECOST, A., 1980. Letter dated 8th March 1980.

PETERS, K. E., ISHIWATARI, R. and KAPLAN, I.R., 1977. Colour of Kerogen as index of organic maturity. Am.Assoc.Petrol. Geol.Bull. 61, 504 - 510.

PETROVA, Yu.N., KARPOVA, P.P. and KASATKINA, N.F., 1955. Cited in Andreev et al., 1968. Transformation of petroleum in nature. Eng.Transl.Intern.Series Monographs in Earth Sciences, 29. Oxford:Pergamon Press, 25.

PHILIPPI, G.T., 1956. Identification of oil source beds by chemical means, In Proc. 20th Intern.Geol.Congr.Mexico,III, 25 - 28.

PHILIPPI, G.T., 1965. On the depth, time and mechanism of petroleum generation. Geochim.Cosmochim. Acta 29, 1021 - 1049.

PHILIPPI, G.T., 1968. Essentials of the petroleum formation process are organic source material and a subsurface temperature controlled chemical reaction mechanism. In Schenck P. and Havenaar, G. eds. Advances in Organic Geochemistry 1968. Oxford:Pergamon Press, 25 - 46.

PHILIPPI, G.T., 1974. The influence of marine and terrestrial source material on composition of petroleum. Geochim. Cosmochim. Acta 38, 947 - 966.

PHILIPPI, G.T., 1975. The deep subsurface temperature controlled origin of the gaseous and gasoline-range hydrocarbons of petroleum. Geochim. Cosmochim. Acta 39, 1353 - 1373.

PHILIPPI, G.T., 1977. Proteins as a possible source material of low molecular weight petroleum hydrocarbons. Geochim. Cosmochim. Acta 41, 1083 - 1086.

PIRT, S.J., 1978. Aerobic and Anaerobic microbial digestion in waste reclamation. J.appl.Chem.Biotechnol.28, 232 - 236.

POWELL, T.G. and McKIRDY, D.M., 1973. The effect of source material, rock type and diagenesis on the n-alkane content of sediments. Geochim. Cosmochim. Acta 37, 623 - 633.

POWERS, R.W., 1962. Arabian Jurassic carbonate reservoir rocks. In Ham, W.E. ed. Classification of carbonate rocks. Am.Assoc.Petrol.Geol.Mem.1, 122 - 192.

PRATT, W.E., 1947. Petroleum on continental shelves. Am.Assoc.Petrol. Geol.Bull.31, 657 - 672.

PRESLEY, B.J. and KAPLAN, I.R., 1968. Changes in dissolved sulphate, calcium, and carbonate from interstitial water of near-shore sediments. Geochim.Cosmochim. Acta 32, 1037 - 1049.

PURDY, E.G., 1963a. Recent calcium carbonate facies of the Great Bahama Bank. 1. Petrography and reaction groups. Jour.Geol.71, 334 - 355.

PURDY, E.G., 1963b. Recent calcium carbonate facies of the Great Bahama Bank.2. Sedimentary facies. Jour.Geol. 71, 472 - 497.

PURDY, E.G., 1968. Carbonate diagenesis: an environmental survey. Geol.Romana 7, 183 - 228.

PURSER, B.H., 1969. Syn-sedimentary marine lithification of Middle Jurassic limestones in the Paris Basin. Sedimentology 12, 205 - 230.

PURSER, B.H., 1975. Sedimentation et diagenese precoce des series carbonatees du Jurassique moyen de Bourgogne. Thesis, University de Paris-Orsay. 383 p.

PURSER, B.H., 1978. Early diagenesis and the preservation of porosity in Jurassic limestones. Petroleum Geology 1, 83 - 94.

PUTSILLO, V.G., 1951. Cited in Andreev, P.F., Bogomolov, A.I., Dobryanskii, A.F., Kartsev, A.A., 1968. Transformation of petroleum in nature. Engl.Transl. Int.Series Monographs in Earth Sciences 29. Oxford: Pergamon Press, 25.

RASHID, M.A. and VILKS, G., Environmental controls of methane production in Holocene basins in eastern Canada. Org. Geochemistry 1, 53 - 59.

RHEAD, M. M., EGLINTON, G. and DRAFFAN, G.H., 1971. Hydrocarbons produced by the thermal alteration of cholesterol under conditions simulating the maturation of sediments. Chem.Geol.8, 277 - 297.

RICHARDSON, R.K., 1924. The Geology and oil measures of S.W. Persia. Jour.Inst.Pet.Tech., 10, 256 - 283.

RIDGEWAY, R., 1912. Colour standards and colour nomenclature. Washington D.C., pub. by author. 43 p.

RITTENBERG, S.C., EMERY, K.O., HULSEMANN, J., DEGENS, E.T., FAY, R.C., GRADY, J.R., RICHARDSON, S.H. and BRAY, E.E., 1963. Biogeochemistry of sediments in experimental Mohole. Jour.Sed.Petrology 33, 140 - 172.

ROBERTS, A.A., PALACAS,J.G. and FROST, I.C., 1973. Determination of Organic carbon in modern carbonate sediments.Jour. Sed.Petrology 43, 1157 - 1159.

ROBERTS III, W.H. and CORDELL, R.T., eds. 1980. Problems of Petroleum Migration, Tulsa, Okla:Am.Assoc.Petrol.Geol. Studies in Geology 10, 273 p.

ROBERTS, W.O., 1967. Science: a wellspring for our discontent. Am. Scientist 55, 3 - 14.

ROBINSON, R.B., 1967. Diagenesis and porosity development in Recent and Pleistocene oolites from southern Florida and the Bahamas.Jour.Sed.Petrology 37, 355 - 364.

ROBINSON, W.E., 1969a. Isolation procedures for Kerogens and associated soluble organic materials. In Eglinton, G. and Murphy, M.T. eds. Organic Geochemistry. Berlin: Springer-Verlag, 181 - 195.

ROGERS, M.A., 1979. Application of organic facies concept to hydrocarbon source rock evaluation. Pre print. 10th World Pet.Congr.Bucharest.London.Heyden and Son. 8 p.

ROGERS, M.A. and KOONS,C.B., 1971. Generation of light hydrocarbons and establishment of normal paraffin preferences in crude oils. Am.Chem.Soc.Monogr.103, 67 - 80.

ROMM, I.I., 1956. Some Geochemical characteristics of Recent Marine sediments. Cited in Veber, V.V. and Gorskaya, A.I., 1965. Bitumen formation in sediments of carbonate facies. Int.Geol.Rev.7, 816 - 825.

RONOV, A.B., 1958. Organic carbon in sedimentary rocks (in relation to the presence of petroleum. Geochem. 5, 497 - 509.

ROTHPLETZ, A., 1892. On the formation of oolite. Am.Geologist 10,279 - 282.

RUMEAU, J.L. and SOURISSE, C., 1972. Compaction, diagenèse et migration dans les sédiment argileux. Bull. Cent. Rech. Pau-SNPA 6, 313 - 345.

RUSNAK, G.A., 1960. Some observations on recent oolites. Jour. Sed. Petrology 30, 471 - 480.

SANDBERG, P.A., 1975. New interpretations of Great Salt Lake ooids and of ancient non-skeletal carbonate mineralogy. Sedimentology 22, 497 - 537.

SAYLES, F.L. and MANHEIM, F.T., 1975. Interstitial solutions and diagenesis in deeply buried marine sediments: Results from the Deep Sea Drilling Project. Geochim. Cosmochim. Acta 39, 103 - 127.

SCALAN, R.S. and 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.

SCHNEIDER, H., GELPI, E., BENNETT, E.O. and ORO, J., 1970. Fatty acids of geochemical significance in microscopic algae. Phytochemistry 9, 613 - 617.

SCHOLL, D.W., 1960. Relationship of the insular shelf sediments to the sedimentary environments and geology of Anacapa Island, Carlifornia.Jour.Sed.Petrology 30, 123 - 139.

SCHRAYER, G.J. and ZARELLA, W.M., 1963. Organic geochemistry of shales. Part 1: Distribution of organic matter in siliceous Mowry Shale of Wyoming.Geochim.Cosmochim.Acta 27, 1033 - 1046.

SCHAEFER, R.G., LEYTHAEUSER, D. and WEINER, B., 1978a. Single step capillary GC method for extraction and analysis of sub-ppb quantities of hydrocarbons (C_2 - C_8) from rock and crude oil samples and its application in petroleum geochemistry. J. Chromatogr. 167, 355 - 363.

SCHAEFER, R.G., WEINER, B. and LEYTHAEUSER, D., 1978b. Determination of sub-nanogram per gram quantities of light hydrocarbons (C_2-C_9) in rock samples by hydrogen stripping in the flow system of a capillary gas chromatograph.Anal.Chem.50, 1848 - 1854.

SHEARMAN, D.J.and SKIPWITH, P.A. D'E., 1965. Organic matter in Recent and ancient limestones and its role in their diagenesis. Nature 208, 1310 - 1311.

SHEARMAN, D.J., TWYMAN, J. and KARIMI, M.Z., 1970. The genesis and diagenesis of oolites.Proc.Geol.Assoc.(Engl.) 81, 561 - 575.

SHIMKUS, K.M. and TRIMONIS, E.S., 1974. Modern sedimentation in Black Sea. In Degens, E.T. and Ross, D.A. eds. The Black Sea - Geology, Chemistry and Biology. Memoir 20. Tulsa, Okla: Am.Assoc.Petrol.Geol., 249 - 278.

SHIMOYAMA, A. and JOHNS, W.D., 1972. Formation of alkanes from fatty acids in the presence of $CaCO_3$. Geochim.Cosmochim. Acta. 36, 87 - 91.

SIEBOLD, E., 1962. Untersuchungen zur kalkfällung und kalklösung an Westrand der great Bahama Bank.Sedimentology 1, 50 - 74.

SILLIMAN,Jr., B., 1846. Chemical examination of several natural waters. Am.Jour.Sci.2, 218 - 228.

SILVERMAN, S.R. and EPSTEIN, S., 1958. Carbon isotopic composition of petroleums and other sedimentary organic materials. Am.Assoc.Petrol.Geol.Bull. 42, 998 - 1012.

SISSLER, F.D., 1962. Microbiology and biochemistry of the sediments and overlying water. In Cloud, P.E. Environment of calcium carbonate deposition, Bahamas. U.S.G.S. Prof.paper 350, 64 - 69.

SMITH, C.L., 1940. The Great Bahama Bank.1. General hydrographic and chemical factors.2. Calcium carbonate precipitation. J.Marine Research 3, 1-31; 147 - 189.

SMITH, Jr., P.V., 1952. The occurrence of hydrocarbons in Recent sediments from the Gulf of Mexico.Science 116, 437 - 439.

SMITH, Jr.,P.V., 1954. Studies on origin of petroleum: Occurrence of hydrocarbons in Recent sediments. Am.Assoc.Petrol. Geol.Bull.38, 377 - 404.

SNIDER, L.C., 1934. Current ideas regarding source beds for petroleum. In Wrather, W.E. and Lahee, F.H. eds. Problems of Petroleum Geology. Tulsa, Okla: Am.Assoc.Petrol. Geol., 51 - 66.

SNOWDON, L.R. and McCROSSAN, R.G., 1973. Identification of petroleum source rocks using hydrocarbon gas and organic carbon content. Geol.Surv.Canada Paper 72 - 36, 12 p.

SOKOLOV, V.A., 1933. New methods of prospecting for oil and gas deposits. Trudy Neftyanoi.

SOKOLOV, V.A., 1948. Essays on the origin of petroleum. Moscow: 'Gostoptechizdat' Publ.House.

SOKOLOV, V.A., 1959. Possibilities of formation and migration of oil in young sedimentary deposits. In Problems of oil formation and Migration. Proe Lvov Conference. May,1957. Moscow: 'Gostoptechizdat' Publ.House.

SOKOLOV, V.A., ZHUSE, T.P., VASSOEVICH, N.B., ANTONOV, P.L., GRIGORYEV,G.G., and KOZLOV, V.P., 1963. Migration processes of gas and oil, their intensity and directionality. In Proc.6th World Pet.Congr.Frankfurt.Hamburg: Verein Zur Forderung, Des 6. Welt-Erdol-Kongresses, 493 - 505.

SOKOLOV, V.A., TICHOMOLVA, T.V. and CHERMISINOV, O.A., 1972. The composition and distribution of gaseous hydrocarbons in dependence of depth, as the consequence of their generation and migration. In Gaertuer, H.R.V. and Wehner, H. eds. Advances in Org.Geochemistry 1971. Oxford:Pergamon Press, 479 - 486.

SORBY, H.C., 1879. The structure and origin of limestones. Proc.Geol. Soc.London 35, 56 - 95.

SORENSEN, L.O. and CONOVER, J.T., 1962. Algal mat communities of Lyngbya conferoides (C.Agardh) Gomont. Pub.Marine Sci 1, Port Arkansas, Texas, 8, 61 - 74.

SOURON, C., BOULET, R. and ESPITALIE, J., 1977. Etude par spectrometrie de masse de la decomposition thermique de roches sédimentaries coutenant de la matière organique de deux types differents et comparison avec les kerogen correspondants. In Campos, R. and Goni, J., eds. Advances in Organic Geochemistry 1975. Madrid: Enadimsa, 797 - 820.

STAPLIN, F.L. 1969. Sedimentary organic matter, organic metamorphism, and oil and gas occurrence. Bull.Can.Petrol.Geol. 17, 47 - 66.

STEINEKE, M., BRAKAMP, R.A. and SANDER, N.J., 1958. Stratigraphic relations of Arabian Jurassic oil. In Weeks, L.G., ed. Habitat of Oil: A symposium. Tulsa Okla:Am.Assoc. Petrol.Geol., 1294 - 1329.

STEVENS, N.P., BRAY, E.E. and EVANS, E.E., 1956. Hydrocarbons in sediments of Gulf of Mexico. Am.Assoc.Petrol.Geol.Bull. 40, 975 - 983.

SUESS, E., 1968. Calcium carbonate interaction with organic compounds. Unpublished Ph.D Thesis. Marine Science Center, Lehigh University, Bethlehem, Penna. 153 p.

SUESS, E., 1970. Interaction of organic compounds with calcium carbonate - 1. Association phenomena and geochemical implications. Geochim.Cosmochim.Acta 34, 157 - 168.

SUESS, E., 1973. Interaction of organic compounds with calcium carbonate - II. Organo-carbonate association in Recent sediments. Geochim.Cosmochim.Acta 37, 2435 - 2447.

SUESS, E. and FUTTERER, D., 1972. Aragonitic ooids: Experimental precipitation from seawater in the presence of humic acid. Sedimentology 19, 129 - 139.

SWAIN, F.M., 1970. Non-Marine Organic Geochemistry. Cambridge: University Press. 445 p.

TAGUCHI, K., 1975. Panel Discussion. In Proc.9th World Pet.Congr. Tokyo 2. London: Applied Science Pub.Co., 199 - 205.

TEICHMULLER, M., 1974. Generation of petroleum-like substances in coal seams as seen under the microscope. In Tissot, B. and Bienner, F. eds. Advances in Organic Geochemistry, 1973. Paris: Editions Technip, 379 - 407.

THOM Jr., W.T., 1934. Present status of the carbon-ratio theory. In Wrather, W.E. and Lahee, F.H. eds. Problems of petroleum Geology. Tulsa, Okla: Am.Assoc.Petrol. Geol., 69 - 95.

THOMAS, A.N., 1950. The Asmari Limestone of S.W. Iran. Proc.18th Int. Geol.Cong.London VI London: Co-op Press, 35 - 44.

THOMPSON, R.R. and CREATH, W.B., 1966. Low molecular weight hydrocarbons in Recent and fossil shells. Geochim.Cosmochim. Acta 30, 1137 - 1152.

THORP, E.M., 1936. Calcareous shallow-water marine deposits of Florida and the Bahamas. Papers Totugas Lab, Carnegie Inst. Wash.Pub. 452, 37 - 143.

TICHOMOLOVA, T.V., 1970. The possible Ways of Light Petroleum Hydrocarbons formation. Dissertation. IGIRGI, Moscow.

TIRATSOO, E.N., 1967. Natural Gas. London: Scientific Press Ltd. 386 p.

TISSOT, B., CALIFET-DEBYSER, Y., DEROO, G. and OUDIN, J.L., 1971. Origin and evolution of hydrocarbons in early Toarcian shales, Paris Basin, France.Am.Assoc.Petrol. Geol.Bull. 55, 2177 - 2193.

TISSOT, B., DEROO, G. and HOOD, A. 1978. Geochemical study of Uinta Basin: formation of petroleum from the Green River formation. Geochim. Cosmochim. Acta 42, 1469 - 1485.

TISSOT, B., DURAND, B., ESPITALIE, J. and COMBAZ, A., 1974. Influence of nature and diagenesis of organic matter in formation of petroleum. Am.Assoc.Petrol.Geol.Bull. 58, 499 - 506.

TISSOT, B., PELET, R., ROUCACHE, R. and COMBAZ, A., 1977. Utilisation des alcanes comme fossiles geochimiques indicateurs des environnements géologiques. In Campos, R. and Goni, J., eds. Advances in Organic Geochemistry 1975. Madrid:Enadimsa, 117 - 154.

TISSOT, B. and WELTE, D.H. 1978. Petroleum Fromation and Occurrence. Berlin: Springer-Verlag. 538 p.

TRASK, P.D., 1928. Limestones as a source of oil. Am.Assoc.Petrol. Geol.Bull. 12, 556 - 557.

TRASK, P.D. and PATNODE, H.W., 1942. Source beds of Petroleum. Tulsa, Okla: Am.Assoc.Petrol.Geol., 566 p.

TRASK, P.D. ed., 1955. Recent marine sediments: A symposium. Tulsa Okla: Am.Assoc.Petrol.Geol. 736 p.

TRICHET, J., 1968. Étude de la composition de la fraction organique des oolites. Comparison avec celle de membranes des bacteries et des cyanophycées. Compt.Rend.267, 1492 - 1494.

TRAVERSE, A. and GINSBURG, R.N., 1966. Environments and sediments, Great Bahama Bank. Marine Geology 4, 417 - 459.

TWENHOFOEL, W.H., 1928. Oolites of artificial origin. J. Geology 69, 564 - 568.

USPENSKII, V.A., 1949. Cited in Andreev, P.F., Bogomolov, A.I., Dobryanskii, A.F. and Kartsev, A.A., 1968. Transformation of Petroleum in nature. Engl. Transl.Intern.Series Monographs in Earth Sciences 29. Oxford:Pergamon Press, 25.

VALITOV, N.B., 1974. Elemental sulphur as a factor in the generation of hydrogen sulphide in deep lying carbonate reservoir rocks. Dokl.Akad.Nank SSR 219, 206 - 208.

VAN TUYL, F.M., 1916. A contribution to the oolite problem. Jour.Geol. XXIV, 792 - 797

VASSOEVICH, N.B., KORCHAGINA, Yu.I., LOPATIN, N.V., CHERNISCHEV, V.V., 1970. The main stage of petroleum formation.Int.Geol.Rev. 12, 1276 - 1296.

VAUGHAN, T.W., 1914. Preliminary remarks on the geology of the Bahamas, with special reference to the origin of the Bahaman and Floridian oolites. Papers Tortugas Lab., Carnegie Inst.Wash.Pub. 182, 47 - 54.

VAUGHAN, T.W., 1918. Some shoal-water bottom samples from Murray Island, Australia, and comparison of them with samples from Florida and the Bahamas. Papers Tortugas Lab., Carnegie Inst.Wash. Pub. 213, 235 - 288.

VEBER, V.V. and GORSKAYA, A.I., 1965. Bitumen formation in sediments of carbonate facies. Int. Geol.Rev.7, 816 - 825.

VEBER, V.A. and MAXIMOV, S.P., 1976. Early diagenetic generation of hydrocarbon gases and their variations dependent on initial organic composition. Am.Assoc.Petrol. Geol.Bull.

VEBER, V.V. and TURKELTAUB, N.M., 1958. Gaseous hydrocarbons in Recent sediments. Geol.Nefti 2, 39 1 44. Eng.Trans. in Petrol.Geol.2, 737 - 742.

VEBER, V.V., SAZONOV, M.L., MOROZOVA, D.Ye., GERSHANOVICH, I.P. ZARIKHIN and CHERNOV, V.I., 1977. Generation of hydrocarbon gases in modern sedimentary and volcanogenic-sedimentary formations of the eastern and southern parts of the Atlantic Ocean. Int.Geology. Rev.19, 1399 - 1403.

VERNADSKIY, V.I., 1924. La Geochimie. Paris: Libr.Felix Algyan.

VAN VLEET, E.S. and QUINN, J.G., 1979. Early diagenesis of fatty acids and isoprenoid alcohols in estuarine and coastal sediments. Geochim.Cosmochim.Acta 43, 289 - 303.

WALTHER, J., 1888. Die Korallenriffe der Sinaihalbinsel. Abhandl.Sachs.Akad.Wiss.Leipzig, Math.Naturw.Kl.14, 437 - 506.

WALTHER, J., 1891. Die Denudation in der Wuste und ihre Bedeutung. Abhandl.Sachs.Akad.Wiss.Leipzig.Math.Natuurw.Kl.16, 345 - 569.

WEEKS, L.G., 1950. Discussion of papers by Lees, G.M., Henson, F.R.S., Thomas, A.N., O'Brien, C.A.E., Gee, E.R. and Tasman, C.E.In Proc.18th Int.Geol.Congr. London 6, 68 - 73.

WEEKS, L.G., 1958. Habitat of oil and factors that control it. In Weeks, L.G. ed. Habitat of Oil: A symposium. Tulsa, Okla:Am.Assoc.Petrol.Geol., 1 - 60.

WEEKS, L.G., 1961. Origin, migration and occurrence of petroleum. In Moody, G.B. ed. Petroleum Exploration Handbook. New York: McGraw-Hill, Chap.5.

WEEKS, L.G., 1962. In Gehman, H.M., 1962. Organic matter in limestones. Geochim. Cosmochim. Acta 26, 885 - 897.

WEEKS, W.B. and ALEXANDER, C.W., 1942. Schuler Field, Union County, Arkansas. Am.Assoc.Petrol.Geol.Bull. 26, 1467 - 1516.

WEISS, A., 1963. Organic derivatives of mica-type layer-silicates. Angew.Chem., Internat.Edit.2, 134 - 144.

WELLER, J.M., 1959. Compaction of sediments. Am.Assoc.Petrol.Geol. Bull. 43, 273 - 310.

WELLS, A. J. and ILLING, L.V., 1964. Present-day precipitation of calcium carbonate in the Persian Gulf. In Van Straaten, L.M.J.U. ed. Deltaic and Shallow Marine Deposits. Amsterdam: Elsevier Pub.Co., 429 - 435.

WELTE, D.H., 1965. Relation between petroleum and source rock. Am.Assoc.Petrol.Geol.Bull. 49, 2246 - 2268.

WENGERD, S.A., 1958. Origin and habitat of oil in the San Juan Basin of New Mexico and Colorado. In Habitat of oil: A sumposium. Tulsa, Okla: Am.Assoc. Petrol.Geol., 366 - 394.

WHELAN, J.K., 1979. C_1-C_7 hydrocarbons from IPOD Holes 397 and 397A. In Ryan, W.B. and Rad von, U.eds. Deep-Sea Drilling Proj.47. Washington D.C.: U.S. Govt.Printing Office, 531 - 539.

WHELAN, J.K. and HUNT, J.M., 1978. C_1-C_7 hydrocarbons in Holes 379A, 380/380A and 381. In Ross, D., Neprochnov, Y., et al, eds. Initial Repts. Deep-Sea Drilling Proj.42. Washington D.C.: U.S. Govt. Printing Office, 673 - 677.

WHITE, D., 1915. Geology: Some relations in origin between coal and petroleum. J.Wash.Acad.Sci.5, 189 - 212.

WILSON, L.R. 1971. Palynological techniques in deep basin stratigraphy. Shale Shaker 21, 124 - 139.

WILSON, H.H. 1975a. Time of hydrocarbon expulsion, paradox for geologists and geochemists. Am.Assoc.Petrol.Geol. Bull. 59, 69 - 84.

WILSON, H.H., 1977. 'Frozen-In' hydrocarbon accumulations or diagenetic traps-exploration targets. Am.Assoc.Petrol.Geol. Bull. 61, 483 - 491.

WOLF, K.H., 1965. 'Grain Dimunition' of algal colonies to micrite. Jour.Sed.Petrology 35, 420 - 427.

YOUNGBLOOD, W.W., BLUMER, M., GUILLARD, R.L. and FIORE, F., 1971. Saturated and unsaturated hydrocarbons in marine benthic algae. Marine Biology 8, 190 -201.

ZANKL, H., 1969. Structural and textural evidence of early lithification in fine-grained carbonate rocks. Sedimentology 12, 241 - 256.

ZIMMERSCHEID, W.J., DINERSTEIN, R.A., WEITKAMP, A.W., and MARSCHNER, R.F., 1950. Crystalline adducts of urea with linear aliphatic compounds. Indust.Eng.Chem. 42, 1300 - 1306.

ZOBELL, C.E., 1946b. Studies on redox potential of marine sediments. Am.Assoc.Petrol.Geol.Bull.30, 477 - 511.

ZOBELL, C.E., 1951. Contributions of bacteria to the origin of oil. In Proc.3rd World Pet.Congr.Hague 1. Leiden: E.J. Brill, 414 - 420.