AN INVESTIGATION OF SOME POTENTIAL JURASSIC HYDROCARBON SOURCE ROCKS OF SOUTHERN ENGLAND

By:

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October, 1984

To:

My two daughters, Mfon and Itoro

ABSTRACT

Rock samples from the three major Jurassic mudrock formations in Southern England - the Lower Lias, the Oxford Clay and the Kimmeridge Clay - have been characterized using x-ray diffraction and organic geochemical techniques. Organic geochemistry of three reservoired oils from Dorset has also been investigated.

The Lower Lias and the Kimmeridge Clay show a wide range of lithologies - from shales through mudstones to limestones. Alternations of these lithologies occur at various stratigraphic levels in the two formations. By contrast, the Oxford Clay consists mainly of shales in the lower part and mudstones in the upper part. The clay mineralogies of the three formations are similar. The main clay minerals are discrete illite and illite-smectite mixed layers. The mixed layers are mainly ordered.

Organic carbon contents in almost all the rock samples analysed are in excess of the minimum required for potential hydrocarbon source rocks. Relationships between lithology, sedimentation rate, and organic matter content are noted.

The kerogen facies range from chemical type II to type IV in the Lower Lias and the Oxford Clay whereas only types II to III are identified in the Kimmeridge Clay. Amorphous organic material constitutes the most abundant fraction of all the kerogen samples.

Organic matter in the Oxford Clay and the Kimmeridge Clay are immature in most parts of southern England.

They are well mature only in the central parts of the Mesozoic Wealden Basin. The distribution of mature Lower Lias sections is found to be more extensive.

The Lower Lias on the southern side of the Purbeck - Isle of Wight Disturbance appears to be the main source of the Dorset oils on the bases of adequate maturity, n-alkane distribution, alkane ratios, and stable carbon and hydrogen isotope ratios.

Application of the modified Lopatin method of basin analysis suggests the Lias in the Weald as the probable source for the natural gas deposit in Surrey.

ADDENDA

1. Cuticle

The term "cuticle" is employed in this thesis (Chapters 6-8) for any thin translucent, tissue-like material in the Jurassic kerogen concentrates, and does not necessarily refer to the waxy layer coating of leaf or stem epidermis (Masran and Pocock, 1981)*.

2. Vitrinite Reflectance

Values of this parameter quoted for all samples analysed in this research project were estimated from spore/pollen colour based on Waples' (1980) TAI - R_o conversion chart.

3. Thermal Alteration Index (TAI): Accuracy of Determination

Values of this parameter are given to two decimal places in this thesis. Such a high level of accuracy may seem unrealistic to the reader. Since the scale is not a linear one with increasing depth of burial (or temperature), the second decimal place was used to indicate small maturity differences between samples.

4. Time-Temperature Dependence of Organic Maturity

Barnard et al. (1981)* have indicated some differences in the respective responses of spore/pollen materials and vitrinite grains to heating due to the chemical differences between the two groups. Vitrinite reflectivity has been noted by the authors to show greater dependence on heating time than the spore/pollen colour which tends to be controlled almost exclusively by the maximum subsidence temperature. Viewed in this context, the direct correlation of the two maturation indicators as shown in this thesis, based on Waples (1980), may not be totally unchallenged.

5. The Geologic Time Scale

The scale of Van Eysinga is used in this thesis for sedimentation rate calculations (Chapter 5) and basin analysis (Chapter 9). The most recent geologic time scale is by Harland et al. (1982)*.

* See 'Additional References' (page 450)

ACKNOWLEDGEMENT

I am very grateful to Dr. R.R.F. Kinghorn, my supervisor, for all the assistance he has given during this project. To Professor R. Stoneley, I should like to express my gratitude for his interest in this research, his guidance on the geology of southern England and for his help in the collection of some of the outcrop samples.

I wish to thank the University of Port Harcourt, Nigeria for the Staff Development Award, and the Committee of Vice Chancellors and Principals of the Universities of the United Kingdom for the Overseas Research Students Award (ORS); without these financial assistances this project could not have been completed. My thanks are also due to the Director of the Institute of Geological Sciences (now the British Geological Survey) for allowing me access to most of the borehole rock samples and well data used for this project, to the Managements of Shell U.K. Exploration and Production for the provision of rock samples from the Cooles Farm No. 1 Well, B.P. Petroleum Development Limited for the provision of the Cornbrash Oil from the Kimmeridge Bay, and the British Gas Corporation for allowing me access to the oils from the Wytch Farm Oilfield. I wish to express my gratitude to Mr. P. Grant for his assistance in the collection of most of the Kimmeridge Clay and Oxford Clay outcrop samples.

I am very grateful to Mr. M. Rahman for his guidance with the maceration of the rock samples and the

transmitted-light microscopic examination of insoluble organic matter, and for stimulating discussions on various aspects of sedimentary organic matter. I wish to thank Dr. H. Shaw and Messrs. R. Curtis and M. Gill for their assistance with the X-ray diffraction analysis and interpretations of whole-rock and clay mineralogies, Mr. A.R. Hodgkinson for his help with instrumentations in the Organic Geochemistry Laboratory of this Department, and Mr. J. Bilton of the Chemistry Department of this College for his guidance on the HPLC analysis. I am very grateful to Drs. B. Spiro and J. Rouse of the Isotope Geology Unit of the British Geological Survey for their guidance on the stable carbon and hydrogen isotopic analyses and the interpretation of organic matter isotope data.

Finally, many thanks are due to my friends and colleagues for their useful discussions and moral support during the course of this research.

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CHAPTER I

INTRODUCTION

INTRODUCTION

1.1 GEOGRAPHICAL LOCATION OF THE STUDY AREA

The area considered in this study includes the southern counties of England south of Latitude 52°N. Particular attention is focussed on the Mesozoic sedimentary basins in the Bristol - Gloucester area, Hampshire Basin, and Wealden District (see Figs. 1.1 and 1.2).

1.2 HYDROCARBON EXPLORATION AND DISCOVERIES IN SOUTHERN ENGLAND

1.2.1 The Main Basis for the Early Search for Oil and Gas

The story of the exploitation of hydrocarbons or their precursors in southern England goes as far back as the Iron Age when the oil shales of the Kimmeridge Clay (Upper Jurassic) were used as local fuel substitute for coal (Gallois, 1978b). In the 18th Century, they were used as heat source for alum and sea-salt industries at Kimmeridge in Dorset. The Hampshire Basin and the Wealden District constitute hydrocarbon provinces where surface oil indications and the early accidental discovery of natural gas accumulation in coal borings at Heathfield (East Sussex) have stimulated a quest for economic productions for about half a century. Today, surface oil seepages and impregnations can be seen along the Dorset coast between Weymouth and Swanage in the Upper Jurassic rocks of the Corallian and Purbeck Beds, and in the Lower Cretaceous Wealden Sands. In the Weald, surface

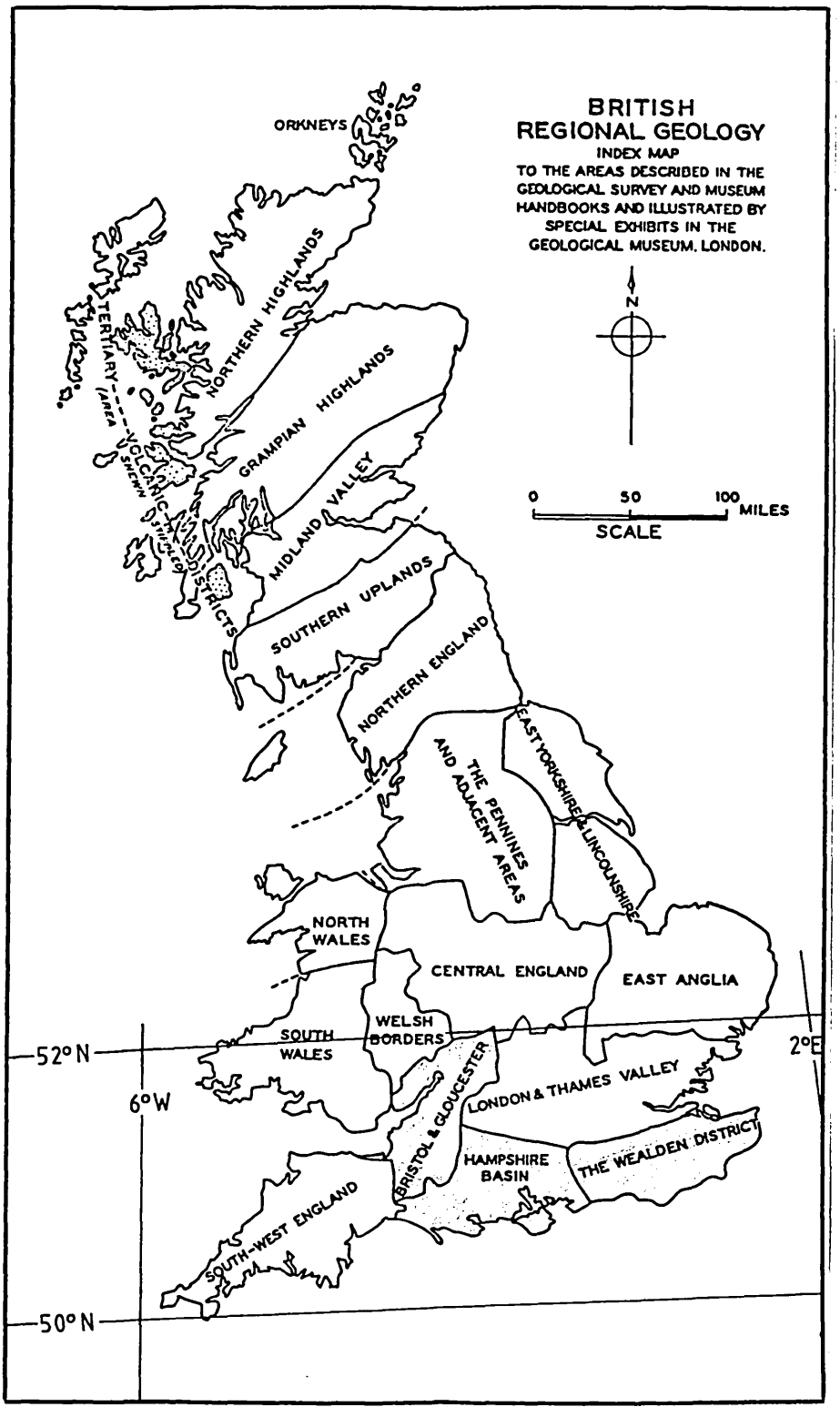


FIG.1.1- BRITISH REGIONAL GEOLOGY MAP SHOWING THE MAIN DISTRICTS IN S. ENGLAND CONSIDERED IN THE PRESENT STUDY.



FIG.1·2 – MAP OF SOUTHERN ENGLAND SHOWING COUNTIES

oil indications occur in the Purbeck inliers and in the Wealden Sands at Chilley near Pevensey (Lees and Cox,1937).

Apart from these surface oil indications, southern England contains a zone of well developed folds in the Mesozoic rocks extending from about the longitude of Weymouth to the Kent coast. Most of these folds are believed to have been emplaced during the Miocene orogenic phase, while the rest are pre-Miocene in age and were probably produced by the important earth-movements which took place between Aptian and Albian times (Brunstrom, 1963).

The surface oil shows together with the clear surface expression of many anticlines became the major geological basis for the early search for oil in southern England. This early exploration was begun in the early 1930s by the D'Arcy Exploration Company (now the British Petroleum Company) (Lees and Cox, 1937). Hydrocarbon exploration in this area has been in two main phases - the first before the Second World War and the second after the War.

1.2.2 Exploration Before the Second World War

This first phase of explorative activity was mainly a drilling programme based on surface geological studies by the staff of the D'Arcy Exploration Company under the leadership of Dr. G.M. Lees. The first deep borehole was drilled in 1936 - 1937 on Portsdown Hill, overlooking the Portsmouth harbour, on a prominent surface anticline (Taitt and Kent, 1958). This was followed by boreholes at Henfield (ten miles northwest of Brighton), at Kingsclere in northern Hampshire, and at Hankham on Pevensey anticline in Sussex.

At about the same time, two deep boreholes were drilled in the Weald by other oil companies - one by the Gulf Exploration Company at Penshurst in Kent, and the other by the Anglo-American Oil Company near Hellingley (Grove Hill) in Sussex (Lees and Taitt, 1946; Terris and Bullerwell, 1965) (see Fig. 1.3). The results of these early drillings were very disappointing and only sub-commercial oil shows were encountered. However, the drillings confirmed the presence of a thick and complete Jurassic succession in what seemed to be a single depositional basin extending from Dorset through Hampshire and Sussex to east Kent. A slight attenuation of some of the Upper Jurassic and Lower Cretaceous subdivisions at Portsdown was interpreted as reflecting a gentle swell in the sub-Mesozoic floor in this part of the basin. Similarly, the contrast in thickness of the Jurassic between Penshurst and Grove Hill led to the recognition of a Jurassic arch near the south coast in line with the Paris Pladge ridge (Kent, 1949; Terris and Bullerwell, 1965).

In addition to deep wells, the D'Arcy Exploration Company also embarked on several shallow drillings designed to test the Wealden and the Upper Jurassic Beds containing oil residues at outcrops. Notable amongst them were boreholes drilled on the Poxwell anticline, on the Purbeck anticline at Broadbench, and on the pitching end of the Osmington - Ringstead anticline at Chaldon Down (Lees and Taitt, 1946) (see Figs. 1.3 and 1.4). Though the Poxwell and Chaldon Down boreholes proved the existence underground of evidences of complex pre-Albian earth movements (Taitt and Kent, 1939; Arkell, 1947), the result of these shallow

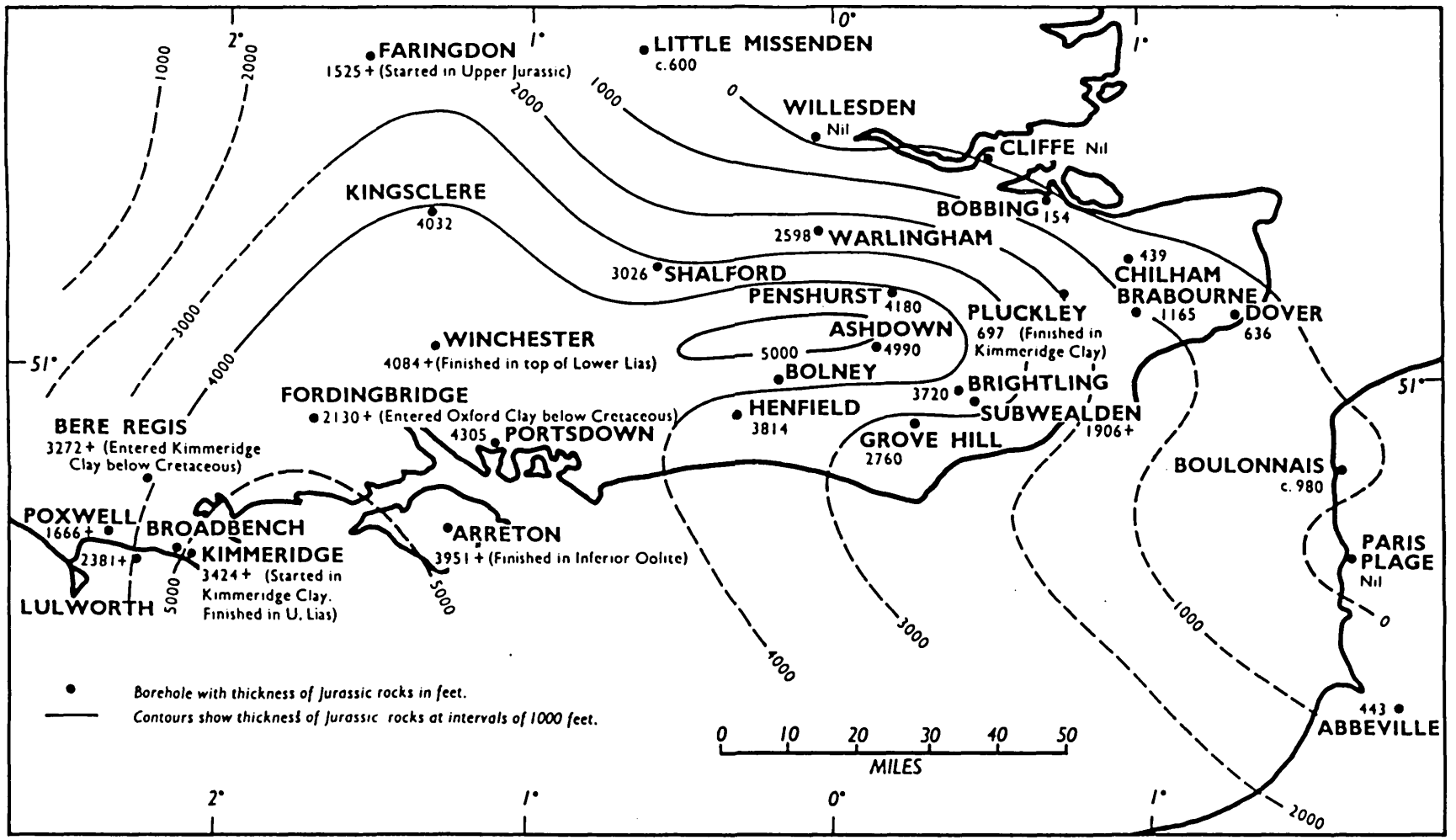


FIG. 1.3 - LOCATION MAP SHOWING EARLY EXPLORATORY BOREHOLES IN S. ENGLAND (AFTER TERRIS AND BULLERWELL, 1965)

drillings, in terms of commercial hydrocarbon discovery, was also disappointing. A second well was started at Chaldon Down in 1939 but was abandoned following the outbreak of the Second World War and it was not completed until after the War.

This initial failure in discovering commercial hydrocarbon accumulations in southern England was blamed on the lack of porosity in all rocks below the Wealden rocks, and also on the insufficient knowledge of the underground structures (Lees and Taitt, 1946).

1.2.3 Post-War Exploration and Oil and Gas Discoveries

In the second phase of the exploration after the War, exploratory drillings were based not only on surface structures but also on geophysical anomalies delineated by seismic and gravity surveys. And in this next stage, the basis of exploration by the British Petroleum Company Ltd. was broadened to include search for natural gas on behalf of the Gas Council and in conjunction with Imperial Chemical Industries (Falcon and Kent, 1960). With gas shows at Heathfield (in the Purbeck Beds) and at Henfield (in the Great Oolite of Middle Jurassic), the Weald area was given serious consideration for its gas prospects.

In the period between 1945 and 1955 inclusive, a number of boreholes were drilled. The first of the surface anticlines to be drilled was at Chaldon Herring - a superficially simple fold which was proved by four boreholes to be a complex structure at depth flanked by a fault with a large pre-Albian throw. The distorted fault plane was indicative of an

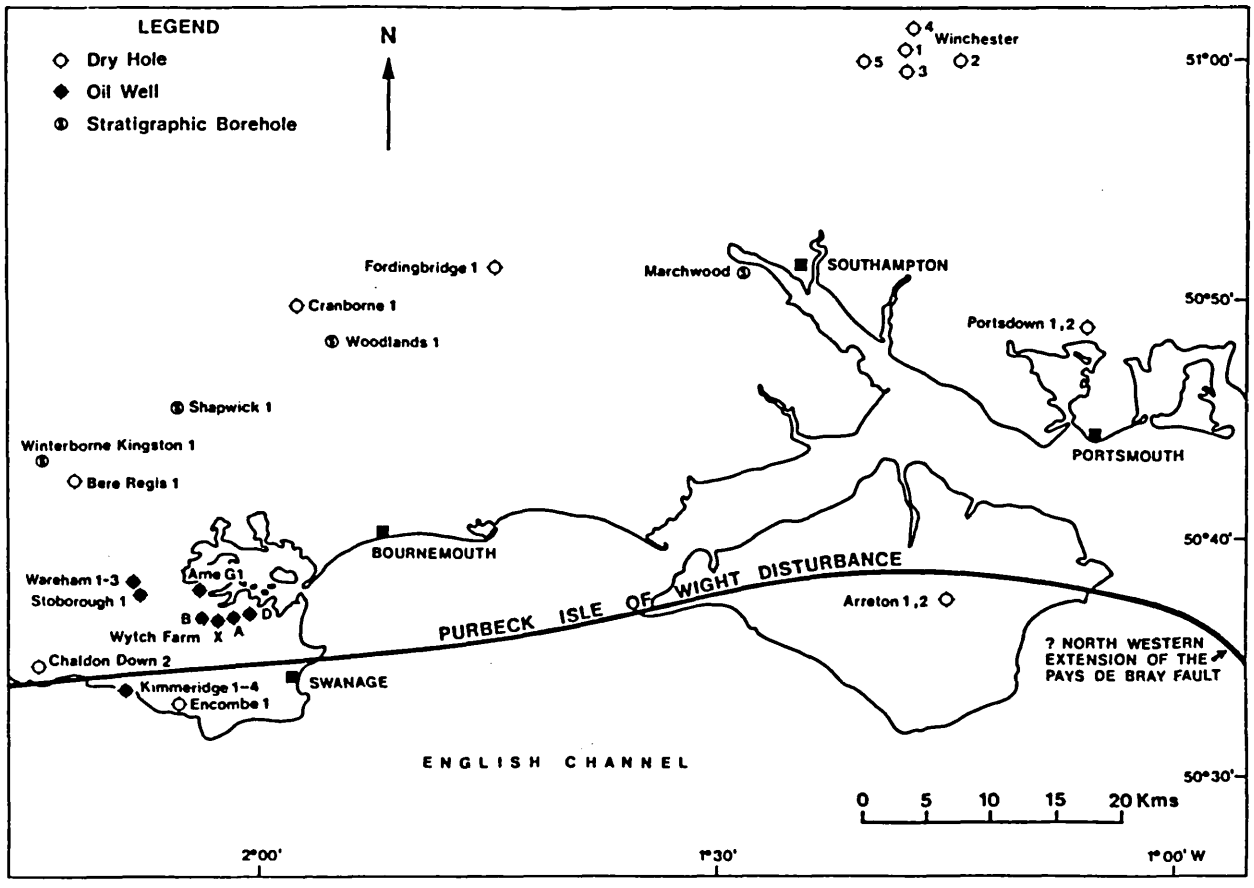


FIG. 1.4 - PART OF HAMPSHIRE BASIN SHOWING LOCATIONS OF SOME RECENT BOREHOLES (AFTER COLTER AND HAVARD, 1981)

additional complication of the structure by the Tertiary Alpine Orogeny (Falcon and Kent, 1960; Terris and Bullerwell, 1965). In the Isle of Wight a borehole, Arreton No. 1, was drilled on a domal structure located by surface geology, gravity work, and seismic reflection survey in the centre of the island. The drilling which started in the Ferruginous Sands (Aptian) was stopped at 5161 ft. (1573 metres) in the Middle Jurassic Inferior Oolite. Apart from proving a normal, fully developed succession of the Lower Cretaceous and the Jurassic Beds down to the Inferior Oolite, no hydrocarbon discovery was made (Falcon and Kent, 1960; Terris and Bullerwell, 1965). With the development of interest in gas prospects, a number of wells were drilled in the Weald. The first structure to be considered was the Ashdown anticline - a large surface structure in the Wealden Beds near Crowborough, Sussex. After preliminary detailing of the crestal part by shallow boring and by a seismic reflection survey, a Well, Ashdown No. 1, was drilled to 4,500 ft. (1,372 metres) finishing in the Inferior Oolite. The result of this drilling which was considered encouraging, necessitated another drilling at the highest part of the structure at depth established by seismic survey. The second borehole, Ashdown No. 2, was drilled one mile south-east of the first well and was continued to the Mesozoic floor. It found the Lower Jurassic resting unconformably on red beds of Carboniferous or Devonian age. An encouraging oil show was found in the Lower Lias but it was not considered enough to justify further development in an area with many surface obstructions (Falcon and Kent, 1960). In an attempt to

investigate the size of gas accumulation at Heathfield and possibly increase production, two projects were undertaken - firstly, an additional boring to the Portland Beds (Upper Jurassic) at Heathfield itself, and secondly, a deep boring to test the whole of the Jurassic near Brightling on the structurally highest point of the Wealden Anticline. The Heathfield test produced gas at sub-commercial level from the Portland Beds. Similarly, the Brightling hole found gas show in the Portland Beds and some gas and oil shows in the Middle Jurassic Kellaways Beds. An interesting structural feature revealed in the Brightling borehole was a reversed fault evidenced by a repitition of part of the Upper, Middle, and most of the Lower Lias. The fault's throw of about 500 ft. (152 metres) was clearly established by ammonite evidence (Falcon and Kent, 1960).

The year 1956 saw the continuation of the exploration programme by the British Petroleum Company (BP) in southern England. Further number of boreholes were drilled including Shalford No. 1, Fordingbridge No. 1, and Bere Regis No. 1. During this period, the Esso Petroleum Company drilled a borehole at Bolney (Fig. 1.3). In 1958, the BP drilled the Radipole borehole near Weymouth. The exploration by BP continued with very little success until 1959 when a shallow borehole, Kimmeridge No. 1, drilled at Kimmeridge Bay on the Purbeck anticline made an important oil discovery in the fractured Cornbrash limestone (Middle Jurassic) at a depth of 1,791 ft. (546 metres) (Brunstrom, 1963; Terris and Bullerwell, 1965). Three more producing wells (Kimmeridge Nos. 2-4) have been drilled on the structure since then. The pressure in the fractured oil reservoir is substantially

below hydrostatic and hence pumps are used to force the oil to the surface separators (see Plate 1.1).

In 1964, the Wareham No. 1 Well in Dorset was drilled by BP and it produced oil at the rate of approximately 23 barrels/day from the thin Inferior Oolite (16 ft or 5 metres) and the top 9 ft (about 3 metres) of the Upper Liassic Bridport Sands. The Well was suspended and was not production tested until November, 1970 (Colter and Havard, 1981). Between 1968 and 1972, the exploration of the Wessex Basin (the Mesozoic Dorset - Hampshire Basin) became the joint responsibility of the BP and the Gas Council based on an agreement reached in 1967 to share equally all hydrocarbon discoveries. On completion in 1970, the initial oil production from the Wareham No. 1 Well was in excess of 100 barrels/day which rapidly declined in time until shut-in in 1979 to conserve energy. Wareham No. 2 was drilled down-dip from the No. 1 Well and it found the Inferior Oolite to be wet but produced oil from the Cornbrash limestone at a rate of approximately 14.5 barrels/day after fracturing and acidizing. The Well was later abandoned (Colter and Havard, 1981). During this period, oil was also discovered in a well drilled at Stroborough close to Wareham (see Fig. 1.4). In addition to exploratory wells, stratigraphic boreholes such as Shapwick and Woodlands were also drilled (Fig. 1.4).

In 1972, The Gas Council (Exploration) Limited became in-charge of the full hydrocarbon exploration operation in the Wessex Basin. Based on the discovery of adequate porosity and permeability in the Bridport Sands in Wareham and Bere Regis No. 1 Wells from micrologs and drill stem test (DST)



PLATE 1.1 - AN OIL PUMPING INSTALLATION IN THE KIMMERIDGE BAY OILFIELD (THE CORNBRASH OIL RESERVOIR IS UNDERPRESSURED)

data, the Wytch Farm No. 1 Well was drilled (in Dorset) in December 1973 to test the Sands. The Well was drilled on a structure mapped from seismic data earlier acquired in the area by the BP geophysicists. The Bridport Sands were found to be oil-bearing, producing oil at an average rate of 600 barrels/day on a drill stem test (Colter and Havard, 1981). Oil shows were found in the Cornbrash limestone at sub-commercial level. The oil discovery in the Wytch Farm No. 1 was subsequently followed by other production drillings.

In 1977, based on a theoretical oil migration mechanism from a deep faulted Jurassic source rock up into Triassic reservoirs, the Wytch Farm D5 Well was deviated to the Triassic Sherwood Sandstone Group below the Bridport Sands. This Well made a significant oil discovery in these Triassic Sandstones (Colter and Havard, 1981). Today, oil is being produced in the Wytch Farm Oilfield from both the Bridport Sands and the Sherwood Sandstone Group. In contrast to the underpressured reservoirs of the Bridport Sands, those of the deeper Sherwood Sandstones are sufficiently pressured and oil is being produced naturally from the 'Christmas trees' fixed directly to the well heads. The Triassic reservoir is believed to contain about 50 million barrels of recoverable oil but could contain up to 150 million barrels (Sinclair, 1983).

The Wytch Farm Jurassic discovery was first brought on stream in the spring of 1979. Average daily production from the Bridport Sands reservoir climbed steadily from 2,500 barrels/day in 1979 to 5,300 barrels/day in 1982 (Sinclair, 1983). It is believed that if the deeper Triassic

Sherwood reservoir is fully developed, the Wytch Farm could produce at least 40,000 barrels/day. At present, the Wytch Farm Field constitute the biggest onshore oil discovery in the United Kingdom (Sinclair, 1983).

The big oil finds in the Wytch Farm resulted in intensified interest in exploration in the Dorset - Hampshire Basin as well as in the Weald. The majority of new targets, identified through improved seismic survey techniques together with cumulative drilling knowledge, are believed to be within the Jurassic System (Sinclair, 1983). In 1980, oil was found at Humbly Grove near Basingstoke in Hampshire and during the early part of 1983, another field was discovered at Horndean in the same county. The Humbly Grove Field is thought to contain around 12 million barrels of recoverable oil reserves while, according to seismic surveys, the Horndean Field could be about three times larger. Commercial development of the Humbly Grove was expected to begin in the later part of 1983 or in 1984, although the field has been producing small trial quantities of oil since 1980 (Sinclair, 1983). Also in 1983, a natural gas discovery of possibly commercial status was made by Conoco (UK) at Godley Bridge near Chiddingfold in Surrey and more recently, oil accumulation has been found by the same Company at Palmer's Wood near Godstone in the same county (Dolan, 1984).

The locations of the known oil and gas fields in southern England are shown in Fig. 1.5.

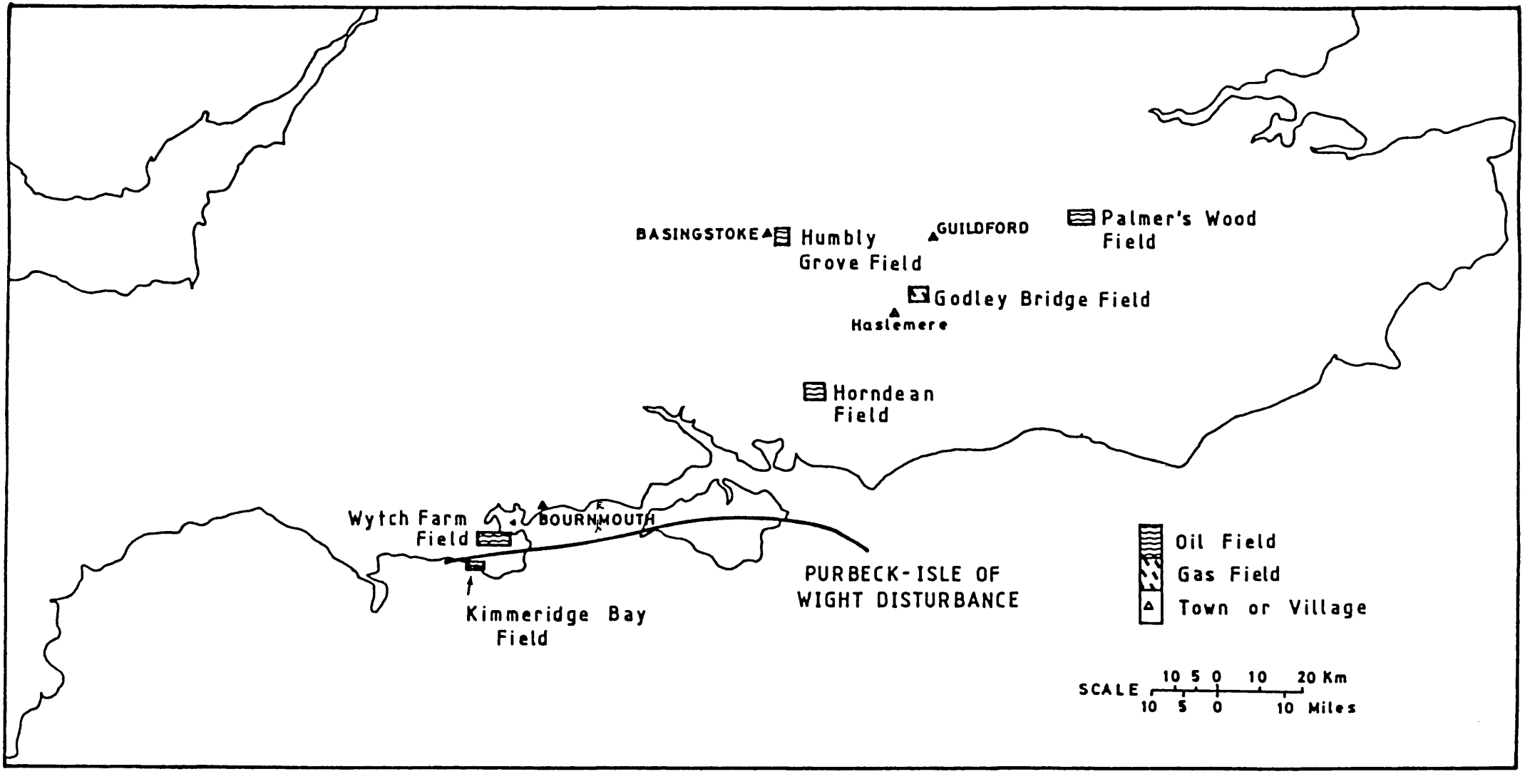


FIG. 1.5 - MAP OF SOUTHERN ENGLAND SHOWING LOCATIONS OF KNOWN OIL AND GAS FIELDS

1.3 PREVIOUS WORK ON HYDROCARBON SOURCE-ROCK INVESTIGATIONS AND RELATED STUDIES OF THE JURASSIC MUDROCKS IN S. ENGLAND

The Jurassic System of southern England contains three major mudrock-formations namely:- the Lower Lias, the Oxford Clay, and the Kimmeridge Clay. The term 'mudrock' is used here to include all fine-grained sedimentary rocks - both argillaceous and calcareous (Selley, 1982). The rocks of these formations occur both on outcrop sections as well as in the subsurface at various depths across southern England. Very little appear in the literature so far on co-ordinated source-rock studies of these formations with the ultimate objective of identifying mature hydrocarbon source horizons across the study area.

Davies (1978), from his organic geochemical investigations of outcrop samples of the Kimmeridge Clay and the Oxford Clay Formations along the Dorset Coast, concluded in his Ph.D. thesis that the organic matter in both formations were immature. Williams and Douglas (1980) and Douglas and Williams (1981) investigated the organic geochemistry of Kimmeridge oil shales from outcrops and shallow boreholes in the study area as well as in other parts of Britain. They concluded that the Kimmeridge shales represent an organic rich, but immature sequence which was deposited in a reducing marine environment in which lower plants, probably algae, played a significant part. The only known publication to date with a reference to oil source-rock studies of subsurface samples of the three Jurassic mudrock formations from deep boreholes in southern England is that of Colter

and Havard (1981). Borehole samples from the Wytch Farm Oilfield (Dorset) and Arreton No. 2 Well in the Isle of Wight were considered. The results of the organic geochemical analyses of these samples carried out by BP Research Centre at Sunbury-on-Thames in 1976 showed that not only were the Lias and Oxford Clay samples from the Wytch Farm organically poor but also immature. However, samples of the Kimmeridge Clay, Oxford Clay, and the Lias from Arreton No. 2 Well were found to be rich in marine-type organic matter, and they were also found to be at or close to maturity. On the basis of carbon isotope data obtained from the Wytch Farm oil ($\delta^{13}C$ of -29‰) a restricted marine or a deltaic coastal swamp was invoked for its source material. Though no oil-source rock correlation was attempted, the Jurassic rocks in the locality of Arreton No. 2 Well were indicated to be the probable source for the Wytch Farm oils. The more recent analyses by Geochem Laboratories (UK) Ltd. have identified rich potential source rock materials in both the Oxford Clay and the Liassic shales in the Wytch Farm and have also confirmed their immaturity (Colter and Havard 1981).

There are a number of reports on various related aspects of hydrocarbon source-rock studies of the Lower Lias, the Oxford Clay, and the Kimmeridge Clay in southern England. Downie in 1955 (in Morris, 1980) reported on the nature and origin of the Kimmeridge oil shale. He recognized 141 partial or complete lithologic cycles of mudstone - bituminous shale - oil shale in 200 m (656 ft.) of the sequence. He also noted the dramatic variation in organic matter content in the sequence with the mudstones having

the least total organic carbon values (1-2%) and the oil shales the highest (up to 35%). Gallois (1976; 1978a) also described the nature and the oil source potential of the various lithologic units of the Kimmeridge Clay. Employing the idea of phytoplankton bloom, he attempted an explanation of the cyclic sequence of the Kimmeridge Clay units. Other notable works on the origin/depositional environment of the Kimmeridge Clay are those of Tyson et al. (1979) and Morris (1980) - both of which were based mainly on faunal and floral evidences. The bituminous shales of the Lower Oxford Clay Formation have been described by Morris (1980) in the context of organic richness, mineralogical composition, mineral diagenesis, and depositional environment. Reports on the general lithologic character, the depositional environments, and the bituminous sequences of the Lower Lias Formation on outcrops are contained in the works of Hallam (1960, 1964, and 1975), Bitterli (1963), and Sellwood (1970, 1972). The results of clay mineralogical investigations of the three formations indicating illite or illite with illite-smectite mixed layers as the dominant clay mineral component(s) have been published by a number of workers (Perrin, 1957, Freeman, 1964; Hallam and Sellwood, 1968; Sellwood, 1972; Hallam, 1975; Gallois, 1978a; and Morris, 1980). There has, however, been no publication yet on the clay mineral diagenesis in the three potential Jurassic hydrocarbon source-rock formations and its possible relation to hydrocarbon generation and migration in southern England.

1.4 THE PRESENT WORK

This is an organic petrographic and geochemical as well as a mineralogic investigation of both outcrop and borehole rock samples of the Lower Lias, the Oxford Clay, and the Kimmeridge Clay Formations across southern England. The organic geochemistry of some Dorset reservoired crude oils (- the Kimmeridge Bay and the Wytch Farm oils) is also considered.

The main objectives of this study are:-

(i) to investigate the sedimentary organic matter facies and their hydrocarbon potentials in each of the three Jurassic formations.

(ii) to investigate the relationships between the organic matter richness and facies of these formations and their lithologies and depositional environments.

(iii) to investigate the levels of maturation of their organic materials in Jurassic sections across the study area, and possibly identify the source rock(s) for the known oil and gas accumulations.

(iv) to relate organic matter maturity and hydrocarbon generation in these formations to the structural history of the area.

(v) to investigate their clay mineral diagenesis and its possible relations to hydrocarbon generation and migration in these formations.

CHAPTER II

REVIEW OF GEOLOGICAL HISTORY AND GENERAL GEOLOGY OF SOUTHERN ENGLAND

REVIEW OF GEOLOGICAL HISTORY AND GENERAL GEOLOGY OF SOUTHERN ENGLAND

2.1 PRE-DEVONIAN TIMES

During the Pre-Cambrian to Silurian times, southern England was part of the Armorican geosyncline of Western Europe, and this extended westwards from Poland across Germany, Belgium, northern France to southwest Ireland (Edmonds et al., 1975). Sedimentation from the open sea of the geosyncline may have continued from the Late Pre-Cambrian to the end of the Carboniferous Period. Onshore southern England, vestiges of ancient crystalline basement of supposed Pre-Cambrian age are seen at Lizard Point and in the area around Start Point in Cornwall (Terris and Bullerwell, 1965) (Fig. 2.1). Great orogenic movements, which may have ranged in time up to Late Cambrian, imposed an ENE-WSW structural trend in northern France and south Wales. Isotopic age determinations suggest that earth-movements of similar age affected sediments of southern England (Edmonds et al., 1975). Today, the crystalline basement complexes of the Lizard Point and Start Point areas are found faulted or thrusted on their northern sides against Devonian sediments. This structural setting is believed to have been emplaced during the orogenic movements of Permo-Carboniferous age.

Outcrops believed to be of Ordovician and Silurian ages respectively, occur in the area immediately to the north of the Lizard Point Complex, and they occur as discontinuous outcrops or lenses in what is termed the

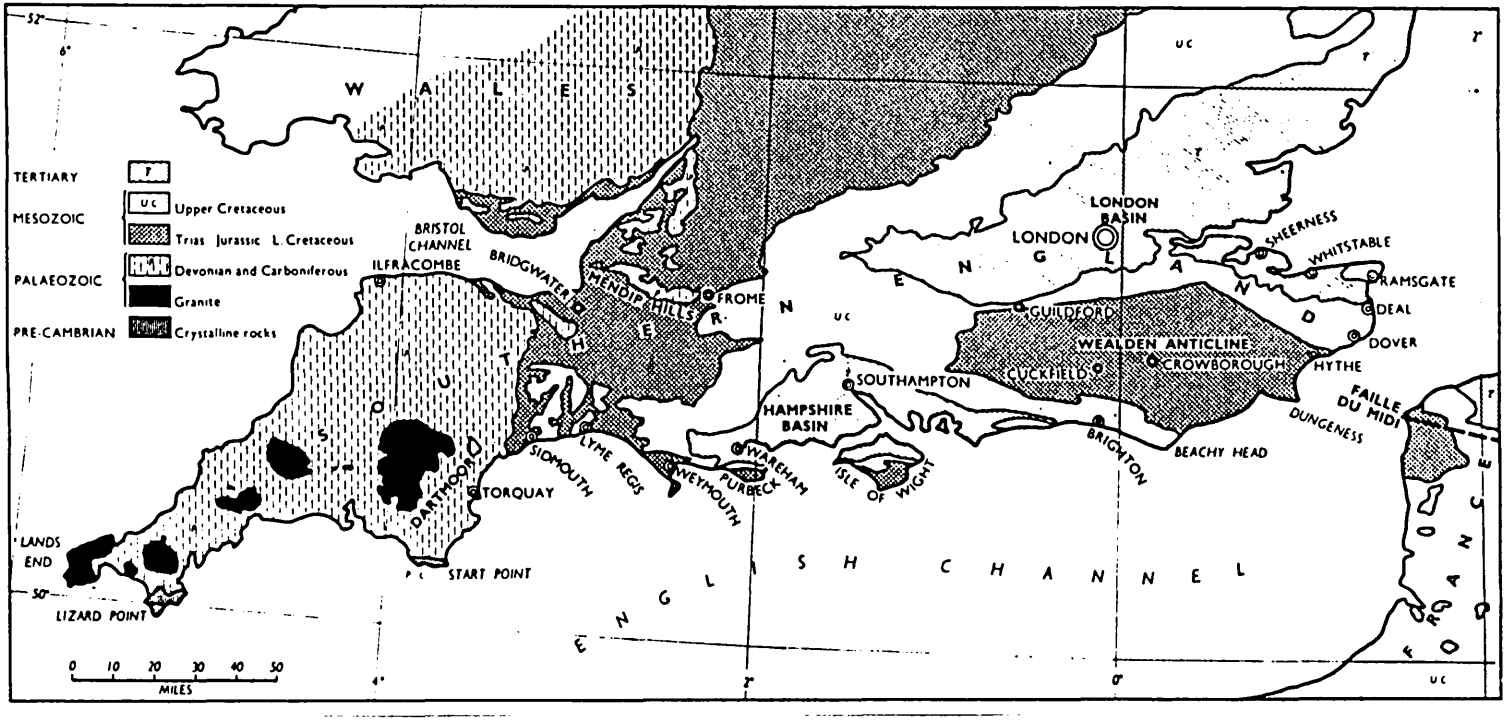


FIG. 2.1 SKETCH MAP OF SURFACE GEOLOGY OF SOUTHERN ENGLAND (AFTER TERRIS AND BULLERWELL, 1965)

Meneage Crush Zone (Bennison and Wright, 1969). This is an area of brecciated rocks, chiefly shales of Late Devonian age. The dating of these lenses have been based on their contained fossils.

A major phase of the Early Paleozoic Caledonian Orogeny occurred during the Late Silurian to Early Devonian times. Though southern England was not affected by this episode, it resulted in the uplift of land to the north of the Armorican geosyncline and imposed a NE-SW structural trend to the mountain chains formed. The landmass formed by this orogeny has been named the Old Red Sandstone (ORS) Continent (Bennison and Wright, 1969).

2.2 DEVONIAN PERIOD

During the Devonian, most of southern England lay to the south of the ORS Continent and still formed part of the Armorican geosyncline. Deposition of marine facies from the sea continued in south England as opposed to the continental facies in the uplifted continent. Paralic facies were deposited in the nearshore environments. Sporadic outbursts of vulcanicity occurred throughout much of the Devonian Period and resulted in the formation of coarse agglomerates, greywackes, tuffs and spillitic lava (Edmonds et al., 1975). Outcrops of Devonian rocks are seen today in the South-West Peninsula of England - comprised of Cornwall and Devon (Fig. 2.1).

An uprising of the land area to the south of SW Peninsula (possibly the southern boundary of the Armorican geosyncline) was recorded during the Late Devonian (Edmonds et al., 1975). The rising land area provided coarse

debris for conglomeratic sedimentation in south Cornwall.

From Devon and Somerset the Devonian rocks are now found to disappear eastwards under the Mesozoic cover. They are known from several borings in the east and south-east England (Rayner, 1981).

The Late Devonian also witnessed the start of a major marine transgression northwards into Wales and central England.

2.3 CARBONIFEROUS PERIOD

The palaeogeographic conditions were highly variable during much of this period. The Early Carboniferous saw the continuation of the northward extension of the Devonian geosyncline. This period records the history of the spread of marine conditions with the gradual incursion of the former Old Red Sandstone Continent by chiefly shallow epicontinental seas to the north whilst to the south, marine sedimentation continued in the geosyncline (Bennison and Wright, 1969). In the Bristol - Somerset area, marine shelf facies of largely limestone successions were deposited conformably over the low lying alluvial plains of the ORS Continent. In the geosynclinal area to the south, Early Carboniferous marine beds are found to follow the Devonian ones conformably (as noted in Devon and Cornwall). The whole sequence of the geosynclinal marine Carboniferous rocks of south-west England (dominantly argillaceous with cherty and arenaceous beds) is sometimes referred to as the "Culm" from the presence of occasional thin seams of impure coaly material. The Culm is divided into the Lower and the Upper parts as deposits of the Early and Late Carboniferous respectively

(Rayner, 1967). Volcanic activity was locally vigorous during the deposition of the Lower Culm, and spillitic lava and tuffs have been found within this unit.

In the Mid-Carboniferous (Late Visean to Early Namurian) there was a major uplift of hinterland and basin margin areas, and this probably initiated the advent of large new fluvial drainage system during the Namurian (Anderton et al., 1979). The deltaic facies deposited at this time is known as the Millstone Grit - a sequence of sandstones and shales. This sequence has been observed in places in the Bristol - Somerset area though the Namurian is not fully represented here as the Coal Measures of the Later Carboniferous Period are found to rest unconformably upon Early or Pre-Namurian beds (Bennison and Wright, 1969). There is no record of the Millstone Grit in the SW Peninsula. The Lower Culm conditions persisted in this area and fossil evidences suggest that part of the Upper Culm was deposited at this time.

The general palaeogeography of the Westphalian Age (Late Carboniferous) resembled that of the Namurian with the Caledonian Orogenic Structure - the Wales - Brabant Massif - still remaining a positive feature and the associated fluvial drainage flowing southwards into the open sea. Fluvial erosion of the coastal area produced vast flat areas which became the sites of spread of deltaic materials. Periodically, sedimentation exceeded the rate of subsidence and swamp forest grew and soil formed. Being close to the sea small changes in the sea level, possibly due to small-scale epeirogenic movements, resulted in minor

transgressions and regressions. The Carboniferous Coal Measures were deposited during this period (Bennison and Wright, 1969; Anderton et al., 1979). In southern England, coalfields have been worked in two main areas - Somerset - Gloucester and east Kent (Fig. 2.2). In the Somerset - Gloucester area, about 75% of the Coal Measures are concealed by the Mesozoic strata leaving only isolated outcrops, whereas they are completely hidden by younger strata in the Kent Coalfield (Bennison and Wright, 1969). In the SW Peninsula, the deposition of the Upper Culm continued under a condition possibly similar to that of the Coal Measures further north. The combined evidence of goniatites, non-marine lamellibranchs and plant remains indicates that much of the Upper Culm is of Westphalian age (Bennison and Wright, 1969).

In the Latest Carboniferous (Late Westphalian - Stephanian) times, the deltaic "Coal Measure" type condition of deposition in the SW Peninsula was succeeded by a return of deep (turbiditic) marine deposition. There was a change in the depositional condition at the sites of Coal Measures formation as a result of a gradual uplift of the area and termination of marine transgression. Sediments deposited at this time were predominantly continental red beds.

Towards the end of the Carboniferous after the deposition of the Coal Measures, there was a culmination of the Variscan or Hercynian Orogeny into an important mountain building episode (Bennison and Wright, 1969; Edmonds et al., 1975). The loci of this orogeny lay to the south of Britain and as a result, southern England was one of the areas seriously affected by the earth movements. Faulting

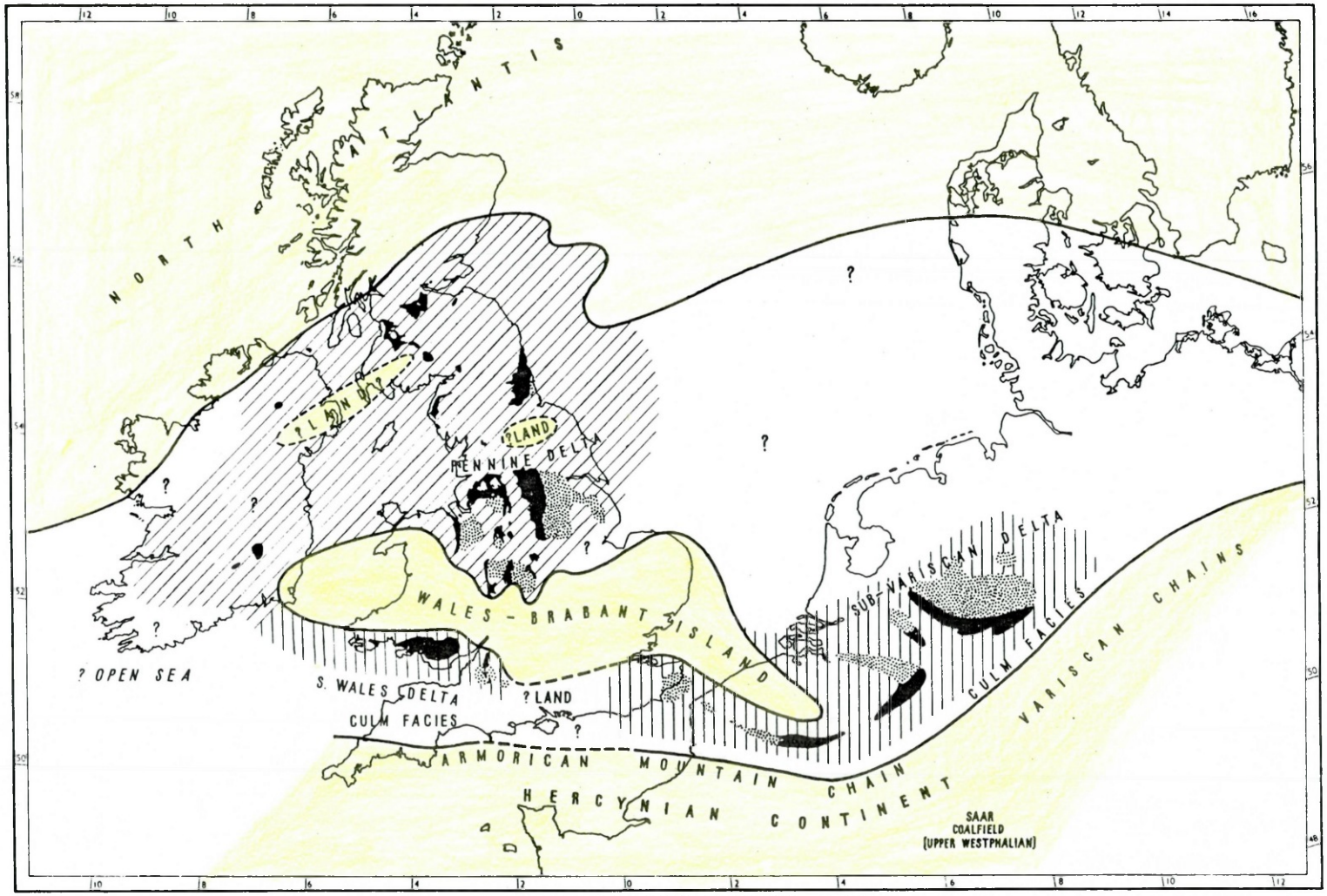


FIG. 2.2 LATE CARBONIFEROUS (EARLY WESTPHALIAN) PALAEOGEOGRAPHIC MAP SHOWING THE DISTRIBUTION OF COALFIELDS IN BRITAIN (AFTER WILLS, 1951)

and folding of the Devonian and Carboniferous rocks with relatively low dips resulted in most parts of southern England except in the SW Peninsula where thrusting and overfolding were produced accompanied by metamorphism (Bennison and Wright, 1969). Associated with this orogenic phase were widespread igneous intrusions (mainly granites) and mineralization in the south west England (see Fig. 2.1). An important Variscan feature occurs in the Bristol - Gloucester area - the Mendip Hills (Figs. 2.1 and 2.3). These comprise three periclinal folds arranged en echelon and they have been eroded to reveal Devonian age rocks in their cores.

2.4 PERMO-TRIASSIC TIMES

Following the deformation of the Devonian and Carboniferous rocks and the emplacement of granite bodies at the end of the Carboniferous, southern England (as well as other parts of Britain) experienced arid climatic conditions during the Permo-Triassic times (Edmonds et al., 1975; Rayner, 1981). The weathering and erosion by wind and torrential streams of the folded Paleozoic rocks and granitic bodies in the west resulted in the deposition of red continental facies with evaporites in broad depressions and temporary lakes towards the east. The continental rocks formed during this period have been grouped together and popularly referred to as the New Red Sandstones. In Devon area, active volcanic eruptions occurred during the Permian and today, several types of volcanic rocks which crop out as isolated remnants of the formerly extensive lava flows are grouped together

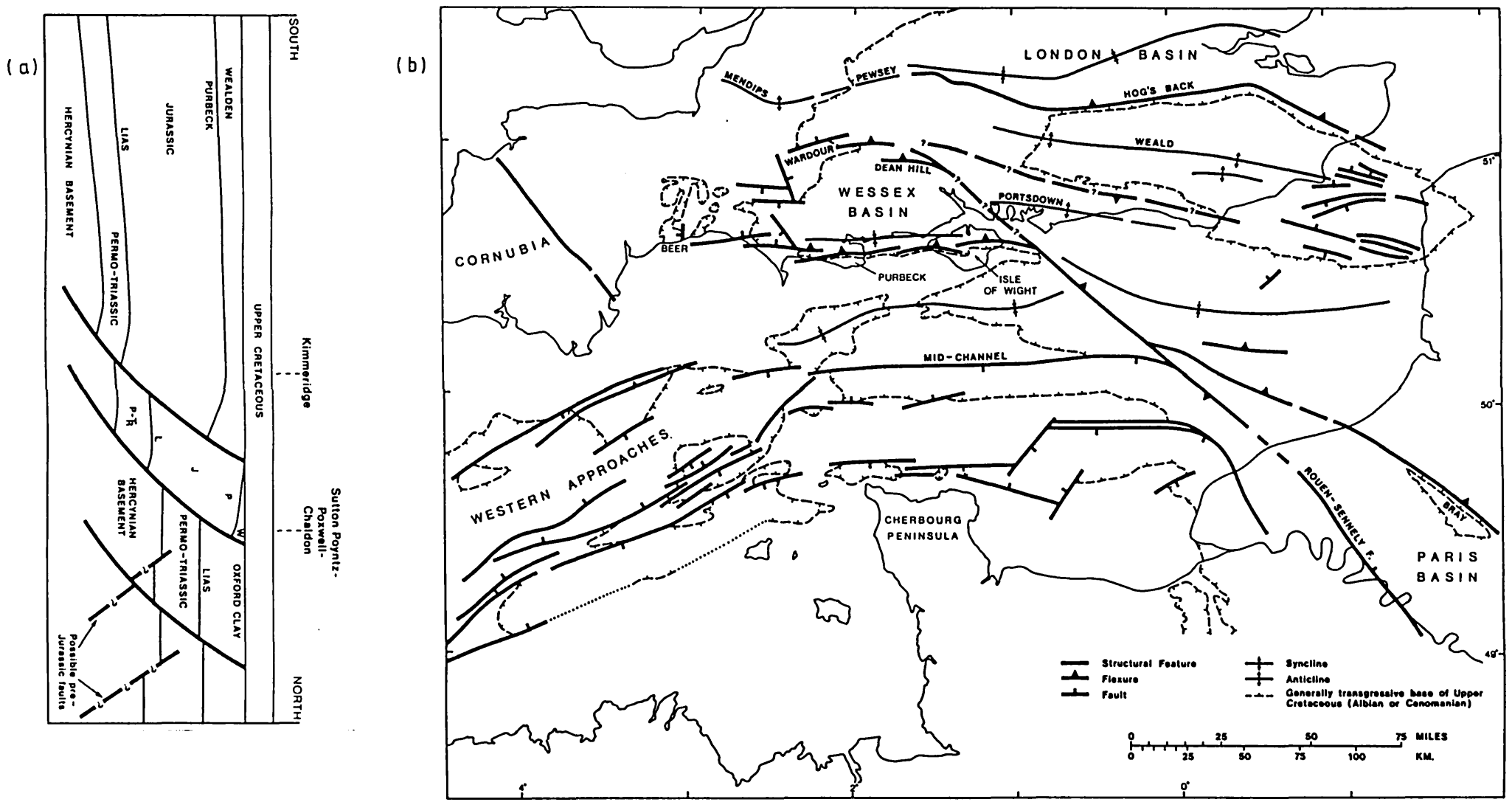


FIG. 2.3 (a) INTERPRETED PROFILE ACROSS SOUTH DORSET AT THE CLOSE OF THE CRETACEOUS
(b) MESOZOIC - TERTIARY STRUCTURAL FEATURES OF S. ENGLAND AND NEIGHBOURING AREAS (AFTER STONELEY, 1982)

under the name the Exeter Volcanic Series (Edmonds et al., 1975). The Mendip Hills and the London Platform constituted the main positive elements towards the east during this period and the New Red Sandstones have not been found on these highs. Outcrops of these red beds occur over much of east Devon and west Somerset with good sections along the coasts.

Towards the close of the Triassic, in the Rhaetic times, much of southern England came under the influence of marine transgression from the Tethys Sea (the Mesozoic Mediterranean Sea) which spread across the area as shallow epicontinental sea and resulted in the deposition of marine beds (see Fig. 2.4).

Warrington et al. (1980) have subdivided the Triassic portion of the Permo-Triassic deposition into three major groups. The basal unit is the Sherwood Sandstone Group consisting of variably cemented red to brown, fine to coarse arkosic sandstones which grade into claystones in a series of fining-upward cycles. On outcrops, they are noticed to be cross-bedded and contain intra-formational conglomerates - showing these sandstones to be mostly fluviatile in origin. However, some possibly eolian units occur with very thick sets containing long low foresets (up to 1 metre or 3 ft.), no intraformational shales or claystones, and even though finer than the fluvial sands contain very little clay matrix. The Sherwood Sandstone Group constitutes the lower major oil reservoir rocks in the Wytch Farm Oilfield (Dorset). It is about 550 ft. (168 metres) thick in the Wytch Farm (Colter and Havard, 1981). This basal unit is overlain by the Mercia Mudstone

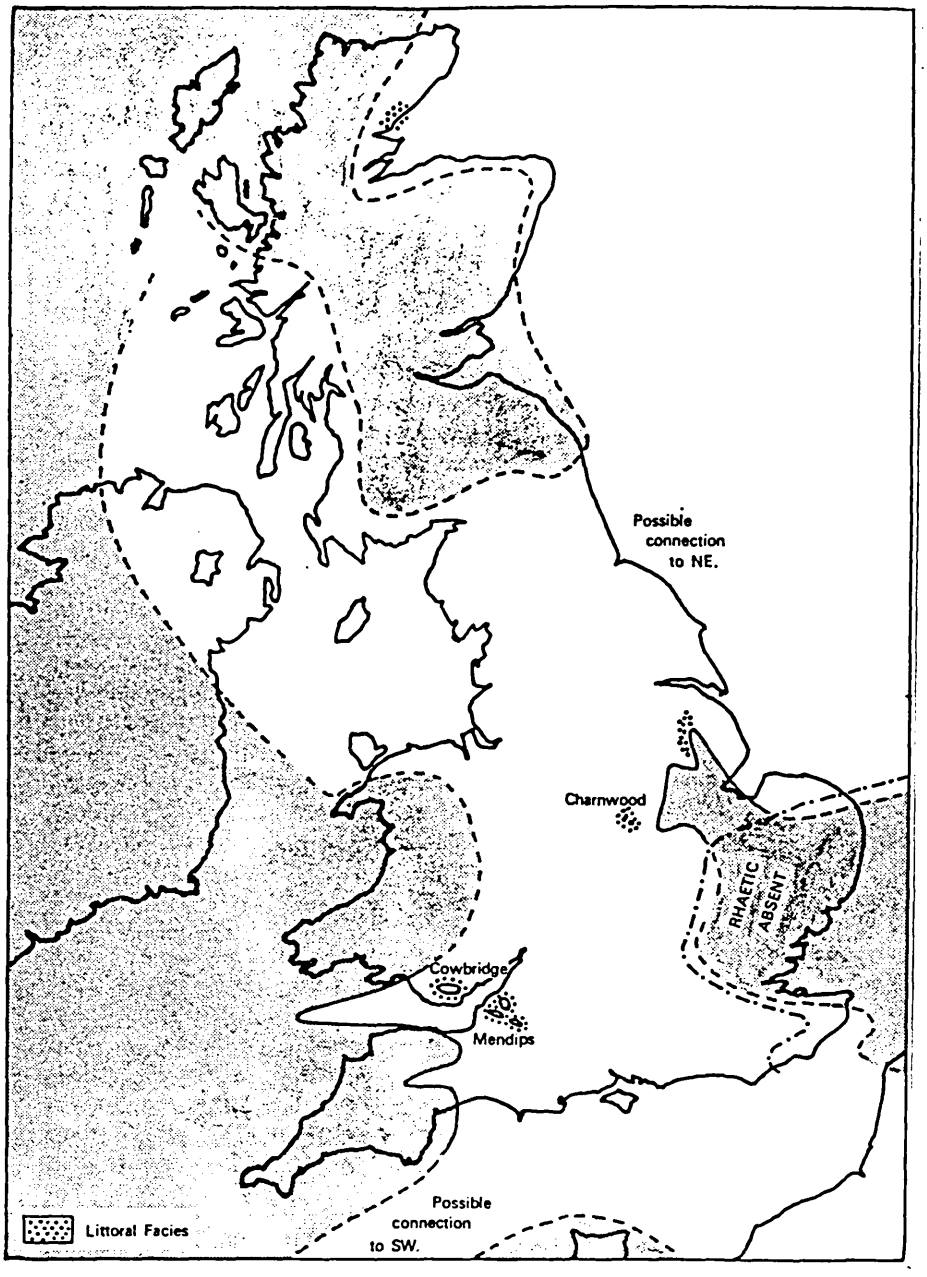


FIG.2.4- THE PROBABLE PALAEOGEOGRAPHY OF RHAETIC TIMES (After Bennison and Wright,1969).

Group (formerly called the Keuper Marls). This group is composed dominantly of red, and less commonly, green and grey mudstones and subordinate siltstones with thick halite-bearing units in the basinal areas. Thin beds of gypsum and anhydrite are widely developed at particular horizons. Deposition of this group is believed to have been mainly in subaqueous environments - probably in playas or inland sabkhas with intermittent connections to a sea. Thicknesses of 1145 -1199 ft. (349 - 366 metres) have been recorded in the Wytch Farm (Colter and Havard, 1981). The uppermost Triassic unit is the marine Penarth Group representing the various beds deposited during the Rhaetic marine transgression of the area. This group consists of three main sub-units namely the Westbury Beds at the base consisting of black shales with thin beds of limestones and sandstones; the Cotham Beds which comprise greenish grey shales and thin limestones; and the White Lias Limestone Formation at the top consisting mainly of white to pale grey micritic limestone. The Penarth Group is about 70 ft. (21 metres) thick in the Wytch Farm Field (Colter and Havard, 1981).

Today, the remains of the highly denuded Armorican Mountains in the south-west England is referred to as the Cornubian Uplands (Fig. 2.3).

The formation of the Mesozoic basins in southern England (in Central Somerset, Dorset-Hampshire and the Weald) are believed to have been initiated in the Permian times by the onset of the rifting episode associated with the early attempted opening of the North Atlantic Ocean.

The rifting was highly accelerated during the Triassic and is believed to have continued through the Jurassic to the Early Cretaceous times (Ziegler, 1975; Kent, 1977; Stoneley, 1982). Evidence from drillings in the Mesozoic Wessex Basin and geometrical constructions have shown that these vertical movements occurred along listric normal faults and were downwarping to the south (Stoneley, 1982). The theoretical profile of these faults have been found to intersect the free surface at 45^{o} (Hose and Danes, 1973).

2.5 JURASSIC PERIOD

The Late Triassic marine condition continued into the Jurassic Period. The story of the Jurassic is largely one of subsidence into fully marine conditions. The subsidence episode was rather uneven over southern England. This resulted in the development of basins between adjoining swells or axes some of which, like the Mendips and the Landon-Brabant Massif, though subsiding differentially acted as positive areas throughout most of the Mesozoic times (Bennison and Wright, 1969; Anderton et al., 1979). There was, as a result, a general variation in the thicknesses of the various deposited sedimentary units and some facies changes across southern England. The gradual opening of the North Atlantic Ocean affected the old fold axes and fault planes from time to time beneath the basins of deposition. These constituted minor disturbances which also affected the Jurassic sedimentation.

The Early Jurassic marked a deepening rather than an extension of the shallow Rhaetic Sea, and the dominantly fine-grained marine Lower Liassic Formation (consisting of shales, mudstones and calcilutites) attests to this condition (Fig. 2.5). There was a distinct shallowing of the sea in the Late Lias Epoch with the resultant deposition of coarser detrital materials (sands and silts) commencing in the Somerset-Gloucester area and spreading southwards later. The Bridport Sands, which constitute a major reservoir rock in the Wytch Farm Oilfield, were deposited at this time. The Sands consist of generally very bio-turbated, moderately well sorted coarse silt to very fine-grained sandstone. A striking feature of this unit is the rapid alternation of hard and friable bands due to variation in calcite cementation (Colter and Havard, 1981; Melville and Freshney, 1982). Along the Dorset Coast, a thickness of 140 ft. (about 43 metres) has been reported (Chatwin, 1960) while in the Wytch Farm, the Sands vary in thickness from 150 to 240 ft. (46 to 73 metres) (Colter and Havard, 1981).

In the Middle Jurassic times, there was a general shallowing of the Liassic Sea with the production of environments in which marine shoal deposits such as oolitic and coral-reef limestones, shallow marine sands and iron-stones were laid down. These shoal deposits of the Mid-Jurassic have been subdivided into two broad groups - the Inferior Oolite (Aalenian and Bajocian Stages) and the Great Oolite (Bathonian Stage). In the Late Bathonian, after the deposition of the last varied units of the Great



FIG.2.5- LIASSIC PALAEOGEOGRAPHY, WITH ISOPACHYTES IN METRES(After Bennison and Wright,1969)

Oolite series, there was a widespread change of marine conditions which resulted in a general extension and transgression of the sea. The deposits of this sea are now referred to as the Cornbrash, and two divisions of this formation are recognisable - the Lower Cornbrash consisting chiefly of marly rubble and compact limestones; and the Upper Cornbrash made up of sandy marl, concretionary limestone and flaggy beds of hard pinkish limestone. On outcrops in Dorset, this formation does not exceed 30 ft. (9 metres) in thickness (Chatwin, 1960). In the Kimmeridge Bay, oil is at present commercially produced from the fractured Cornbrash Formation.

The beginning of the Late Jurassic (Callovian - Early Oxfordian) was marked by the deepening of the Bathonian shallow sea, and sedimentation resulted in the formation of deep water facies now named the Oxford Clay Formation. This dominantly argillaceous formation is believed to have been deposited under conditions generally similar to those of the Lower Lias (Bennison and Wright, 1969). The passage from the uppermost Cornbrash to the deposits of the Oxford Clay was marked by the deposition of transition beds - the Kellaways Beds - consisting of clays at the base and hardened sands at the top.

By Mid-Oxfordian the sea again became shallow and warm with the resultant formation in places of calcareous grits, oolitic and coralline limestones. This shallow water facies, the deposition of which lasted till the end of the Oxfordian Age, is referred to as the Corallian Beds - so named from the abundance of scleractinian corals (Bennison and Wright, 1969). A full sequence of the beds is well exposed along

the Dorset Coast between Osmington and Ringstead and also in cliffs south of Weymouth (Bennison and Wright, 1969).

At the end of the Corallian times, changes in geographical conditions resulted in a gradual subsidence of the area and a long continued deposition of muddy sediments. The Kimmeridgian thus marked a deepening of the sea, and the Kimmeridge Clay Formation was deposited during this period. Variation in lithology occur in this formation. In addition to thick clays and shales, there are bands of cementstones and siltstones, while further north a sandy facies developed towards the top of the succession in Wiltshire, Oxfordshire and Buckinghamshire (Bennison and Wright, 1969). A full development of this formation is found in the Kimmeridge Bay area (Dorset). Another significant coastal expsoure occurs in the Ringstead Bay area (see Fig. 2.6).

Shallowing and a reduction in the extent of the sea occurred at the end of the Kimmeridgian due to a general uplift of the area. Shallow water facies - mainly sandstones and limestones - were laid down during the Early Portlandian. This series of facies has been named the Portland Beds - consisting of the clastic Portland Sands overlain by the calcareous Portland Stone. Towards the end of this Age, once again, the relative distribution of land and sea underwent considerable modification (Bennison and Wright, 1969). The shallow sea under which the Portland Beds were deposited retreated and its place was taken by an oscillating area - sometimes a land surface and sometimes covered by swamps and fresh-water lakes or brackish waters

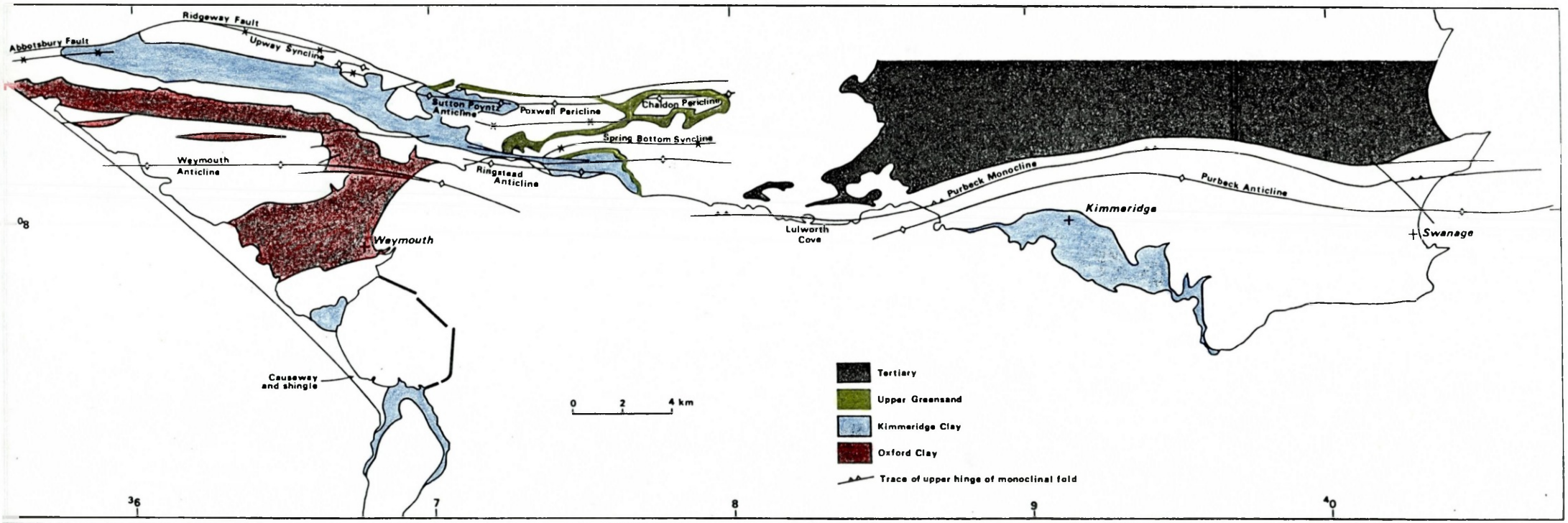


FIG. 2.6 MAJOR STRUCTURAL ELEMENTS OF THE WEYMOUTH - SWANAGE AREA (FROM MELVILLE AND FRESHNEY, 1982)

or occupied by mud flats. From time to time the sea invaded this unstable area. As a result of these changes, a varied series of deposits accumulated, and since they are particularly well developed in the Isle of Purbeck, they are known as the Purbeck Beds.

2.6 CRETACEOUS PERIOD

Since the Late Triassic times southern England, excepting most of the SW Peninsula, had remained a persisting site of mostly marine sedimentation till the end of the Jurassic. At the beginning of the Cretaceous, most of the British Isles was land as a result of a marked uplift that affected the area. The only exception was southern England where, at the site of the persisting marine sedimentation, a great freshwater delta with lagoons was built up by a river or rivers flowing mainly from the west (Wills, 1951; Chatwin, 1960) (Fig. 2.7). The non-marine deltaic facies deposited at this time have been named the Wealden Beds. They constitute a cyclic sedimentary sequence of alternating clays and sands. Total thickness of up to 2950 ft. (899 metres) has been recorded for the Wealden Beds in the south-east England (Gallois, 1965). The absence of these beds beneath the Tertiary London Basin has been interpreted to imply that the London Platform was still a positive area and possibly formed one of the source areas for the supply of detritus for the delta (Rayner, 1981).

A major phase of pre-Albian earth movement occurred following the formation of the Wealden Beds. This resulted in the faulting and folding of the Wealden Beds and the Jurassic rocks. The main structural features emplaced

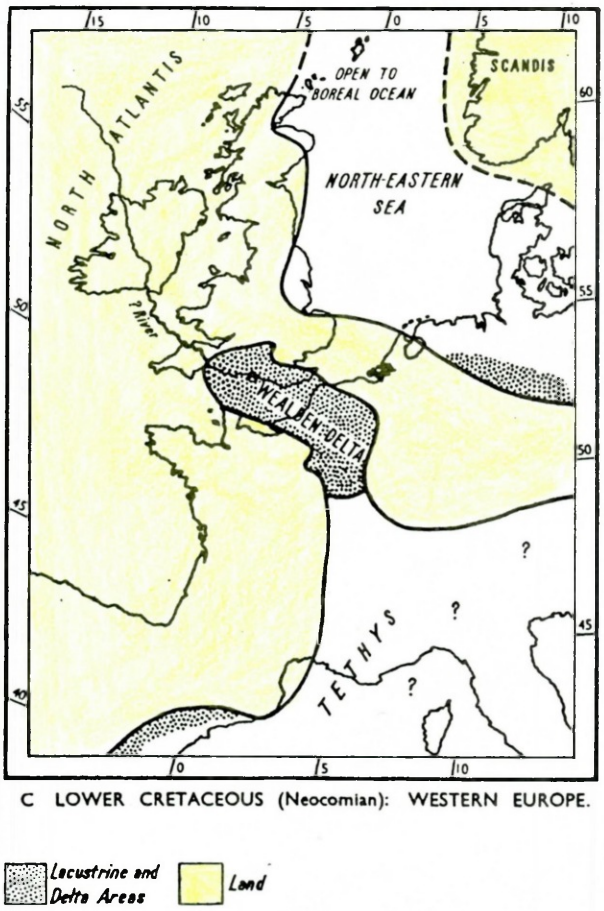


FIG.2.7- EARLY CRETACEOUS PALAEOGEOGRAPHY(After Wills ,1951).

by this disturbance include the Weymouth Anticline and the Abbotsbury fault in Dorset (House, 1961; Perkin, 1977) (see Fig. 2.6). The deformation led to the erosion of the rocks which, in some places, went as far down into the Jurassic as the Oxford Clay and the Great Oolite (Perkins, 1977).

Following the disturbance, marine transgression affected most of southern England from Early Aptian to Early Albian (- the Aptian Transgression) (Perkin, 1977). This led to the deposition of the Lower Greensand Formation in the area. The formation is mainly composed of glauconitic and ferruginous sands with sandy limestone, calcareous sandstones, and silty mudstone beds. A maximum thickness of about 800 feet (244 metres) has been recorded for this formation in the Isle of Wight (Bennison and Wright, 1969). The London Platform was still positive at this time. The Lower Greensand was not as extensive westwards as the Wealden Beds. It is observed to thin out very rapidly towards west Dorset (Rayner, 1981).

After the deposition of the Lower Greensand, a second major Cretaceous earth movement was experienced which led to the tilting and submergence of the region (Perkins, 1977). This was again followed by another marine transgression (- the Albian Transgression) which lasted till Late Albian. The Gault Clay and the Upper Greensand of Southern England, which extend further west and north than the Lower Greensand, were deposited during this transgression. They are however, found to be concordant with the Lower Greensand, the Wealden and the Upper Jurassic Beds in the Weald - east Purbeck

area, whereas in the west (Swanage to Devon) they overlap and overstep the more steeply dipping earlier Cretaceous, Jurassic and even Triassic Beds onto the Paleozoic rocks (Gallois, 1965; Edmonds et al., 1975; Rayner, 1981). The Gault Clay is mainly an argillaceous deposit typically made up of dark grey, stiff and tenaceous clay. The Upper Greensand covers a considerable lithologic range from glauconitic sandstones to marls and chert. Thicknesses of up to 300 feet (91 metres) and 200 feet (61 metres) have been reported for the Gault Clay and the Upper Greensand respectively in the Wealden District (Gallois, 1965). For the first time during the Mesozoic Era, this marine sedimentation spread across the London Platform.

Marine conditions spread across most parts of the British Isles in the Later Cretaceous times, and in south England this period was dominated by the deposition of Chalk. This is a nearly pure calcium carbonate formation made up mainly of a mixture of coccoliths and varying proportions of shell debris and foraminifera. A thickness of about 1720 feet (524 metres) has been recorded for this formation in the Isle of Wight (Melville and Freshney, 1982).

The differential vertical movements initiated in the Permian along listric normal faults are believed to have continued through the Jurassic till the Mid-Cretaceous (Arkell, 1947; House, 1961; Ziegler, 1975; Kent, 1977). During this period subsidence was accompanied by continuing gentle faulting along persistent lines of weakness which formed elements of crustal fracture system (Melville and Freshney, 1982). One of these lines, which has long been

known, is the south Dorset - Isle of Wight Belt (Arkell, 1947; House 1961) or the Purbeck-Isle of Wight Disturbance (Colter and Havard, 1981) (see Fig. 1.4 and Fig. 2.3). This regime of north-south stretching associated with the vertical movements was terminated by the Aptian after which a period of relative stability prevailed until the latest Cretaceous times. This was then followed by a tendency to reverse the earlier sense of vertical displacements which may have become effective by the beginning of the Cenozoic Era (Arkell, 1947; Stoneley, 1982).

2.7 TERTIARY PERIOD

After the deposition of the Chalk in the Senonian, there was a withdrawal of the Chalk Sea and southern England experienced a long period of non-deposition, erosion and slight earth movements which produced gentle tilting and folding of the rocks (Bennison and Wright, 1969). The formation of a large sedimentary basin - the Anglo-Parisian Cuvette in the Early Tertiary marked the return of marine conditions in southern England (Bennison and Wright, 1969). This Early Tertiary Sea covered mainly the south-eastern part of England extending as far west as Dorset. Beds of marine facies, marginally interdigitating with continental facies, were thus laid down unconformably over the eroded and sligthly tilted Chalk surface. These strata are now found preserved in the Tertiary Basins of Hampshire and London (Fig. 2.1). A major marine argillaceous formation - the London Clay - was deposited in these areas in the Early Eocene during a widespread transgression from the North Sea. Measured thicknesses of upto 328 feet (100 metres) have

been reported for this formation in the Hampshire Basin (Melville and Freshney, 1982). The crustal instability which preceded the Miocene orogenic episode gave rise to a cyclic series of oscillation between marine and non-marine conditions. Sedimentation continued till the Early Oligocene times and this marked the end of any major marine influence onshore southern England.

During the Miocene Epoch, the crustal instability since the Late Cretaceous believed to be associated with the Alpine Orogeny, culminated in a major mountain building phase. The focus of this orogenic episode lay far to the south of Britain and as a result, only the southern part of England was seriously affected. It produced the folding, faulting and minor thrusting of the rocks with an imposed E-W trend (Gallois, 1965; Rayner, 1981; Melville and Freshney, 1982). The important structures emplaced in southern England include the Wealden Anticline with its two complementary Tertiary-bearing synclines of the London and Hampshire Basins, and the Purbeck - Isle of Wight Monocline (see Fig. 2.3). This Dorset - Isle of Wight monoclinal flexure has long been noticed to correspond in position with one of the major lines of weakness initiated by the Permo-Triassic rifting (Arkell, 1947). According to Stoneley (1982), the Purbeck - Isle of Wight belt is not a continuous, more or less straight line commonly shown on maps (e.g. see Fig. 1.4) but rather it consists of a number of en echelon segments not all offset in the same sense, and each in plan scalloped to the south (see Fig. 2.3). The Miocene orogenic phase is believed to have resulted in a crustal shortening expressed along pre-existing

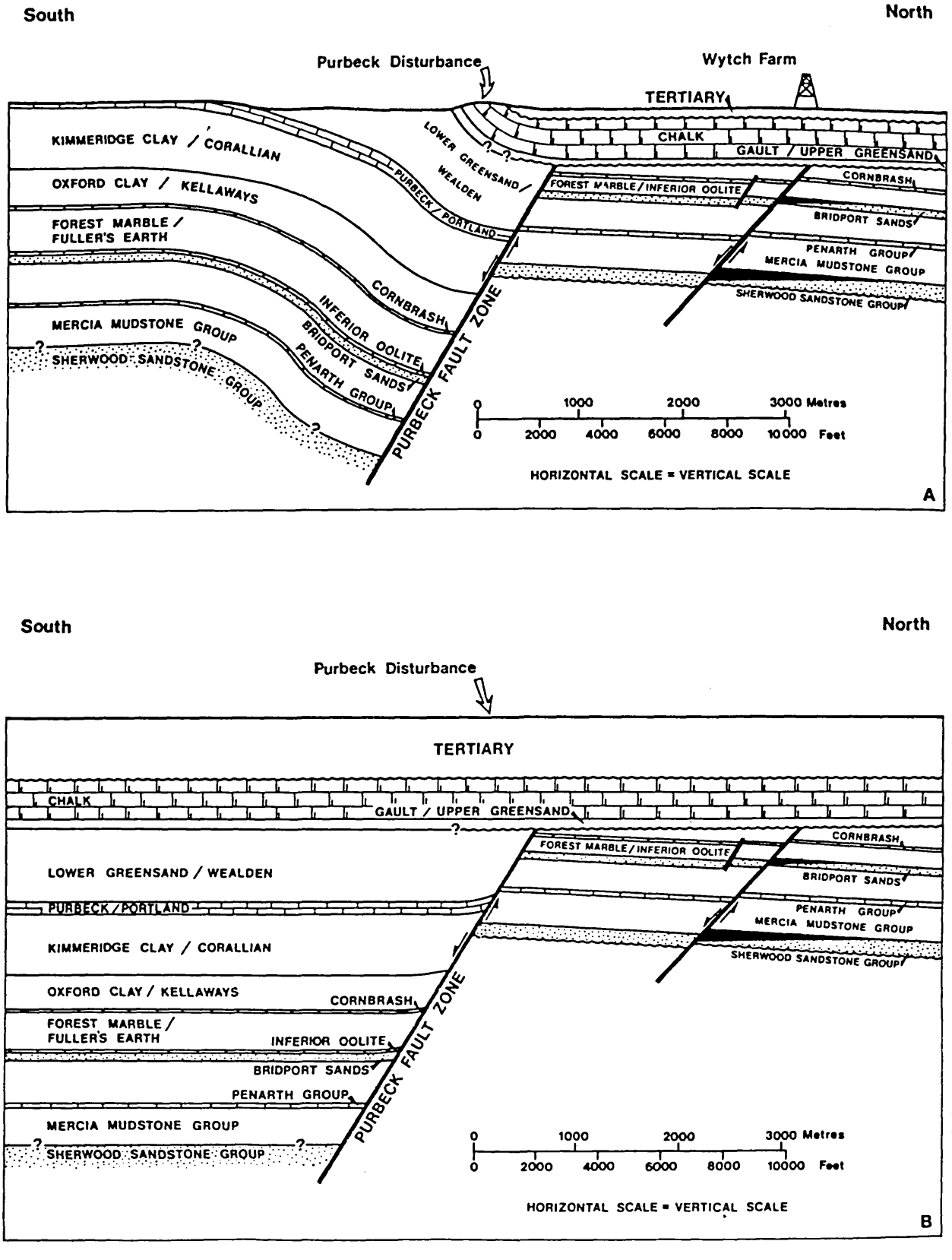


FIG.2.8- INTERPRETED STRUCTURAL SECTIONS THROUGH WYTCH FARM FIELD AND PURBECK DISTURBANCE.(A) PRESENT DAY (B) TERTIARY,BEFORE ALPINE EARTH MOVEMENTS (From Colter and Havard, 1981).

lines of weakness as monoclines. These flexures are thought to have been produced mainly by northwards compressive movements along the former listric normal faults (Stoneley, 1982). This has been inferred from the northerly dip of the monoclinal structures well expressed in the Mesozoic and Tertiary strata along the Dorset coast. These Alpine compressive movements thus resulted in a reversal of the sense of the initial regime of vertical displacement along the faults.

This idea of a Miocene tectonic inversion has been illustrated by Colter and Havard (1981) in the Wessex Basin based on evidences from drillings and outcrops in the vicinity of the Wytch Farm Oilfield (Fig. 1.4 and Fig. 2.8). Previously deeply buried Mesozoic strata on the southern side of the Purbeck - Isle of Wight Disturbance were brought to shallow depths by this tectonic episode. In the Kimmeridge Bay, some of these uplifted strata are well exposed at the surface (see Fig. 2.6 and Fig. 3.7).

A major tectonic inversion was also produced in the Weald by the Miocene Alpine orogenic phase. This area constituted an important basin of deposition throughout most of the Mesozoic and Early Cenozoic Eras. But in the Miocene, the basin was deformed into a fold - the Wealden Anticline. This anticline is essentially a simple structure with low regional dips and the axial region is indicated by the presence of three faulted inliers of the Upper Jurassic Purbeck Beds in the Lower Cretaceous Wealden Beds (Fig. 2.9). These inliers indicate zones in the Weald where the Miocene inversion became very drastic and therefore form the structurally highest parts of the

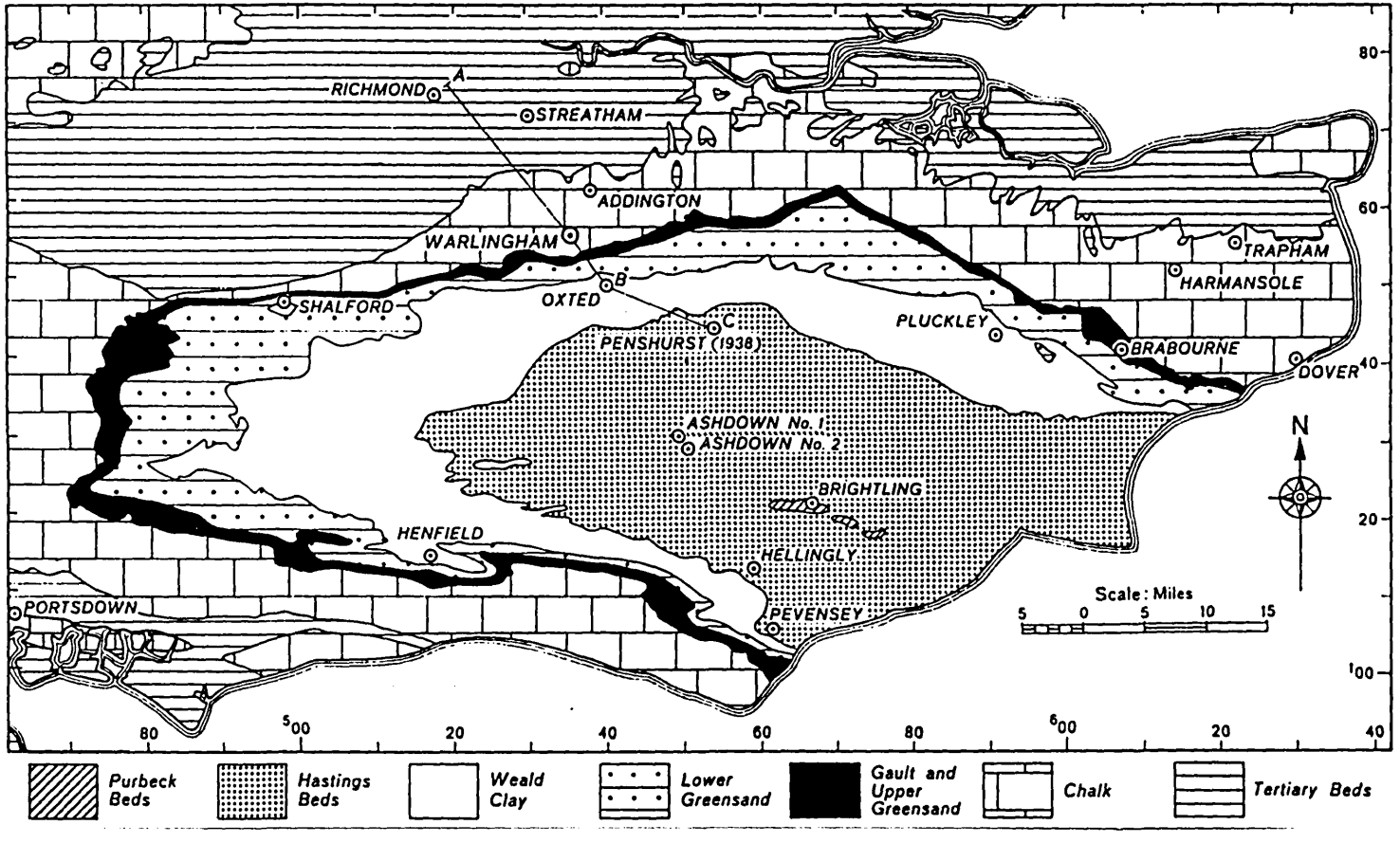


FIG. 2.9 GEOLOGICAL SKETCH MAP OF THE WEALD SHOWING THE PURBECK INLIERS AND POSITIONS OF IMPORTANT BOREHOLES IN THE AREA (AFTER WORSSAM AND IVIMEY-COOK, 1971)

Wealden Anticline (Terris and Bullerwell, 1965). The reversal sense of movement produced by the Miocene Alpine orogenic phase in this area has been confirmed by the presence of a reversed fault in the Brightling Well drilled by the BP (Fig. 2.10). This is evidenced by the repetition of part of the Upper, Middle and most of the Lower Lias in this borehole (Terris and Bullerwell, 1965).

N/B:

The reader is also referred to Ziegler (1982)* for a general overview of the tectonic and stratigraphic framework of Western and Central Europe together with a summary of its evolution since the Late Silurian times.

* See 'Additional References' (page 450).

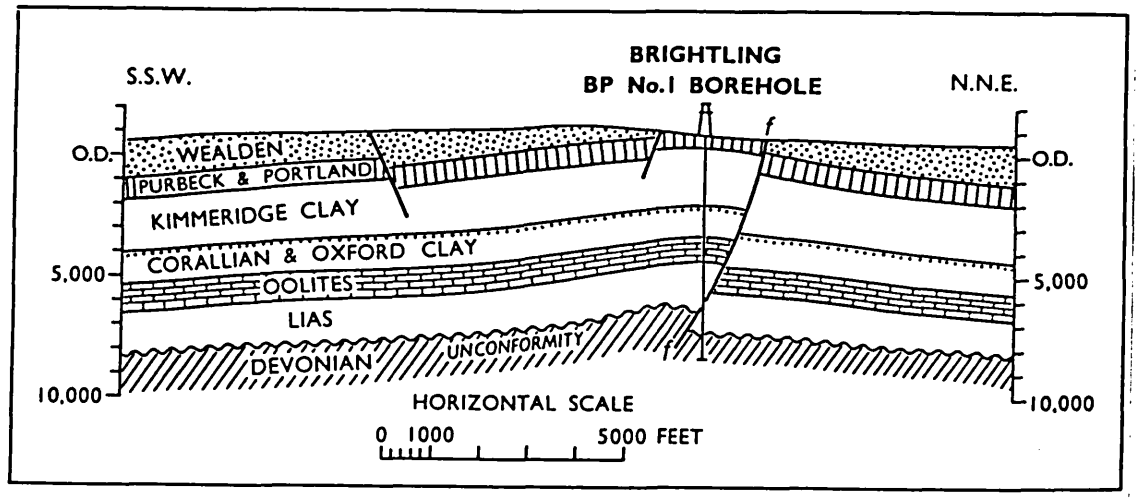


FIG.2.10- STRUCTURAL CROSS-SECTION THROUGH THE BRIGHTLING BOREHOLE, SUSSEX (From Terris and Bullerwell, 1965).

CHAPTER III

JURASSIC STRATIGRAPHY AND THE DESCRIPTION OF THE LOWER LIAS, THE OXFORD CLAY AND THE KIMMERIDGE CLAY FORMATIONS

JURASSIC STRATIGRAPHY AND THE DESCRIPTION OF THE LOWER LIAS, THE OXFORD CLAY AND THE KIMMERIDGE CLAY FORMATIONS

3.1 A SUMMARY OF THE JURASSIC STRATIGRAPHIC COLUMN

The Jurassic System is subdivided into the Lower (Lias), Middle and Upper units. The boundaries of these units have been the subject of continuing controversy. The Stage and Zonal subdivisions adopted in this thesis are based on those reported by Hallam (1975) and Rayner (1981). Fig. 3.1 is a summary of the Jurassic Stratigraphic Column in southern England. The sedimentary facies of the various lithological divisions are deduced from their litholgic characters, sedimentary structures and their contained fauna (Melville and Freshney, 1982; Selley, pers. comm.).

The Column shows the Jurassic to contain three major mudrock-formations - the Lower Lias, the Oxford Clay and the Kimmeridge Clay - deduced to have been deposited in marine environments below the wave base. These three formations contain organic-rich black shale sequences (Bitterli, 1963; Morris, 1980). The mudrock units are succeeded by shallow water (marine shoal /paralic) sands. The sandy units include the Downcliff Sands, the Thorncombe Sands and the Bridport Sands of the Lias, the calcareous grits of the Corallian Beds, and the Portland Sands. The sandy formations are generally overlain by shallow marine carbonates including skeletal and oolitic packstones and grainstones. These include the Inferior and Great Oolite series and the Cornbrash of the Middle Jurassic, the Osmington Oolite of the Corallian Beds, and the Portland Stone of the Upper

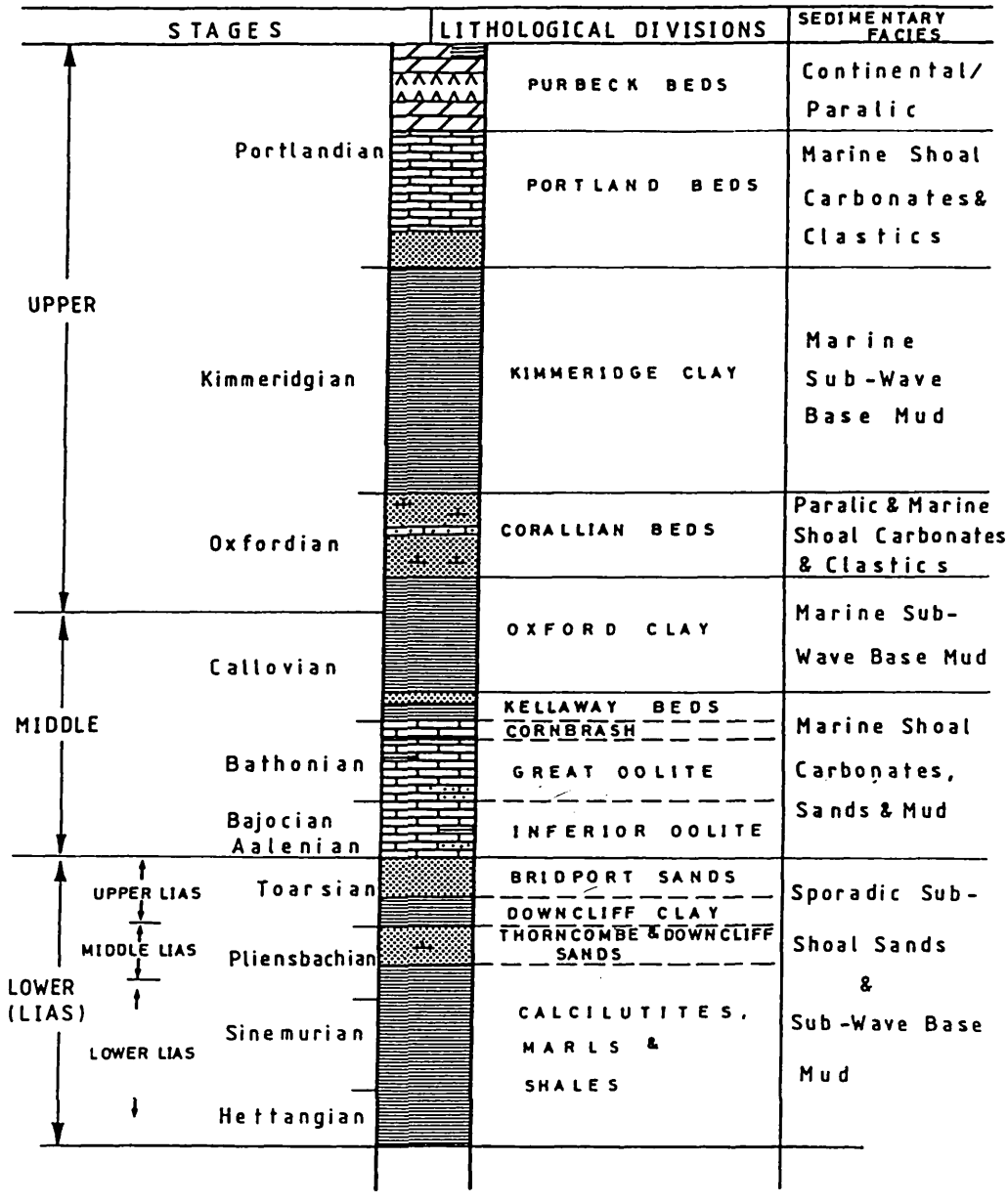


FIG. 3·1 - SUMMARY OF JURASSIC STRATIGRAPHIC COLUMN IN SOUTHERN ENGLAND.

Jurassic. Both the sands and the limestones, though generally of rather low porosity and permeability, act as petroleum reservoir rocks in southern England.

The Jurassic Period ended with the deposition of the Purbeck Beds which contain paralic and non-marine sub-units - attesting to the highly unstable palaeogeographic conditions at that time.

3.2 THE JURASSIC STRATIGRAPHIC MODEL

A close study of the Jurassic Stratigraphic Column (Fig. 3.1) reveals that the sediments of the Jurassic consist essentially of three main facies - the marine sub-wave base mud, the shallow water sands and the marine shoal carbonates. These facies tend to be arranged in transgressive - regressive cycles. Each cycle commences with the widespread transgressive and deep water facies - the basinal mud - which can be rich in organic matter depending on the primary organic productivity and the depositional conditions (Demaison and Moore, 1980). Where the bottom condition was reducing, with a consequent rarity of benthic fauna, the basinal muds formed laminated bituminous shale sequences (Morris, 1980). This basal facies is overlain by the shallow water sands, and the top of each cycle is occupied by the shallow marine carbonates. Fig. 3.2 is a diagrammatical illustration of a typical Jurassic sedimentary cycle. According to Melville and Freshney (1982), the basal mud facies often forms the thickest member in each cycle. As shown in Fig. 3.1, the Jurassic section in southern England is made up of three main repetitive sedimentary cycles.

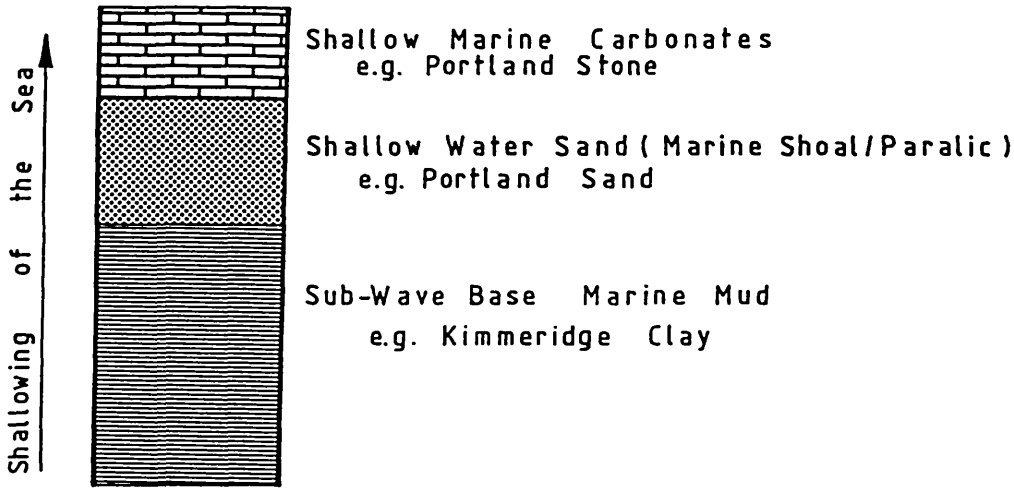


FIG. 3·2 - A TYPICAL JURASSIC SEDIMENTARY CYCLE

3.3 THE LOWER LIAS FORMATION

3.3.1 Introduction

This constitutes the lowest major mudrock unit in the Jurassic stratigraphic column (see Fig. 3.1). The Lower Lias, which is classically exposed to either side of Lyme Regis in Dorset, is seen to succeed the Penarth Group (Rhaetic) near Pinhay Bay (Devon). Palmer (1972b) suggested the Lower Lias sections between Pinhay Bay in Devon and Seatown in Dorset to be the candidate best qualified as Type Section for the formation. The thickness of the Lower Lias strata exposed in the cliffs and foreshore in the proposed type sectional area is about 600 feet (183 metres) (Palmer, 1972b).

The Lower Liassic Stages, Ammonite Zones and Lithologic Divisions in Dorset are given in Table 3.1.

3.3.2 The Blue Lias

This forms the basal lithologic division of the Lower Lias in Dorset. At Pinhay Bay, to the west of Lyme Regis, it is found to rest on the eroded top of the 'White Lias' - which is of Rhaetic age. It includes the Planorbis, Liasicus and Angulata Zones of the Hettangian Stage as well as the Bucklandi and the lower part of Semicostatum Zone of the Lower Sinemurian Stage. This unit has been described by Hallam (1960) as an offshore facies, and it is characterised by a pattern of regular small-scale alternations of four principal rock types: the normal limestones (calcilutites), marls, finely laminated limestones and bituminous shales. This rythmically bedded Blue Lias (about 105 ft in Dorset)

TABLE 3.1: THE LOWER LIASSIC STRATIGRAPHIC DIVISIONS

STAGES	AMMONITE ZONES	LITHOLOGIC DIVISIONS IN DORSET*
LOWER PLIENSBACHIAN	*Prodactylioceras davoei*	Green Ammonite Beds (105 ft.)
	Tragophylloceras ibex	Belemnite Marls (75 ft.)
	Uptonia jamesoni	
SINEMURIAN	*Echioceras raricostatum*	Black Ven Marls (150 ft.)
	Oxynoticeras oxynotum	
	Asteroceras obtusum	
	Caenisites turneri	Shales-with-Beef (70 ft.)
	Arnioceras semicostatum	Lyme Regis Beds or Blue Lias (105 ft.)
	Arietites bucklandi	
HETTANGIAN	*Schlotheimia angulata*	
	Alsatites liasicus	
	Psiloceras planorbis	

* The thicknesses indicated are according to Bennison & Wright (1969)

has for a long time attracted the attention of many geologists. Pyrite, occurring as microscopic cubes or framboidal aggregates, is known to be quite common in the rocks of the Blue Lias. It is considered to have formed early in the diagenesis under anaeroboic condition within the sediments and not necessarily indicative of anoxic bottom waters (Hallam, 1960; 1975).

The origin of the small-scale alternations of limestones and shales in the Blue Lias has been the subject of controversy amongst geologists for many years. Formed originally as muds in the Early Jurassic Seas, the shales suggest deeper water phases while the limestones should indicate periods of shallower and clearer water. The point in dispute has been whether the alternations are original sedimentary features or products of diagenesis. A primary origin would imply a regularly varying environmental condition (for example a pulsating sea floor) so that sediments were deposited with the distinct layering we now see in them. A secondary origin would, on the contrary, imply uniform depositional conditions with the original sediment being a uniform lime-rich mud which was rythmically unmixed on compaction during the solidification of the deposit. Field evidences considered to favour either mode of origin are summarized in Table 3.2 based on Hallam (1960; 1964) and Perkins (1977). However, geologists have now resolved the apparent conflict of evidence by accepting that both primary and secondary factors have contributed to the rythmic succession (Perkins, 1977). Epeirogenic activity and/or variation in humidity (rainfall) on land have been suggested to

TABLE 3.2 - EVIDENCES FOR THE ORIGIN OF THE LIMESTONE - SHALE RYTHMS IN THE BLUE LIAS

Favouring Primary Origin	Favouring Secondary Origin
1. Burrowing activities producing trace fossils like Chondrites and Diplocrateron affecting both the lighter, more calcareous and the darker, more argillaceous layers.	1. Presence of bands of ellipsoidal calcareous nodules symmetrical about planes of bedding which may pass laterally into regular limestone bands.
2. Occurrence of smaller-sized benthic fauna in the shales in contrast to the large and well preserved fossils in the calcareous bands - suggesting oxygen deficient depositional environment for the shales.	2. Some continuous limestones have highly irregular, hummocky surface which could not be supposed to represent the original configuration of the sea bottom.
3. Areal extent and extra-ordinary regularity of certain limestone bands.	3. Better preservation of fauna in limestones but crushed and decalcified in the shales.
4. The microlaminae in the laminated limestones and bituminous shales are interpreted as varves due to annual fall of plankton into anaerobic bottom waters in contrast to the normal limestones and marls deposited under oxic bottom conditions.	4. The thicker the Blue Lias the more limestone bands there are. 5. Thickening of limestone bands around large fossils.

account for primary sedimentary variations. More calcium carbonate was precipitated in shallower, higher temperature and lower pressure water either inorganically or by the action of bacteria. The shale units are considered to represent deeper water facies with anaerobic bottom water and an influx of more clayey sediments. These primary variations were subsequently accentuated by secondary diagenetic processes (Hallam, 1964; Perkins, 1977).

According to Hallam (1960), the bituminous shales and the laminated marl/limestone bands are organic rich with total organic carbon (TOC) contents of up to 8%, whereas the normal limestones and marls are poorer in organic matter often with TOC less than 2%. From his transmitted light study of the isolated organic material, he noted that the great bulk of the matter was structureless with rare occurrence of plant spores and hystricosphaeroids (phytoplankton).

3.3.3 The Shales-with-Beef

Upward in the Lower Lias section in Dorset, the rythmical character of the Blue Lias merges rather gradually into a more homogeneous bituminous lithological unit called the 'Shales-with-Beef'. This corresponds to the Upper Semicostatum and the Turneri Ammonite Zones. The unit is about 70 feet thick at Black Ven Cliff (Dorset) and consists of dark shales, paper-shales and marls with occasional indurated bands of limestone and nodule-beds. The word 'beef' is a local term for fibrous beds of calcite which show cone-in-cone structure and may have been secondarily deposited (Bennison and Wright, 1969; Stoneley, 1983).

The fine lamination exhibited by these shales and marls is an indication of deposition in an oxygen deficient bottom water. This unfavourable environmental condition must have restricted extensive colonization of the sea floor by benthic fauna, and hence the good preservation of delicate laminae in the sediments.

3.3.4 The Black Ven Marls

The Shales-with-Beef are overlain by a thick series (about 150 feet) of dark clays and marls which constitute the Black Ven Marls (Obtusum - Raricostatum Ammonite Zones). This division is characterized by several layers of nodules and lenticular limestone bands often enclosing ammonites. The flattened ellipsoidal shape of the nodules is suggestive of a secondary origin.

Sellwood (1970, 1972) has noted that Raricostatum to Jamesoni Lower Liassic sequence (i.e. top part of Black Ven Marls to the basal part of the overlying Belemnite Marls) is characterized by rythmic units. The units are defined by variations in either the carbonate to clay content or sand and silt to clay content. Two major types of cycles or rythms have been identified (Sellwood, 1970). In the first type, each cycle coarsens upwards from shales at the base to a bioturbated argillaceous sandstone at the top. The scour surfaces, and the diverse body- and trace-fauna exhibited by the bioturbated sandstones are believed to be indicative of shallow water and high energy depositional conditions. By contrast, the restricted fauna of the shale intervals suggest deposition in a deeper and poorly oxygenated water. The second type of rythms consist of limestone-marl

alternations similar to that of the Blue Lias.

3.3.5 The Belemnite Marls (Jamesoni - Ibex Ammonite Zones)

The top of the Black Ven Marls is marked by a band of nodular limestone called the Hummocky Limestone (Sellwood, 1972). Above this, the rythmic Belemnite Marls commence with calcilutite - marl rythms at the base succeeded by a sequence of marls and bituminous shales. A thickness of about 75 feet has been recorded along the Dorset coast for this unit (see Table 3.1).

3.3.6 The Green Ammonite Beds (Davoei Zone)

This lithologic unit consists of mainly marly clays with ferruginous bands and it is sandy towards the top. The monotony of these clays is interrupted by three irregular limestone bands. These marly clays have been found to be slightly bituminous (Bitterli, 1963). The unit is about 105 feet thick along the Dorset coast. These beds take their name from the occurrence in them of the ammonites (Androgynoceras lataecosta) with chambers filled with greenish crystalline calcite (Chatwin, 1960).

3.3.7 Clay Mineralogy of the Lower Lias

Published reports on clay mineral studies of the Lower Lias in southern England show that by far the most important clay mineral is illite (90-100%) with kaolinite present in subordinate amounts (normally less than 5-10%). Vermiculite and smectites are either totally absent or present as faint traces. Chlorite has not been detected at all (Perrin,

1957; Hallam and Sellwood, 1968; Sellwood, 1972; Hallam, 1975).

3.3.8 Stratigraphic Correlation of the Lower Lias across southern England

3.3.8.1 Dorset - Somerset

In the Somerset area, the full succession of the Dorset Lower Lias Ammonite Zones is present in the north-central and south-eastern parts. In the north-western part, the section comprises zones up to and including the Semicostatum Zone, the remaining zones having been removed by post-Lias erosion (Kellaway and Welch, 1948; Cope et al., 1980; Palmer, 1972a). In the north-central and south-eastern Somerset, above the basal 'Blue Lias' type lithology, the bulk of the Lower Lias consists of clays, marls and shales with occasional nodular or lenticular limestones.

In contrast to the relatively undisturbed outcrops of Lower Lias succession along Devon and Dorset coasts, the coastal outcrops of northwestern Somerset are interrupted by numerous E-W trending faults. According to Palmer (1972a), in the Watchet area (north-western Somerset), the Lower Lias Ammonite Zones from Planorbis to Semicostatum are present in a thickness of 178.9 metres (587 feet) compared to 47.6 metres (140 feet) for the equivalent zones in Dorset and 119 metres (350 feet) in Glamorgan (South Wales). The comparison shows a remarkable expansion of those zones in north-western Somerset.

The north and north-western Somerset coastal Lower Lias is composed of the 'Blue Lias' type alternations

of blue-grey limestones and black shales or marls (Palmer, 1972a). However, the succession is not a uniform series of limestone - shale alternations but is interrupted by thick development of shales and paper-shales. Palmer (1972a) noted that the Blue Lias lithology in this area gives way to thick shales three times and it is succeeded by grey marls. According to him, in these shales the intervals between widely spaced limestone nodules can be as much as 6.1 metres (20 ft.).

3.3.8.1 Dorset - Wealden District

In the Wealden District of southern England, the Lower Lias is comprised mainly of grey shales and mudstones with subordinate thin limestones. Near the deepest part of the Mesozoic trough in the Ashdown No. 2 Well, the formation is 840 feet (256 metres) thick, and the full sequence of the Dorset Ammonite Zones is probably present (Gallois, 1965). It is noticed to thin rapidly towards the edge of the basin and is only 3.5 feet (about 1 metre) thick at Harmansole (see Fig. 2.9) where only the topmost zone of the Lower Lias - the Davoei Zone is present (Gallois, 1965). In the Warlingham Borehole (see Fig. 2.9), a thickness of about 326 feet (99.4 metres) has been recorded (Worssam and Ivimey-Cook, 1971). Here the upper 170 feet 3 inches (52 metres) (corresponding to the Davoei Zone) of the Lower Lias consists predominantly of silty or shaly mudstone. This overlies 155 feet 4 inches (47.3 metres) of the 'Blue Lias' type facies of alternating mudstone and limestone bands which rest, with a possibly faulted junction, on a

Rhaeto-Liassic conglomerate 3 feet 1 inch (about 1 metre) thick (Worssam and Ivimey-Cook, 1971). The 'Blue Lias' facies at Warlingham extends up to the top of the Ibex Zone and therefore it is much later in persistence than in Dorset.

3.4 THE OXFORD CLAY FORMATION

3.4.1 Introduction

The Oxford Clay constitutes the middle major Jurassic mudrock unit in southern England (see Fig. 3.1). Its deposition commenced during Early Callovian and marked a widespread transgression of offshore and deepwater facies which clearly reflected a relative rise of sea level (Hallam, 1975). A widespread argillaceous facies persisted until the Late Oxfordian when it gave way to the shallow water calcareous facies of the Corallian.

The Oxford Clay Formation is subdivided into the Upper, Middle and Lower parts (Fig. 3.3). According to Callomon and Cope (1971), this subdivision is on the grounds of convenience and lithology only and the boundaries are not necessarily iso-chronous horizons.

In Dorset, the formation is well exposed by the shores of the East Fleet and in the brickyard at Chickerell (Fig. 3.4).

3.4.2 Lithology and Distribution

Oxford Clay is essentially an argillaceous formation consisting of clays, mudstones and bituminous shales. The formation is uniform in character and distribution

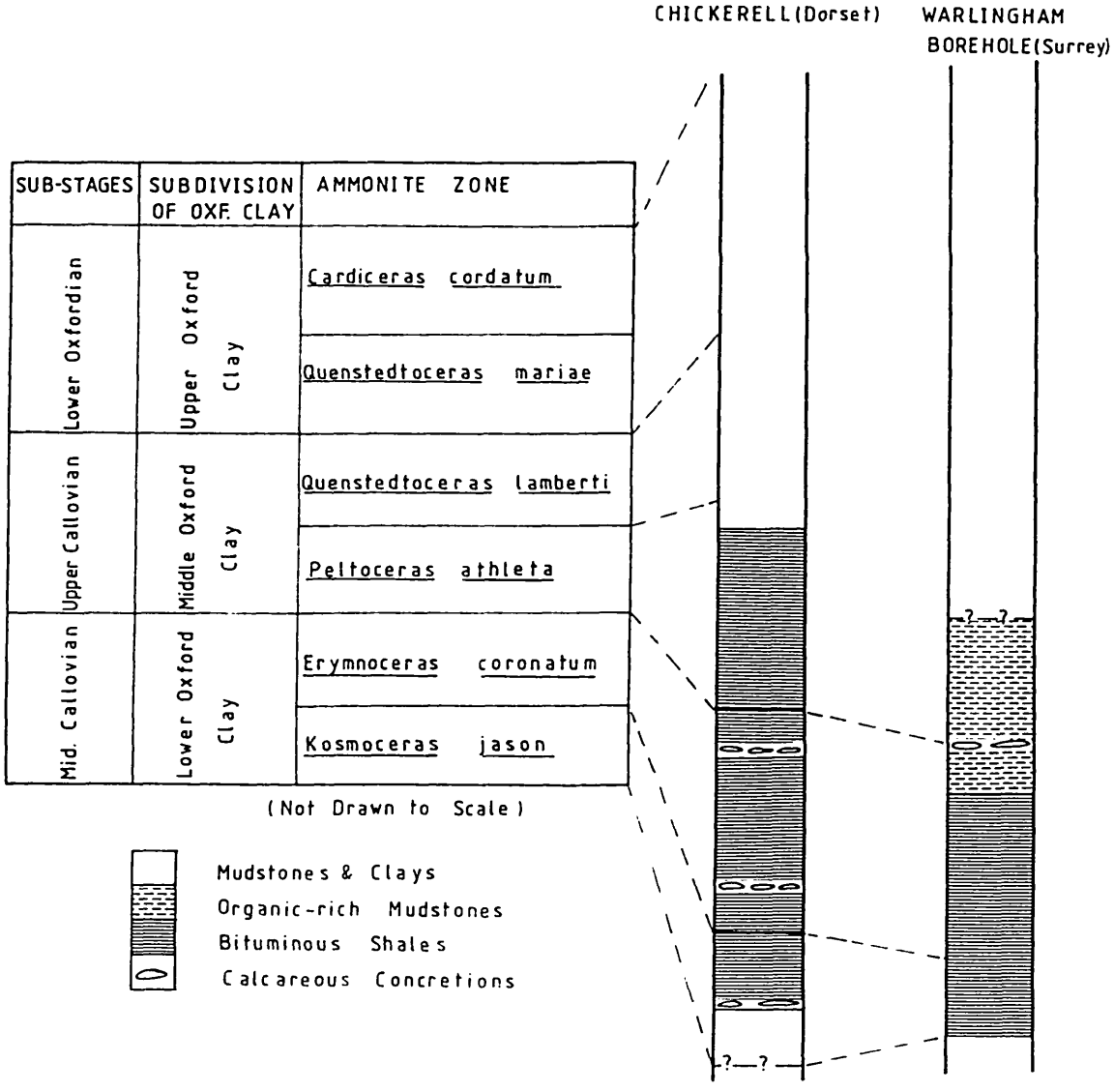


FIG. 3.3 STRATIGRAPHIC SUBDIVISIONS AND DISTRIBUTION OF OXFORD CLAY IN SOUTHERN ENGLAND

throughout southern England though its thickness is known to vary. From a maximum thickness of about 550 feet (168 metres) in Dorset (Bennison and Wright, 1969) it thins to 320 feet (97.5 metres) in the Warlingham Borehole in north-eastern Surrey (Worssam and Ivimey-Cook, 1971). As observed by Arkell (1947), Callomon and Cope (1971), and Morris (1980), the bituminous shales are characteristically limited to the Lower Oxford Clay and the basal part of the Middle Oxford Clay (the Jason - Lower Athleta Ammonite Zones) (see Fig. 3.3). These shales are overlain by the relatively organic-poor mudstones and clays. In the Warlingham Borehole, an intermediate fairly organic-rich series occur (Callomon and Cope, 1971) (see Fig. 3.3). In Dorset, the basal organic-rich shales attend a thickness of about 56 feet (17 metres) (Arkell, 1947), whereas in the Warlingham Well, a thickness of about 37 feet (11 metres) is ascribed to these bituminous shales.

The shales are generally poorly calcareous (2-8% $CaCO_3$) with clay minerals making up the bulk of the shales (40-60%) (Morris, 1980). Pyrite is ubiquitous though present in amounts less than 5%. According to Morris, illite, mixed-layer clay (illite-smectite), kaolinite and smectite are the major clay minerals with chlorite present in subordinate amounts. However, both Perrin (1957) and Freeman (1964) reported that the clay mineral fraction of this formation consisted predominantly of illite with kaolinite being farily plentiful (10-20%) and other clay minerals being either absent or present in trace quantities. Total organic carbon contents of 2 to 6.5% have been reported for the bituminous shales (Morris, 1980).

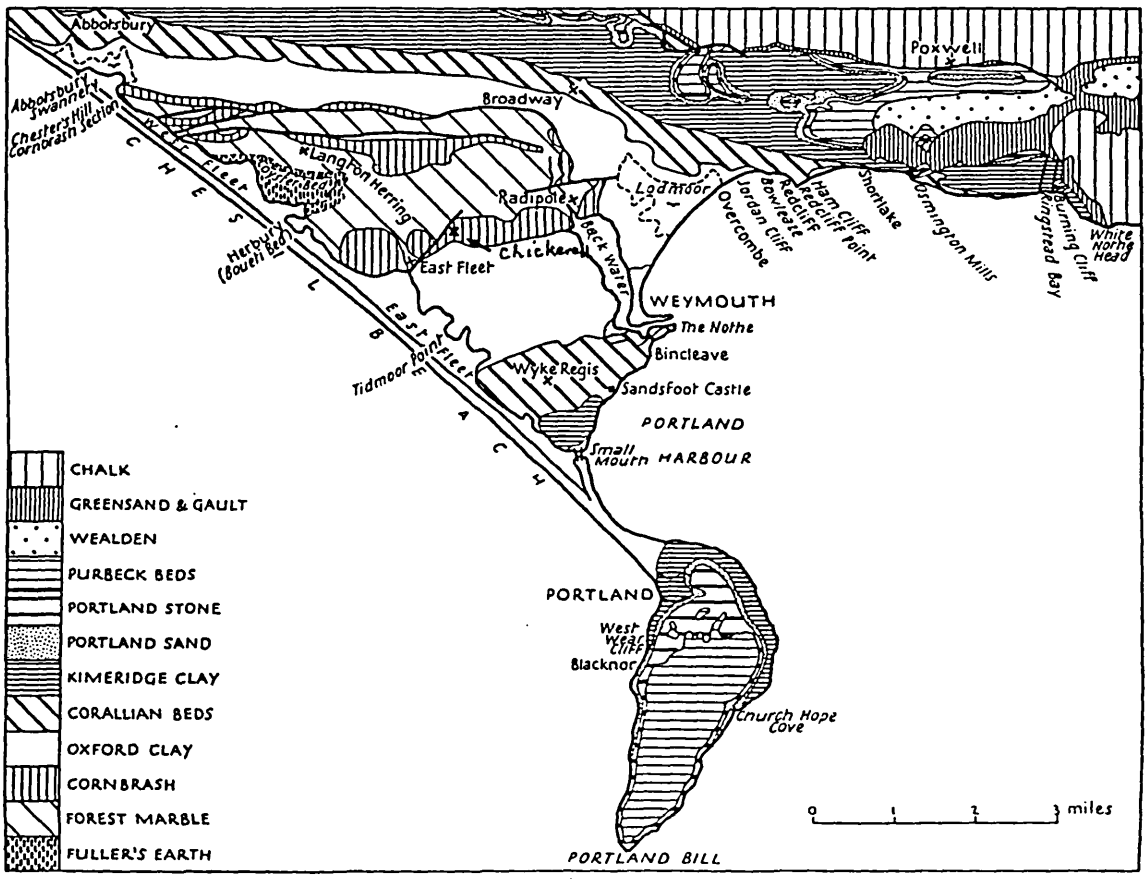


FIG. 3.4 SKETCH MAP OF WEYMOUTH AND PORTLAND SHOWING OXFORD CLAY OUTCROPS AT EAST FLEET AND CHICKERELL (FROM ARKELL, 1933)

Calcareous concretions constitute a common feature in the Lower Oxford Clay shales. They are believed to have started forming early in the diagenetic process at shallow burial depths of 5 metres (16 feet) or less (Raiswell, 1976). According to Morris (1980), the formation of these early concretions were possibly accomplished by the combination of calcium ions (derived from the solution of aragonitic shells in the anoxic layer with reduced pH) with bicarbonate ions produced by sulphate reducing bacteria. The solution of calcium bicarbonate so formed then migrated upwards and subsequently precipitated at shallow depths in the sites of locally reduced pH - for example around decaying ammonites. Ammonites enclosed by these concretions are often found uncrushed thus supporting an early origin for the concretions.

3.4.3 Depositional Environment

Based on faunal evidence and lithologic character, Morris (1980) concluded that the Lower Oxford Clay was deposited in mildly oxygenated bottom waters which, together with the slow burial rate of the sediments, allowed aerobic breakdown of the sedimented organic matter for a considerable length of time. This prolonged oxidation of organic matter is suggested to be responsible for the relatively low values of preserved organic carbon found in these rocks today. In apparent agreement with this line of diagnosis, Hallam (1975) remarked that the southern English Lower Oxford Clay is not composed of typical laminated shales and that it contains a rich benthos. The apparent lack of lamination in the clays

and mudstones of the Middle and Upper Oxford Clay with their abundant and diversified benthic fauna clearly suggest the deposition of these higher units is well oxygenated bottom waters.

3.5 THE KIMMERIDGE CLAY FORMATION

3.5.1 Introduction

The Kimmeridge Clay forms the uppermost principal mudrock formation in the Jurassic of southern England. It is the thickest and most organic-rich shale sequence in the British Jurassic (Morris, 1980). Figs. 3.5 and 3.6 show the distribution, stratigraphic subdivisions and the correlation of the formation across southern England. It is best exposed along the Dorset coast in the Kimmeridge Bay area between Broad Bench and Chapman's Pool (Fig. 3.5 and Fig. 3.7). The total reported thickness of the Kimmeridge Clay in this area is about 1,650 feet (503 metres) - of which about 1,070 feet (326 metres) is exposed along the coastal cliffs and the remainder (about 581 feet) below the Euxodus Zone is known only from boreholes (Arkell, 1947; Gallois, 1978a).

3.5.2 Lithology and Distribution

In contrast to the Oxford Clay, the Kimmeridge Clay is highly variable in lithologic character. It consists of rapidly alternating beds of organic poor mudstones and clays, organic-rich shales (bituminous shales) and highly organic-rich shales - the 'oil shales'. In the Upper Kimmeridge Clay, particularly in the Hudlestoni and

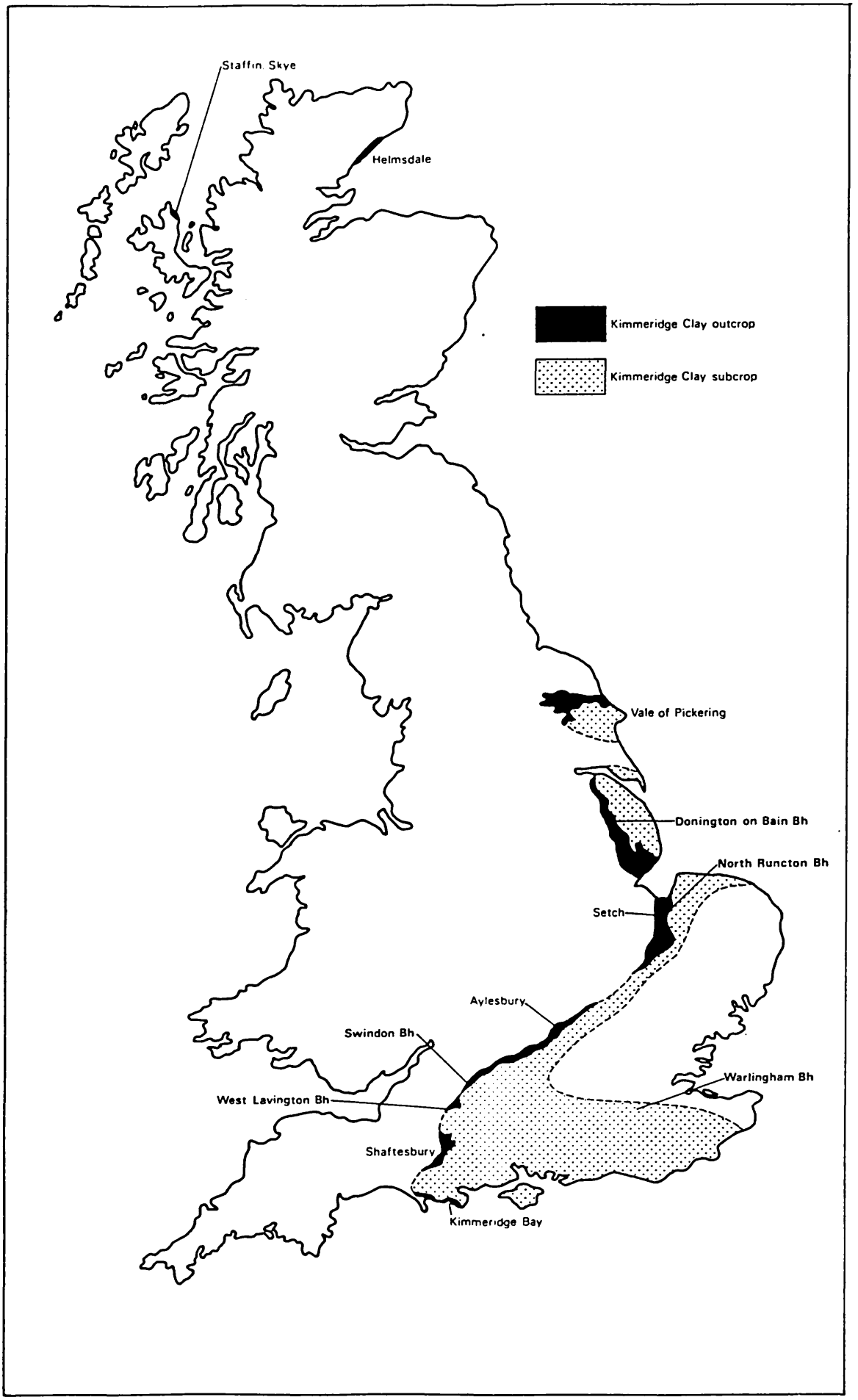


FIG.3.5- MAP SHOWING THE KIMMERIDGE CLAY OUTCROP AND SUBCROP IN SOUTHERN ENGLAND AND OTHER PARTS OF BRITAIN (AFTER GALLOIS,1978a).

Pectinatus Zones, impure chalks (coccolith limestones) are found. They often occur associated with the oil shales (Gallois, 1976; 1978a). Calcareous and dolomitic concretions and cementstone horizons occur at intervals throughout the sequence. Five very organic-rich 'oil shale' bands have been recognised in the sequence and named after the ammonite zones in which they occur (Gallois, 1978a). They are the Lower Euxodus Band, the Upper Euxodus Band, the Elegans Band, the Wheatleyensis Band and the Pectinatus Band (see Fig. 3.6).

The distribution of the Kimmeridge Clay in southern England (and in other parts of Britain) is fairly well known from the pilot study of oil shale occurrences in this formation carried out by the Institute of Geological Sciences (now the British Geological Survey) (Gallois, 1978a) (Fig. 3.5). In the southeastern England the Kimmeridgian, though of variable thickness across the Mesozoic Wealden Basin, exhibits similar lithologic character to the sequence on the Dorset coast. In the Warlingham Borehole (in Surrey) towards the edge of the basin, the formation is 712 feet (217 metres) thick (Worssam and Ivimey-Cook, 1971) whereas it thickens to 1,242 feet (379 metres) in the Penshurst Well (west Kent) towards the centre of the basin. It is only in the Swindon - Oxford region that any significant lithologic differences are found - much of the Upper Kimmerdgian is developed in a sand facies (see Fig. 3.6).

The organic-poor mudstones are homogenous and show no conspicuous lamination. The organic-rich 'bituminous shales' are better laminated while the 'oil shales', which

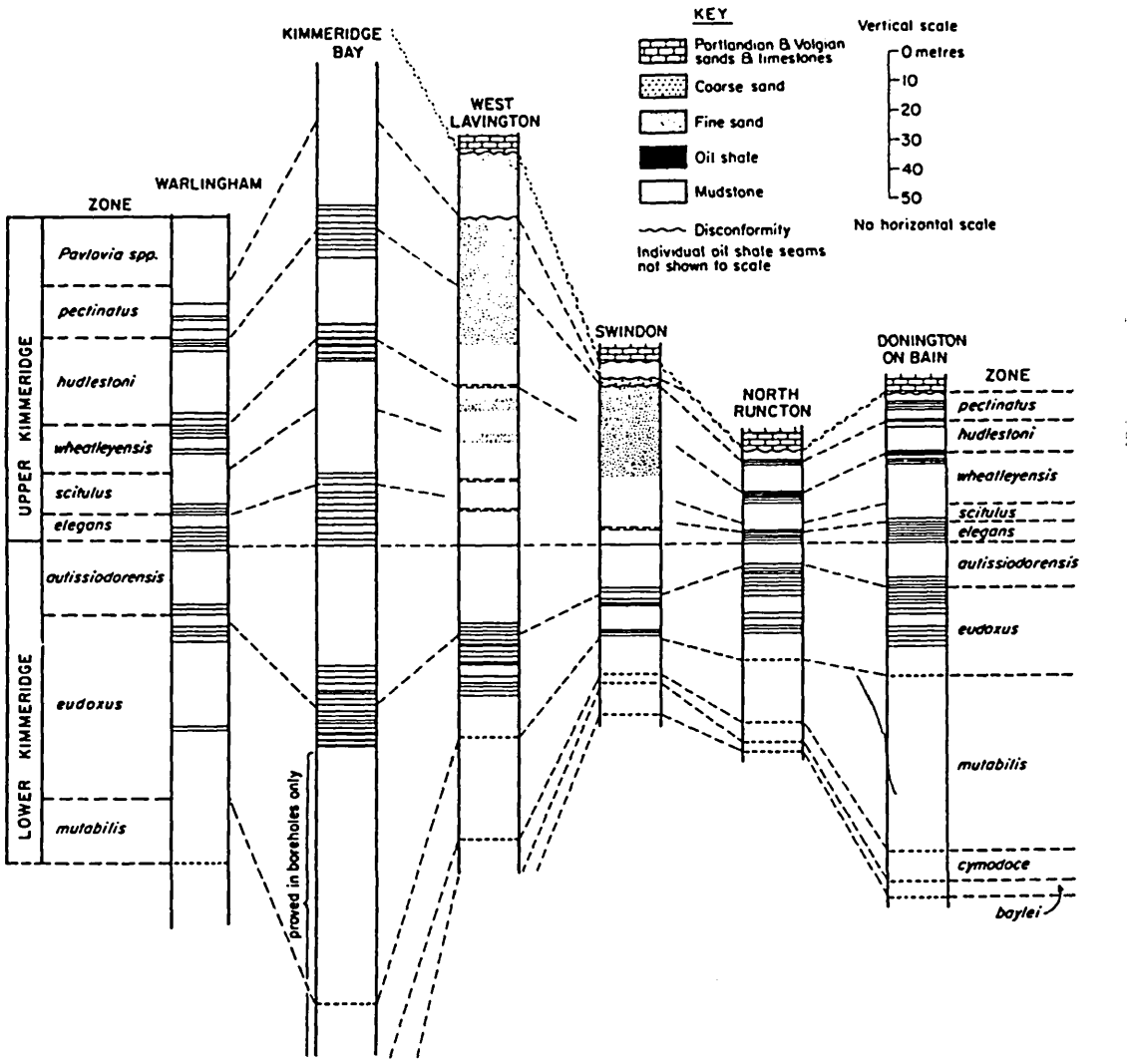


FIG.3.6- STRATIGRAPHIC DIVISIONS AND CORRELATION OF KIMMERIDGE CLAY(LOCALITIES OF CORRELATION SHOWN IN FIG.3.5) (From Morris,1980)

though appearing laminated in hand specimen, are not finely laminated in thin section (Morris, 1980). Bioturbation is restricted to distinct horizons, particularly at the junctions of bituminous and organic-poor mudstones. This consists mainly of Chondrites and thin pyritic burrows. Larger burrows including Rhizocorallium, Teichichnus and Tigillites are seen in some coccolith limestone horizons (Morris, 1980).

Vertical lithologic changes are accompanied by some changes in faunal content. The mudstones contain a fairly abundant low diversity macrofauna of small, thin-shelled benthonic bivalves plus a nektonic element including ammonites, fish and reptiles. The plankton includes dinocysts, coccoliths and the rare acritarchs. In the bituminous shales, the macro-fauna is similar to that of the mudstones and clays but it tends to occur only at discrete horizons (Tyson et al., 1979). In the oil shales and the coccolith limestones, benthic fossils are rare or absent and the non-carbonate organic content consists dominantly of amorphous sapropel with above average proportions of terriginous palynomorphs (Ioannides et al., 1976; Tyson et al., 1979).

The mineralogy of the organic-rich shales reported by Morris (1980) shows that they consist mainly of clay minerals (20-60%) - dominated by illite (up to 80%) with little mixed layering. Kaolinite forms the most common subordinate clay mineral and varies up to 31% while chlorite and vermiculite are absent or present in small amounts. A similar clay mineral composition was reported

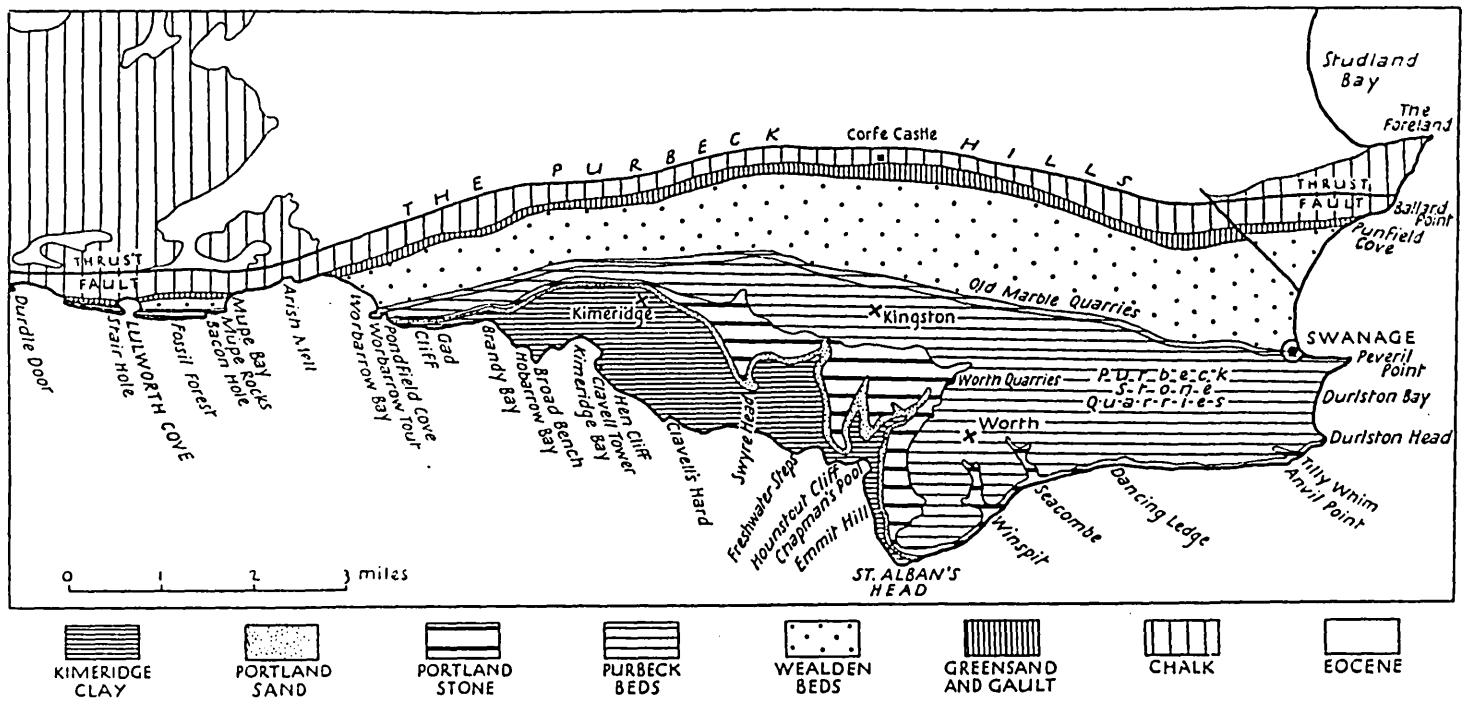


FIG. 3.7 SKETCH MAP OF "ISLE" OF PUBBECK SHOWING KIMMERIDGE CLAY OUTCROPS (FROM ARKELL, 1933)

by Perrin (1957). The mineralogy of the mudstones and clays are similar to that of the bituminous shales (Tyson et al., 1979). Pyrite is ubiquitous in the Kimmeridge Clay though present in small amounts. The cementstones which occur commonly in the Kimmeridge Clay sequence consist of microspar (10-15 μm) ranging from ferroan dolomite to ankerite. Carbonates comprise upto 85% of the cementstones. Discrete carbonate nodules occurring in the organic-rich shale horizons consist of non-ferroan calcite microspar (< 10μm) and are usually pyritic (Tyson et al., 1979).

Results of total organic matter analysis reported by Tyson et al. (1979) for the Kimmeridge Clay rocks show that the organic matter is predominantly amorphous sapropel with the clays/mudstones containing up to 10%, the bituminous shales up to 30% and the 'oil shales' up to 70% organic matter. The dolomitic cementstones are also noted to contain amorphous kerogen either as dispersed fragments or discontinuous laminae about 0.25 mm thick. Two varieties of coccolith limestones have been identified - one homogenized by bioturbation and the other showing microlaminations of alternating dark coloured sapropel-rich material and light coccolith layers (Tyson et al., 1979).

3.5.3 Depositional Environment

The origins of the high organic-rich horizons and the clay/mudstone - bituminous shale - oil shale - coccolith limestone lithologic associations characteristic of the type Kimmeridge Clay have remained a subject of controversy in recent years. From his observation of the intimate

association of the coccolith limestones with oil shales, and also from faunal evidence, Gallois (1976) suggested that the organic content of the Kimmeridge Clay was largely derived from phytoplankton blooms. According to him, these blooms by de-oxygenating and poisoning the water themselves provided the temporary anaerobic bottom conditions required to ensure the preservation of their organic content. He rejected the idea that widespread anaerobic bottom conditions developed beneath a layer of undisturbed effectively stagnating sea water, suggested by Hallam (1967, 1975), for the Lower Lias, could have been responsible for the formation of the Kimmeridge Clay oil shales. The rejection of Hallam's idea for the Kimmeridge Clay type situation was on evidences of plentiful benthic fauna in the oil shales, regional occurrence of thin seams of oil shales independent of the shape of sea floor or distance from shoreline, and the occurrence of oil shales in juxtaposition with a variety of lithologies representing differing bottom conditions.

However, Tyson et al. (1979) by comparison with similar sediments of Quarternary age in the Black Sea and Mediterranean, and also using faunal and palynologic evidences proposed that the characteristic lithologic association observed in the Kimmeridge Clay can be attributed to the vertical movement of the O_2:H_2S interface in a temporarily stratified water column. They rejected Gallois' phytoplankton bloom hypothesis. According to Tyson et al. (1979), the mudstones/clays were deposited under oxygenated bottom conditions below normal wave base,

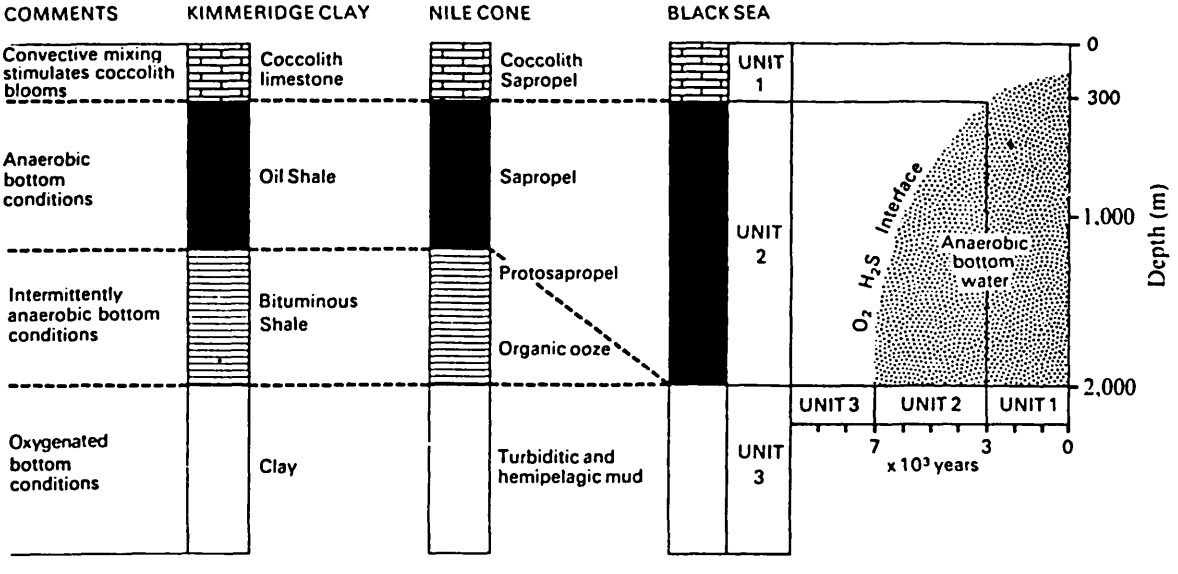


FIG.3.8- A MODEL FOR ORIGIN OF KIMMERIDGE CLAY LITHOLOGIC CYCLES(Tyson et al.,1979).

and the bituminous shales formed during periods of fluctuating aerobic/anaerobic conditions with a consequent preservation of greater amounts of organic matter. The oil shales were formed in predominantly anaerobic conditions and they marked an intermediate phase in the upward progression of the O_2:H_2S (Fig. 3.8). They believed the coccolith limestones marked the maximum development of anaerobic bottom water in the Kimmeridgian Water column. At this time the top of the H_2S zone had migrated to a level where seasonal convective processes could provide its nutrients to the euphotic zone and there stimulated a coccolith bloom.

In partial agreement with the above hypothesis of Tyson et al., Morris (1980), using essentially faunal evidence, remarked that the ubiquitous occurrence of epifauna together with a low diversity, low-oxygen tolerant, infauna in the bituminous and oil shales suggest deposition of these sediments in an environment where anoxic conditions extended up to the sediment surface. But according to him, free H_2S was not released into the bottom waters for any length of time.

CHAPTER IV

SAMPLING AND ANALYTICAL TECHNIQUES

SAMPLING AND ANALYTICAL TECHNIQUES

4.1 GENERAL STATEMENT

A total of 151 selected samples were variously analysed in this study. These included 25 outcrop- and 123 borehole-rock samples together with three reservoired oil samples. All the rock samples were generally fine-grained, and sampling was restricted to the Lower Lias, the Oxford Clay and the Kimmeridge Clay Formations of the Jurassic. The localities of sample collection are indicated in Fig. 4.1.

4.2 SAMPLING

4.2.1 Outcrop Samples

These were collected in the Dorset coastal area. The Lower Lias was sampled at Charmouth and Lyme Regis. The sampling of the Oxford Clay outcrops was at Shortlake and in the Chickerell area mostly from brickpits (see Fig. 3.4). The Kimmeridge Clay was sampled at two main localities separated by the Purbeck - Isle of Wight monocline - the Ringstead Bay area to the north, and the Kimmeridge Bay to Chapman's Pool area to the south of the line of disturbance. Stratigraphic sampling by ammonite zonation was carried out for the Oxford Clay at the two mentioned localities, and for the Kimmeridge Clay in the Kimmeridge Bay - Chapman's Pool area.

Most of the outcrops were found to be covered with a weathering layer. Fresh samples were obtained by breaking off large pieces of rocks with a hammer and chipping off the weathered portions. Unweathered samples were also

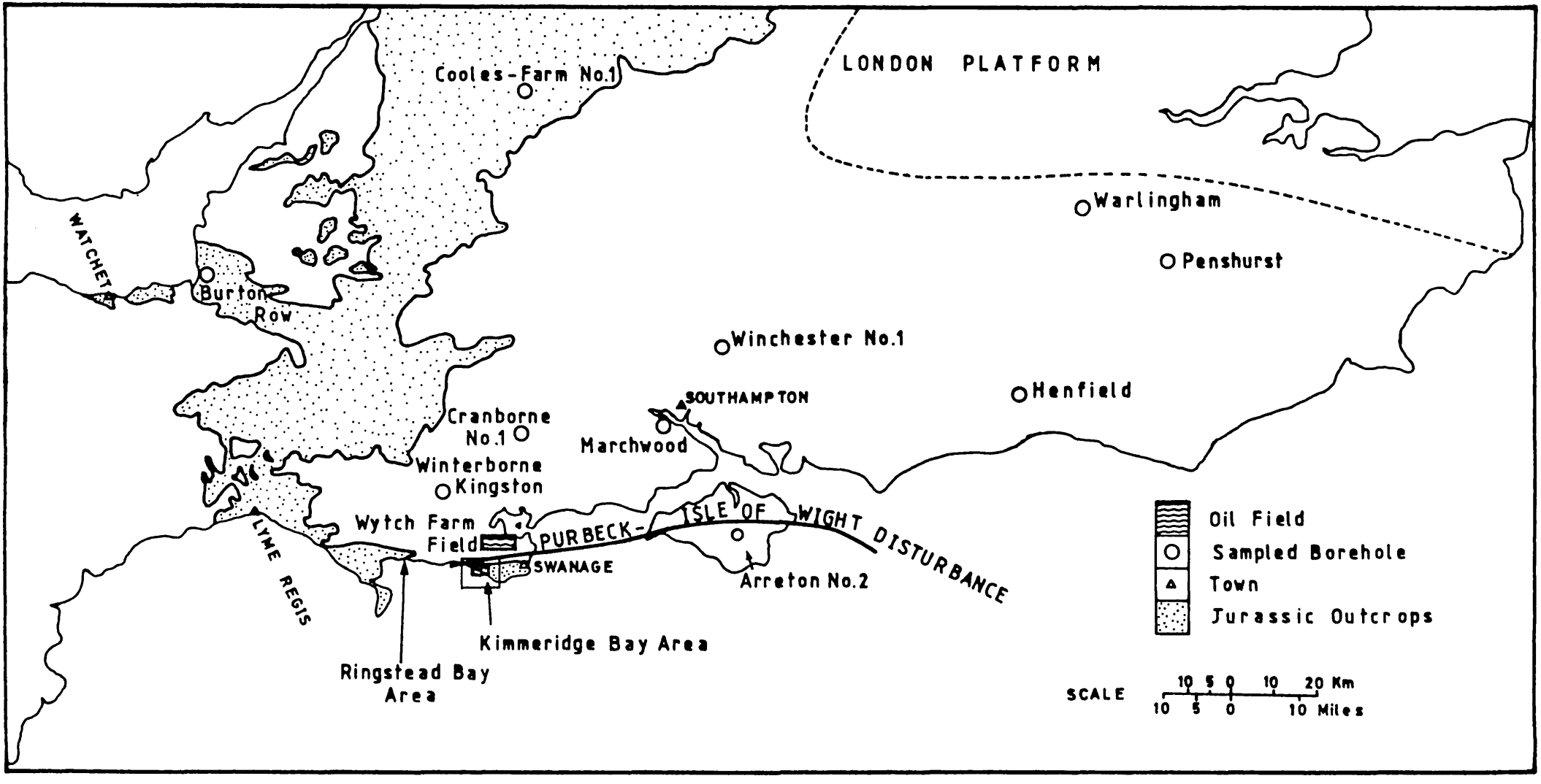


FIG. 4.1 MAP SHOWING SAMPLED LOCALITIES

obtained from brickpits where available. Each sample was transported to the laboratory in labelled non-plastic containers.

4.2.2 Borehole Samples

Rock samples were obtained from ten boreholes for this study. The boreholes are Marchwood, Warlingham, Winterborne Kingston, Cooles Farm No. 1, Cranborne No. 1, Burton Row, Winchester No. 1, Arreton No. 2, Henfield and Penshurst (see Fig. 4.1). Samples from all the boreholes, except the Cooles Farm, were kindly supplied by the Institute of Geological Sciences (now the British Geological Survey) from its collections. The Shell Petroleum Company supplied samples from the Cooles Farm No. 1 borehole. The present depths of the three sampled formations in these boreholes are shown in Fig. 4.2.

The samples from Arreton No. 2, Cooles Farm No. 1, Cranborne No. 1 and Penshurst (Lower Lias only) Wells were ditch cuttings whereas those from the the other wells and from the Oxford Clay and the Kimmeridge Clay Formations, of Penshurst borehole were conventional core materials.

A number of problems were encountered in obtaining the desired samples from the author's choice of boreholes for this research. The first was that samples from some boreholes considered appropriate for this study were still under confidential lists and therefore could not be released. Secondly, was the problem of sampling cored materials from the horizons or intervals of interest. This was because many of the samples kept by the Institute of Geological Sciences are used, among other things, for stratigraphic

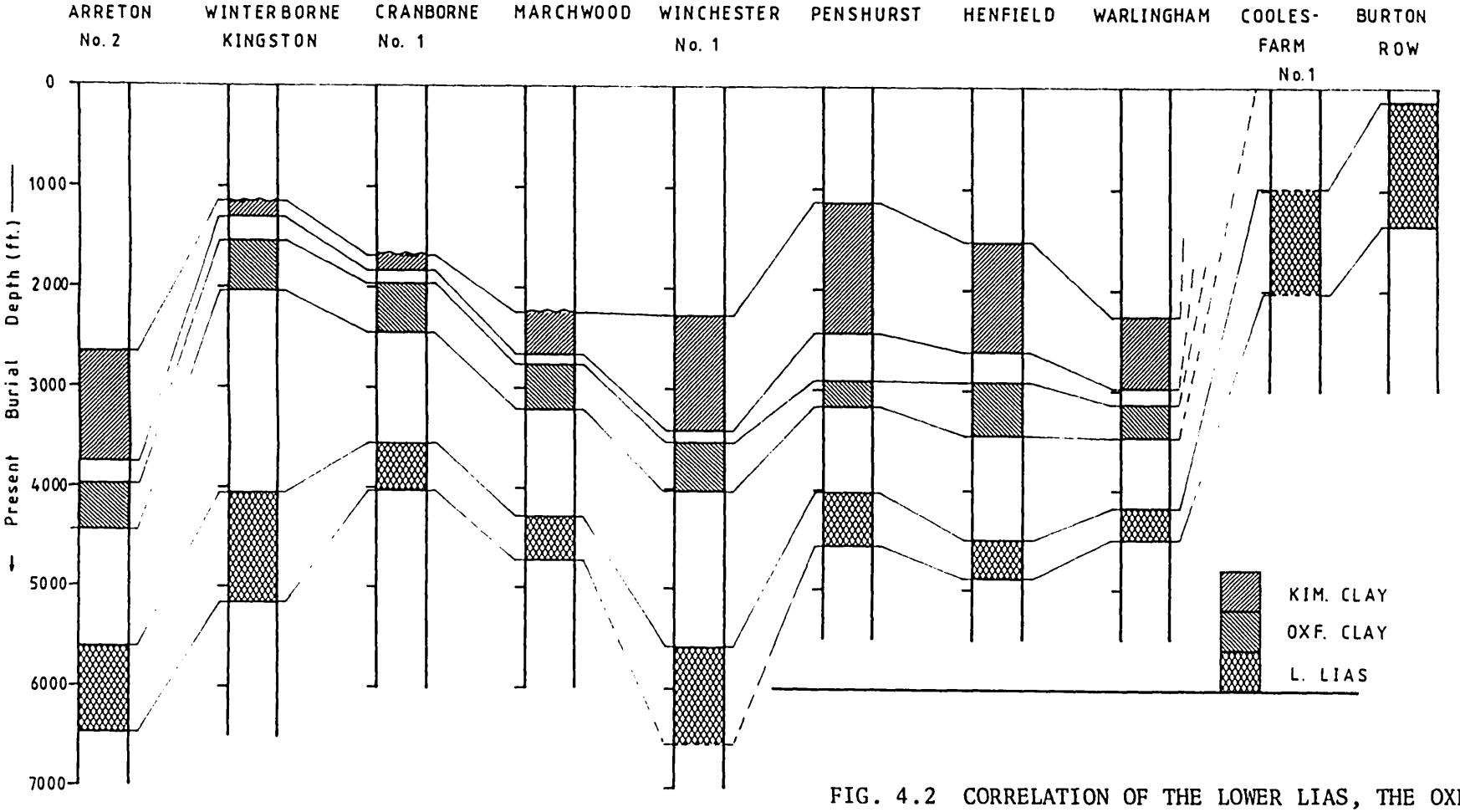


FIG. 4.2 CORRELATION OF THE LOWER LIAS, THE OXFORD CLAY AND THE KIMMERIDGE CLAY FORMATIONS IN THE SAMPLED BOREHOLES

studies and hence any sampling that tended to destroy or displace any contained fossil or fossil evidence was highly discouraged. More so, coring of the Lower Lias, the Oxford Clay and the Kimmeridge Clay in many of the boreholes was not continuous and in some cases no coring at all was carried out in a formation of interest. Where cuttings were lacking, sampling had to be restricted to cored intervals. The amount of sample (measured by weight) made available for this study were in many cases quite inadequate with the worst situation encountered with the Arreton No. 2 borehole where samples of only 5 g per 100 ft of formation were supplied. The limitation in the size of sample obviously restricted the number of analyses a sample was subjected to and in some cases alternate samples in a borehole had to be subjected to different analyses.

4.2.3 Oil Samples

The three oils analysed in the present study were produced from three main reservoir rocks in Dorset. They are - the oil from the fractured Cornbrash obtained from the Kimmeridge No. 1 Well (Kimmeridge Bay), and the two oils from the Wytch Farm Oilfield produced respectively from the shallow Bridport Sands (depth: 3038 - 3225 feet) and the deeper Sherwood Sandstone Group (depth: 5156 - 5594 feet). The three oils are referred to, respectively in this thesis, as the Cornbrash or Kimmeridge No. 1 Oil, the Bridport Oil and the Sherwood Oil. The Cornbrash Oil was supplied by British Petroleum Development Limited and was a bottom hole sample taken on the 29th April, 1959.

The two Wytch Farm Oils were collected from a production platform on the 15th November, 1982. The oils were topped at $40^{o} \pm 2^{o}C$ for 24 hours and stored in glass tubes in nitrogen atmosphere at room temperature prior to analyses.

4.2.4 Sample Identification

The location and the formation of a rock sample may be identified from its combined letters and number code. The first group of letters before a stroke indicates the sample location or name of borehole: MD/ = Marchwood; CN/ = Cranbourne-1; WM/ = Warlingham; WK/ = Winterborne Kingston; BR/ = Burton Row; CF/ = Cooles Farm-1; WCH/ = Winchester-1; HN/ = Henfield; AR/ = Arreton-2; PH/ = Penshurst; and OSD/ = Outcrop Sample, Dorset. The next pair of letters immediately after the stroke indicate the name of sample formation: KC = Kimmeridge Clay; OC = Oxford Clay; and LL = Lower Lias. The number at the end of a sample code indicates the stratigraphic position of the sample in terms of age and for each formation, samples are numbered in order of increasing depth/age. As a result of the occurrence of the Kimmeridge Clay units of same age in both Ringstead Bay and Kimmeridge Bay - Chapman's Pool areas the outcrop samples of Kimmeridge Clay numbered 1-3 belong to the Ringstead Bay area (not stratigraphically arranged) and those numbered 4-12 belong to the Kimmeridge Bay - Chapman's Pool area (stratigraphically arranged).

An example of a sample code is HN/KC-2. This implies the second Kimmeridge Clay sample (in order of depth/age) from the Henfield Borehole.

4.3 ANALYTICAL TECHNIQUES

4.3.1 Initial Preparation of Rock Samples

The ditch cuttings were first hand-picked with the aid of a hand lens to remove caving materials and drilling mud contaminants. All the rock samples were hand washed with distilled water in an attempt to remove any contaminating material from the samples surfaces and then dried at $40^{o} \pm 2^{o}C$ in an oven. A pestle and mortar of cast iron was used to reduce each dried sample to about 1 mm grain size. The crushed sample was divided into two portions. One portion, sieved clean of the fines, was stored for maceration and clay fraction preparation. The other portion, with the fines from the first portion was further reduced to a particle size of less than 75 microns using a Pascal Mechanical Mortar and Pestle-Mill and a 200 mesh sieve. The rock powder was stored in stoppered glass tubes/bottles to be used for bitumen extraction, pyrolysis, total organic carbon determination and whole rock x-ray diffraction analysis.

Throughout every stage of the operation, every possible precaution was taken to prevent contamination. This included thorough washing of the mortar and pestle using detergent and brush before rinsing them with distilled water and then dried with a jet of compressed air in between samples. The sieves were also cleaned using brushes and a jet of compressed air after each sample.

4.3.2 Maceration and Insoluble Organic Matter Fractionation

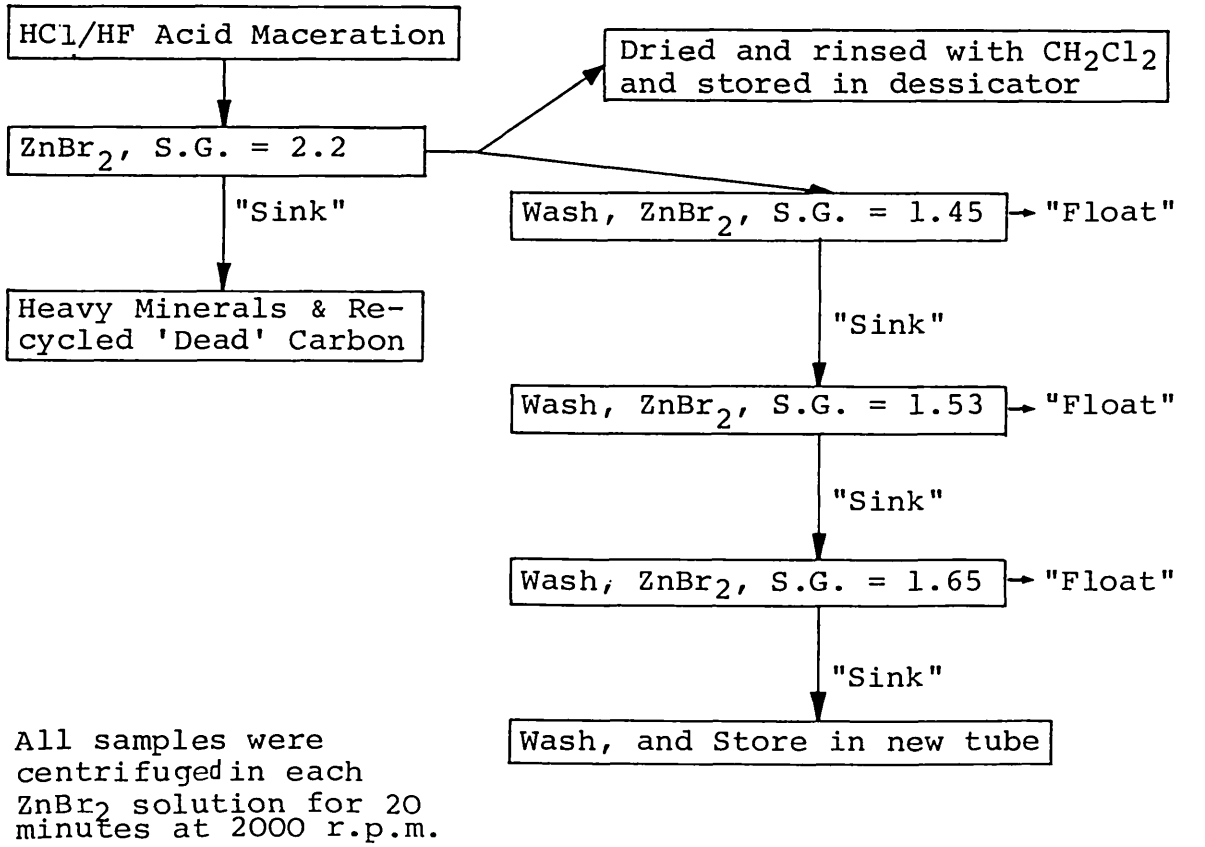
Maceration is the term applied to various chemical and physical processes by which insoluble organic matter is extracted from sedimentary rocks. The maceration method used in this project was adapted from that described by Barss and William (1973) for palynological preparations.

5-50 g of each selected rock sample, previously crushed to 1 mm grain size, were placed in a 600 ml plastic beaker and treated with 100 ml-portions of 10% Hydrochloric acid (technical grade) to eliminate the carbonates. The Hydrochloric acid (HCl) treatment was continued until the reaction ceased to be observable. The residue was washed in distilled water to neutrality in an attempt to remove all the calcium ions. The residue was allowed sufficient time to settle and the clear distilled water was decanted off. The concentrate was acidified with a few millilitres of 5% HCl and then treated with two 50 ml-portions of concentrated Hydrofluoric acid (60% HF, technical grade) to completely digest the silicate minerals. The Hydrofluoric acid (HF) treatment was carried out over a period of 48 hours. Care was taken to avoid any form of heating or oxidation of the organic matter. The reason for acififying the residue with 5% HCl prior to HF treatment was to prevent any calcium ions that may have been present from forming fluoride complexes (Saxby, 1970; Bostick and Alpern, 1977). The HCl/HF acid insoluble residue was washed to neutrality with distilled water.

The insoluble organic matter was subjected to a density fractionation procedure similar to the one

described by Kinghorn and Rahman (1980, 1983) using zinc bromide solutions with specific gravities of 2.2, 1.65, 1.53 and 1.45 (see Fig. 4.3). The inorganic heavy minerals which are known to be insoluble in non-oxydising acids (e.g. HCl and HF) such as pyrite were separated from the organic fraction by centrifuging the total residue in a zinc bromide solution of specific gravity 2.2 in 30 ml plastic centrifuge tube at 2000 r.p.m. for 20 minutes. The heavy recycled and 'dead' organic matter also separated out along with the heavy minerals. The organic matter (the floating fraction) was decanted and washed three times by centrifuging in 1% HCl and then a further twice in distilled water. The washed organic matter obtained from this procedure was divided into two portions. One portion was

Fig. 4.3 Method for fractionating acid insoluble organic matter



centrifuged for 20 minutes at 2000 r.p.m. successively in solutions of zinc bromide of specific gravity 1.45, 1.53 and 1.65. After each centrifugation, the "float" and "sink" fractions were separated by decantation into new tubes and washed as described above, three times with 1% HCl. The "float" fraction from each density-grade separation was finally washed with distilled water and stored in distilled water for mounting. The "sink" fraction was then centrifuged in the next higher specific gravity solution of zinc bromide. The process was continued until the heaviest organic components had been separated. The "sink" fraction of the 1.65 specific gravity was washed as before and stored in distilled water as the 1.65 - 2.2 density fraction. Thus four fractions of the organic matter were obtained from this fractionation process: of density less than 1.45, 1.45 - 1.53, 1.53 - 1.65, and 1.65 - 2.2 The separated four fractions were allowed to settle down in distilled water in the graduated centrifuge tubes for a period of 24 hours. The percentage separations of the four fractions were then volumetrically estimated. A representative part of each of the fractions was mounted in glycerine jelly on standard glass slides for microscope or optical examination.

The second portion of the float fraction of the initial (specific gravity 2.2) centrifugation was dried in an oven at $40^{o} \pm 2^{o}C$ in a nitrogen atmosphere. The drying was continued until the organic concentrate reached a fairly constant weight. The dried organic matter was then ground in a clean agate mortar using an agate pestle and rinsed twice, in a glass tube, with 20 ml-portions of

dichloromethane (boiling point = 38°C) in order to remove any bitumen (soluble organic matter) left on the insoluble organic fraction after the HCl/HF treatment (Peters et al., 1983). The kerogen was dried again under the same conditions as above for a day and then stored in a stoppered glass tube in a dessicator.

A total of 138 samples were subjected to this maceration and fractionation procedure.

4.3.3. Elemental Analysis

A Perkin Elmer Model 240 Elemental Analyser was used to determine the total organic carbon (TOC) contents of 137 whole rock samples, and also to analyse 138 kerogen samples for their carbon (C), hydrogen (H), nitrogen (N) and oxygen (O) contents.

The Model 240 Elemental Analyser determines the carbon, hydrogen, nitrogen and oxygen in organic compounds by detecting and measuring their combustion products such as carbon dioxide (CO_2), water (H_2O), and Nitrogen (N_2). For CHN analysis, combustion occurs in pure oxygen under static conditions. But for oxygen analysis, the oxygen is shut off and combustion is carried out in a Helium atmosphere.

4.3.3.1 Kerogen CHN Analysis and the Whole Rock Total Organic Carbon (TOC) determination by Perkin Elmer Model 240 Elemental Analyser

Three systems in the Elemental Analyser perform the determinations. These are the combusion train, the analytical system, and the electronics. Each is a separate

portion of the instrument to insure optimum operating conditions. The combustion train and the analytical system are shown in a simplified configuration in Fig. 4.4. As shown, Helium and pure oxygen (for CHN analysis only) supplies are required. Helium is used to carry the combustion products from the combustion train, through the analytical system, to atmosphere. Gas flows are determined by solenoids valves A through G, controlled by a cam-operated programmer in the sequence shown in Fig. 4.5. Valves H and I (see Fig. 4.4) are used for maintenance purposes. A helium bath surrounds the thermal conductivity cells to guard against small leaks.

The combustion train (Fig. 4.6) includes independently heated combustion and reduction furnaces maintained at about 950°C and 650-700°C respectively during analysis, and each with the appropriate reaction tube. The convenient sample inlet fitting plug at the end of the combustion tube facilitates rapid introduction of sample into the train for combustion. A known weight of sample in a platinium boat is introduced into the combustion train on a quartz ladle operated by a magnet. The reduction tube is packed with copper, and functions to reduce any oxides of nitrogen and removes any residual oxygen from the combustion train.

The analytical system (see Fig. 4.7) consists of a mixing volume (in which the sample combustion products - CO_2, H_2O, and nitrogen are mixed with helium to a homogeneous, equilibrated mixture), a pressure switch, sample volume, detectors, and adsorption traps. Three pairs of thermal

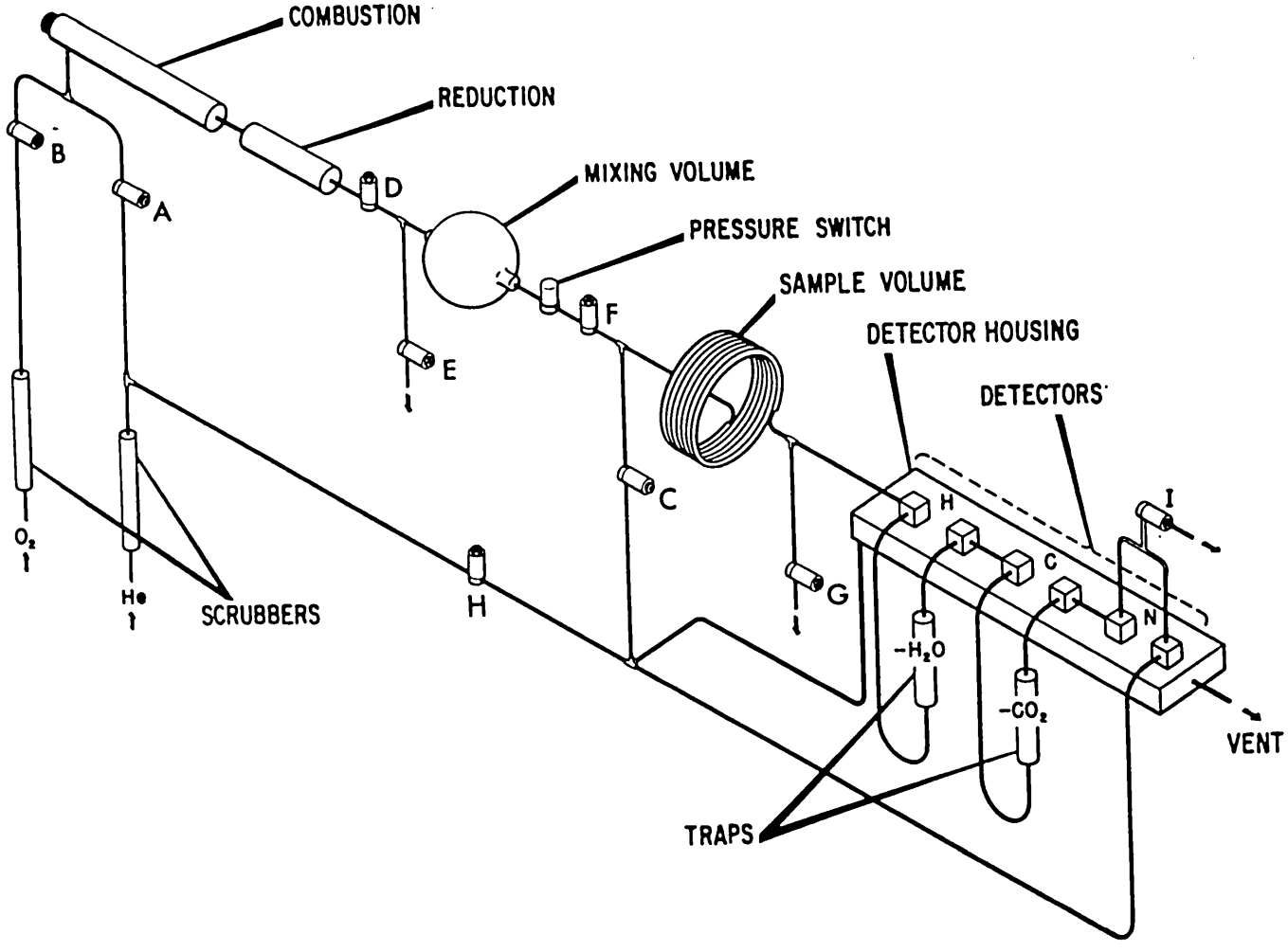
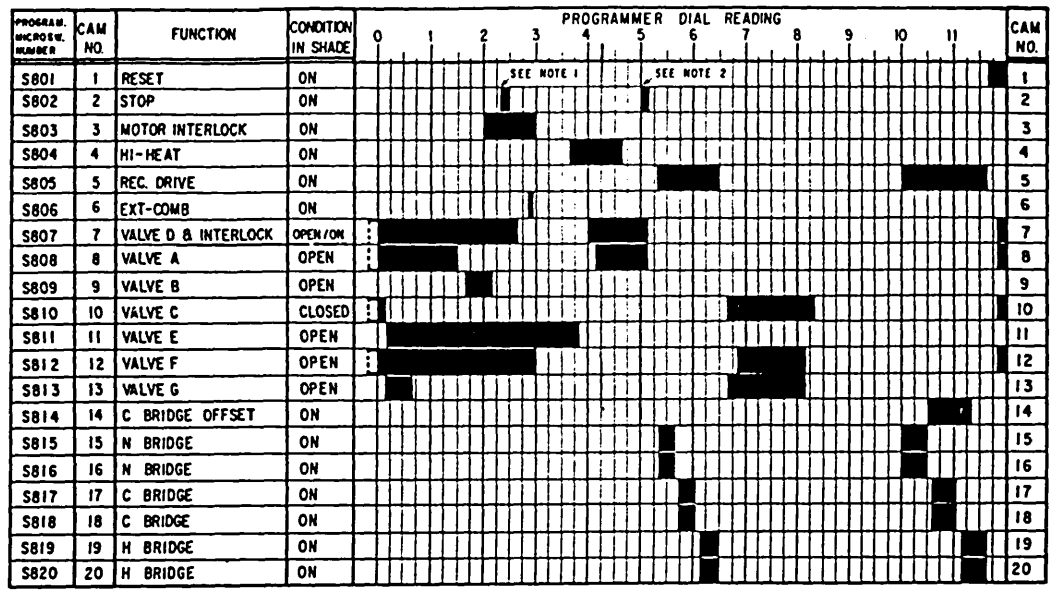


Fig. 4·4 - Simplified Diagram of Combustion Train and Analytical System

conductivity cells, in series, are used for detection, one pair each for water, carbon dioxide, and nitrogen. The platinum filaments of each cell are connected differentially in a Wheatstone bridge-type circuit so that any difference in the contents of the two cells will result in an electrical signal. A magnesium perchlorate trap between the first pair of cells (Fig. 4.8) adsorbs any water from the gas mixture before it enters the second cell so that the signal obtained from the corresponding bridge circuit is proportional to the amount of water removed. Likewise, an adsorbing trap between the second pair of cells results in a signal in proportion to the carbon dioxide removed from the sample. The last pair of cells detects nitrogen by comparing the thermal conductivity of the remaining sample gas with that of pure helium. The output signals from the bridge circuits are applied, through adjustable attenuators, to a 1-millivolt recorder or to the Perkin Elmer Model 240 Data Station Interface, which processes the data to the Data Station. When the Model 240 Data Station is used, the signals are seen at maximum sensitivities, therefore the attenuators are not used. With the 1-mV recorder, values of zero and read for each detector are displayed in a bar graph form.

Between 1-3 mg of each kerogen sample were used for this analysis and the carbon, hydrogen and nitrogen contents were expressed as percentages by weight of the kerogen. For TOC determinations in whole rock samples, between 3-4 mg of each powdered rock (<75 μm grain size) were weighed into a platinium boat and the sample was treated

PROGRAM. MICROSW. NUMBER	CAM NO.	FUNCTION	CONDITION IN SHADE	CAM NO.
S801	1	RESET	ON	1
S802	2	STOP	ON	2
S803	3	MOTOR INTERLOCK	ON	3
S804	4	HI-HEAT	ON	4
S805	5	REC. DRIVE	ON	5
S806	6	EXT-COMB	ON	6
S807	7	VALVE D & INTERLOCK	OPEN/ON	7
S808	8	VALVE A	OPEN	8
S809	9	VALVE B	OPEN	9
S810	10	VALVE C	CLOSED	10
S811	11	VALVE E	OPEN	11
S812	12	VALVE F	OPEN	12
S813	13	VALVE G	OPEN	13
S814	14	C BRIDGE OFFSET	ON	14
S815	15	N BRIDGE	ON	15
S816	16	N BRIDGE	ON	16
S817	17	C BRIDGE	ON	17
S818	18	C BRIDGE	ON	18
S819	19	H BRIDGE	ON	19
S820	20	H BRIDGE	ON	20



NOTES: PROGRAM STOPS UNTIL COMBUST BUTTON IS PUSHED.
2. PRESSURE IN MIXING CHAMBER RISES TO APPROXIMATELY 1500 MM Hg. (PROGRAM WILL STOP IF IT DOES NOT.) THEN PRESSURE SWITCH S401 OPENS AND CAUSES SOLENOID VALVE D TO CLOSE AND THE PROGRAM TO CONTINUE.

Fig. 4 · 5 - Model 240C Elemental Analyzer Program

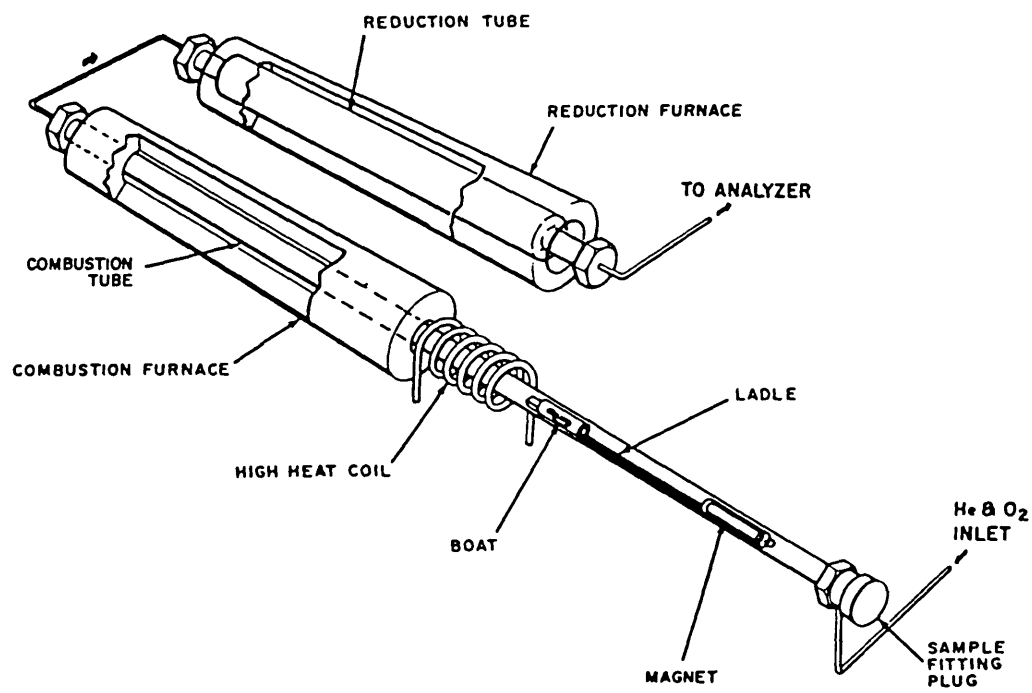
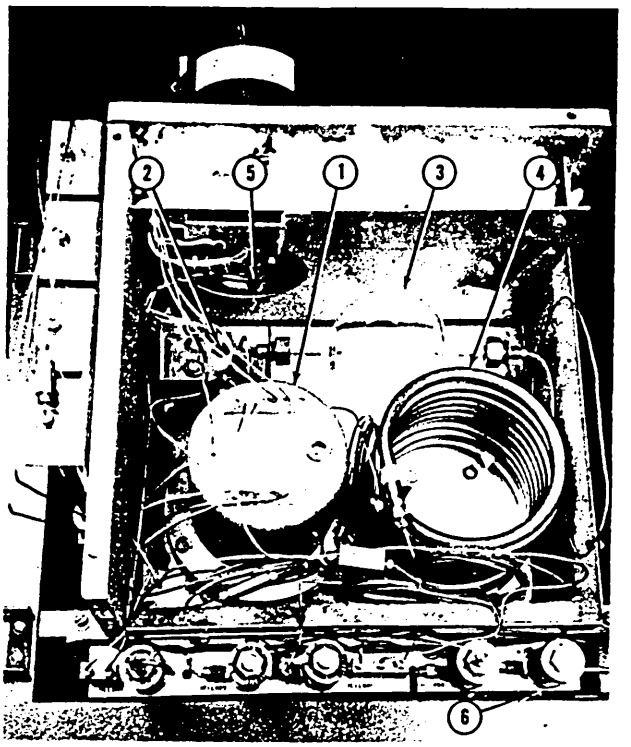


Fig. 4 · 6 - Combustion Train



1 *Detector Assembly*
2 *Pressure Switch*
3 *Mixing Volume*
4 *Sample Volume*
5 *Oven Thermistor*
6 *Heated Tube Assembly*

Fig. 4·7- Analytical System, Cover Removed

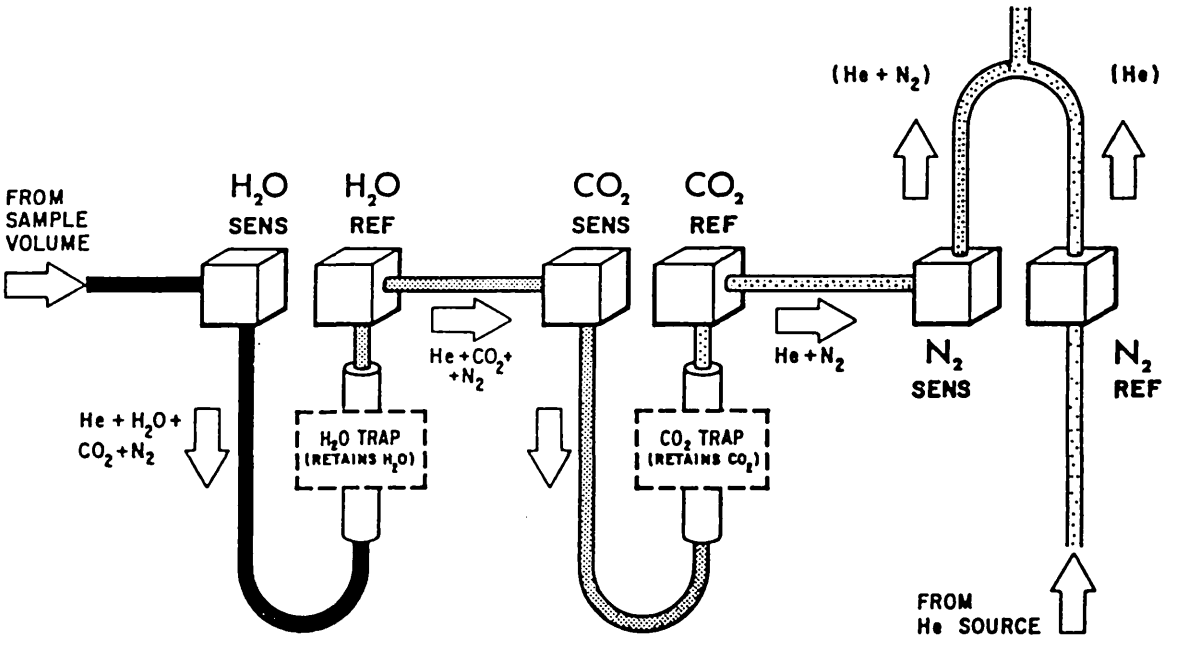


Fig. 4·8 - Detector Flow Diagram

with 30% HCl to destroy the carbonates. Addition of the acid was continued until no further reaction was visible. The acid treated sample was then dried in an oven at $40^{o} \pm 2^{o}C$ in a nitrogen atmopshere for about 3 hours before being subjected to the organic carbon analysis. The total organic carbon content of each sample was expressed as a percentage by weight of the whole rock sample.

The instrument was calibrated each day for CHN using Acetanilide (composition: C = 79.09%, H = 6.71%, N = 10.36%, O = 11.84%) as a standard before any sample analysis - the calibration values having to be within certain recommended limits.

4.3.3.2 Oxygen analysis of Kerogen samples by Perkin Elmer Model 240 Elemental Analyser

The kerogen oxygen analysis was performed separately from the CHN analysis following a modification to the combustion train (see Fig. 4.9). The analytical and the electronic systems remain unchanged. Between 1-3 mg kerogen sample is pyrolysed in helium at $975^{o}C$, over platinized carbon, and the resulting oxygen is converted to carbon monoxide. The carbon monoxide and other gases pass through free copper at $900^{o}C$, and through an external 'U' tube of Colorcarb where any acid gases are removed. The carbon monoxide and the remaining gases pass through copper oxide in the Oxidation tube at $670^{o}C$, where the carbon monoxide is converted to carbon dioxide. Any basic gases are removed by a water trap. The read out of the carbon detector is then recorded and used for the calculation of the oxygen content (expressed as a percentage by weight

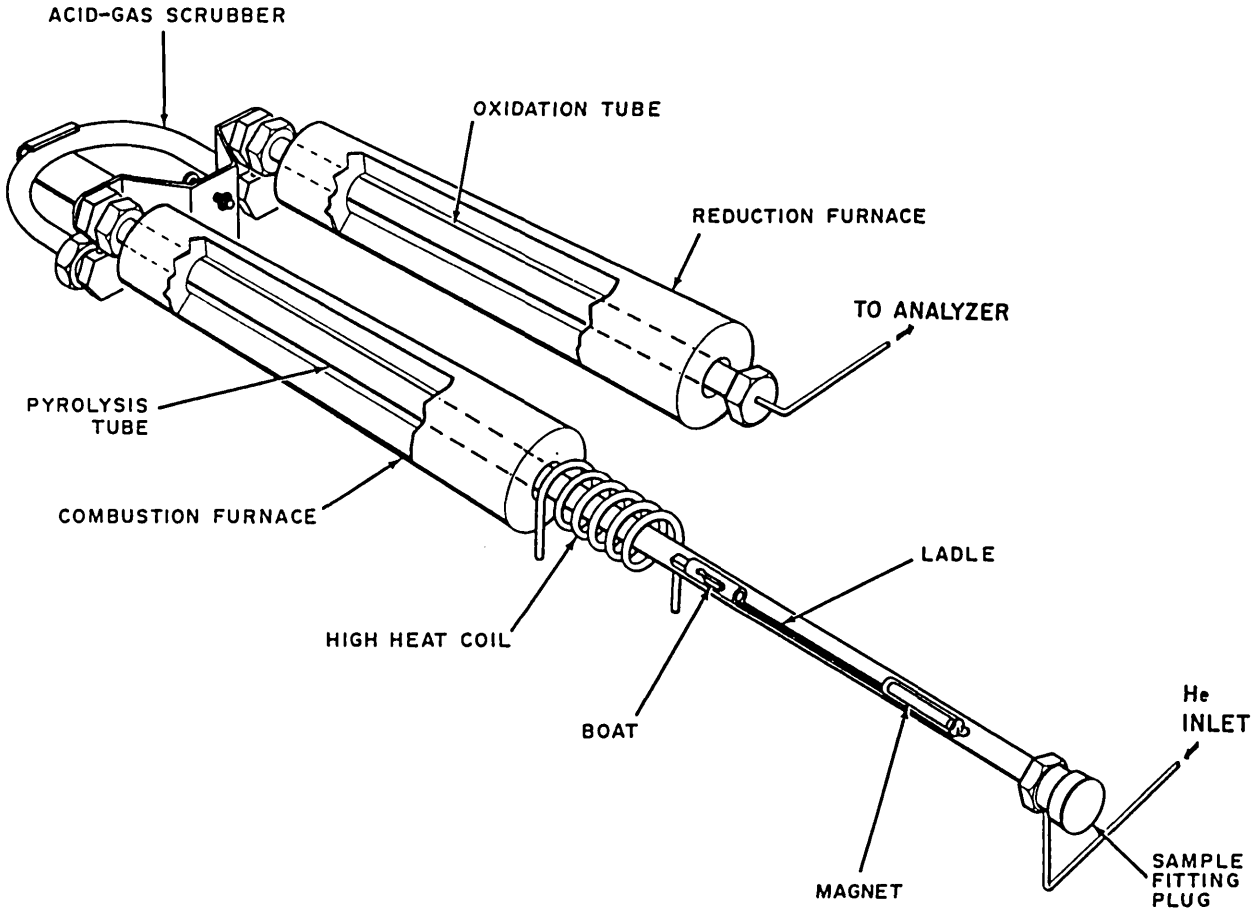


Fig.4·9 - Combustion Train, Oxygen Analysis

of the kerogen sample). The removal of any acid and basic gases is necessary to prevent an erroneously high read out from the carbon detector.

The oxygen, normally admitted through valve B (see Fig. 4.4) during CHN analysis, is shut off and the sample pyrolysis is carried out in an oxygen-free atmosphere.

The equipment was calibrated for oxygen each day using Benzoic Acid (Composition: C = 68.6%, H = 4.95%, O = 26.45%; N = O%) as the standard before kerogen analysis. The calibration value had to be within the recommended limits before kerogen samples were analysed.

4.3.4 Solvent Extraction of Soluble Organic Matter (bitumen) from rock samples

Extraction of soluble organic matter from powdered rock samples was carried out with the use of a stirrer. The stirrer consisted of an electrically driven rotor which revolved a stirring head. The stirring head (see Fig. 4.10) was a demountable unit consisting of a steel rod vertically fitted through two circular brass plates (3.3 cm diameter). The lower plate had six curved vanes each with a vertical projection of 0.6 cm from the plate surface. Each plate had six small holes arranged close to the edge.

5g of rock powder (<75 μ grain size) were extracted with 75 ml of distilled dichloromethane (boiling point = 38^{o}C) by stirring at 4000 r.p.m. for 30 minutes in a 252 ml-glass bottle. During the stirring, the mouth of the glass bottle was covered with a clean piece of aluminium foil

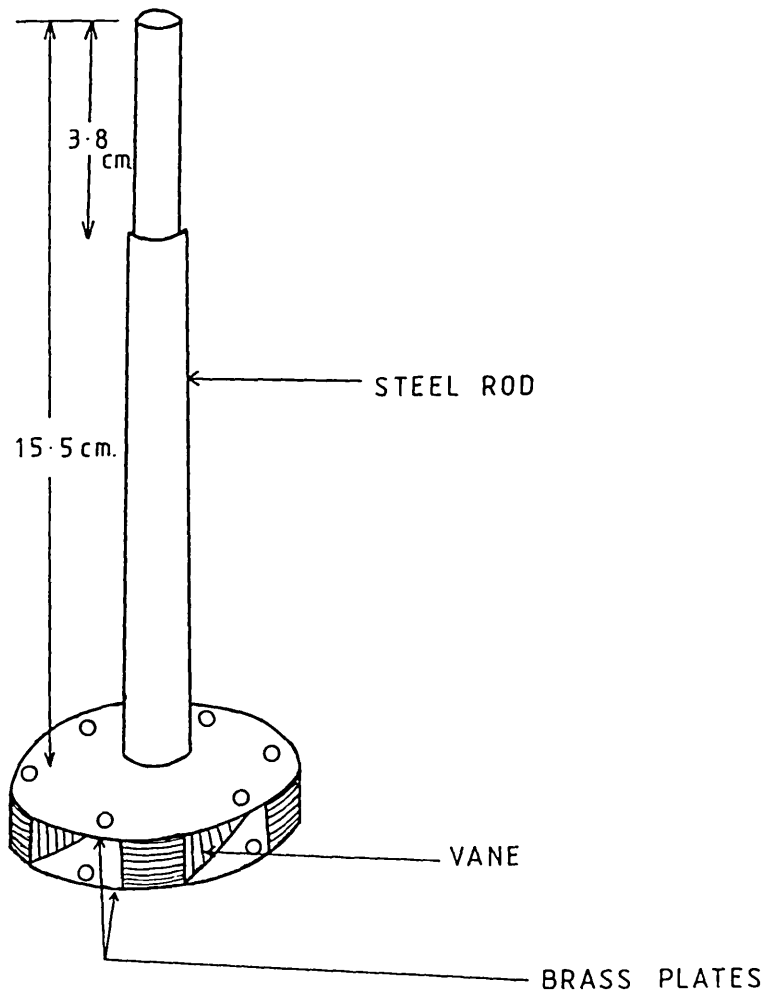


FIG. 4.10 THE STIRRING HEAD USED FOR BITUMEN EXTRACTION

(cleaned by dipping in dichloromethane for 5 minutes) to prevent excessive evaporation of the solvent. After stirring, a few millilitres of the solvent was used to wash the stirring head into the bottle, and everything was filtered through a pre-cleaned GF/C glass microfibre filter paper (retention: 1.2 μm) into clean pre-weighed glass tubes (10.0 x 2.5 cm). The procedure adopted for cleaning the filter paper consisted of wrapping it with aluminium foil and leaving in an oven at 350°C for one hour. The glass tubes were cleaned by washing with detergent, rinsed several times with distilled water, dried in air and then rinsed with dichloromethane. Neat solvent was used to wash the rock power on the filter as many times as necessary to ensure that most of the bitumen were removed from the rock sample. The filtrate was evaporated in an oven at 40° ± 2°C in a nitrogen atmosphere. Evaporation of the solvent was allowed till the weight of the extract (bitumen) was reasonably constant and the weight of the extract was recorded in milligrams.

Depending on the amount of rock sample available and also on bitumen richness of sample single, duplicate or triplicate extraction(s) per sample was carried out. Twenty eight (28) samples were extracted by the above described method in this project.

4.3.5 De-asphaltening of Rock Organic Extracts and Oils

In order to successfully fractionate the organic extracts (from rock samples) and the three oils (from Dorset) into saturates, aromatics and resins using high performance liquid chromatography (HPLC), it was necessary to first of

all precipitate out their contained asphaltenes. Asphaltenes are very high molecular weight, often undesirable, hetero-compounds in organic extracts and oils which, if not removed, can block HPLC columns with the consequent generation of back pressures which can cause leakage from the sample introduction devices.

4.3.5.1 Procedure for Extracts

n-Heptane (G.P.R. - I.P. Specification) was the organic solvent used for the asphaltenes precipitation. 200 micro-litres (μl) of solvent per milligram of extract was added to each bitumen sample in 10 x 2.5 cm pre-cleaned glass tubes. The added solvent was gently swirled around in the tube to dissolve out the hydrocarbons and the resins leaving the asphaltenes in precipitated form. After swirling the solvent for about 5 minutes, the tube with its content was centrifuged (using a bench centrifuge) at 3000 r.p.m. for 5 minutes. The centrifugation resulted in a compacted precipitation of the asphaltenes at the bottom of the tube leaving a clear solution above. By the use of a one-millilitre syringe and needle, the clear solution was trans-ferred to another clean tube and the precipitation procedure repeated. After the second precipitation, the solution of the de-asphaltened extract was transferred to a clean pre-weighed glass tube and the solvent was evaporated in an oven at $45^{o} \pm 2^{o}C$ in a nitrogen atmosphere. The solvent removal was continued until the weight of the de-asphaltened extract was constant within reasonable limits. The final weight of the extract was recorded (in mg). Similarly, the precipitated asphaltenes fraction was dried and its

weight recorded. Using these resulting two weights and the initial weight of total extract, it was possible to determine both the percentage recovery of extract and the proportion of asphaltenes in total extract. The percentage recovery for all the samples was always in excess of 94%.

4.3.5.2 Procedure for the Oils

Due to the very small quantities of asphaltenes in the Dorset oils, the above described method for extract was unsuitable for these oils. Hence a different procedure had to be adopted. n-Heptane was used as the asphaltenes precipitating solvent here. 500 µl of solvent per mg of topped oil were added to each oil in 10 x 2.5 cm cleaned glass tube. After gently swirling the solvent around in the tube for about 5 minutes, the mixture was left to stand for about 3 hours with the open end of the tube covered with cleaned aluminium foil. Each mixture was then filtered through a pre-cleaned and pre-weighed glass microfibre filter paper (with a retention of 1.2 µm) in a glass funnel. The cleaning procedure for the filter paper was the same as described under extraction, and involved heating the filter, wrapped in aluminium foil, at 350^{o}C for about 1 hour in an oven. The filtrate was collected in cleaned glass tubes. Using neat solvent (n-Heptane), the retained asphaltenes on the filter paper were washed several times to remove as much of the soluble materials as possible. The filter paper (with the retained asphaltenes) was dried in an oven at 45^{o} $\pm$ 2^{o}C and the weight of the filter paper

plus asphaltenes determined. The weight of the asphaltenes was then obtained by difference and the percentage of the asphaltenes in the total oil was calculated. The filtrate was evaporated in the oven to remove the solvent and the final weight of the deasphaltened oil was recorded. The calculated percentage recovery varied from 89% - 92% for the 3 oils. The relatively low recoveries recorded for the oils may be attributed partly to the very long period needed to remove all the solvent from the filtrate at $45^{o} \pm 2^{o}C$. This may have resulted in excessive loss of the light ends in the de-asphaltened oils.

Since it cannot be guarranteed that all the Heptane-soluble fraction was washed off the filter papers/asphaltenes during filtration, and also that there were no slight changes in the weights of the filter papers due to repeated washings, the asphaltenes percentages arrived at for the oils can only be regarded as approximate values.

4.3.6 Fractionation of the De-asphaltened Organic Extracts and the Oils into Saturates, Aromatics and Resins (Nitrogen, Sulphur, and Oxygen heterocompounds) by High Performance Liquid Chromatography (HPLC)

4.3.6.1 The Equipment

The HPLC set up used for this project is the system in Tilden Laboratory in the Chemistry Department of this College. It consists essentially of four main components - the solvent preparation and pressurisation unit, the sample introduction device, the column, and the detectors.

The solvent preparation and pressurisation component consists basically of a motorised piston pump from which a teflon tube, having a metal filter of 10 μm porosity at its end, leads to a solvent reservoir. The metal filter is to ensure that a clean, particle-free, solvent is pumped through the HPLC system. The pump used delivers solvent at a constant flow rate irrespective of the back pressure.

The sample introduction device consists of a micro-sampling injection valve with a detachable external sample loop. Sample loops of various capacities from 0.5 μl to several millilitres can be attached. But throughout this project only the 100 μl loop was used. The sample injection valve has two switches or setting positions: INJECT and LOAD. At the INJECT position, the loop is cut off from the general flow system, and it is at this position that a sample is injected into the loop using a syringe and needle. To introduce the sample into the carrier solvent (mobile phase), the valve is switched to the LOAD position - which opens the sample loop to the flow system.

The column used for the fractionation was a Spherisorb stainless steel column (S5W) of dimension 250 mm x 4.5 mm, packed with silica of particle size 5 μm. To further ensure that no particulate impurities entered the column, a pre-column packed with 10 μm silica was connected between the column and the sample introduction device. This acted as a filter to remove any suspended impurities in the sample introduced or in the mobile phase or in both. This precaution was necessary to prevent any column blockage

and the consequent buildup of back-pressure.

Two detectors - the Differential Refractometer (Model 1107 Refracto-Monitor) and the Double Beam Ultra Violet (UV) Detector (Cecil Instrument CE515) - were used to monitor the major components of the de-asphaltened oils and extracts. Both detectors employ for their detection two detector cells - the Reference and the Sample cells. The UV detection was at 254 nm wave-number. The minimum structural requirement of an organic compound for UV detection at 254 nm is usually a double-bonded chromophore to which is attached some structure with unapired electrons which enhances UV absorption: $\overset{X}{\underset{W}{|}} = Y$, where X and Y are carbon-contained molecular fractions (Snyder and Kirkland, 1974). As a result of the above requirement for UV detection, UV detectors are insensitive to the saturated compounds in oils and extracts and hence the use of a refractometer for their detection. The Differential Refractometer is a bulk-property detector which detects by continuously monitoring the difference in the refractive index (RI) between a Reference mobile phase (in the Reference detector cell) and a mobile phase containing a sample (in the Sample detector cell) as it elutes from the column. The Refractometer performance is often sensitive to temperature fluctuations if the HPLC system is operated at high flow rates (in excess of 1 ml/min). This is because high flow rates cause thermal equilibrium problems. This results from insufficient residence time for many organic solvents in the detector cell chamber to reach thermal equilibrium. And hence a temperature regulator is often necessary for operation at high flow rates.

4.3.6.2 The HPLC Operational Conditions

To eliminate the need for a temperature control unit, the solvent flow rate was set at 0.84 ml/min (i.e. less than 1 ml/min). The Differential Refractometer sensitivity was set at 4 (The Sensitivity Range is 1-32, with the sensitivity increasing with decreasing number). The sensitivity of the Double Beam UV Detector was set at 1.0 AUFS. The stationary phase was Normal Phase silica of 5 μm particle size packed in stainless steel column (250 x 4.5 mm) (S5W). Two mobile phases of different polarities were used to elute the three components (saturates, aromatics and resins) from the column. n-Heptane was first used to elute the saturates and the aromatics (the less polar components), followed by the use of a mixture of Dichloromethane (75%) and the Isopropanol (25%) to elute the resins - which are the more polar components. Elution of the three components was in order of increasing polarity: Saturates - Aromatics - Resins.

To elute the resins from the column, apart from the change in the mobile phase, other changes were necessary on the equipment settings. Due to the very strong adsorption of the resins to the polar surfaces of the column packing material (5 μm silica), in addition to the use of a polar mobile phase, the solvent flow rate of 0.84 ml/min was increased to 2.24 ml/min to enhance the elution of the resins. The Differential Refractometer was disconnected after the detection of saturates and aromatics before the changes in mobile phase and flow rate. The elution of the polars (resins) was thus indicated only by the UV detector.

The Double Beam UV detectors are not suitable for gradient elution (i.e. changes in mobile phase during a sample fractionation) due to the presence of a reference detector cell which, for a single sample analysis, can only be filled with the first mobile phase. Since the background UV absorptions are different for different solvents, any change in the mobile phase during a sample analysis results in detector outputs which cannot be compared. As a result, the UV detector output for the aromatics could not be compared with that for the resins.

The outputs of the two detectors were simultaneously recorded by a chart recorder operated at a chart speed of 10 mm/min.

4.3.6.3 Sample Analysis and collection of fractions

De-asphaltened bitumen was made up to a standard concentration of 2 mg/100 µl of n-Heptane, and 100 µl of sample solution were injected via a 100 µl sample loop. Elution of the 3 fractions was achieved as described above. Before each sample run, a standard mixture of pure hydrocarbon compounds was run to check the column performance. Examples of recorded outputs of the detectors for a standard and a sample are shown in Figs. 4.11 a and b respectively. It was noticed that after each complete sample analysis, the ability of the column to adequately separate the saturates from the aromatics in the standard (i.e. the column resolution) was seriously lowered - probably due to the effect of the fairly strong polar component (isopropanol) in the second mobile phase (see

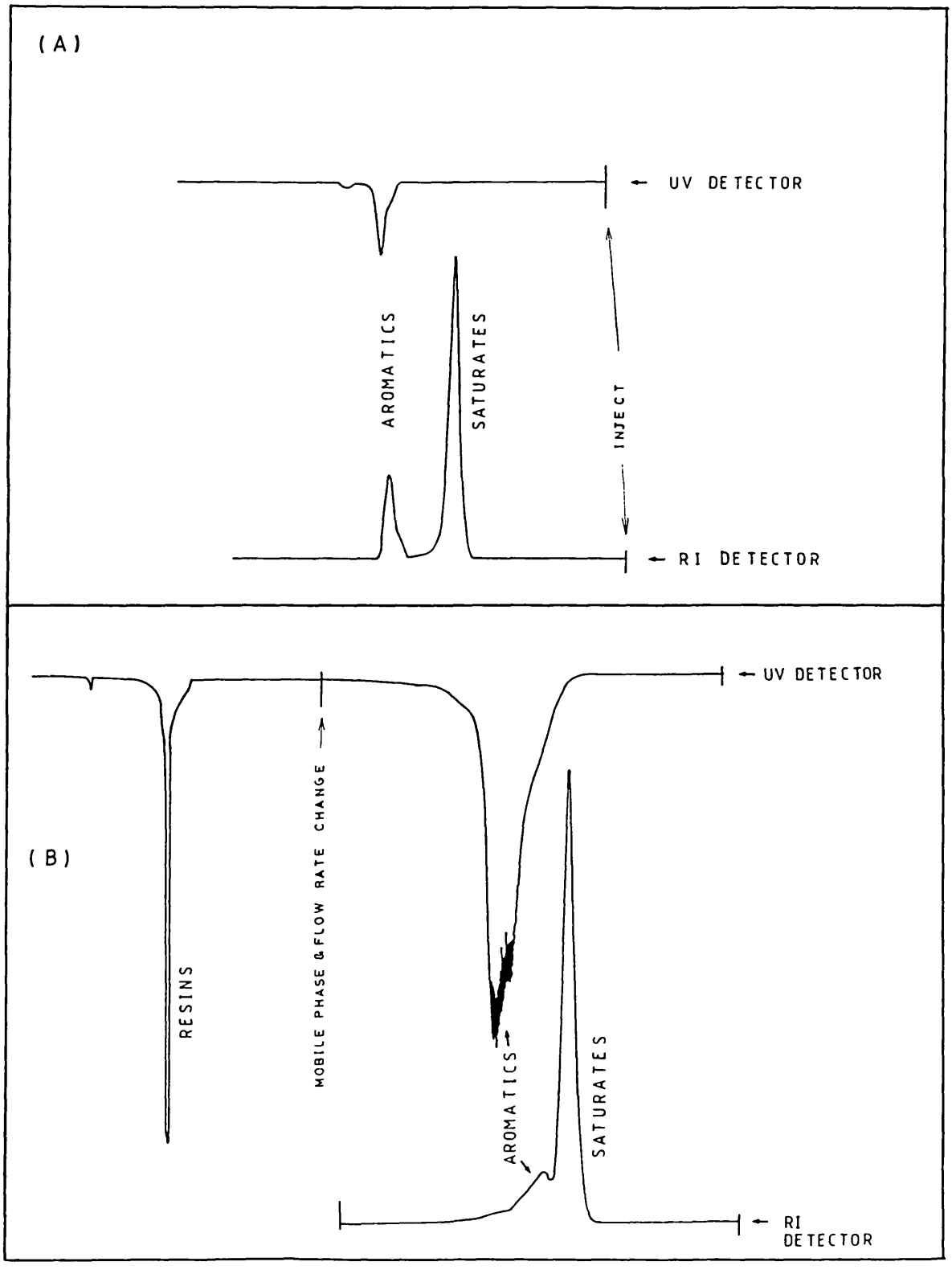


FIG. 4.11 EXAMPLES OF HPLC DETECTOR TRACES: (A) A 9:1 STANDARD MIXTURE OF SATURATES AND AROMATICS (B) A DE-ASPHALTENED SAMPLE (CORNBRASH OIL)

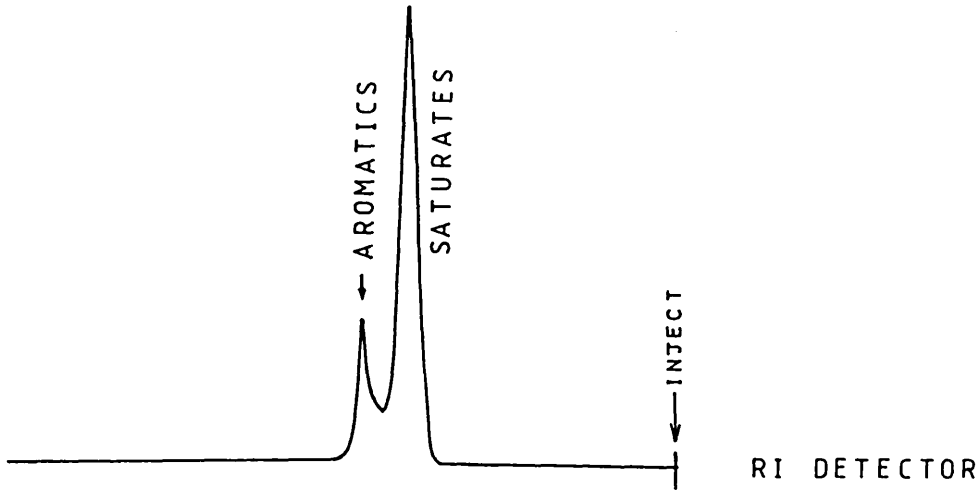


FIG. 4.12 A REFRACTIVE INDEX (RI) DETECTOR TRACE OF THE 9:1 STANDARD MIXTURE IMMEDIATELY AFTER A SAMPLE ANALYSIS INDICATING REDUCED COLUMN RESOLUTION

Fig. 4.12). To recondition the column after each sample analysis, the following procedure was adopted: (a) flush dichloromethane through the column at a flow rate of 2.24 ml/min for 40 mins (b) flush n-heptane through the column also at 2.24 ml/min flow rate for 40 mins. (c) Change the n-Heptane flow rate to 0.84 ml/min and allow the column and the detectors to reach equilibrium before running a standard.

It was observed that due probably to the presence of compounds of intermediate polarities between the purely saturated and the aromatic compounds in the samples, the chromatographic separation of these two groups was not very good (see Fig. 4.11b). Separate collection of the saturates and the aromatics was thus very difficult. To avoid losing any of the hydrocarbons, both groups (saturates and aromatics) were collected together as the Hydrocarbon fraction, and the resins were collected separately as the Non-Hydrocarbon fraction. Collections of the hydrocarbon and the non-hydrocarbon fractions were made using cleaned pre-weighed 10 cm x 2.5 cm glass tubes. In order to obtain sufficient separated fractions for quantitation purposes by weighing, duplicate runs were made for all the oils and the selected rock extracts. After collection of the fractions, the solvents were evaporated in an oven at $45^{o} \pm 2^{o}C$ in a nitrogen atmosphere till the weights of the fractions were reasonably constant. These weights (in mg) were recorded.

4.3.6.4 Calibration of the Relative Refractometer Responses to Saturates and Aromatics

In order to estimate the saturates/aromatics weight ratios in the deasphaltened oils and extracts using the refractometer responses, it was found necessary to calibrate the detector's relative responses to these two groups of compounds by the use of standard hydrocarbon mixtures. First of all, a mixture of saturated compounds and another of aromatic compounds were prepared using some of the authentic compounds known to be common constituents of petroleum (Hunt, 1979, p. 46; Kinghorn, 1983, pp. 72-79). The mixture of saturates was made from 4 ml of dodecane, 2 ml of cyclohexane, 2 ml of pristane and 2 ml of isooctane (2, 2, 4 trimethyl pentane); while the aromatic preparation comprised dissolving 30 mg of naphthalene in 6 ml of toluene. Standard solutions, containing varying weight ratios of the saturated and aromatic mixtures, were then prepared by adding 100 µl of n-heptane per 2 mg of the total hydrocarbon mixture (i.e. saturates + aromatics). The standard hydrocarbon solutions prepared for the calibration are shown in Table 4.1.

100 µl of each standard solution/mixture were injected into the HPLC mobile phase (n-Heptane) as described before. The two hydrocarbon groups were completely separated by the silica column and the responses of the detector were displayed by the chart recorder as two separate peaks. As stated before, being a normal phase liquid chromatography, the less polar component (saturates) were eluted first. Each standard solution was chromatographed twice as a check on the reproducibility of detection. The refractometer

TABLE 4.1 STANDARD SOLUTIONS USED FOR THE CALIBRATION OF THE DIFFERENTIAL REFRACTOMETER

Standard Solution No.	Wts. of Hydrocarbon Mixtures used for Standard Solution Preparation		Saturates/ Aromatics Wt. Ratio	Volume of Solvent (n-Heptane) used (ml)	Saturates/ Aromatics Peak Area Ratio
	Saturates (mg)	Aromatics (mg)			
1	108	12	9:1	6	3.80
2	96	24	4:1	"	1.55
3	90	30	3:1	"	1.08
4	84	36	7:3	"	0.90
5	72	48	3:2	"	0.59
6	60	60	1:1	"	0.39

responses to the saturated and aromatic components in the Standard Solution No. 1 have been shown on Fig. 4.11a. Before running each Standard mixture, care was taken to ensure that the column material and the refractometer cells were in good equilibrium with the mobile phase - as indicated by the relative steadiness of the recorder baseline. An electronic digitizer was used to compute the peak areas of the saturates and aromatics on each standard's chromatogram, and the saturates/ aromatic Peak Area Ratio calculated. These ratios, shown in Table 4.1 above, were used to construct a calibration curve for the Differential Refractometer (see Fig. 4.13).

4.3.6.5 Quantitative Estimations of the Compositions of the Analysed Oils and Extracts

Using the Detector Calibration curve (Fig. 4.13), the weight ratios of the saturates/aromatics in the hydrocarbon fractions were computed. As noted earlier, the separation of the saturates and the aromatics in the samples were not as good as observed for the standard solution. However, the peak area of each hydrocarbon group on a sample chromatogram was measured by dropping a perpendicular from the valley between the two peaks to the baseline (Synder and Kirkland, 1974). By using the saturates/ aromatics weight ratio (obtained from the calibration curve), the relative amounts of the Hydrocarbon and Non-Hydrocarbon fractions in the deasphaltened sample (from HPLC), and also the percentage of asphaltenes in total sample, the composition of each oil/extract was worked out as shown below, using as an example, sample OSD/KC.12 (extract).

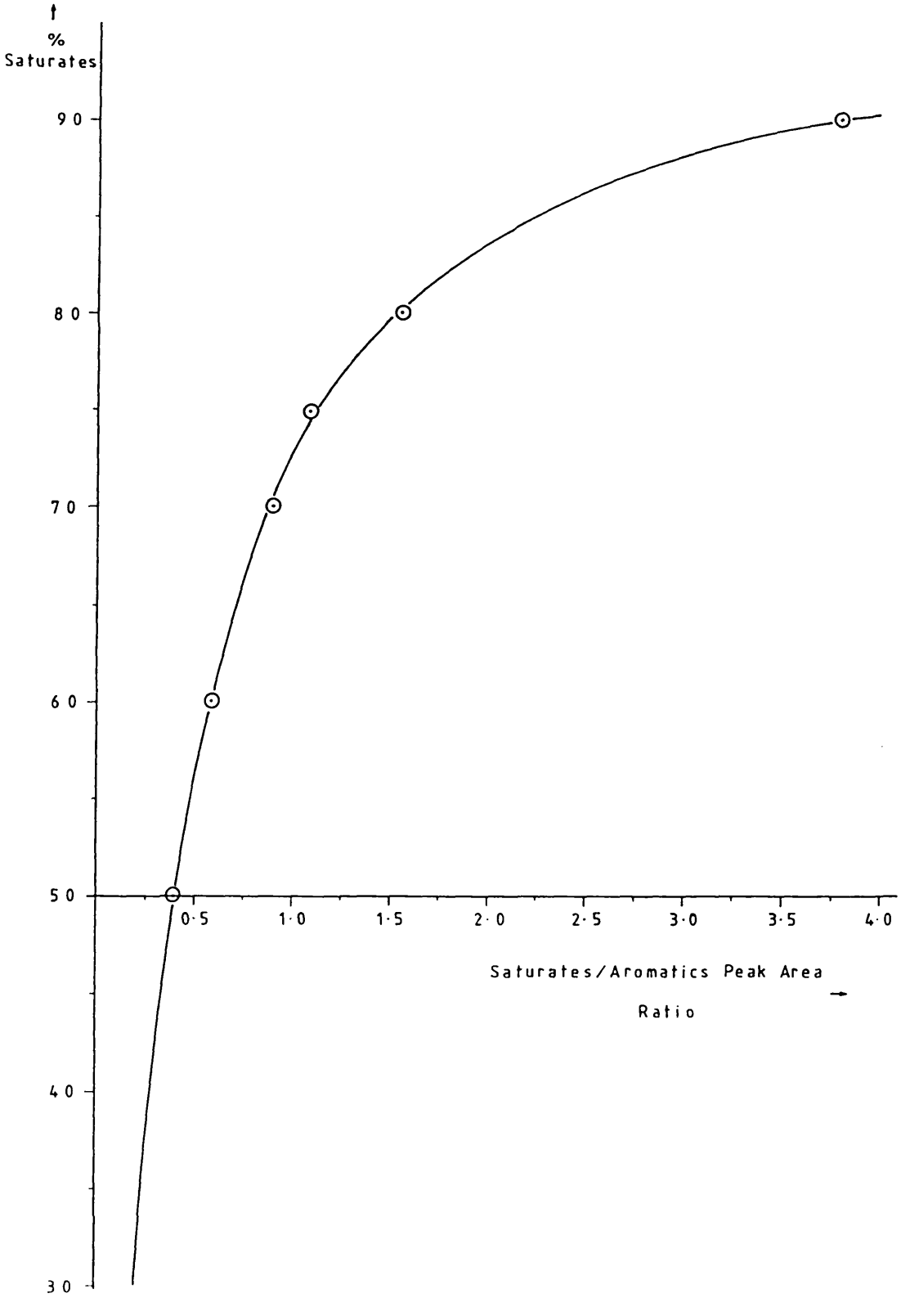


FIG. 4.13 CALIBRATION CURVE FOR THE HPLC DIFFERENTIAL REFRACTOMETER

Wt% of Asphaltenes in Total Extract = 23.72%

Wt% of Hydrocarbon Fraction in De-asphaltened Extract = 51.81%

Wt% of Non-hydrocarbon fraction in De-asphaltened Extract = 48.19%

Saturates/aromatics Peak Area Ratio = 0.98

Saturates/Aromatics Wt. Ratio (from calibration curve) = 2.57:1.00

Wt% of Saturates in De-asphaltened Extract = $\frac{(2.57)}{(2.57+1.00)}$ x 51.81%

= 37.30%

Wt% of Aromatics in De-asphaltened Extract = (51.81 - 37.30)%

= 14.51%

By re-calculation, taking into account the asphaltenes content of Total Extract :

The Wt% of Saturates in Total Extract = 28.45%

" " " Aromatics " " " = 11.07%

" " " Resins " " " = 36.76%

Adding: The Wt% of Asphaltenes in Total Extract = 23.72%

Total = 100.00%

A total number of 17 samples were analysed by this HPLC method.

4.3.7 Gas Chromatographic Analysis of the Oils and Organic Extracts

4.3.7.1 Principles of Analysis

The method of gas chromatography has been widely used in the compositional analysis of crude oils and soluble organic extracts from sedimentary rocks. In this method, the various components in a sample are separated in the gas phase. Separation is effected by passing the

sample vapour in a stream of inert "Carrier" gas (the mobile phase) through a chromatographic column which contains relatively non-volatile materials (stationary phase) that are capable of reversibly absorbing or adsorbing the components of the sample. This "sorption" process retards a component in its passage through the column to a degree that depends upon its partition ratio between the stationary and mobile phases. Since the ratio is different for the various components, they pass through the column at different rates, and are eluted in sequence from the end of the column through a detector, which gives an electrical signal related to the changing composition of the gas passing through it. This signal is converted to a suitable form for operating a potentiometric recorder, which draws a curve (the "chromatogram") showing the change in composition of the gas passing through the detector, thus illustrating the composition of the sample. It may be necessary to supply an output from the instrument to a data-handling system, such as an electronic integrator, if simultaneous quantitative analysis of the sample is required.

4.3.7.2 The Equipment and Sample Analysis

The apparatus used was a Perkin Elmer Model F30 Gas Chromatograph equipped with a 40 metre x 0.5 mm i.d. glass support coated open tubular (SCOT) capillary column, with GSC/OV101 as the stationary phase. An oxygen-free nitrogen (at 15 psi pressure control) was used as the carrier gas. A schematic diagram of the equipment is shown on Fig. 4.14.

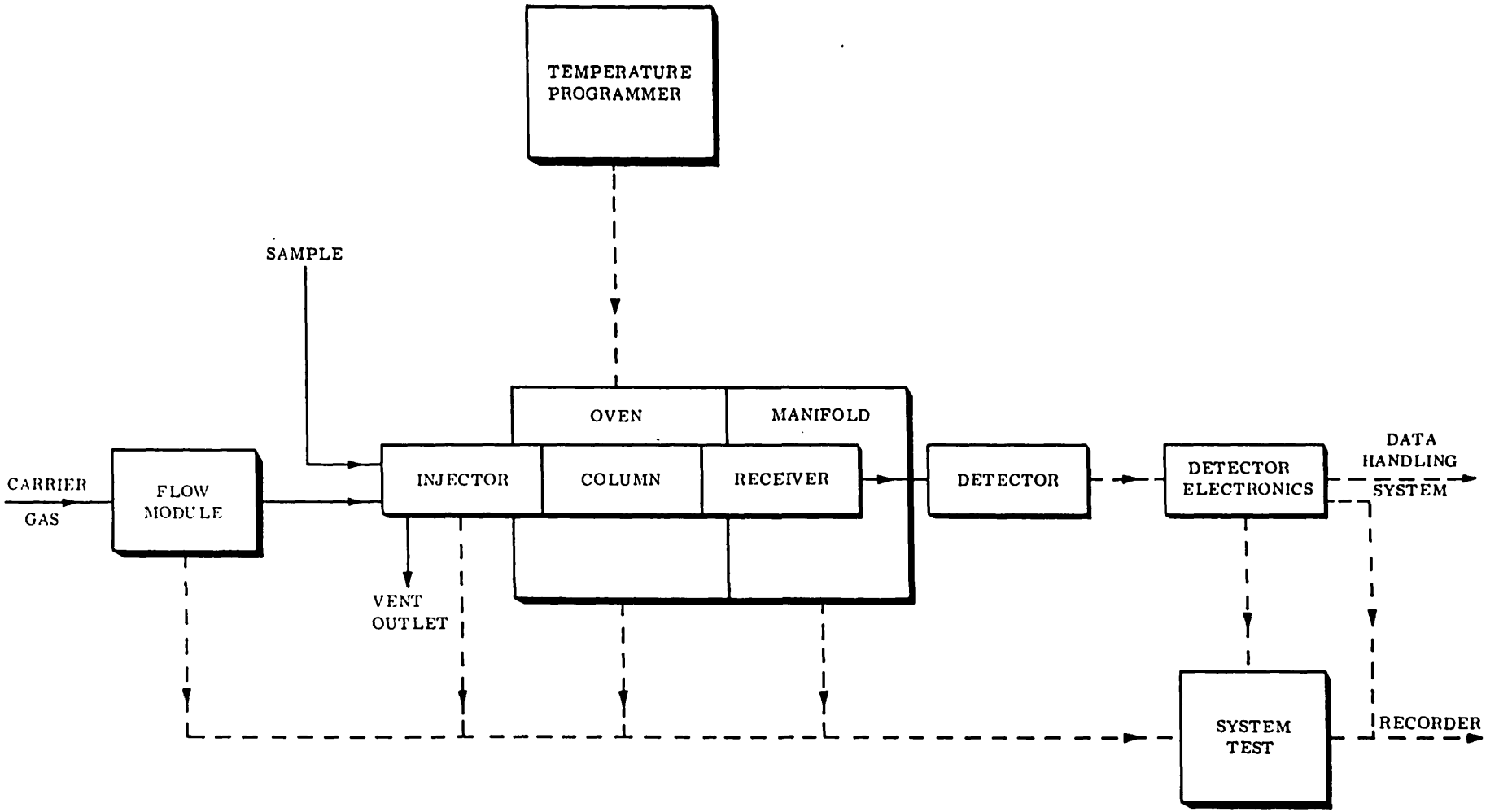


Figure 4-14 Model F30 Schematic Diagram

A sample was introduced into the column with the help of a 1 μl syringe and needle via a $^{1}/16$ inch (0.16 cm) injector maintained at 350°C. The temperature of the injector zone was selected to vaporize the sample into the carrier stream. The bulk of the column is suspended in an oven. The oven temperature, with an initial setting of 80°C, was programmed to rise during the course of each sample analysis, at the rate of 4°C/minute, to 270°C in order to accelerate the passage of sample components through the column. The other end of the column is connected to a receiver block, mounted in a thermal interface (the "manifold ") through which the gas passes to the detector. The detector used was a flame ionization detector (F.I.D.), and detection was by the changes that the sample components in the carrier gas produce in the electrical conductivity of a hydrogen flame (see Fig. 4.15). As shown, hydrogen gas and compressed air are separately supplied to the F.I.D. and their flow, like for the carrier gas, was regulated by pressure controls in the flow module set at 18 psi and 12 psi respectively. The temperature of the detection zone was maintained at 350°C. The detector output passes through an amplifier unit where the output sensitivity is adjusted before being displayed by a chart recorder. The chart recording speed was 5 mm/minute.

A total of 27 samples were analysed by this method, and these included the hydrocarbon fractions (from HPLC) of the 3 oils and 14 organic extracts, and 10 whole extract samples. The analysis was carried out under stringent dilution/injection/instrument sensitivity conditions.

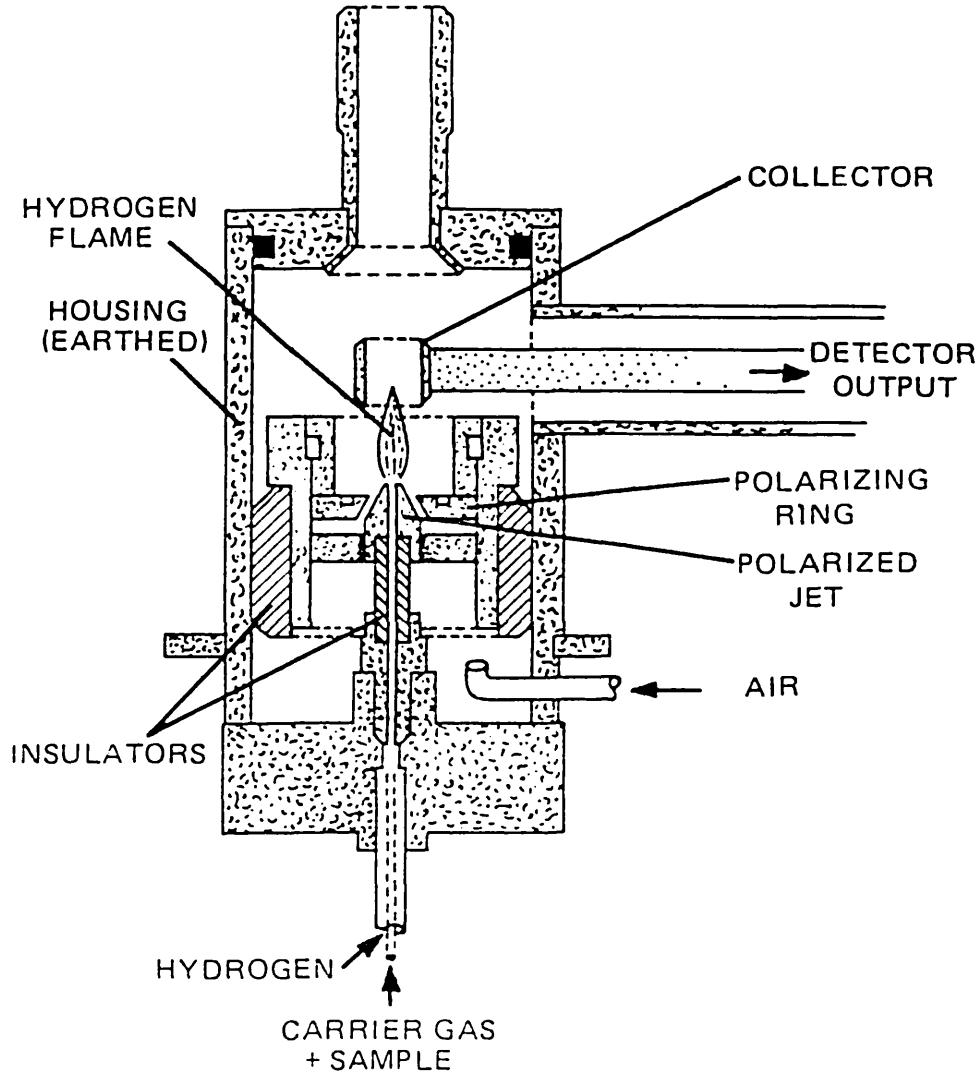


FIG.4.15- FID SCHEMATIC DIAGRAM.

In all cases, the solvent used for dilution of sample was distilled iso-octane. The addition of this solvent to the whole extract samples also helped in precipitating the asphaltenes so that only the solutions of the hydrocarbons plus the resins were injected into the column.

4.3.7.3 Identification of the eluted sample components and Quantitative Analysis of the Sample

Only the n-alkanes and the isoprenoids - Pristane and Phytane - were identified. Their identification was achieved by comparison of their retention times with those of authentic compounds in a standard mixture.

The quantitative estimate of each identified sample component was carried out by its peak area or peak height measurement on the chromatogram. As a result of the tall and narrow peak shapes, and the relatively poor separation, in many cases, between pristane and n-C_{17} and between phytane and n-C_{18}, the quantitative estimate of each of these four components was by peak height measurement (Stock and Rice, 1974). These peak height values were used for the calculation of $^{Pristane}/_{Phytane}$, $^{Pristane}/_{n\text{-}C_{17}}$, $^{Phytane}/_{n\text{-}C_{18}}$ and $^{(Pristane + Phytane)}/_{(n\text{-}C_{17}+n\text{-}C_{18})}$ ratios. For normal alkane components with carbon number from 19 to 30, estimates of their relative amounts was by peak area measurement - approximated by multiplying the peak height by the peak width at half the peak height (Schenck and Eisma, 1964; Albrecht et al., 1976). Carbon Preference Index (CPI) in the C_{24} - C_{30} n-alkane range was calculated using the method of Vandenbroucke et al. (1976) with:

$$CPI = \frac{2(n\text{-}C_{25} + n\text{-}C_{27} + n\text{-}C_{29})}{n\text{-}C_{24} + 2(n\text{-}C_{26}) + 2(n\text{-}C_{28}) + n\text{-}C_{30}}$$

In an attempt to check on the marine/non-marine origin of the oils the ratio: $(n\text{-}C_{21} + n\text{-}C_{22})/(n\text{-}C_{28} + n\text{-}C_{29})$ was calculated for the oils and some organic extract samples (Phillipi, 1974).

4.3.8 Pyrolysis Techniques

4.3.8.1 Introduction

The artificial maturation of kerogen, whether with or without its accompanying inorganic rock matrix, in the absence of oxygen is referred to as pyrolysis (Kinghorn, 1983). This analytical technique has useful applications in assessing sedimentary organic matter type, its hydrocarbon generating potential, as well as the level of maturation. This organic matter study technique is basically an extension of the pyrolysis of oil-shales to produce commercially useable quantities of hydrocarbons, but on a much smaller scale. Being a laboratory simulation of the thermal generation of hydrocarbons in the subsurface, pyrolysis of organic matter often requires heating at much higher temperatures than obtained in the subsurface. The high pyrolytic temperatures are designed to compensate for the very short periods of the laboratory simulation experiments.

There are two main groups or types of pyrolysis techniques currently being employed in organic matter study (Kinghorn, 1983) - the variable or programmed

temperature pyrolysis and the fixed temperature pyrolysis. The programmed temperature pyrolysis entails the subjection of organic matter to a progressively increasing temperature over a given period of time, whereas the fixed temperature type is the one in which the organic matter is heated for a given period of time at a constant temperature. In this project, two pyrolysis methods, both of variable temperature type, were used to investigate the organic matter type, maturity and generation potential - (i) programmed temperature pyrolysis of whole rock samples with Flame Ionization Detection of evolved hydrocarbons (ii) programmed temperature pyrolysis of kerogen sample with a gas chromatographic analysis of the generated bitumen.

4.3.8.2 Programmed-Temperature Pyrolysis of Whole Rock Samples

4.3.8.2.1 Principles of the Method:-

Organic matter in sedimentary rocks is often composed of two phases - the already generated liquid material (bitumen) which is solvent extractable, and the partially converted (thermal) solid kerogen. These will be present in varying amounts depending upon the maturation level and, to a lesser degree, the occurrence of migration (Barker 1974; Tissot and Welte, 1978; Kinghorn, 1983). Thus, when a rock sample is heated at a steadily increasing temperature the first thing that happens is the volatilization of the free, already generated hydrocarbons present as such in the rock at a low temperature. Second is the evolution of hydrocarbons from the thermal breakdown of kerogen at a much increased temperature.

The pyrolysis of the rock sample is carried out in a temperature - programmable oven in the presence of an oxygen-free carrier gas which prevents oxidation of the organic matter and sweeps any evolved materials during the heating process into a flame ionization detector (FID). The detector responds only to the total amount of the hydrocarbon fraction of the product and not to the inorganic components such as water and carbon dioxide. The thermal distillation of the already generated bitumen in the rock results in a low temperature response of the FID in the form of a peak (called P_1). The hydrocarbons generated by the pyrolytic degradation of the kerogen produce a second peak response by the detector (called P_2). The pyrolysis temperature at which the maximum amount of P_2 compounds are generated is referred to as the T_{max} (Peters et al., 1983; Dembicki et al, 1983).

The generative potential of a suspected source rock is given by the ratios of the peak sizes (P_1/P_2, P_1/P_1+P_2). In general, as the sample depth or maturity increases, the relative size of the low temperature peak (P_1) increases and the T_{max} value also increases (Barker, 1974; Tissot and Welte, 1978, Dembicki, 1983; Peters et al., 1983). In the absence of migration, the ratio of the first peak to both peaks (i.e. P_1/P_1+P_2), referred to as the Transformation Ratio (Tissot and Welte, 1978) or the Generative Index (Barker, 1974), gives the relative amount of hydrocarbons generated to the total potential of hydrocarbon generation. This ratio increases with increasing maturity of the rock.

The absolute pyrolysis temperatures at which the second peak reaches maximum detector response (i.e. T_{max}) are known to have no significance because they vary with the heating rate (Brown, 1957; Juntgen and Van Heek, 1968). However, it has been shown that for any given heating rate T_{max} values increase with increasing organic maturity (Van Krevelen et al., 1951; Juntgen and van Heek, 1968; Espitalie et al., 1977; Dembicki et al., 1983; Peters et al., 1983), and it may be related to other maturation parameters, for example vitrinite reflectance values (R_o%) (Ekweozor and Gormly, 1983). As noted by Dembicki et al., (1983) T_{max} being a bulk chemical parameter is influenced by both maturity and kerogen type. At any given level of maturity, and for a given heating rate, significant variations in T_{max} may occur. The variation depends on the relative concentration of kerogen components in the rock sample and their normalized pyrolytic yields (Girling, 1963; Tissot et al. 1974; Larter et al., 1977).

4.3.8.2.2 Equipment:-

The pyrolysis apparatus used for this whole rock analysis was made in our Organic Geochemistry Laboratory consisting of the following components (Fig. 4.16). The central unit is a stainless steel pyrolysis tube lined on the outside with a quartz tube, and brazed at one end to a rectangular heated block (maintained at 320^{o}C). From the heated block, a short upright tube of 1.5 mm internal diameter leads to a flame ionization detector (FID)

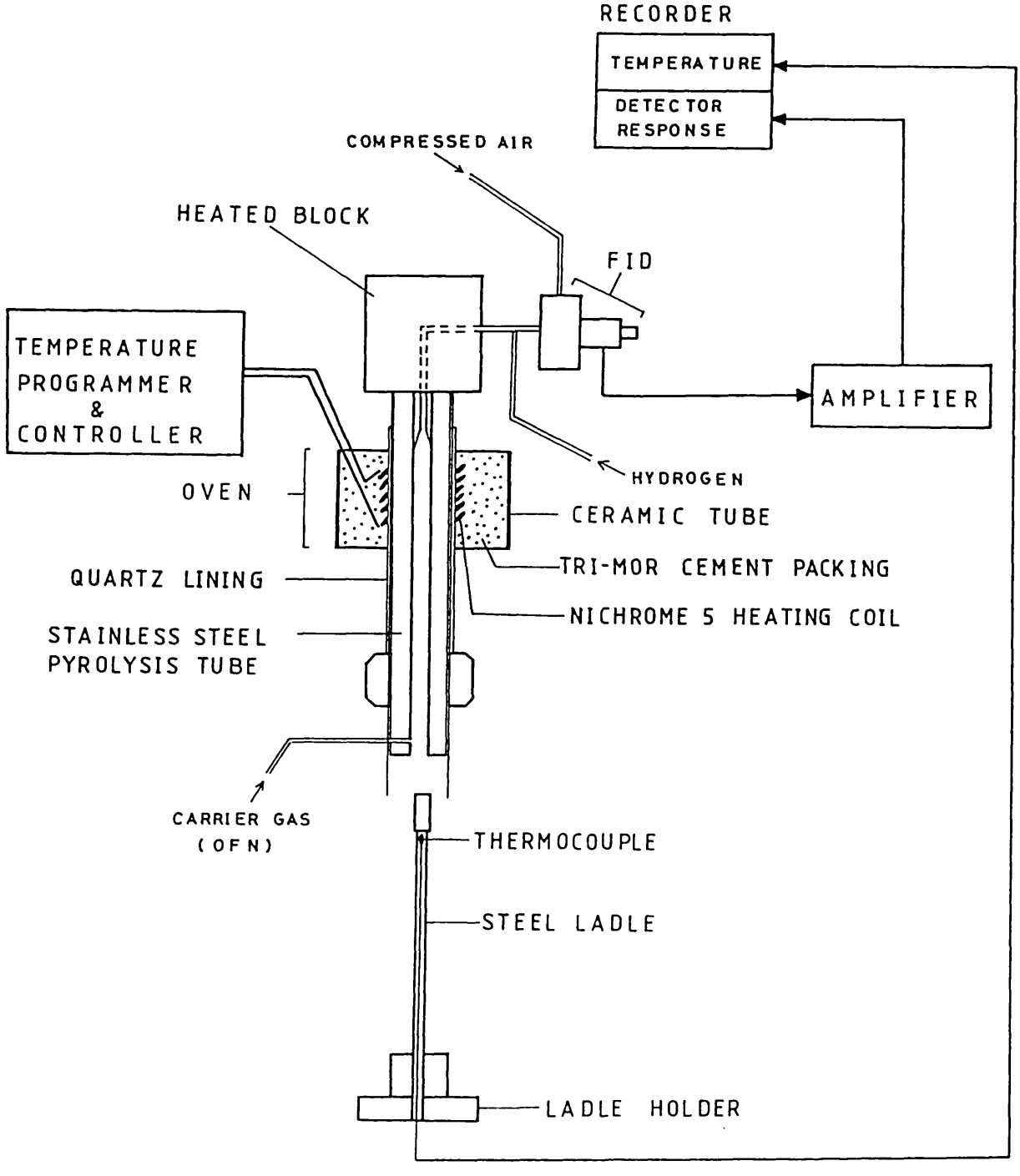


FIG. 4.16 SCHEMATIC DIAGRAM OF THE WHOLE-ROCK PROGRAMMED-TEMPERATURE PYROLYSIS APPARATUS

which is maintained at 210°C. The pyrolysis tube is 16 cm long and has a variable internal diameter, as shown in Fig. 4.16. The bore of the tube is 5 mm from the open end to about the end of the heated zone, after which it narrows to 1.5 mm. A bore of similar diameter (i.e. 1.5 mm) passes through the heated block to the F.I.D.. The fine size of the bore from the oven to the detector was designed to keep the dead volume down as much as possible to avoid excessive temperature drop. The stainless steel tube is heated by a small tubular oven (about 1.5 cm long) close to the heated block end. The oven, which consists of a fine Nichrome 5 heating coil (0.9 mm diameter) wound round the quartz liner on the steel tube, is controlled via a transformer by a Eurotherm Temperature Programmer - Controller unit. To prevent any significant heat loss, the heating coil is covered by a considerable thickness of TRI-MOR air setting cement packed in a ceramic tube. The cement is able to withstand temperatures of up to 1400°C before getting brittle. The oven is maintained at an initial temperature of 250°C.

The carrier gas used was oxygen-free nitrogen (OFN) at a flow rate of 20 cc/min. Hydrogen gas and compressed air are separately introduced into the F.I.D. (see Fig. 4.16) at flow rates of 140 and 60 cc/min respectively. The detector output is displayed via an amplifier on a chart recorder.

A weighed rock sample in a nickel boat is introduced into the hot zone of the pyrolysis tube by the help of a steel ladle. The ladle carries a thermocouple fixed very close to the sample thus making it possible to

accurately record the temperature of the heated zone during the temperature programming, and hence the determination of T_{max}. The ladle is fitted through an O-ring in the holder and this enables a to- and fro-movement of the ladle through the holder while preventing entry of air into the pyrolysis tube. The ladle holder is fitted tightly to the open end of the pyrolysis tube with the help of another O-ring. A thin steel partition separates the thermocouple from the sample compartment of the ladle to prevent the escape of the carrier gas to the outside through the ladle.

4.3.8.2.3 Operating Procedure and Sample Analysis:-

A known weight (5 - 30 mg) of powdered rock sample (<75 μm grain size) was placed in a nickel boat. After making sure the equipment has attained its optimum operating conditions (as mentioned in previous section), the steel ladle with the holder was removed from the pyrolysis tube and allowed to cool to ambient temperature. The boat with the sample was loaded into the ladle. By moving the ladle through its holder, the sample was first introduced into the cold part of the steel tube and the ladle holder was then tightly fitted to the open end of the pyrolysis tube. The set-up was purged for 3 minutes - to sweep out any oxygen introduced into the system during the loading of the sample. Again by moving the ladle through the O-ring in its holder, the sample was injected into the hot zone at 250^{o}C and left at this temperature for 5 minutes to volatilize the already generated bitumen in the sample. The programmer was then started and the kerogen

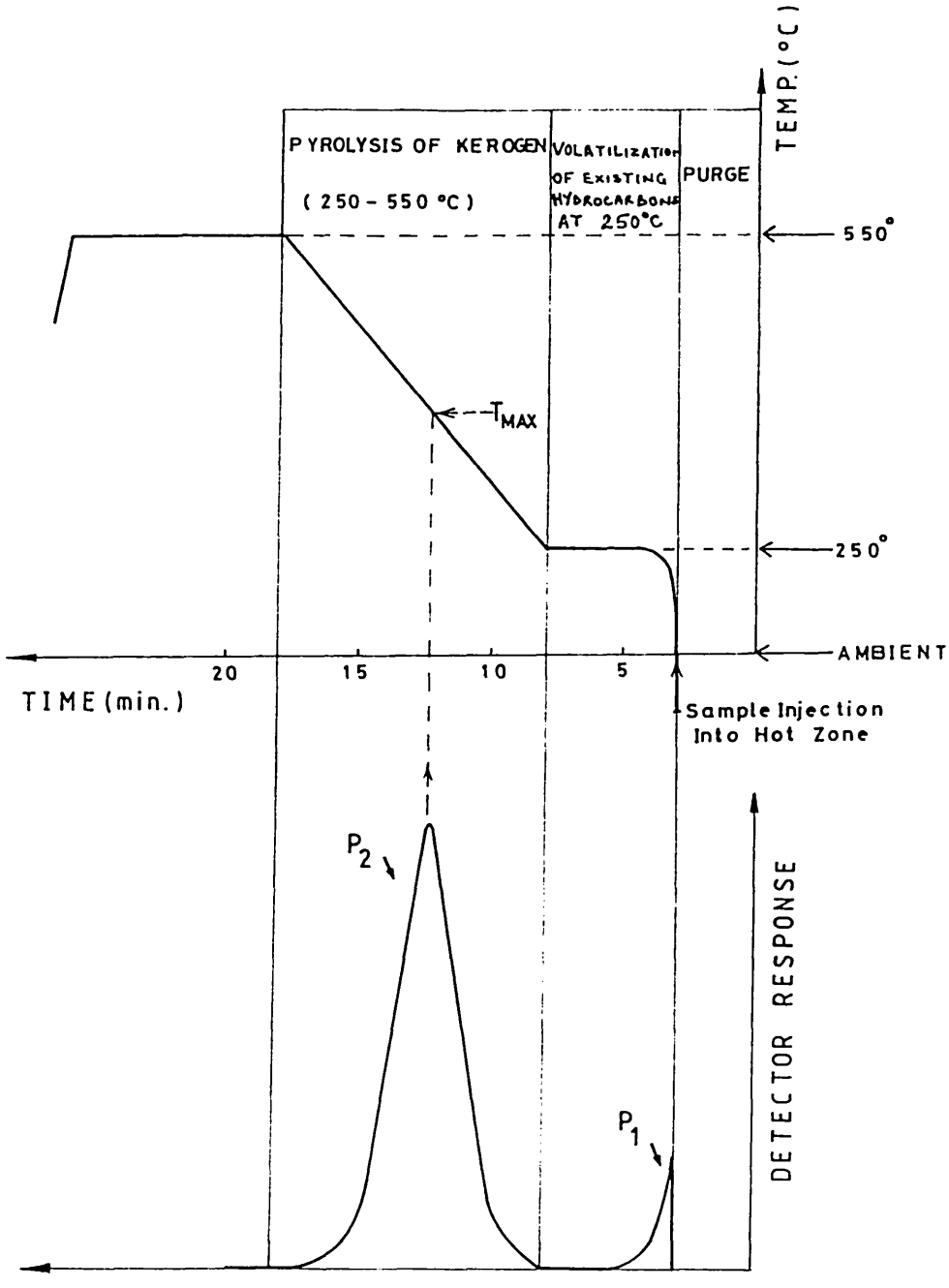


FIG. 4.17 PROGRAMMED PYROLYSIS: A DIAGRAMATICAL ILLUSTRATION OF ANALYTICAL STEPS AND AN EXAMPLE OF A RECORDED DETECTOR RESPONSE (PYROGRAM)

was pyrolysed by heating the sample from 250^{o} to 550^{o}C at the rate of 29.4^{o}C/minute. A diagrammatic illustration of the stages of sample analysis and an example of a recorded detector response is shown in Fig. 4.17. At the end of the temperature programme, sufficient time was allowed for the detector response to return to the background level and the programmer was switched off. The oven then cooled gradually back to 250^{o}C.

A total of twenty seven whole rock samples were analysed by this method.

4.3.8.2.4 Influence of Sediment Mineralogy on the Evolution of organic compounds by pyrolysis:-

It is now known that sedimentary minerals are capable of retaining and altering both the polar and non-polar organic compounds by surface and/or inter-layer effects (Jurg and Eisma, 1966; Henderson et al. 1968; Galwey, 1969; Shimoyama and Johns, 1971). To demonstrate the retention properties of sedimentary minerals, Dembicki et al. (1983) adsorbed normal eicosane (n-C_{20}) on various minerals and then subjected the adsorbed alkane to programmed temperature pyrolysis. The result of the pyrolysis indicated that although the total product yield was not severely altered in any case, the minerals retarded the release of the n-eicosane to varying degrees, thus resulting in organic material that should belong in P_1 being released at a higher temperature and included in P_2. Espitalie et al. (1980) showed that the yields of kerogen pyrolysates are controlled by the concentration and type of mineral

substrates. The pyrolysates appeared to be trapped on active sites and subsequently released by thermal cracking at higher temperatures. This mineralogy effect was most noticeable with rock samples that had low organic carbon concentrations (less than 1.0%). In rich samples with TOC > 1.0% the retention and/or cracking effect was found to be unimportant - possibly due to the de-activation of the reactive sites by the pyrolysates (Dembicki et al., 1983).

In this project, only rock samples with total organic carbon content in excess of 1% were analysed by this pyrolysis method to minimize the mineralogy effect.

4.3.8.3 Kerogen Programmed Temperature Pyrolysis - Gas Chromatography

The programmed-temperature pyrolysis - gas chromatography set-up employed essentially a Perkin Elmer Model F30 Gas Chromatograph in which the injector had been replaced with a programmable stainless steel furnace. The furnace was heated by low resistant wires and the furnace temperature was controlled via a step-down transformer by a muffle-furnace temperature controller. The gas chromatograph detector (FID) response was displayed via an amplifier unit by a chart recorder operated at a speed of 5 mm/min.

Kerogen sample (0.5 - 2 mg), in a nickel boat loaded into a steel ladle, was first introduced into the cold zone of the furnace, and the furnace was purged for 2 minutes. The chart recorder was started as soon as the

sample was placed in the cold zone of the furnace. After the two minute purge, the sample was injected into the hot zone at 150°C and immediately the temperature programmer was started by adjusting the temperature controller setting to the furnace temperature equivalent of 550°C. The kerogen was then rapidly pyrolysed from 150° - 550°C (in helium carrier gas) in 9 minutes. On completion of the pyrolysis, the gas chromatograph oven was closed, and after 2 minutes its temperature programme was started and the kerogen pyrolysis products were then analysed by gas chromatography. The gas chromatograph temperature programme involved a 3-minute purge and a temperature rise from 80° - 270°C at the rate of 4°C/minute (the gas chromatograph settings here were similar to the ones described under gas chromatographic analysis of oils/extracts).

Identification of the normal alkane components of the pyrolysates was achieved by comparison of their retention times with those of authentic compounds in a standard mixture gas chromatographed (after disconnecting the pyrolysis furnace) using the same procedure as for the pyrolysates.

Thirteen kerogen samples were subjected to this analytical procedure.

4.3.9 Infra-Red (IR) Spectroscopic Analysis of Kerogen and Oil Samples

4.3.9.1 Principles of the Method

The application of Infra-Red Spectroscopic technique in organic geochemical studies is based on the fact that

molecular vibrations of certain functional groups/radicals in sedimentary organic matter are known to absorb characteristic radiation frequencies in the Infra-Red region of the spectrum.

A molecule may be considered to be a group of atoms bound together in a certain geometric configuration by elastic bonds formed by the electron clouds around atomic nuclei. These elastic bonds allow the atoms to vibrate about a mean position. These apparently random molecular vibrations have been shown to consist of an integral number of periodic vibrations each of a definite frequency. Molecular vibration frequencies are found to be of the same order as those of the Infra-Red radiations - 12 x 10^{13} to 0.6 x 10^{13} cycles/second (or 4000 - 200 cm^{-1} wave-number units). If a characteristic vibration causes a periodic change in electric dipole moment of the molecule, electromagnetic radiation of the same frequency will interact with the molecule. This interaction excites the fundamental vibrational mode and results in a resonant energy transfer in which radiation energy is absorbed by the molecule.

A record of the absorption of Infra-Red energy as a function of the frequency of the incident radiation gives the Infra-Red spectrum of the sample. The molecular groups present in the organic matter are indicated by the frequencies or wave numbers at which absorption bands are observed. And since the degree of absorption is proportional to the amount of molecular species present, a sedimentary organic matter can be characterised in terms of type and/or maturity from its Infra Red Spectrum.

4.3.9.2 Instrumentation

The spectra of the kerogen samples were run using a Perkin Elmer Model 457 Grating Infra-red spectrophotometer with a wavenumber scan range of 4000 to 250 cm^{-1}, whereas those of the oil samples were run with a Perkin Elmer Model 157 Sodium Chloride Infra-red Spectrophotometer The wave number scan range of the Model 157 is from 4000 to 650 cm^{-1}.

The wave number scale of the Model 457 is graduated in three regions: 4000 to 2000 cm^{-1}, 2000 to 600 cm^{-1}, and 600 to 250 cm^{-1}, corresponding to the second and first orders diffraction of the 100 lines per millimetre (100 l/mm) and the first order of the 25 l/mm grating respectively. During a complete operating cycle of the instrument, seven different filters are automatically placed in the radiation path. The sequence of the gratings and their orders and the filter sequence are listed in Table 4.2 below.

TABLE 4.2 SEQUENCE OF THE GRATINGS AND THEIR ORDERS AND THE FILTER SEQUENCE IN A COMPLETE ANALYTICAL CYCLE OF MODEL 457 INFRA-RED SPECTROPHOTOMER (Perkin Elmer)

Region (cm^{-1})	Grating	Order	Filter Range
4000 to 2000	100 l/mm	Second	1. 4000 to 3100 2. 3140 to 2480 3. 2520 to 2000
2000 to 600	100 l/mm	First	4. 2000 to 1150 5. 1170 to 700
600 to 250	25 l/mm	First	6. 720 to 410 7. 425 to 250

By contrast, the Model 157 does not have the grating system but relies on a complicated and delicate optical system between the sample area and the detector - some components of which are manufactured from sodium chloride (rock salt) which is very hygroscopic. For proper functioning of this model care had to be taken not to upset the preset optical system and also to maintain the optical compartments as dry as possible using a good dessicant such as silica gel.

In both models, the radiated energy from the source is split into two beams by a set of mirrors - one beam passes through the sample which absorbs certain characteristic wavelengths whilst the other serves as a reference.

For the spectrum scan of each sample the following instrument settings were used: the SLIT control was at Normal; the Gain setting was Moderate; and the Scan Mode was at Slow - for high resolution scanning. Each day before use, the equipment was switched on, left to warm up for 30 minutes and then calibrated by scanning a Polystyrene film supplied with the instrument as the Standard.

4.3.9.3 Kerogen Sample Preparation and Analysis

2 mg of dry kerogen sample and 200 mg of potassium bromide (KBr - Analytical grade) were homogenized by grinding to a fine powder using a clean agate mortar and pestle. Care was taken to avoid introduction of impurities. The sample mixture was dried for 24 hours in an oven at $40^{o} \pm 2^{o}C$ and then left in a dessicator for about a week for further drying.

A micro Die with a trade name SPECADIE, supplied by Analytical Accessories Ltd., Kent BR5 3QX, UK, was used to press the dried KBr-sample mixture into pellets of 9 mm diameter. The micro Die consists of a Short Bolt, a Short Bolt Seal, an Evacuation Tube, the Die Body, a Long Bolt and a Long Bolt Seal (see Fig. 4.18a). Before each sample pellet preparation, all the metallic components of the Die which actually make contact with sample (the Short Bolt, the Die Body, and the Long Bolt) were thoroughly washed in an organic detergent, rinsed in distilled water and blown dry using compressed air from a tap. A bench spanner, of the type shown on Fig. 4.18c, was used to hold the Die securely upright when charged with sample mixture and during pressing and evacuation. To prepare a pellet, the following steps were followed:-

(a) the Short Bolt, holding the Short Bolt Seal, was screwed into the Die Body so that the Short Bolt Seal was compressed by about 25% thus ensuring a vacuum tight seal.

(b) the Short Bolt head was inserted into the female hexagon of the bench spanner, thus keeping the Die (with one end open) upright.

(c) Using a clean glass funnel, about 0.2 ml of KBr-sample mixture was poured into the Die aperture. The sides of the Die Body were lightly tapped so that the mixture was evenly distributed across the face of the Short Bolt.

(d) The Long Bolt, with its Seal, was screwed into the Die Body, as shown on Fig. 4.18a until the seal was slightly compressed forming a vacuum tight seal.

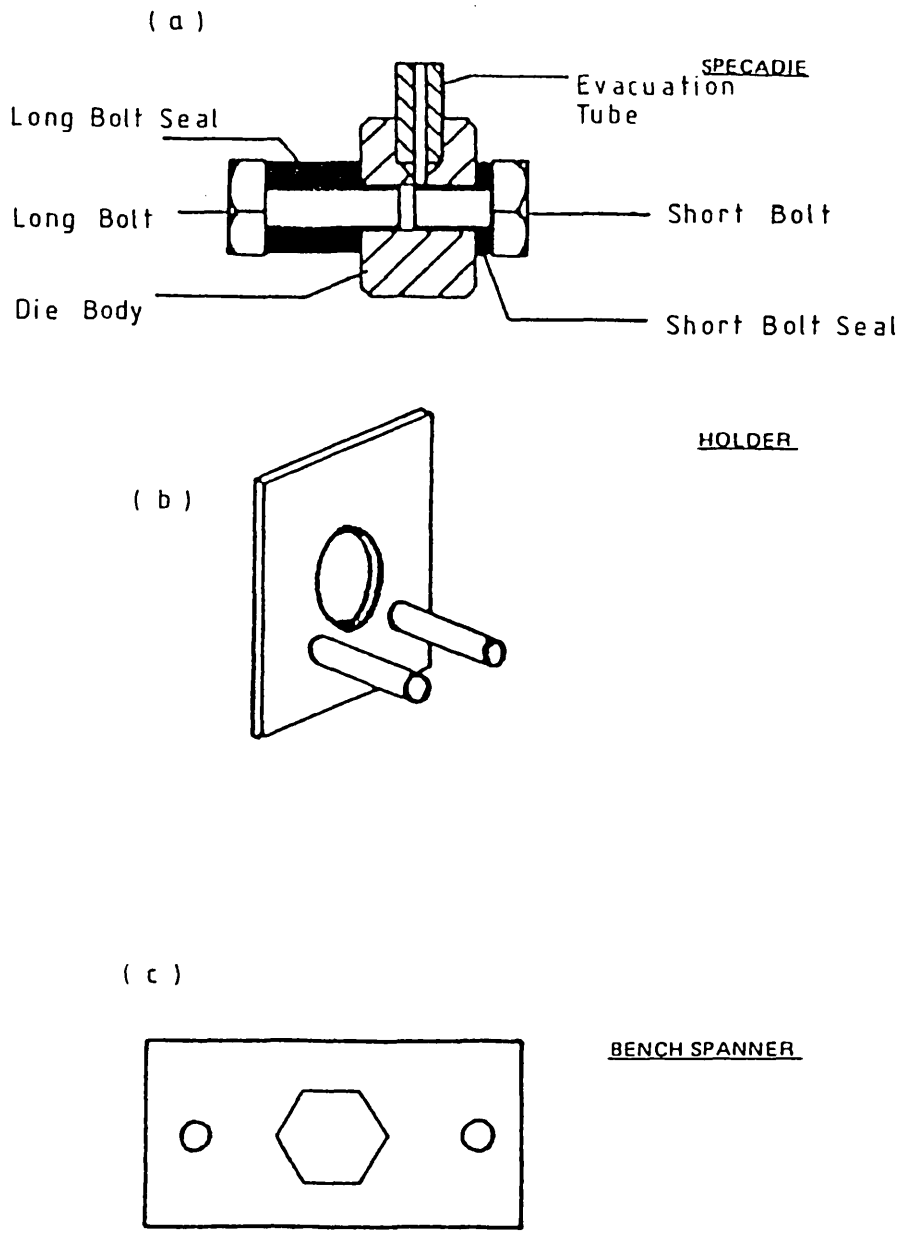


FIG. 4.18 COMPONENTS USED FOR KBr-KEROGEN PELLET PRESSING AND MOUNTING

(e) The Die and its sample now ready to press and evacuate, the Evacuation Tube was connected to a good vacuum pump - capable of providing a pressure of about 1 cm Hg.

(f) The Long Bolt was tightened using a long adjustable spanner until the sample was well compressed. At this point, the vacuum pump was switched on and the die was evacuated for about 1 minute. The tightening of the Long Bolt was continued throughout the evacuation period till the sample mixture was fully compressed.

(g) Both the Short Bolt and the Long Bolt were then loosened and removed leaving a well formed sample disc in the Die Body. The Die Body was then used as the pellet holder.

To run a spectrum, the Die Body was then seated securely on the two supporting arms of a Die Holder (see Fig. 4.18b). The Die Holder was then inserted into the spectrophotometer sample compartment with the pellet well situated in the sample beam region. Each kerogen sample pellet was scanned from 4000 to 600 cm^{-1} wave number range.

Because of the low transmittance of the KBr- kerogen sample pellets, a reference beam attenuator was used to raise the baseline at the starting point (i.e. at 4000 cm^{-1} wave number) to between 20 to 40% transmittance.

A total of six kerogen samples from Winchester No. 1 and Arreton No. 2 Wells were prepared and analysed by this method.

4.3.9.4 Analysis of the Oils

The analysis of oils by the Model 157 NaCl Spectrophotometer required the use of accessories including pairs of NaCl windows and a demountable cell. The cell consisted of two aluminium plates which support a pair of rectangular windows separated by a spacer and four quick-release nuts (see Fig. 4.19). To run a spectrum, a thin film of sample was placed between a clean pair of NaCl windows before the cell was assembled. The cell was then fitted to the sample area of the spectrophotometer and the sample was scanned from 4000 to 650 cm^{-1} wave number range.

As a result of the intense hygroscopic nature, the NaCl windows were always stored in a dessicator when not in use. After each sample run, the windows were cleaned using a 2:1 solvent mixture of Chloroform and Ethanol and then dried in a dessicator. Blank runs before sample analysis were often necessary to ascertain the cleanliness and dryness of the NaCl windows.

The three oils were subjected to this analysis.

4.3.9.5 Kerogen and Oil Spectral Absorption Bands

Fig. 4.20 is a typical Infra-red spectrum of a kerogen sample showing the characteristic absorption bands of sedimentary organic matter. The identification of the absorption bands is based on the work of Espitalie et al. (1973) (in Durand and Espitalie, 1976), Dypvik et al. (1979), and Rouxhet et al. (1980):

(a) the bands at about 2900 cm^{-1}, 1450 cm^{-1} and 1375 cm^{-1} are due to saturated C-H molecular groups. Their

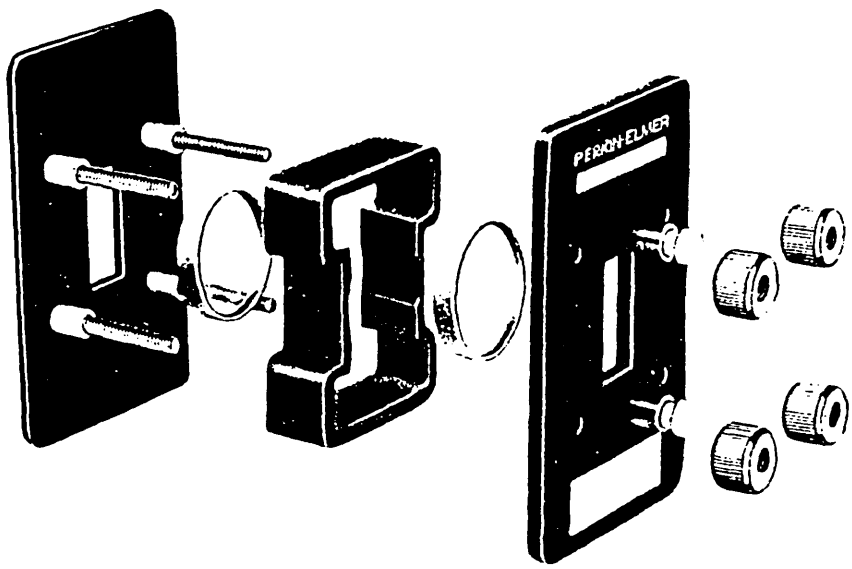


FIG.4.19- ACCESSORIES FOR INFRA-RED SPECTROSCOPIC ANALYSIS OF LIQUID SAMPLES: NaCl WINDOWS AND A DEMOUNTABLE CELL.

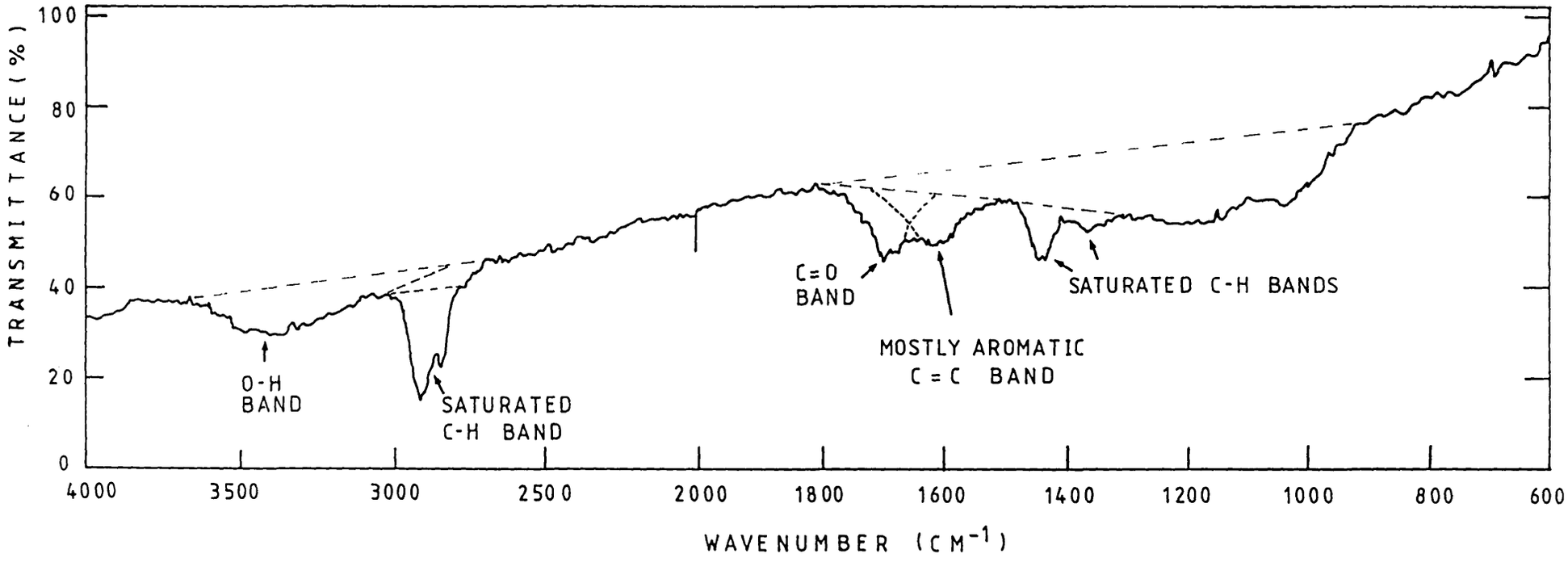


FIG. 4.20 EXAMPLE OF A KEROGEN (SAMPLE: WCH/OC.2) INFRA-RED SPECTRUM

occurrence indicate the presence of alkanes and/or alkyl groups in the organic matter.

(b) A broad band at about 1700 cm^{-1} is due to C = O stretching indicating the presence of oxygenated functions from acids, ketones, esters, and aldehydes.

(c) A broad absorption band at about 1600 cm^{-1} is believed to be mainly due to C = C stretching in aromatic substances. However, according to Durand and Espitalie (1976), other contributions to this band are not unlikely.

(d) An absorption band often appearing at about 3500 cm^{-1} (very broad) attributed to O-H stretch. This band can be due to OH groups in immature organic matter and/or atmospheric moisture adsorbed by KBr or NaCl windows during sample preparation and analysis.

(e) Absorption bands in the region 700 to 900 cm^{-1} (in some samples) due to aromatic C-H deformation bending out of plane.

4.3.10 Carbon and Hydrogen Stable Isotope Analyses of Organic Matter

4.3.10.1 Theory of Analysis

Isotopes of an element are atoms of that element having the same number of protons but different numbers of neutrons in their nuclei. The mass of an atom is the sum of its protons and neutrons plus electrons.

The element hydrogen has two main stable isotopes in nature: a major one constituting 98.948% with one proton and one neutron designated H, and a minor one with one proton and two neutrons constituting 0.016% of the total

and designated D (deuterium). Similarly, carbon has two main stable isotopes: a major one - ^{12}C (6 protons and 6 neutrons and constitutes 98.89% of the total) and a minor one -^{13}C with 6 protons and 7 neutrons and forms 1.11% of total occurrence of carbon in nature.

For an isotopic analysis, the sample is first converted to a suitable gas that can be conveniently analysed by a mass spectrometer. The suitability of a gas is determined by its relative stability and non-reactiveness. Carbon dioxide and hydrogen gas are the ones used for carbon and hydrogen isotopic analyses respectively (Schoell et al. 1983). Carbon dioxide (CO_2) is a compound of carbon and oxygen, and oxygen has 3 main isotopes [^{16}O - 99.76% (Major), ^{17}O = 0.04% (Minor), and ^{18}O = 0.20% (Minor)]. Therefore the gas CO_2 occurs in various combinations of carbon and oxygen isotopes. However, the two combinations - $^{13}C^{16}O^{16}O$ (total mass of 45) and $^{12}C^{16}O^{16}O$ (total mass - 44) - containing only the major oxygen isotope are selected for carbon isotopic analysis. The $^{12}C^{16}O^{16}O$ ($^{44}CO_2$) combination is referred to as Major because it contains the major carbon isotope and the other $^{13}C^{16}O^{16}O$ ($^{45}CO_2$) is referred as the Minor combination on account of its content of the minor carbon isotope.

The carbon (C) and hydrogen (H) in organic matter sample are first oxidised to CO_2 and Water (H_2O) in the presence of oxygen at elevated temperature. The CO_2 gas produced is used for carbon isotopic analysis while the water (H_2O) is reduced to hydrogen gas before being subjected to hydrogen mass spectrometric analysis.

The mass spectrometric isotopic analysis of gaseous samples is based on the central principle that a charged particle accelerated through a magnetic field bends in such a way that the radius of curvature of the path depends on its mass and charge. And therefore, to make a measurement on a molecule or particle, a charge has to be added to it. A mass spectrometer has two main regions - the source and the collecting regions. The source region charges the particles/molecules and accelerates them through a magnetic field. The collecting region consists of metallic cups which serve to collect different mass groups of charged particles accelerated through the magnetic field for isotopic analysis.

The results of isotopic analysis are often expressed in the delta (δ) scale:

$$\delta = \left[\frac{R \text{ sample}}{R \text{ standard}} - 1 \right] \times 1000$$ and the units are in

parts per mil (‰); where R is the ratio of the Minor to the Major isotopes. For purposes of comparison of results between laboratories, two gases are analysed at the same time - a sample gas and an internationally recognized reference (or standard) gas. In some laboratories an intermediate standard, with known isotope value/data relation to an international standard, is used during measurements.

4.3.10.2 Sample Preparation and Analysis

43 dried kerogen, 4 soluble organic extracts and 3 oil samples were prepared and analysed for their carbon and hydrogen isotopes using the equipments at the Isotope

Geology Unit of the British Geological Survey in London.

Between 4 - 6 mg of organic matter were introduced into a quartz tube containing about 0.5 g of copper oxide (CuO). Both the tube and the CuO had previously been cleaned of any carbonaceous contaminant by baking at 800°C for 2 hours. A small roll of silver (Ag) wool was added to the mixture to help in the removal of any traces of sulphur during the reaction. The quartz tube with the content was then carefully evacuated to about 3×10^{-5} torr (1 torr = $^{1}/_{760}$ std. atmosph.) using rotary and diffusion pumps. The sample mixture in the tube was then sealed off by closing the neck of the tube using oxyacetylene blow pipe flame. The oxidation of the organic matter carbon and hydrogen was carried out by placing the sealed tube with the sample mixture in an oven at 800°C for 2 hours.

The oxidation products - mainly carbon dioxide (CO_2) and water (H_2O) were first extracted from the quartz tube and frozen into a multiple trap submerged in liquid nitrogen using extraction lines operated by a high vacuum system. CO_2 was separated from H_2O by replacing the liquid nitrogen trap with a freezing isopropanol (about - 70°C) trap and this resulted in CO_2 sublimating off leaving H_2O in its frozen state. Both CO_2 and H_2O in their cleaned state were then separately collected in pre-cleaned glass vessels. Before each sample extraction, about 0.25 g of zinc granules was weighed into the vessel to be used for H_2O collection.

The collected water was reduced to hydrogen gas by the reaction with zinc on a hot plate at 430°C for about an hour.

The CO_2 samples were analysed for carbon isotopes using a triple-collector mass spectrometer. A double-collector mass spectrometer was used for the hydrogen isotope analysis. Intermediate reference samples were used during both analyses. The CO_2 intermediate reference sample was prepared from a carbonate material (MCS-7) by reaction with 100% phosphoric acid at 25.18°C. The intermediate reference for hydrogen analysis was prepared from a gypsum sample by reaction with zinc on a hot plate at 430°C.

The isotope data obtained from the analyses were, after correction, expressed in the usual δ-notation and related to the Peedee Belemnite Standard for Carbon ($\delta^{13}C_{PDB}$) and Standard Mean Ocean Water for hydrogen (δD_{SMOW}). The extraction method of this analysis was checked by using the international reference material NBS 22 with $\delta^{13}C_{PDB}$ = -29.8‰ and δD_{SMOW} = -119.2‰ (Schoell et al., 1983). Reproducibility of lower than 0.2‰ for $\delta^{13}C$ and 2.0‰ for δD was obtained from duplicate analyses.

4.3.11 Whole-Rock Analysis by X-Ray Diffraction Technique

4.3.11.1 Sample Preparation and Analysis

About one gram of each selected whole-rock sample powder (less than 75 μm grain size) was further reduced to the required optimum particle size range of 2 - 40 μm by grinding in an agate mortar for about 15 minutes (Tatlock, 1966). The resulting powdered sample was then back loaded into an aluminium cavity holder for X-ray diffraction analysis.

A Philips PW1060 diffractometer, equipped with a linear recorder, was used for the analysis. The equipment employed an iron filtered CoK_{α} radiation generated at 38 KV and 24 mA power supply settings. Scanning was carried out over the 4^{o} - 70^{o} 2θ range at 1^{o} 2θ per min, and a proportional counter with pulse height analysis served as the detection system. 1^{o} divergent and anti-scatter slits were used throughout in conjunction with a 0.1 mm receiving slit.

4.3.11.2 Semi-quantitative Estimation of the Whole Rock Mineralogy

A semi-quantitative estimation of the relative amounts of the principal minerals in each sample was made based on the method outlined by Schultz (1964). Briefly, this involved comparing the intensities of particular diffraction peaks of various minerals when present at 100% of the specimen with the intensities of the same peaks in the sample being analysed.

The areas of the characteristic peaks of the minerals present were measured using an electronic digitizer and were considered to the equivalent to their intensities. They were then multiplied by their correction factors before direct comparison. Table 4.3 gives the characteristic peak of each mineral and its correction factor after Schultz (1964). Fig. 4.21 is a typical whole-rock x-ray diffraction trace showing the characteristic peaks of the various minerals identified in this study.

TABLE 4.3: FACTORS FOR X-RAY DIFFRACTION SEMI-QUANTITATIVE ESTIMATION OF MINERALS (AFTER SCHULTZ, 1964)

Mineral	hkl	d(hkl)Å	Intensity factor (Counts per sec. per 100%)	Correction Factor
Quartz	101	3.34	2000	x 1
Plagioclase	040	3.18	1000	x 2
Potassium Feldspar	040	3.24	1000	x 2
Calcite	104	3.04	1000	x 2
Dolomite	104	2.89	1000	x 2
Gypsum	020	7.56	1500	x 1.3
Siderite	104	2.79	1000	x 2
Pyrite	200	2.71	500	x 4

Intensity factors of 600 and 250 counts per sec. per 100% were recommended by Schultz (1964) for Siderite and pyrite respectively when present in amounts less than 10%. But in this study, uniform values of 1000 and 500 c.p.s. per 100% respectively have been adopted for all samples where siderite and pyrite occur.

It was difficult to measure the peak area of the (001) muscovite due to the fact that it is superimposed on the broad diffuse (001) illite and illite-montmorillonite mixed layer mineral reflection. Therefore it was calculated with the clay minerals.

For the estimation of the "clay minerals" present in the whole-rock samples, the variation made by Shaw (1971) to the Schultz method was used. This involved measuring the intensities of the principal clay mineral reflections

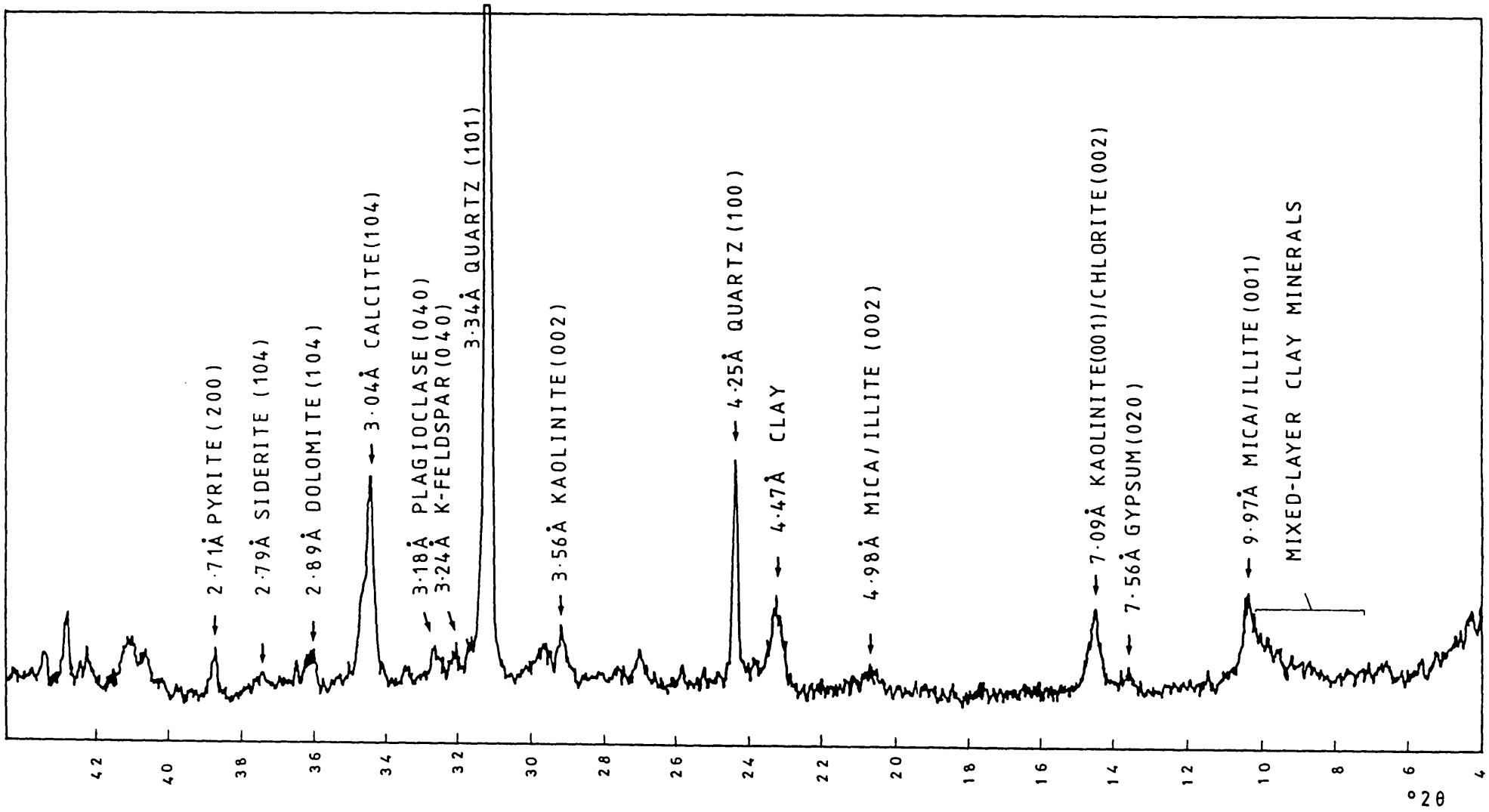


FIG. 4.21 A TYPICAL WHOLE-ROCK X-RAY DIFFRACTOGRAM (SAMPLE NO.: PH/KC.1) SHOWING THE CHARACTERISTIC PEAKS OF THE MINERALS IDENTIFIED IN THIS STUDY

[the illite and muscovite (001) at 10Å including the low angle tail due to mixed layer mineral, and the kaolonite (001) plus chlorite (002) at 7Å], correcting them for differences in diffracting ability relative to each other, and then comparing the total corrected intensity directly with that of quartz (101) reflection.

Example: The semi-quantitative estimation of the whole-rock mineralogy of sample PH/KC.1:

Mineral	Measured Intensity	Intensity x Correction Factor	Corrected Intensity
Quartz (101)	5.28	5.28 x 1	5.28
Calcite (104)	2.23	2.23 x 2	4.46
Dolomite (104)	0.60	0.60 x 2	1.20
Gypsum (020)	0.50	0.50 x 1.3	0.65
Potassium Feldspar (040)	0.54	0.54 x 2	1.08
Plagioclase (040)	0.67	0.67 x 2	1.34
Siderite (104)	0.37	0.37 x 2	0.74
Pyrite (200)	0.31	0.31 x 4	1.24
Illite + Muscovite + mixed layers	4.24 x 2.5)	[(4.24 x 2.5)+ 1.22] x 1	11.82
Kaolinite (001) + Chlorite (002)	1.22)		———
		Σ Corrected Intensity =	27.81

% Quartz = 5.28/27.81 x 100 = 19%

% Calcite = 4.46/27.81 x 100 = 16%

% Dolomite = 1.20/27.81 x 100 = 4%

% Gypsum = 0.65/27.81 x 100 = 2%

% Potassium Feldspar = 1.08/27.81 x 100 = 4%

% Plagioclase = 1.34/27.81 x 100 = 5%

% Siderite = 0.74/27.81 x 100 = 3%

% Pyrite = 1.24/27.81 x 100 = 4%

% "Clay" = 11.82/27.81 x 100=43%

Total = 100%

4.3.12 Clay Mineral Analysis by X-Ray Diffraction Method

4.3.12.1 Sample Preparation and Analysis

5-15 g of each selected sample (previously crushed to about 1 mm grain size) were soaked in distilled water for about one week. The soaked sample was stirred vigorously for 10 minutes to enhance the release of clay minerals from the rock particle surfaces into the distilled water. The fine-grained mineral suspension was divided into two portions and transferred into 250 ml plastic centrifuge bottles. After washing each portion twice in de-ionized water by centrifugation (at 1500 rpm for 4 minutes) and decantation, the < 2 μm fraction (mostly clay minerals) in one portion was separated by centrifuging the fine-grained mineral concentrate, thoroughly dispersed in de-ionized water, at 1000 rpm for 4 minutes (Tanner and Jackson, 1947). All the minerals with particle size greater than 2 μm were forced to settle down leaving the clay fraction in suspension. However, it was noted that clay minerals in many samples flocculated and settled with the other minerals by this separation procedure. To prevent the flocculation, 10 ml of ammonia solution were added to each fine-grained mineral

suspension prior to the separation step. Oriented clay mineral specimen was then prepared using the separated clay suspension. The method used for this preparation (oriented clay mount) was adopted from Shaw (1971, 1972) and it involved filtering a clay suspension by suction onto a ceramic tile.

The fine-grained mineral concentrate in the second portion was treated with 40 ml of 1M Mg^{2+} solution (using $MgCl_2.1OH_2O$ - Analytical grade) for 24 hours. This treatment was carried out to aid in subsequent differentiation of vermiculite and smectite clay minerals. The suspension was then washed several times in de-ionized water till chloride-free. Each washing was done by centrifugation at 1500 rpm for 4 minutes and decantation. When chloride-free (as confirmed by $AgNO_3$ test), the <2 μm fraction was separated and oriented clay mount prepared as described above.

Thus two oriented clay specimens were prepared per sample: one untreated and the other treated with Mg^{2+} ions. The specimens were left in a dessicator to dry before the x-ray diffraction analysis.

The equipment and the equipment settings used for the clay fraction analysis were the same as for the whole-rock analysis already described. However, in examining the clay fraction of the selected rock samples, the following experimental procedure was carried out:-

(a) Air-dried oriented clay mounts (treated and untreated) scanned from 2^{o} - $35^{o}2\theta$.

(b) The untreated specimen solvated with ethylene glycol and scanned from 2^{o} - $25^{o}2\theta$.

(c) The Mg^{2+} treated specimen solvated with glycerol scanned from 2^{o} - $20^{o}2\theta$.

(d) The clay mounts heated at $390^{o}C$ for 1½ hours and scanned from 2^{o} - $20^{o}2\theta$.

(e) The clay mounts heated at $550^{o}C$ for 1½ hours and scanned from 2^{o} - $16^{o}2\theta$.

4.3.12.2 Clay Mineral Identification

Clay minerals were identified from the positions of their basal reflections on the x-ray diffractograms (Fig. 4.22).

Illite was represented by its (001) peak which occurred about the 10Å position and remained unshifted when the sample was solvated and heated.

Chlorite was identified from its integral series of basal reflections with a first order (001) peak at 14Å position which was unaffected by glycerolation or glycolation and by heating at $390^{o}C$. Generally, upon heating to $550^{o}C$ the (001) reflection intensity increased together with a slight peak shift to higher angles while the (002), (003) and (004) reflections decreased or disappeared as the brucite layer decomposed.

The presence of kaolinite was indicated by its (001) reflection which occurred between 7Å and 7.2Å and remained unaffected by solvation with either glycerol or glycol and by heating at $390^{o}C$. The significant reduction or disappearance of this (001) peak on heating to $550^{o}C$ confirmed the presence of both kaolinite (001) and chlorite (002) or either of them. The presence of the (002) reflection at 3.56Å was considered in the identification

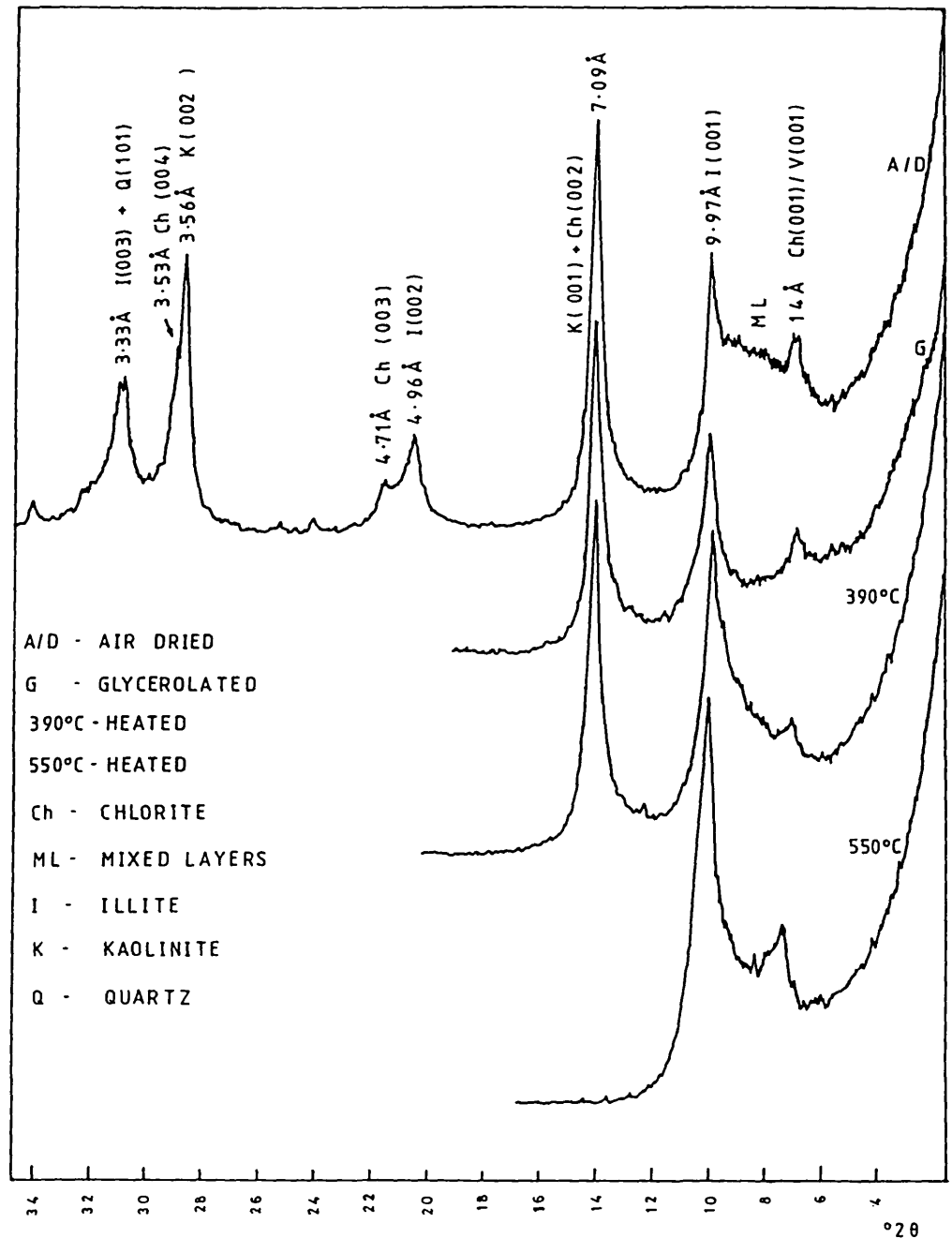


FIG. 4.22 X-RAY DIFFRACTOGRAMS OF Mg^{2+} - TREATED CLAY FRACTION OF A BOREHOLE SAMPLE (WK/LL:1)

of kaolinite.

Vermiculite was identified from analysis of Mg^{2+} treated specimens. Its presence was indicated by the occurrence of its first order (001) reflection at about 14Å position which remained unshifted by glycerolation, but disappeared when the specimen was heated to 390°C. The disappearance was due to the collapse of its structure with the resultant transformation to illite. In cases where the 14Å peak in glycerol solvated specimens merely reduced (not disappeared) upon heating to 390°C, such samples were considered to contain both vermiculite and chlorite.

The presence of illite-smectite mixed layer minerals was indicated by the occurrence of either a low angle tail on the illite (001) peak or by the presence of a broad shoulder between the illite (001) 10Å peak and the 14Å chlorite/vermiculite peak in air-dried specimens. The presence of random mixed layer phase was shown by the full expansion to 17Å on the glycolation of the untreated specimen (Reynolds and Hower, 1970) and contraction to 10Å on heating to 550°C. That the mineral was a random illite-smectite mixed-layer phase and not primary smectite was indicated by the shape of the 17Å (glycolated) peak which was broad with a higher low angle background than for discrete smectite (Pearson et al., 1981). The presence of ordered or regular illite-smectite mixed-layer mineral was shown by a slight shift in its position towards a lower angle on glycolation and its collapse to 10Å position (illite/mica) on heating to 550°C. A similar behaviour of the mixed-layer minerals

was observed in Mg^{2+} - treated specimens except that on solvation with glycerol the random phase expanded to 18.0Å position.

4.3.12.3 Estimation of the proportion of Expandable (smectite) layers in Illite-Smectite Mixed-layer clay minerals

The percentages of smectite layers in both the random and regular/ordered mixed layer minerals were estimated by using the combined criteria of Reynolds and Hower (1970) and Rettke (1981). Reynolds and Hower, in 1970, demonstrated that the 5.6Å smectite-glycol (003) reflection migrates with progressive illitisation towards the 5.0Å illite (002) reflection. Thus they showed that the d-spacing of this reflection can be related directly to the % of smectite layers in the illite-smectite mixed layer mineral (see Table 4.4 and Fig. 4.23).

TABLE 4.4 THE d-SPACINGS OF THE (003) ILLITE-(GLYCOL) SMECTITE REFLECTIONS AND THE CORRESPONDING PROPORTIONS OF SMECTITE LAYERS (AFTER REYNOLDS AND HOWER, 1970)

d-spacing (Å)	Percent Expandable (smectite)
5.02	0
5.06	10
5.16	20
5.34	40
5.48	60
5.58	80
5.61	100

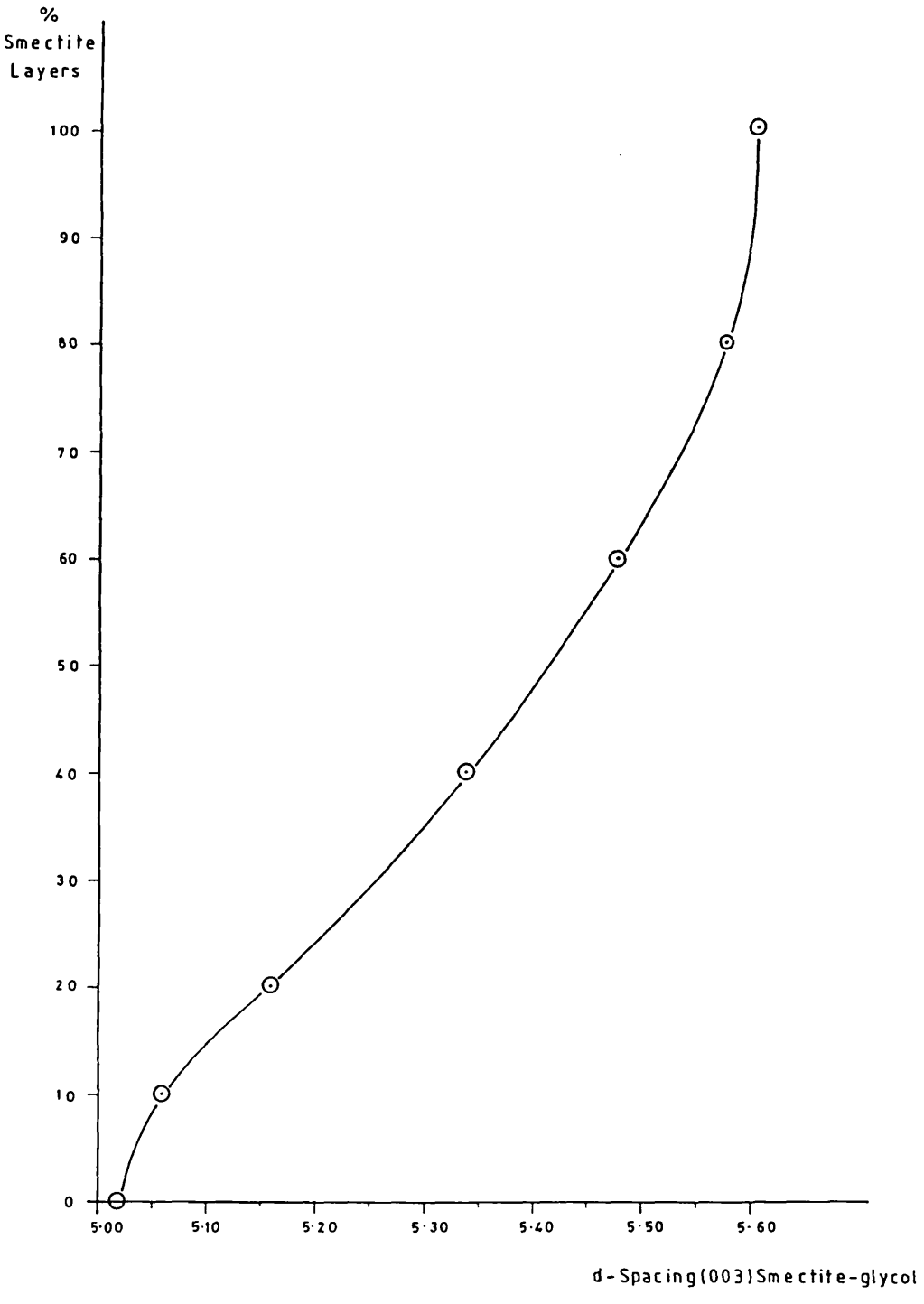


FIG. 4.23 PLOT OF d-SPACING (003) ILLITE-SMECTITE-GLYCOL AGAINST THE PERCENTAGE OF SMECTITE LAYERS (BASED ON DATA FROM REYNOLD AND HOWER, 1970)

But Pearson et al. (1981) noted that in clay mixtures with discrete mica/illite, this direct relation of d-spacing of the (003) reflection of mixed layer-glycol to the % of smectite layers is often made difficult through interference by the 5.0A reflection of the discrete illite/mica. Working on various mixtures of illite and random illite-smectite mixed-layer minerals, Rettke (1981) noted that there was a relationship between the % of smectite layers in the mixed-layer minerals and the low angle "saddle"/17Å reflection intensity ratios in glycolated specimens, and that the smectite contents also depended on the ratio of the amounts of discrete illite to illite-smectite mixed layers in the mixtures. The relationships are illustrated in Fig. 4.24.

4.3.12.4 Semi-quantitative Analysis of the Clay Minerals

The relative proportions of the clay minerals in each sample were estimated from the intensities of their strong basal reflections. The area under the peak of a reflection was considered to be equivalent to the peak intensity and was regarded to be proportional to the quantity of that mineral present. The peak areas were measured using an electronic digitizer. In measuring the peak area, the background level of the peaks had to be projected by joining up the background levels on either side (see Fig. 4.25).

The procedure adopted for the semi-quantitative estimations of the clay minerals was a modified version

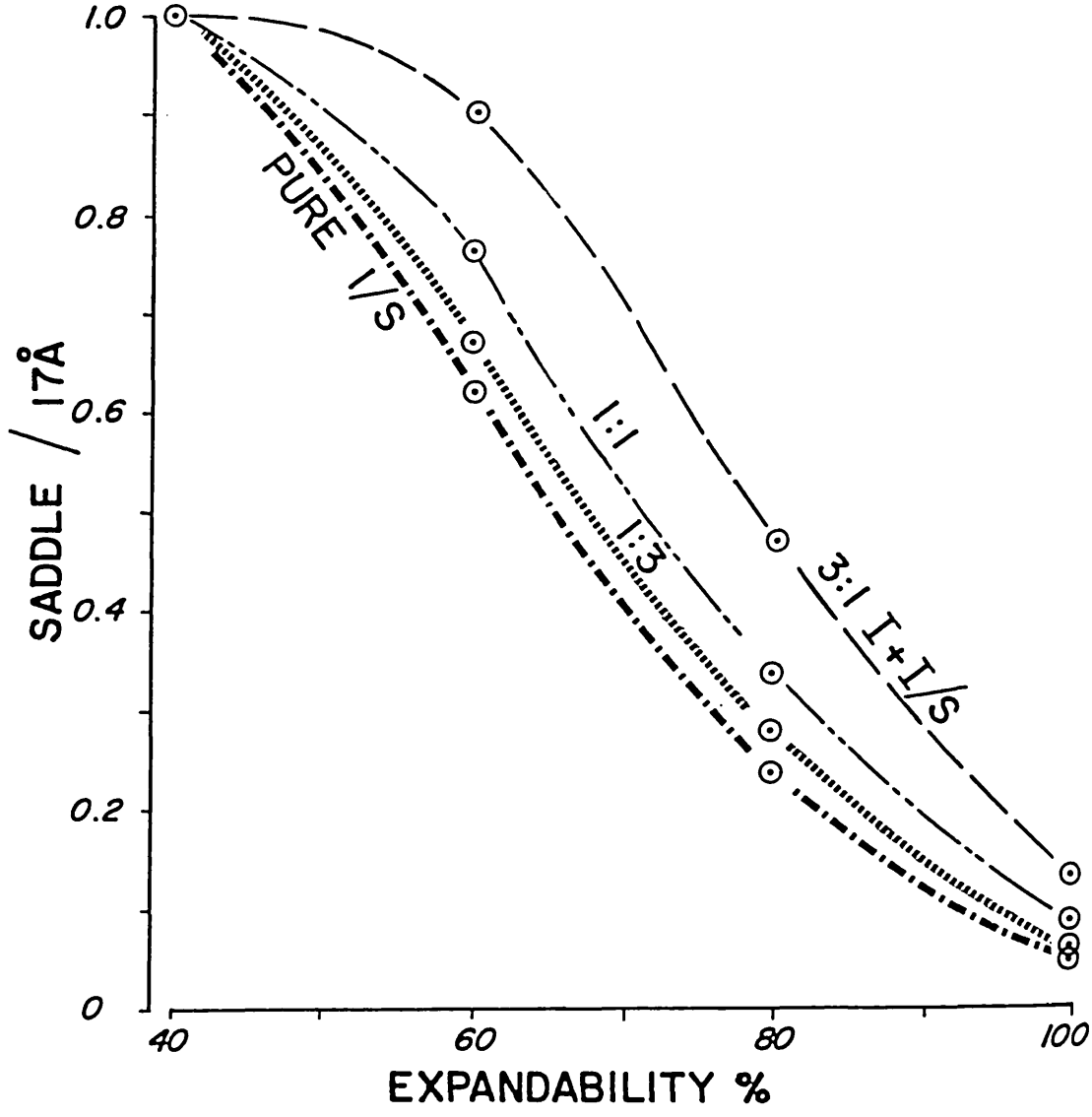


FIG.4.24- GRAPH OF"SADDLE"/17Å INTENSITY RATIO AS A FUNCTION OF ILLITE/SMECTITE (I/S) EXPANDABILITY FOR PURE I/S AND FOR VARIOUS MIXTURES OF I/S WITH DISCRETE ILLITE (After Rettke,1981)

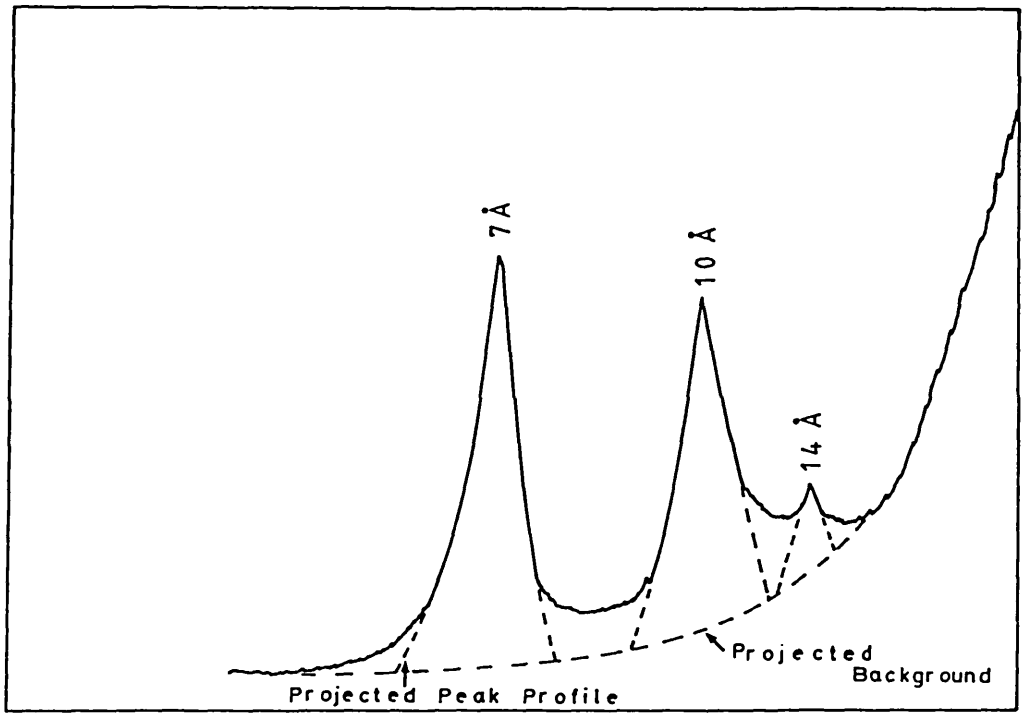


FIG. 4.25 AN ILLUSTRATED DIFFRACTOGRAM OF THE $< 2\mu$ FRACTION SHOWING BACKGROUND AND PEAK PROFILE PROJECTIONS

of the method of Weir et al. (1975), and the diffractograms of the Mg^{2+} treated specimens were used. A list of peaks measured and the X-RD traces used for the measurements are given in Table 4.5 below.

TABLE 4.5 MEASURED CLAY PEAKS AND X-RAY DIFFRACTION TRACES USED FOR SEMI-QUANTITATIVE ESTIMATION OF CLAY MINERALOGY OF A SAMPLE

Peaks Measured	Traces Measured On
Chlorite (001)+ Vermiculite(001) at 14Å ($I_{ch(001)+V}$)	Glycerolated
Chlorite (001) at 14Å ($I_{ch(001)}$)	Heated at 390°C
Illite (001) at 10Å (I_I)	Glycerolated
Illite + Expandables at 10Å (I_{I+Ex})	Heated at 390°C
Kaolinite (001) + Chlorite (002) at 7Å ($I_{K+ch(002)}$)	Heated at 390°C

The measured peak areas were weighted to enable direct comparison of the various peak intensities as follows:

(a) $I_{ch(001)+V} \times 1$ - gave the integrated intensity of chlorite (001) plus vermiculite (001) at 14Å.

(b) $I_{ch(001)} \times 1$ - gave the integrated intensity of chlorite (001) at 14Å.

(c) $I_{k+ch(002)} \times 1$ - gave the integrated intensity of kaolinite (001) plus chlorite (002) at 7Å.

(d) $I_I \times 2.5$ - gave the integrated intensity of illite at 10Å. An intensity correction factor of 2.5 was used here to enable comparison between illite and either kaolinite or chlorite at 10Å and 7Å respectively (Weaver, 1961).

(e) $I_{I+EX} \times 2.5$ - gave the integrated intensity of illite plus expandable minerals. The 2.5 intensity correction factor was again used here based on the assumption that the expanding minerals (vermiculite and illite-smectite mixed layers) collapsing to 10Å on heating gave the same reflection intensity as illite (Weir et al., 1975).

In samples where the illite-smectite mixed-layer minerals did not completely collapse until after heating at 550°C for 1½ hours, the intensity of illite + expandables ($I_{I+EX)}$ was estimated from the 10Å peak after heating at 550°C rather than at 390°C.

By subtracting (d) from (e), the weighted intensity value for expandable clays (I_{EX}) was obtained. Similarly, (a) minus (b) gave the integrated intensity of vermiculite (I_V), and by subtracting I_V from I_{EX}, the weighted intensity of illite-smectite mixed layer mineral (I_{I-S}) was arrived at. The chlorite (002) area/intensity at 7Å was required for the quantitative analysis, but unfortunately in most instances the overlap between kaolinite (001) and chlorite (002) reflections was so great that the two could not be separated. An estimate of each was made by assuming

that the chlorite (002) peak had 1.25 times the intensity of chlorite (001) peak at 14Å (Huggett, 1982). The estimation of the kaolinite (001) intensity was then carried out by subtraction of $I_{ch(001)} \times 1.25$ from (c).

The procedure described above thus resulted in weighted peak areas/intensities for illite, illite-smectite mixed layers, vermiculite, kaolinite and chlorite. The 5 weighted peak areas were summed up, and the weighted peak area of each mineral multiplied by 100 and divided by the sum of the areas gave the "percentage" of each mineral.

CHAPTER V

MINERALOGY AND ORGANIC CARBON RICHNESS OF THE ROCK SAMPLES

MINERALOGY AND ORGANIC CARBON RICHNESS OF THE ROCK SAMPLES

5.1 WHOLE-ROCK MINERALOGY AND LITHOLOGIC DESCRIPTIONS

5.1.1 The Whole-Rock Mineralogy

The results of semi-quantitative estimation of the whole-rock mineralogy, from x-ray diffraction traces, of 100 samples were presented in Table 5.1. This number includes 48 Lower Lias, 20 Oxford Clay, and 32 Kimmeridge Clay samples from Jurassic sections across Southern England. Each sample's identity including present burial depth (in case of borehole samples) is indicated in the table.

Samples from the 3 formations show some broad similarity in mineralogy. Nine minerals were identified in each formation and these include clay (with muscovite), quartz, calcite, dolomite, potassium feldspar, plagioclase, gypsum, siderite and pyrite. A summary of the percentage contents of these minerals in the Lower Lias, the Oxford Clay and the Kimmeridge Clay Formations is shown in Table 5.2. Clay, quartz, and the lime carbonates (calcite and dolomite) constitute the main mineral components of the samples. While the lime carbonates contents of the Kimmeridge Clay and the Lower Lias samples range up to 70% and over, no Oxford Clay sample is found to contain the calcareous carbonates in excess of 50%. Plagioclase was identified in all the Oxford Clay samples whereas it was not detected in some Lower Lias and Kimmeridge Clay samples. Gypsum was identified in 7 Lower Lias samples, 7 samples from the Oxford Clay, and 13 Kimmeridge Clay samples. The presence of gypsum in some of the samples is indicative of the fact that during the deposition of the 3 formations, the salinity of the Jurassic

TABLE 5.1 - WHOLE ROCK MINERALOGY, LITHOLOGY AND TOC VALUES OF SAMPLES FROM OUTCROPS, BURTON ROW, WINTERBORNE KINGSTON, MARCHWOOD, WINCHESTER-1, HENFIELD, WARLINGHAM & PENSHURST WELLS

LOCALITY	SAMPLE NO. & DEPTH (FT.)	FORMATION	AMMONITE ZONE OR FORMATIONAL SUB-DIVISION	TOTAL ORGANIC CARBON (TOC) (Wt.%)	CLAY %	QUARTZ %	CALCITE %	DOLOMITE%	K-FELD.%	PLAGIO-CLASE %	GYPSUM %	SIDERITE %	PYRITE %	LITHOLOGIC DESCRIPTION
Ringstead Bay Area (Dorset)	OSD/KC.1	Kimmeridge	-	2.95	Trace	1	88	-	-	-	2	4	5	Dark greyish brown Limestone
	OSD/KC.2	Clay	-	16.34	43	19	22	-	-	-	5	-	11	Very dark greyish Mudshale
	OSD/KC.3	"	-	10.59	56	16	14	-	-	-	4	3	7	"
Kimmeridge Bay - Chapman's Pool Area (Dorset)	OSD/KC.4	"	Rotunda	1.76	41	26	20	-	-	-	2	5	6	Dark grey Mudshale
	OSD/KC.5	"	Pallasioides	1.62	41	19	24	-	-	3	2	5	6	"
	OSD/KC.6	"	Pectinatus	6.81	51	16	21	-	-	-	4	-	8	"
	OSD/KC.7	"	Hudlestoni	16.37	43	20	23	-	-	-	2	3	9	Black Mudshale
	OSD/KC.8	"	Wheatleyensis	20.48	39	20	23	-	-	4	5	2	7	Very dark greyish brown Mudshale
	OSD/KC.9	"	"	3.26	30	18	33	4	-	-	-	7	8	Very dark grey Calcareous Mudstone
	OSD/KC.LO	"	Elegans	8.44	41	20	19	-	-	4	-	8	8	Black Mudshale
	OSD/KC.11	"	Autissiodorensis	2.50	31	42	7	-	6	5	-	3	6	" "
	OSD/KC.12	"	Euxodus	6.16	43	23	15	-	3	4	-	6	6	" "
Shortlake (Dorset)	OSD/OC.1	Oxford Clay	Cordatum	1.73	41	34	5	-	5	6	3	-	6	Grey Mudstone
Chickerell (Dorset)	OSD/OC.2	"	Athleta	1.50	52	21	-	-	6	5	6	-	10	Greenish grey Mudstone
	OSD/OC.3	"	"	12.36	53	24	-	-	7	8	3	-	5	Very dark greyish brown Mudshale
	OSD/OC.4	"	Coronatum	8.14	56	27	-	-	4	6	3	-	4	"

Table 5.1 (Cont.)

LOCALITY	SAMPLE NO. & DEPTH (FT.)	FORMATION	AMMONITE ZONE OR FORMATIONAL SUB-DIVISION	TOTAL ORGANIC CARBON (TOC) (Wt.%)	CLAY %	QUARTZ %	CALCITE %	DOLOMITE%	K-FELD. %	PLAGIO-CLASE %	GYPSUM %	SIDERITE	PYRITE %	LITHOLOGIC DESCRIPTION
Chickerell (Dorset)	OSD/OC.5	Oxford Clay	Coronatum	5.63	42	28	-	-	7	11	6	-	6	Very dark greyish brown Mudshale
Charmouth (Dorset)	OSD/LL.1	Lower Lias	Black Ven Marls	0.51	9	3	72	9	-	-	-	-	7	Grey Limestone
	OSD/LL.2	" "	" " "	0.70	11	2	3	80	-	-	-	-	4	" "
	OSD/LL.3	" "	Shales-with-Beef	6.18	21	6	29	30	2	2	1	1	8	Dark grey laminated Argillaceous Limestone
	OSD/LL.4	" "	" " "	2.86	11	2	84	-	-	-	1	-	2	Dark grey laminated Limestone
	OSD/LL.5	" "	" " "	7.36	45	14	9	7	6	4	8	-	7	Very dark grey Mudshale
	OSD/LL.6	" "	" " "	6.74	50	16	15	6	-	-	2	-	11	"
Lyme Regis (Dorset)	OSD/LL.7	" "	Blue Lias	0.63	Trace	5	90	-	-	-	-	-	5	Bluish grey Limestone
	OSD/LL.8	" "	" "	5.98	69	17	-	-	10	-	-	-	4	Very dark grey Clay-shale
Burton Row Well (Somerset)	BR/LL.1 (122)	Lower Lias	-	2.35	42	19	16	-	-	9	2	-	12	Very dark grey Mudshale
	BR/LL.2 (214.3)		-	1.44	48	17	12	-	-	12	-	6	5	" "
	BR/LL.3 (360.7)		-	4.54	35	12	33	5	4	4	-	2	5	Very dark grey Calcareous Mudshale
	BR/LL.4 (419.8)		-	1.47	51	17	12	5	4	4	-	2	5	Black Mudshale

TABLE 5.1 (Cont.)

LOCALITY	SAMPLE NO. & DEPTH (FT.)	FORMATION	AMMONITE ZONE OR FORMATIONAL SUB-DIVISION	TOTAL ORGANIC CARBON (TOC) (Wt.%)	CLAY %	QUARTZ %	CALCITE %	DOLOMITE%	K - FELD.%	PLAGIO-CLASE %	GYPSUM %	SIDERITE%	PYRITE %	LITHOLOGIC DESCRIPTION
Burton Row Well (Somerset)	BR/LL.5 (503.5)	Lower Lias	-	3.54	33	11	25	13	3	5	-	-	10	Very dark grey Calcareous Mud-shale
	BR/LL.6 (588.3)			2.24	52	17	8	5	5	5	-	-	8	Black Mudshale
	BR/LL.7 (759·9)			1.70	38	17	18	10	-	9	-	-	8	" "
	BR/LL.8 (969.2)			1.39	20	4	54	11	-	1	-	3	7	Very dark grey Argillaceous Limestone
	BR/LL.9 (1227.6)			2.34	24	11	25	16	-	5	-	-	19	Very dark grey Calcareous Mud-shale
	BR/LL.10 (1317.7)			5.43	28	9	40	8	-	6	-	-	9	Black Laminated Argillaceous Limestone
	BR/LL.11 (1342.2)			3.76	20	4	50	8	-	7	-	-	11	" "
Winterborne Kingston Well (Dorset)	WK/KC.1 (1148)	Kimmeridge Clay	Lower Kimmeridge Clay	2.53	41	21	11	-	6	4	2	4	11	Black Mudshale
	WK/KC.2 (1164.9)		"	3.94	46	19	14	-	4	4	3	-	10	" "
	WK/KC.3 (1179.3)			3.17	49	19	14	-	3	4	-	-	11	" "
	WK/LL.1 (4150)	Lower Lias	Belemnite Marls	2.61	44	20	6	-	4	16	-	2	8	Dark grey Mud-stone
	WK/LL.2 4165.6		Black Ven Marls	1.52	38	24	9	3	4	12	-	4	6	" " "

TABLE 5.1 (Cont.)

LOCALITY	SAMPLE NO. & DEPTH (FT.)	FORMATION	AMMONITE ZONE OR FORMATIONAL SUB-DIVISION	TOTAL ORGANIC CARBON (TOC) (Wt.%)	CLAY %	QUARTZ %	CALCITE %	DOLOMITE%	K-FELD.%	PLAGIO-CLASE %	GYPSUM %	SIDERITE%	PYRITE %	LITHOLOGIC DESCRIPTION
	WK/LL.3 (4198.4)		Black Ven Marls	1.21	40	17	9	3	4	11	-	10	6	Dark grey Mudstone
	WK/LL.4 (4208.2)		" " "	1.18	37	24	9	-	5	12	-	10	3	" "
	WK/LL.5 (5100.4)		Blue Lias	0.72	32	13	23	18	2	4	-	2	6	Dark grey Calcareous Mudstone
	WK/LL.6 (5116.8)		" "	0.78	29	8	43	11	2	3	-	-	4	Very dark grey Argillaceous Limestone
	WK/LL.7 (5143)		" "	0.41	16	3	68	6	-	-	-	3	4	Dark grey limestone
	WK/LL.8 (5149.6)		" "	1.91	21	3	64	5	-	3	-	-	4	" " "
Marchwood Well (Hampshire)	MD/OC.1 (2950)	Oxford Clay	Upper Oxford Clay	0.98	29	24	27	6	2	3	-	6	3	Dark grey Calcareous Mudstone
	MD/OC.2 (2960)		" " "	1.15	39	16	23	6	4	3	-	6	3	Dark grey Mudstone
	MD/OC.3 (2966)		" " "	0.79	24	17	38	6	4	4	-	4	3	Dark grey Calcareous Mudstone
	MD/OC.4 (2970)		" " "	0.81	31	15	36	10	1	2	-	2	3	" "
	MD/LL.1 (4501)	Lower Lias	-	0.70	11	3	76	7	-	-	-	-	3	Grey Limestone
	MD/LL.2 (4505)		-	1.45	16	4	68	6	1	2	-	1	2	" "
	MD/LL.3 (4515)		-	1.16	17	4	60	8	1	3	2	3	2	Grey Argillaceous Limestone
	MD/LL.4 (4519)		-	0.89	15	4	65	8	1	1	-	3	3	Grey Limestone

TABLE 5.1 (Cont.)

LOCALITY	SAMPLE NO. & DEPTH (FT.)	FORMATION	AMMONITE ZONE OR FORMATIONAL SUB-DIVISION	TOTAL ORGANIC CARBON (TOC) (Wt.%)	CLAY %	QUARTZ %	CALCITE %	DOLOMITE %	K-FELD. %	PLAGIO-CLASE %	GYPSUM %	SIDERITE %	PYRITE %	LITHOLOGIC DESCRIPTION
Marchwood Well (cont.)	MD/LL.5 (4525)		-	0.92	27	10	39	18	-	-	-	3	3	Grey Argillaceous Limestone
	MD/LL.6 (4533)		-	1.08	15	4	59	15	-	3	-	3	1	Grey Limestone
Winchester No. 1 Well (Hampshire)	WCH/KC.1 (2342-2345)	Kimmeridge Clay	-	1.52	37	26	15	-	7	6	-	3	6	Very dark grey Mudstone
	WCH/KC.2 (3218-3221)		-	1.51	46	17	17	5	5	-	-	5	5	" " "
	WCH/KC.3 (3230)		-	1.61	46	16	15	5	-	6	-	4	8	Black Mudshale
	WCH/OC.1 (3914)	Oxford Clay	Lower Oxford Clay	7.60	46	16	23	-	3	3	-	-	9	Dark greyish brown Mudshale
	WCH/OC.2 (3942-3944)		" " "	9.43	46	19	10	2	6	5	-	3	9	" "
	WCH/OC.3 (3977)		" " "	6.04	57	11	8	5	4	8	-	2	5	" "
	WCH/OC.4 (4004-4008)		" " "	2.31	50	17	5	-	6	7	-	6	9	Dark greenish grey mudshale
	WCH/LL.1 (5814)	Lower Lias	-	2.75	44	20	6	4	5	9	-	8	4	Very dark grey Mudshale
	WCH/LL.2 (5825-5826)		-	2.92	36	23	8	2	6	7	-	8	10	" " "
	WCH/LL.3 (5837)		-	2.92	52	13	8	-	5	9	-	8	5	" " "

TABLE 5.1 (Cont.)

LOCALITY	SAMPLE NO. & DEPTH (FT.)	FORMATION	AMMONITE ZONE OR FORMATIONAL SUB-DIVISION	TOTAL ORGANIC CARBON (TOC) (Wt.%)	CLAY %	QUARTZ %	CALCITE%	DOLOMITE%	K-FELD.%	PLAGIO-CLASE %	GYPSUM %	SIDERITE %	PYRITE %	LITHOLOGIC DESCRIPTION
Henfield Well (West Sussex)	HN/KC.1 (1585-1587)	Kimmeridge Clay	-	1.47	38	19	27	4	-	-	-	-	12	Black Calcareous Mudshale
	HN/KC.2 (2092-2094)			10.02	34	13	37	-	3	3	-	3	7	" "
	HN/KC.3 (2102)		-	1.05	7	7	9	68	1	2	-	-	6	Black Limestone
	HN/LL.1 (4416)	Lower Lias	-	2.50	27	11	34	15	-	5	-	3	5	Very dark grey Calcareous Mudstone
	HN/LL.2 (4698)		-	1.09	22	31	31	6	-	4	-	2	4	Dark grey calcareous Mudstone
	HN/LL.3 (4707)			1.30	26	21	30	8	-	6	-	3	6	" " "
	HN/LL.4 (4838)		-	1.27	27	36	23	5	-	3	-	2	4	Dark grey Mudstone
	HN/LL.5 (4843.5)			0.78	22	32	34	4	-	3	-	2	3	Dark grey Calcareous Mudstone
Warlingham Well (Surrey)	WM/KC.1 (2279-5)	Kimmeridge Clay	Rotunda/ Pallasioides	1.45	11	10	16	52	1	2	1	-	7	Very dark grey Argillaceous Limestone
	WM/KC.2 (2379.5)		Pectinatus	4.95	30	20	27	9	5	3	-	-	6	Very dark grey Calcareous Mudstone
	WM/KC.3 (2480.5)		Hudlestoni	3.84	28	14	51	2	-	-	-	-	5	Very dark grey Argillaceous Limestone
	WM/KC.4 (2520)		Wheatleyensis	2.20	15	8	73	-	-	-	-	-	4	Very dark grey Limestone

TABLE 5.1 (Cont.)

LOCALITY	SAMPLE NO. & DEPTH (FT.)	FORMATION	AMMONITE ZONE OR FORMATIONAL SUB-DIVISION	TOTAL ORGANIC CARBON (TOC) (Wt.%)	CLAY %	QUARTZ %	CALCITE%	DOLOMITE%	K-FELD.%	PLAGIO-CLASE %	GYPSUM %	SIDERITE%	PYRITE %	LITHOLOGIC DESCRIPTION
Warlingham Well (cont.)	WM/KC.5 (2580)		Scitulus	3.61	28	8	53	-	-	2	2	2	5	Greyish brown Argillaceous Limestone
	WM/KC.6 (2680)		Antissiodorensis	1.20	25	5	53	10	-	-	-	4	3	Grey Argillaceous Limestone
	WM/KC.7 (2779.5)		Euxodus	2.74	26	14	34	13	3	3	-	-	7	Dark grey Calcareous Mudstone
	WM/KC.8 (2880)		"	1.42	29	24	25	11	4	4	-	-	3	"
	WM/KC.9 (2982)		Mutabilis	0.99	24	17	11	28	8	6	-	2	4	"
	WM/OC.1 (3162.5)	Oxford Clay	Cordatum	1.03	33	20	18	17	4	3	1	-	4	Grey Calcareous Mudstone
	WM/OC.2 (3202)		Marie	1.22	27	18	29	11	5	5	-	1	4	"
	WM.OC.3 (3400.3)		Athleta	3.41	43	20	20	2	4	3	1	-	7	Dark grey Mudshale
	WM/OC.4 (3430)		Coronatum	2.27	28	15	34	13	-	3	-	-	7	Dark grey Calcareous Mudshale
	WM/OC.5 (3466)		Jason	5.89	54	19	7	3	4	6	-	2	5	Very dark greyish brown Mudshale
	WM/LL.1 (4200)	Lower Lias	Davoei	1.06	42	28	7	-	-	11	-	6	6	Dark grey Mudstone
	WM/LL.2 (4300)		Davoei	1.32	49	21	9	3	7	10	-	-	1	Dark grey Mudstone

TABLE 5.1 (Cont.)

LOCALITY	SAMPLE NO. & DEPTH (FT.)	FORMATION	AMMONITE ZONE OR FORMATIONAL SUB-DIVISION	TOTAL ORGANIC CARBON (TOC) (Wt.%)	CLAY %	QUARTZ %	CALCITE%	DOLOMITE%	K-FELD.%	PLAGIO-CLASE %	GYPSUM%	SIDERITE%	PYRITE %	LITHOLOGIC DESCRIPTION
Warlingham Well (Cont.)	WM/LL.3 (4350)	Lower Lias	Ibex	0.26	10	3	82	-	-	-	-	3	2	Greenish grey Mudstone
	WM/LL.4 (4400)		Rariocostatum	0.72	36	31	16	-	5	7	-	3	2	Dark grey Mudstone
	WM/LL.5 (4460.5)		Obtusum	0.73	31	46	10	2	3	5	-	-	3	" "
	WM/LL.6 (4480)		Uncertain	1.15	49	31	7	-	-	8	-	-	5	" "
Penshurst Well (Kent)	PH/KC.1 (1174)	Kimmeridge Clay	-	8.38	43	19	16	4	4	5	2	3	4	Very dark greyish brown Mudshale
	PH/KC.2 (2242)			1.68										
	PH/KC.3 (2308-2325)		-	0.98	28	26	11	21	2	9	-	-	3	Dark grey Calcareous Mudstone
	PH/KC.4 (2409-2412)		-	3.30										
	PH/OC.1 (2928)	Oxford Clay		0.87	31	20	31	9	-	4	-	-	5	Dark grey Calcareous Mudstone
	PH/OC.2 (3005)			1.25										
	PH/OC.3 (3139)		-	4.19	36	23	23	4	3	5	-	-	6	Very dark greyish brown Mudshale
	PH/LL.1 (4105-4135)	Lower Lias	-	1.38										
	PH/LL.2 (4200-4233)	Lower Lias	-	1.16										
	PH/LL.3 (4304-4335)	" "	-	1.52	27	17	35	8	2	4	1	2	4	Dark grey Calcareous Mudstone

TABLE 5.1 (Cont.)

LOCALITY	SAMPLE NO. & DEPTH (FT.)	FORMATION	AMMONITE ZONE OR FORMATIONAL SUB-DIVISION	TOTAL ORGANIC CARBON (TOC) (Wt.%)	CLAY %	QUARTZ %	CALCITE %	DOLOMITE %	K-FELD.%	PLAGIO-CLASE %	GYPSUM %	SIDERITE%	PYRITE %	LITHOLOGIC DESCRIPTION
Penshurst Well (Cont.)	PH/LL.4 (4407-4438)		-	1.47										
	PH/LL.5 (4518-4550)		-	1.16	28	21	36	5	2	5	-	-	3	Dark grey Calcareous Mudstone

TABLE 5.2 A SUMMARY OF THE WHOLE-ROCK MINERALOGY OF THE LOWER LIAS, THE OXFORD CLAY AND THE KIMMERIDGE CLAY SAMPLES

Identified Minerals	% Contents		
	Lower Lias	Oxford Clay	Kimmeridge Clay
Clay	Trace - 69	24 - 57	Trace - 56
Quartz	2 - 46	15 - 34	1 - 42
Calcite	0 - 90	0 - 38	7 - 88
Dolomite	0 - 80	0 - 17	0 - 68
Potassium Feldspar	0 - 10	0 - 7	0 - 8
Plagioclase	0 - 16	2 - 11	0 - 9
Gypsum	0 - 8	0 - 6	0 - 5
Siderite	0 - 10	0 - 6	0 - 8
Pyrite	1 - 19	3 - 10	3 - 12

Sea sometimes exceeded 200 parts per thousand and this favoured evaporitic precipitation (Krumbein and Garrels, 1952). All the Jurassic samples are noted to contain pyrite. Siderite was identified in many of the samples which contain pyrite. According to Krumbein and Garrels (1952), pyrite and siderite commonly form under reducing environmental conditions but with pyrite requiring more oxygen-deficient conditions. However, according to Hallam (1960, 1975) the presence of pyrite in fine-grained sedimentary rocks is not necessarily indicative of their deposition in anoxic bottom waters, and their formation could have occurred during the early diagenesis under anaerobic conditions within the sediments. Confined waters particularly in the presence of organic matter are known to rapidly lose their oxygen content. Biochemical reactions initiated by micro-organisms rapidly remove oxygen and at the same time produce carbon dioxide and hydrogen sulphide resulting in a lowering of pH (Tschudy, 1969).

5.1.2 Lithologic Descriptions of the Jurassic Mudrocks

Based on mineralogic composition and visual examination, the 100 Jurassic samples have been classified into 9 lithologic types (see Table 5.1) and these are defined as follows:-

1. Normal Limestones - these are indurated, non-laminated calcareous mudrocks with lime carbonates content of 70% and over.
2. Laminated Limestones - these are similar to Type 1 in mineralogy but differ by being finely laminated (the laminae not more than 1.0 mm in thickness).

3. Normal Argillaceous Limestones - these are indurated, non-laminated mudrocks with clay plus quartz content of 20% or more and lime carbonates content of 50-69%.
4. Laminated Argillaceous Limestones - these are similar to Type 3 in mineralogy but are laminated.
5. Calcareous Mudstones - these are indurated, non-laminated fine-grained rocks with lime carbonates content of 30-49%, clay content of less than 65% and quartz content of less than 65%.
6. Normal Mudstones - these are similar to Type 5 in clay and quartz contents but with content of lime carbonates less than 30%.
7. Calcareous Mudshales - these are the laminated version of Type 5 with similar mineralogy.
8. Normal Mudshales - these are the laminated version of Type 6 with similar mineralogy.
9. Clayshales - these are indurated and laminated mudrocks comprising more than 65% clay.

The above classification of the Jurassic mudrocks is based mainly on the analysis and classification of fine-grained sedimentary rocks by Shaw and Weaver (1965), Potter et al. (1980) and Selley (1982).

As noted from Table 5.1, the Lower Lias and the Kimmeridge Clay samples show a wide range of lithologies. Lithologic Types 1 - 9 have been identified in the Lower Lias whereas Types 1 - 8 are identified in the Kimmeridge Clay. The Kimmeridge Clay Sample OSD/KC.1 is a non-laminated coccolith limestone from the Ringstead Bay area (see Plate 5.1). Tyson et al. (1979) identified both the laminated and the non-laminated varieties of this limestone from the

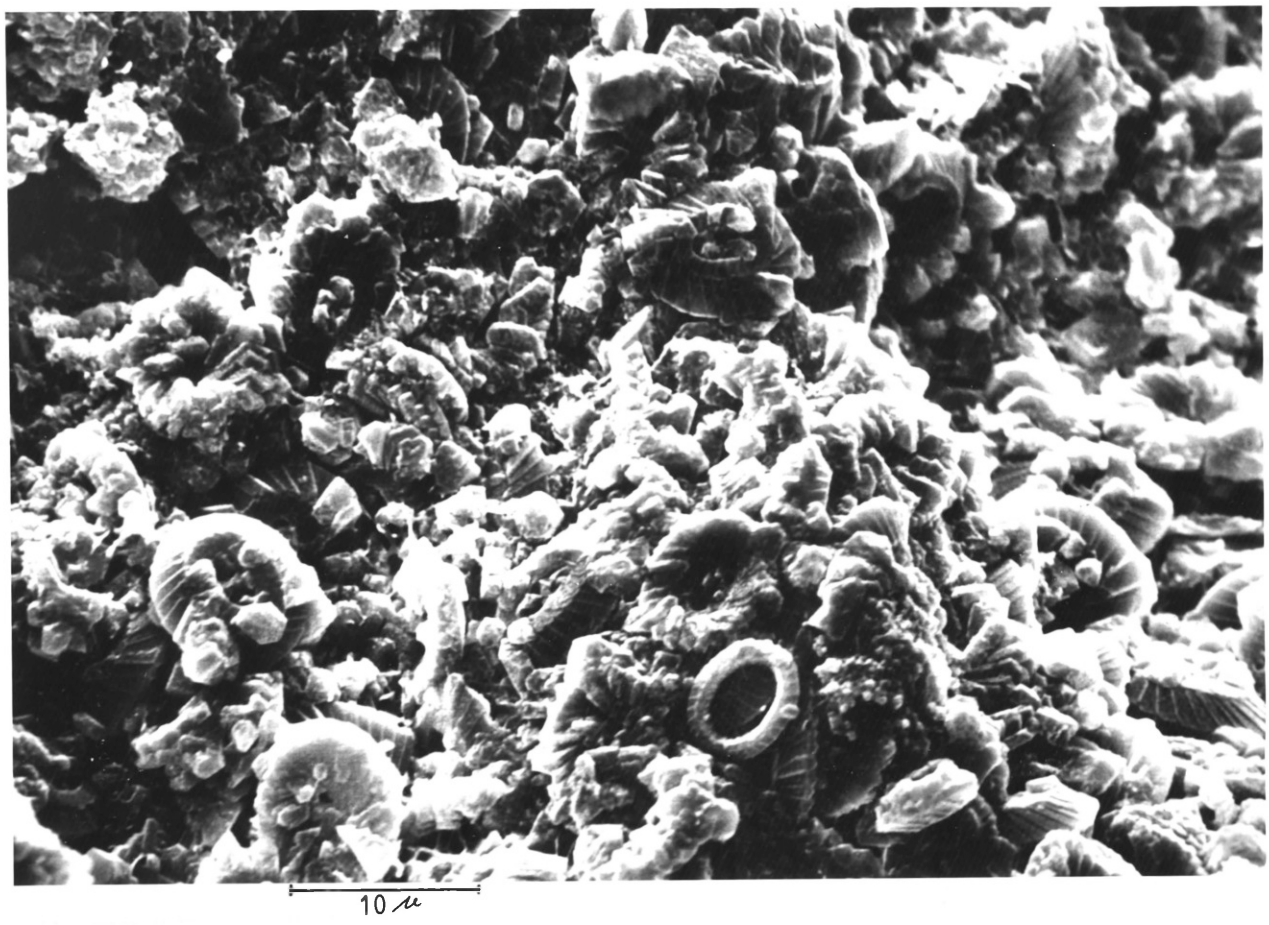


PLATE 5.1 - A NORMAL KIMMERIDGE CLAY COCCOLITH LIMESTONE FROM THE RINGSTEAD BAY AREA (SAMPLE: OSD/KC.1; TOTAL ORGANIC CARBON CONTENT = 2.95%).

Kimmeridge Clay Formation. They described the coccolith limestone bands in this formation as representing the maximum developments of anaerobic bottom conditions in the Kimmeridgian Water Column during which times, the top of the H_2S zone migrated to such high levels that seasonal convective processes provided nutrients to the euphotic zone and there stimulated coccolith blooms. By contrast, the Oxford Clay samples show restricted lithologic variations and only lithologic Types 5-8 have been identified. In the Oxford Clay Formation, the mudstones occur mainly in the upper and middle parts whereas the mud-shales are restricted to the lower part of the formation. No such single litholgic trend is observed for the Kimmeridge Clay and the Lower Lias units. Alternations of the various lithologies tend to occur at various stratigraphic levels in these two formations.

The occurrence of laminated sedimentary rocks are often associated with sediment deposition in relatively undisturbed anoxic bottom waters with very restricted benthic faunal population, and the microlaminae in the rocks are often interpreted as varves due to seasonal fall of plankton (Hallam, 1960, 1964, 1975; Morris, 1980). The absence of lamination (as in normal limestones and mudstones) therefore imply deposition in oxygenated bottom waters where the level of organic matter destruction can be high. If this paleo-environmental deductive hypothesis based on lithology is correct, it follows that there must have been up and down movements in the position of the oxygen-minimum level in the Lower Liassic and the Kimmeridgian Seas in Southern England. A one-directional vertical

shift in the position of this oxygen-minimum level would have been the case for the Oxford Clay Sea with the resultant deposition of anoxic sedimentary facies in the early and non-anoxic facies in the later periods.

The colour of all the Jurassic mudrocks tend to be dark, ranging from grey to black (see Table 5.1). Pettijohn (1975) discussed the relationships of the colour of sedimentary mudrocks to their depositional environments and organic matter richness. The dark coloured rocks are considered to represent oxygen-deficient environments and are believed to be rich in carbonaceous materials. The reddish mudrocks are, by contrast, indicative of highly oxidising depositional environments which are not conducive to organic matter preservation. However, Tissot et al. (1980) have noted that some Middle Cretaceous black shales in Atlantic Basins (marine) even though very organic-rich contain biodegraded marine planktonic organic matter with preferential concentrations of more resistant, hydrogen-poor, terrestrially derived organic matter, and in particular, residual oxidised and/or recycled organic materials which cannot be further degraded, and these are believed to be indicative of oxic depositional conditions.

5.2 CLAY MINERALOGY

5.2.1 Clay Minerals and their Contents in the Jurassic Mudrocks

The results of the semi-quantitative analysis of the clay fraction of 35 samples are presented in Table 5.3. The samples include 19 from the Lower Lias, 5 from the

TABLE 5.3 CLAY MINERAL COMPOSITION IN THE $<2\mu$ FRACTION OF SOME SAMPLES FROM THE LOWER LIAS, THE OXFORD CLAY, AND THE KIMMERIDGE CLAY

SAMPLE	FORMATION AND LOCALITY	ILLITE %	I-S MIXED-LAYERS %	KAOLINITE %	CHLORITE %	VERMI-CULITE %	% SMECTITE LAYERS IN THE MIXED LAYERS	
							RANDOM	ORDERED
OSD/KC.2	Kimmeridge Clay (Outcrop, Dorset)	40	47	10	3	-	90-65	34-18
OSD/KC.4		48	36	14	Trace	2	75-40	36-25
OSD/KC.6		40	48	10	"	2	77-40	36-20
OSD/KC.12		44	42	12	"	2	60-44	27-18
OSD/OC.1	Oxford Clay (Outcrop, Dorset)	41	51	4	4	-	-	30-10
OSD/OC.4		32	54	13	Trace	1	77-40	35-30
OSD/LL.2	Lower Lias (Outcrop, Dorset)	24	66	6	4	Trace	54	20
OSD/LL.3		25	65	6	4	"	65	35-15
OSD/LL.5		33	58	5	4	"	70-65	27
OSD/LL.8		31	68	-	1	-	68-65	27-18
BR/LL.1	Lower Lias (Burton Row Bore-hole)	35	45	13	7	-	45-40	36-20
BR/LL.3		41	51	2	6	-	90	34-22
BR/LL.7		30	57	7	6	-	76	25
BR/LL.9		45	44	5	6	-	-	36-12
BR/LL.11		48	51	-	1	-	n.d.	n.d.
WK/KC.1	Kimmeridge Clay (Winter-borne Kingston)	34	59	5	2	Trace	40	36-10
WK/KC.3		42	51	2	5	-	44-40	36-12
WK/LL.1	Lower Lias (Winter-borne Kingston)	27	56	12	5	-	48	34-20
WK/LL.4		31	56	7	6	-	55	34-12
WK/LL.5		42	53	Trace	5	-	77	30-12
WK/LL.6		50	46	"	4	-	78	30-20
WCH/LL.2	Lower Lias (Winchester No. 1)	33	50	12	5	-	-	27-15

TABLE 5.3 (Cont.)

SAMPLE	FORMATION AND LOCALITY	ILLITE %	I-S MIXED LAYERS %	KAOLINITE %	CHLORITE %	VERMI-CULITE %	% SMECTITE LAYERS IN THE MIXED LAYERS	
							RANDOM	ORDERED
WM/KC.1	Kimmeridge Clay (Warlingham)	44	50	6	Trace	-	73-51	30-20
WM/KC.4		31	59	5	4	-	n.d.	n.d.
WM/KC.9		44	52	1	3	-	64-55	25-15
WM/OC.2	Oxford Clay (Warlingham)	43	47	6	3	1	-	25-18
WM/OC.3		40	51	3	6	-	44	22-15
WM/LL.2	Lower Lias (Warlingham)	28	49	14	1	1	-	36-12
WM/LL.3		36	52	7	5	-	-	30-12
WM/LL.4		40	49	8	Trace	3	-	34-12
WM/LL.6		38	52	6	3	1	-	35-25
PH/KC.1	Kimmeridge Clay (Penshurst)	36	56	6	2	-	72	25-18
PH/KC.4		43	53	Trace	4	-	48	30-22
PH/OC.3	Oxford Clay (Penshurst)	46	42	6	4	2	-	30-15
PH/LL.2	Lower Lias (Penshurst)	50	42	4	4	-	-	27-18

n.d. = not determined

Oxford Clay and 11 from the Kimmeridge Clay.

The mineralogic compositions of the clay fractions from these 3 formations are very similar. The clay minerals identified include discrete illite, illite-smectite mixed layers, kaolinite, chlorite and vermiculite. A summary of the percentage contents of the clay minerals together with the percentages of expandable layers in interstratified illite-smectites in the 3 formations are shown in Table 5.4. Discrete illite and interstratified illite-smectites constitute the most abundant clay minerals in the Jurassic mud-rocks, and they account for over 75% of the clay fraction in all the samples. Kaolinite, chlorite and vermiculite are present in minor amounts with kaolinite being the most common and most abundant of the three and vermiculite the least.

Two characteristic suite of illite-smectite mixed-layers were identified:

(1) highly expandable randomly-ordered phases with percentage of expandable layers of 40% and above (Reynolds and Hower, 1970) (see Fig. 5.1).

(2) less expandable ordered phases (with expandable layer percentages less than 40%) (Fig. 5.2).

The randomly-ordered illite-smectites have varied expandability with smectite layers constituting up to 90% in some Lower Lias and Kimmeridge Clay samples, and up to 70% in some Oxford Clay samples. The occurrence of random phases with varied expandability in a sample was indicated by the presence of a very broad, poorly defined peak at about 17Å in the glycolated clay mount. The

(003) illite-(glycol) smectite reflection of such a sample was noticed to be broad and multi-peaked (see Fig. 5.3). The less expandable illite-smectite mixed layers also have varied expandability and generally formed broad frequently indistinct peaks between 10.5Å and 13.5Å when glycolated, implying ordered illite-smectite inter-stratification with interlayer compositions of less than 40% smectite. Interlayer compositions of as low as 10% smectite have been noted in some samples (Table 5.3).

Many samples contain both the random and the ordered mixed-layer phases (see Fig. 5.3), and in terms of occurrence, the ordered phases tend to be more common than the randomly-ordered phases. The random phases were not identified in some samples whereas the ordered ones are ubiquitous in all the samples.

No discrete smectite was identified in any of the Jurassic samples.

TABLE 5.4 A SUMMARY OF CLAY MINERAL CONTENT (%) AND PERCENTAGE OF EXPANDABLE LAYERS IN INTERSTRATIFIED ILLITE-SMECTITES IN THE SAMPLES FROM THE THREE JURASSIC FORMATIONS

Clay Mineral	Lower Lias	Oxford Clay	Kimmeridge Clay
Discrete Illite	24 - 50	32 - 46	31 - 48
Illite-Smectites	42 - 68	42 - 54	36 - 59
Kaolinite	0 - 14	3 - 13	Trace - 14
Chlorite	Trace - 7	Trace - 6	Trace - 5
Vermiculite	0 - 3	0 - 2	0 - 2
% Expandable layers in Illite-Smectites	10 - 90	10 - 70	10 - 90

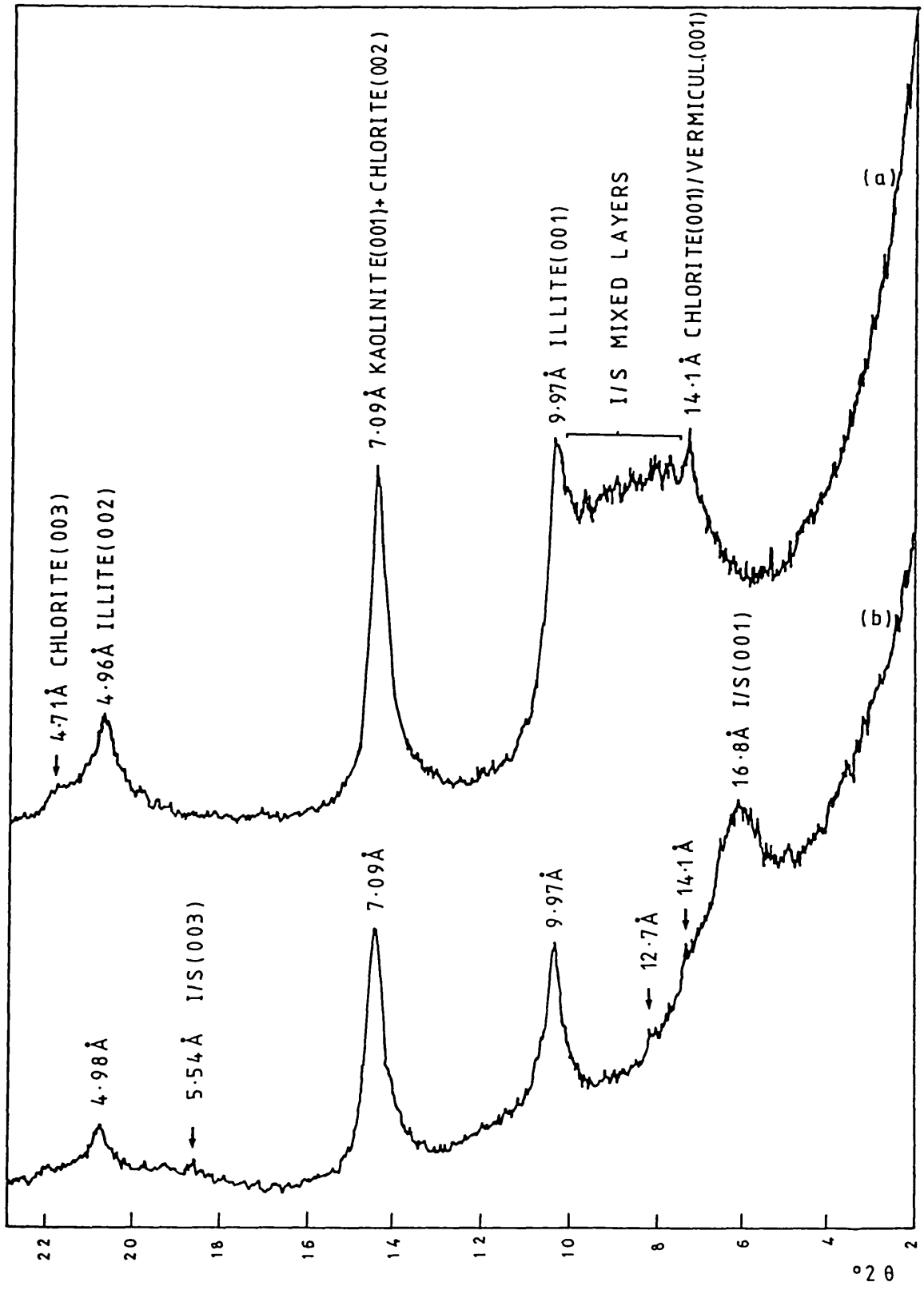


FIG. 5.1 X-RAY DIFFRACTOGRAMS OF $< 2\mu$ FRACTION OF SAMPLE OSD/LL.5 TYPIFIED BY THE PRESENCE OF MAINLY THE HIGHLY EXPANDABLE ILLITE-SMECTITE (I/S) MIXED-LAYERS (a) = AIR-DRIED UNTREATED SAMPLE (b) = GLYCOLATED

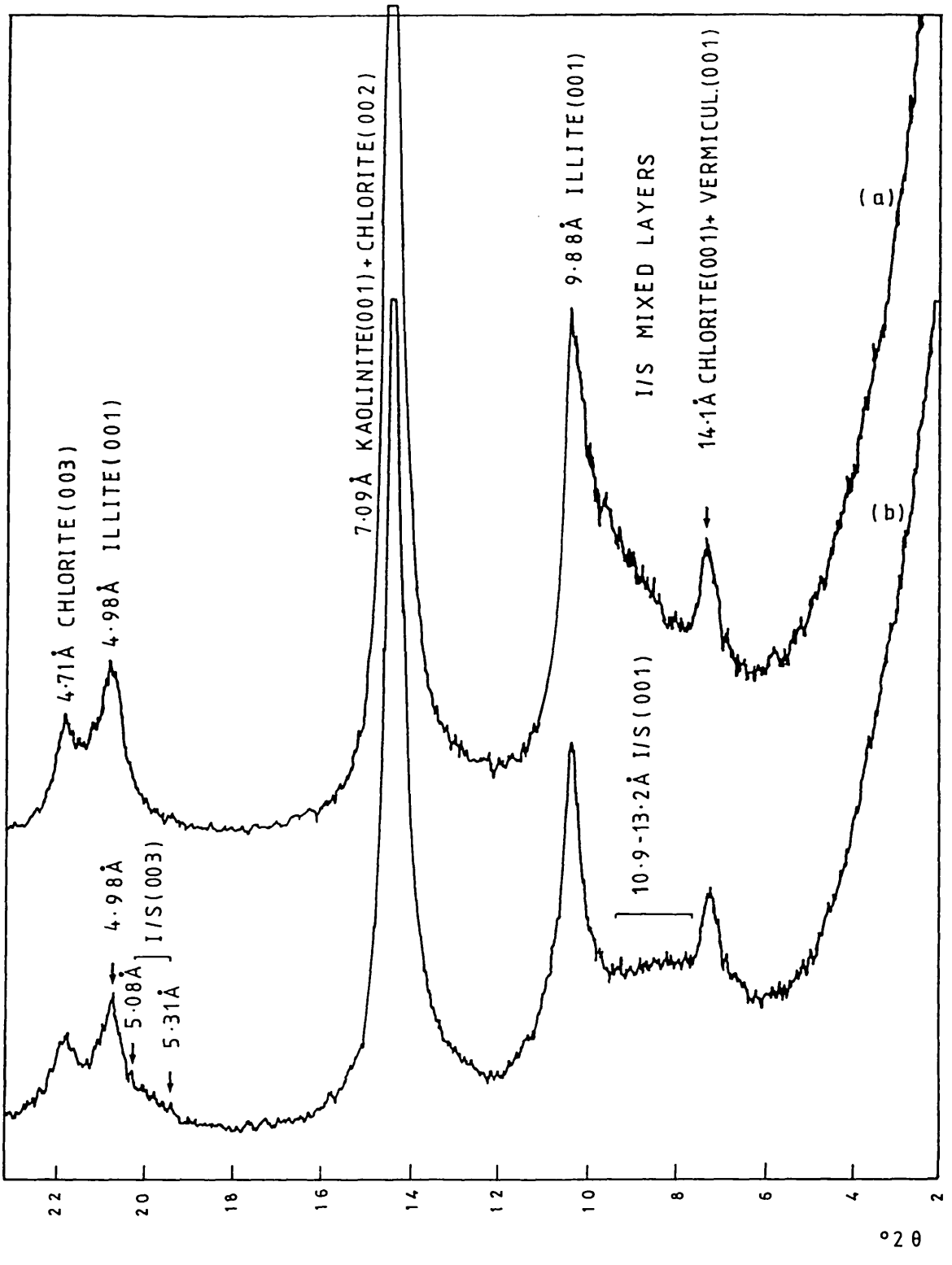


FIG. 5.2 X-RAY DIFFRACTOGRAMS OF $< 2\mu$ FRACTION OF SAMPLE WM/LL.2 (PRESENT BURIAL DEPTH: 4300 FT.) TYPIFIED BY THE PRESENCE OF LOW EXPANDABILITY ORDERED ILLITE-SMECTITE (I/S) MIXED-LAYERS (a) AIR-DRIED UNTREATED (b) GLYCOLATED

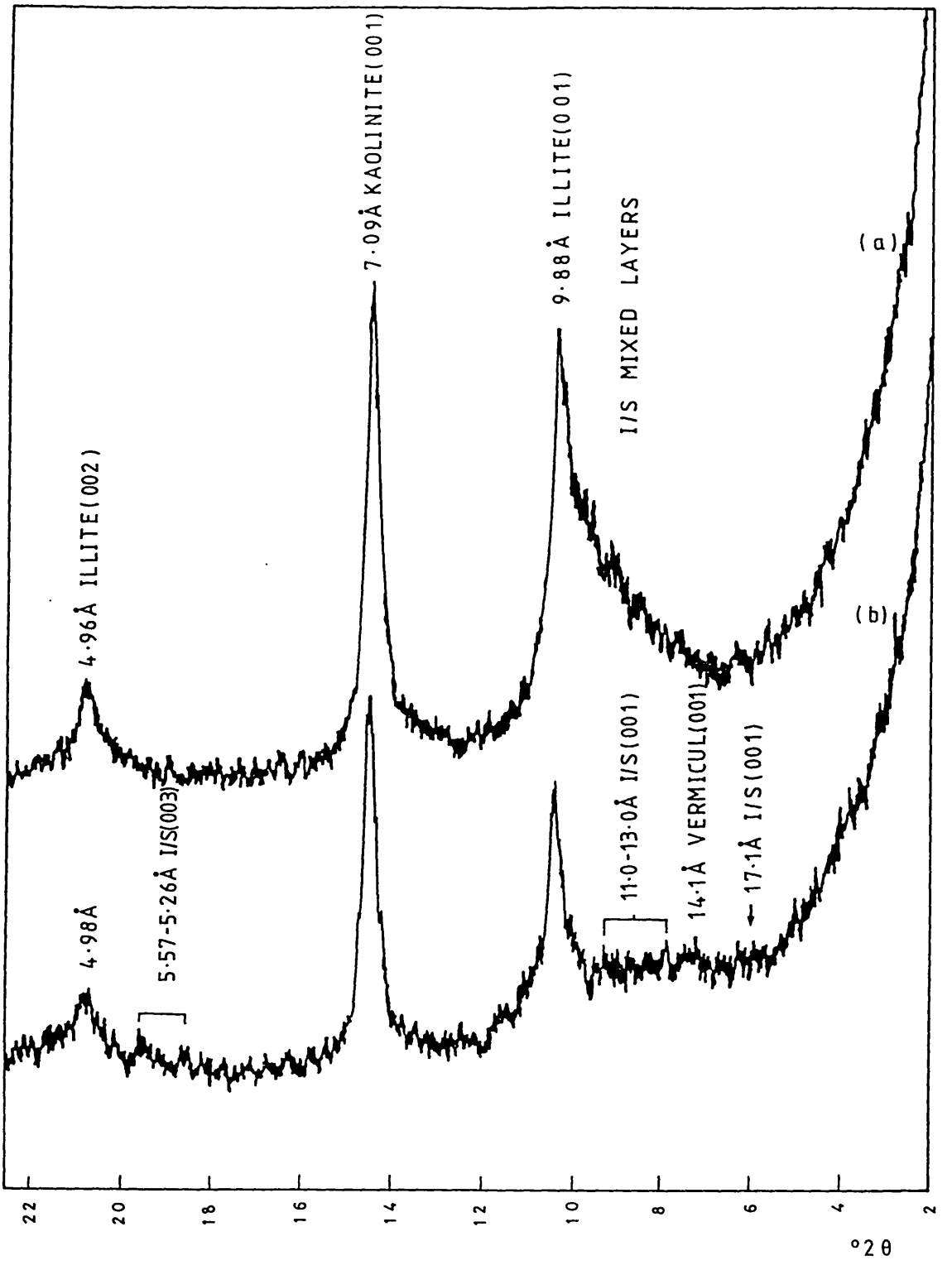


FIG. 5.3 X-RAY DIFFRACTOGRAMS OF $< 2\mu$ FRACTION OF SAMPLE OSD/OC.4 TYPIFIED BY THE PRESENCE OF BOTH RANDOM AND ORDERED ILLITE-SMECTITE (I/S) PHASES (a) = AIR-DRIED UNTREATED (b) = GLYCOLATED

5.2.2 Clay Diagenesis and Possible Source(s) of the Jurassic Clay Minerals

Following the work of Burst (1969) and Perry and Hower (1972) on burial diagenesis of clay minerals in sediments of the Gulf Coast of America, several excellent studies have been carried out in other sedimentary basins. Notable among these have been the work of Heling (1978) on the Rhine Graben of Germany and of Foscolos et al. (1976) and Powell et al. (1978) on basins in N.E. British Columbia and the N.W. Territories of Canada. In each of these studies the disappearance with depth of discrete smectite and the appearance of neo-formed discrete phases such as kaolinite and chlorite were reported. In the majority of cases the loss of smectite has also been accompanied by the appearance of interlayered minerals, most commonly illite-smectites in which illitic layers appear to form by replacement of Si by Al in the smectite tetrahedral sheet and fixation of K^+ at interlayer sites with expulsion of water. Boles and Franks (1979) constructed an approximate temperature scale for inorganic diagenetic changes occurring in interbedded permeable and impermeable sediments in which they proposed that illitisation of smectite clays occurred principally over the range of 50^{o} - $100^{o}C$. And according to Hoffman and Hower (1979), ordered illite-smectites are typical of sediments which have undergone diagenetic modifications at temperatures in excess of $100^{o}C$. Pearson et al. (1981), based on their comparative studies of clay diagenesis and organic maturation in Northern North Sea Middle Jurassic to Oligocene sediments, noted that significant illitisation of detrital smectites

begins at a vitrinite reflectance level of about 0.4% R_o and effectively ceases after the structure becomes ordered at about 0.6% R_o. However, Foscolos et al. (1976) reported the occurrence of this illite-smectite ordering point in the vitrinite reflectance range of 1.0 - 1.5% Ro in the Cretaceous shales of N.E. British Columbia, Canada.

The co-existence of both random and ordered interstratified illite-smectites in many of the Jurassic samples from southern England noted in this study therefore implies that most of these ordered phases have not been produced by the diagenetic transformation of the Jurassic section but have rather been recycled or derived from older (pre-Jurassic) sedimentary rocks. According to Reynolds and Hower (1970), with the onset of illitisation of discrete smectites, the percentage of smectite layers in the random illite-smectite mixed-layers should decrease consistently from 100% to 40% with increasing intensity of diagenetic modification. The lack of such consistent reduction trends in the interlayer compositions of smectite layers with depth of burial (or increasing diagenesis) noted in the Jurassic samples from Burton Row and Winterbourne Kingston Wells seem to imply that some of the random phases in certain Jurassic horizons were also derived from older rocks. The presence of randomly-ordered interstratified illite-smectites in any of the analysed sample may therefore be interpreted to imply that such Jurassic horizon in the locality of that sample has not been heated beyond 100°C. However, the absence of these highly expandable mixed-layer

phases in a sample does not necessarily indicate a diagenetic modification of such a Jurassic horizon at temperatures in excess of 100°C. Hurst (1981) noted the occurrence of both random and ordered illite-smectites in the Jurassic shales from Brora in N.E. Scotland at maximum burial temperature of 50° - 60°C. He identified the Devonian sediments to the N.E. of Brora to be the probable source rocks for the ordered illite-smectites. He interpreted the variable composition of these ordered phases (variable percentages of smectite layers) as being the product of minor alteration during weathering and of compositional variations in the source rocks.

The clay mineralogy of the Carboniferous rocks of the South Wales coalfield, documented by Gill et al. (1979) show a very close similarity to that of the Jurassic mudrocks of southern England. Both random and regular interstratified illite-smectites with expandable layer percentages ranging from 50% to 20% were identified in the Carboniferous rocks. Diagenetic levels of up to the anthracite coal stage (vitrinite reflectance greater than 2% R_o) have been identified in the Carboniferous rocks of the South Wales Coalfield (Gill et al., 1979). As already noted in Chapter 2, the Late Carboniferous Hercynian orogenic phase resulted in the thrusting and overfolding of the Devonian and Carboniferous rocks in S.W. England accompanied by the metamorphism of the rocks. And based on the fact that sections of deformed Palaeozoic rocks (by both the Caledonian and the Hercynian orogenic phases) remained positive areas in the southern part of

Britain throughout most of the Mesozoic Era (Chapter 2), it may be reasoned that some of the Jurassic clay minerals identified in this study together with other sedimentary inorganic and organic (particularly the humic or coaly fragments) materials must have been derived from these older rocks through erosion.

Shaw (1980), Hurst (1981), and others have discussed the origin and occurrence of clay minerals in both recent and ancient sediments. Detrital clay minerals in sediments are derived from two main sources - through erosion of older sedimentary rocks and by primary formation in soils and weathering profiles via the breakdown of pre-existing silicate minerals. Smectites and vermiculites are common products of weathering. The weathering of basic igneous and metamorphic rocks under alkaline and impeded drainage conditions results in the formation of these expandable clay minerals. Active volcanic eruptions in the S.W. England, which resulted in the emplacement of basic igneous rocks, occurred during the Devonian and the Permian times (see Chapter 2). Primary formation of illite is often associated with the weathering of acidic rocks in well drained temperate alkaline environments, whereas primary chlorites are formed under similar conditions but from basic rocks. Widespread intrusions of acidic igneous rocks (e.g. the granite bodies) associated with the Hercynian Orogeny were recorded during the Late Carboniferous in S.W. England (Chapter 2). Kaolinite distribution in modern oceans tend to be concentrated near to major landmasses, particularly adjacent to areas where the climate is warm and humid, and where leaching is the dominant weathering

process (Griffin et al., 1968; Shaw, 1980). No paleoclimatic evidence is known to confirm the presence of lateritic weathering of landmasses in the neighbourhood of S. England during the Jurassic. However, Shaw (1980) pointed out that in some cases clay minerals may be sourced by hydrothermal alterations in active geothermal fields, and noted that the high kaolinite contents in marine sediments off the coast of S.W. England reflect hydrothermally formed kaolinite source material.

The combinations of high temperature polymorph illite-smectites, discrete illite, kaolinite, and chlorite as detrital clays in the Jurassic mudrocks imply that most of the clay fraction would be or was stable up to burial temperatures of at least 100°C (Hoffman and Hower, 1979). Therefore, the expulsion of large volumes of clay interlayer water, frequently proposed to aid primary migration of hydrocarbons, is unlikely from such sediments (Hurst, 1981).

5.3 ORGANIC MATTER RICHNESS OF THE JURASSIC MUDROCKS

5.3.1 Total Organic Carbon (TOC) Contents of the Samples

The petroleum generating potential of a sediment depends on its volume, degree of thermal maturation, organic content, type of organic constituents, and the degree of microbial degradation of the organic materials preserved. Marine sediments are regarded as more oil-prone than terrestrial and deltaic sediments for a given volume,

thermal maturation level, and organic content (Tissot and Welte, 1978). Primary organic constituents such as phytoplankton are more oil-prone than terrestrial organic constituents such as higher plant fragments. There is also a lower percentage of gas - or non-generating degraded and recycled organic matter preserved in marine sediments compared to fluvial or deltaic sediments (Ibach, 1982).

Even when oil-prone organic constituents are preserved in a sediment, the total organic carbon content may be too low to generate commercial quantities of oil under favourable conditions of thermal maturation. For this reason, petroleum source rocks are often initially defined on the basis of total organic carbon (TOC) by weight percent. Clastic (potential) source rocks are defined as containing at least 0.5% TOC, whereas carbonate source or potential source rocks must contain at least 0.3% TOC (Tissot and Welte, 1978).

Results of the TOC analysis of the outcrop samples and the borehole samples from Burton Row, Winchester-1, Marchwood, Henfield, Winterborne Kingston, and Penshurst Wells are shown in Table 5.1 together with the lithologic descriptions of the samples. The TOC data for samples from Cooles-Farm-1, Arreton-2, and Cranborne -1 Wells are shown in Table 5.5. From these tables, it is noted that all the Jurassic rock samples, except one Lower Lias carbonate rock sample (WM/LL.3) from the Warlingham borehole, contain organic carbon in excess of the minimum required to qualify them as potential hydrocarbon source rock materials. The TOC values obtained for the Lower Lias samples vary from 0.26% to 7.36%, while those for the Oxford Clay and

TABLE 5.5 ORGANIC CARBON CONTENTS OF SAMPLES FROM ARRETON-2, CRANBORNE-1 AND COOLES-FARM-1 WELLS

LOCALITY	SAMPLE NUMBER AND DEPTH (FT.)	FORMATION	TOTAL ORGANIC CARBON (TOC) (Wt.%)
Arreton No. 2 Well (Isle of Wight)	AR/KC.1 (2700-2800)	Kimmeridge Clay	-
	AR/KC.2 (2800-2900)		3.02
	AR/KC.3 (2900-3000)		-
	AR/KC.4 (3000-3100)		2.08
	AR/KC.5 (3100-3200)		-
	AR/KC.6 (3200-3300)		5.71
	AR/KC.7 (3300-3400)		-
	AR/KC.8 (3400-3500)		4.59
	AR/KC.9 (3500-3600)		-
	AR/KC.10 (3600-3700)		2.71
	AR/OC.1 (4000-4100)	Oxford Clay	1.30
	AR/OC.2 (4100-4200)		-
	AR/OC.3 (4200-4300)		2.69
	AR/OC.4 (4300-4400)		-
	AR/LL.1 (5500-5600)	Lower Lias	-
	AR/LL.2 (5600-5700)		1.21
	AR/LL.3 (5700-5800)		-
	AR/LL.4 (5800-5900)		1.87
	AR/LL.5 (5900-6000)		-
	AR/LL.6 (6000-6100)		1.32
	AR/LL.7 (6100-6200)		-
	AR/LL.8 (6200-6300)		2.79
	AR/LL.9 (6300-6400)		-

TABLE 5.5 (Cont.)

LOCALITY	SAMPLE NUMBER AND DEPTH (FT.)	FORMATION	TOTAL ORGANIC CARBON (TOC) (Wt.%)
Cranborne No. 1 Well (Dorset)	CN/KC.1 (1718.7)	Kimmeridge Clay	3.26
	CN/OC.1 (1974.6)	Oxford Clay	2.31
	CN/OC.2 (2105.8-2112.3)		2.01
	CN/OC.3 (2230.4-2243.5)		1.75
	CN/OC.4 (2361.6-2374.7)		5.65
	CN/OC.5 (2466.6)		3.66
	CN/LL.1 (3568.6-3575)	Lower Lias	1.62
	CN/LL.2 (3673.6-3680)		1.90
	CN/LL.3 (3739.2-3745.8)		2.97
	CN/LL.4 (3804.8-3824.5)		2.42
	CN/LL.5 (3936-3949.1)		3.10
	CN/LL.6 (4001.6-4014.7)		2.51
Cooles-Farm No. 1 Well	CF/LL.1 (1000)	Lower Lias	2.21
	CF/LL.2 (1200)		1.34
	CF/LL.3 (1400)		2.21
	CF/LL.4 (1500)		2.03
	CF/LL.5 (1700)		0.72
	CF/LL.6 (1800)		1.94
	CF/LL.7 (1900)		0.99

the Kimmeridge Clay samples vary from 0.79% to 12.36% and from 0.98% to 20.48% respectively.

5.3.2 Relationships Between Depositional Environments, Lithologic Variations, and Sedimentation Rates of the Lower Lias, the Oxford Clay and the Kimmeridge Clay Formations and their Organic Carbon Richness

Many authors now agree that the preservation of organic matter in sediments is largely controlled by the extent of microbial degradation (i.e. on oxic-anoxic conditions), with bioturbation being an additional contributing factor (Tissot and Welte, 1978; Coleman et al., 1979; Demaison and Moore, 1980; Kinghorn, 1983). High rates of primary production of organic matter alone do not guarantee that large amounts of that organic matter will be preserved. Microbial degradation results in an elimination of functional groups on the organic molecules. In particular, the hydrocarbon chains and carboxyl groups are easily attacked and carbon dioxide (CO_2) or methane (CH_4) is produced (Tissot and Welte, 1978). Because the presence of long hydrocarbon chains is important to liquid oil formation, reduction of these chains by microbial activity not only reduces the total organic carbon content of the sediment, it also reduces the ability of the organic matter to generate oil as the thermal "oil window" is reached (Ibach, 1982). The preservation of organic-rich sediments capable of generating oil therefore depends on depositional conditions that reduce the efficiency of microbial degradation.

Coleman et al. (1979) described four major zones where organic matter degradation occur with increasing depth of burial (Fig. 5.4). Microbial and benthic activity

Depositional Water	Organic detritus Mineral detritus Dissolved oxygen) by diffusion Dissolved sulphate)] Supplied to sediment column
Aerobic Oxidation Zone	Organic matter decomposed Carbon dioxide produced: lost to depositional water
Sulphate Reduction Zone	Organic matter decomposed. Carbon dioxide produced: carbonate minerals precipitate Sulphate (from depositional water) reduced to sulphides. Sulphides precipitate (pyrite)
Fermentation Zone	Organic matter decomposed. Methane produced. Carbon dioxide produced: carbonate minerals precipitate.
Thermal Maturation Zones	Organic matter altered Carbon dioxide produced by decarboxylation Carbon minerals precipitate
"Oil Window"	Organic matter altered Liquid hydrocarbons form
	Organic matter converted to methane and carbon-rich residues

Organic matter can also be destroyed by reactions with oxidised iron compounds present in the mineral detritus

FIG. 5.4 - ZONES OF ORGANIC DEGRADATION (AFTER COLEMAN ET AL. 1979)

decreases rapidly with depth, so that the most intense degradation of organic matter occurs in the near-surface aerobic oxidation zone and in the sulphate reduction zone. The vertical extent of these zones is limited by the diffusible limit of oxygen (O_2) and sulphates (SO_4) through the sediment column, which is controlled by the sediment composition (Tissot and Welte, 1978; Coleman et al. 1979). Therefore, more organic matter with a higher oil-generating quality is preserved in fine-grained sediments, where the diffusible limit is reduced relative to granular sediments, and in sediments deposited in anoxic bottom waters, where the aerobic oxidation zone has been eliminated.

Sedimentation rate has been noted to be critical in organic matter preservation because it controls the rate of passage of a parcel of sediment through this intense near-surface zone of microbial degradation. Heath et al. (1977) and Muller and Suess (1979) demonstrated in their studies that the organic carbon content of recent marine sediments increases quantitatively with sedimentation rate. Ibach (1982) noted similar quantitative relations between sedimentation rate and total organic carbon content in fine-grained ancient marine sediments of Jurassic, Cretaceous and Cenozoic ages. He also noted that for any given sedimentation rate, the total organic carbon content by weight percent increases from calcareous sediments to calcareous - siliceous sediments to siliceous sediments to black shales. The TOC content was also found to vary with sedimentation rate for each lithology. He pointed out that the increase in TOC content with increasing

sedimentation rate will only be true if the primary productivity of organic matter also increases at a corresponding rate. However, above a critical sedimentation rate, Ibach (1982) observed that the TOC content typically decreases with increasing sedimentation rate owing to clastic dilution.

The lithologic effect on organic matter contents of fine-grained sediments reflects differences in the degree of exposure to microbial degradation. Dark coloured and laminated mudrocks represent oxygen-deficient or anoxic environments of deposition. The relation between the organic content of siliceous and calcareous fine-grained sediments reflects differences in the diffusible limit of O_2 and SO_4, and therefore the vertical limit of the aerobic oxidation and sulphate reduction zones. Krumbein and Sloss (1963) indicated that siliceous sediments are less permeable than calcareous sediments owing to the lower solubility of SiO_2 compared with $CaCO_3$ in near surface sediments. The formation of organo-clay complexes in argillaceous sediments is believed to partially account for enhanced concentration or preservation of organic matter in these sediments (Grim, 1947; Shaw, 1980).

Table 5.6 shows the ranges of TOC contents in the various lithologic types in the Lower Lias, the Oxford Clay and the Kimmeridge Clay Formations. In each of the three formations, the shales (argillaceous) are noted to be richer in organic carbon contents than the limestones (calcareous). The mudstones occupy the intermediate position in organic richness. The TOC contents of the argillaceous limestones are higher than those of the normal

TABLE 5.6 SUMMARY OF TOTAL ORGANIC CARBON CONTENTS (TOC) AND THE RANGES OF IDENTIFIED LITHOLOGIES IN THE LOWER LIAS, OXFORD CLAY AND KIMMERIDGE CLAY

Lithologic Type	Lower Lias	Oxford Clay	Kimmeridge Clay
Normal Limestone: TOC Colour (No. of samples)	0.26 - 1.91 Grey to dark grey (10)	-	1.05 - 2.95 Dark grey to black (3)
Laminated limestone: TOC Colour (No. of samples)	2.86 Dark grey (1)	-	-
Normal Argillaceous Limestone: TOC Colour (No. of samples)	0.78 - 1.39 Grey to very dark grey (4)	-	1.20 - 4.95 Grey to very dark grey (5)
Laminated Argillaceous Limestone: TOC Colour (No. of samples)	3.76 - 6.18 Dark grey to black (3)	-	-
Calcareous Mudstone: TOC Colour (No. of samples)	0.72-2.50 Dark grey to very dark grey (7)	0.79 - 1.22 Dark grey (6)	0.98 - 3.26 Dark to very dark grey (5)
Normal Mudstone: TOC Colour (No. of Samples)	0.72 - 2.61 Dark grey (10)	1.15 - 1.73 Grey to dark grey (3)	1.51 - 2.50 Very dark grey to black (3)
Calcareous Mudshale: TOC Colour (No. of samples)	2.34 - 4.54 Very dark grey (3)	2.27 Dark grey (1)	1.47 - 10.02 Black (2)
Normal Mudshale: TOC Colour (No. of samples)	1.44 - 7.36 Very dark grey to black (10)	2.31 - 12.36 Dark grey to very dark greyish brown (10)	1.61 - 20.48 Dark grey to black (14)
Clayshale: TOC Colour (No. of samples)	5.98 Very dark grey (1)	-	-

limestones. The laminated limestones which represent highly anoxic depositional environments are noted to be very organic rich compared to their non-laminated counterparts.

When the organic carbon contents of samples of similar lithology from the three Jurassic formations are compared, a trend of increasing organic richness from the Lower Lias through the Oxford Clay to the Kimmeridge Clay is noted. The highest TOC values were obtained for the mudshales - the values ranged up to 7.36% for the Lower Lias, 12.36% for the Oxford Clay, and 20.48% for the Kimmeridge Clay. Organic carbon values as high as 35.1% (Williams and Douglas, 1980), and 43.3% (Macdougal and Cawley, 1951) have been recorded for the bituminous Kimmeridge Shales.

In order to establish a possible explanation for this observed trend in organic carbon richness, sedimentation rates for the three formations were calculated in three boreholes (Arreton-2, Winchester-1 and Penshurst) where complete Jurassic sections occur (see Table 5.7 below) in southern England.

The time interval, in million years, for each formation is based on the Geologic Time Table compiled by F.W.B. Van Eysinga (3rd Edition) in 1975. The average sedimentation rates obtained for the formations are 37.7 ft/m.y. for the Lower Lias, 77.5 ft/m.y. for the Oxford Clay, and 290.2 ft/m.y. for the Kimmeridge Clay. This trend of increasing sedimentation rate from the Lower Lias to the Kimmeridge Clay may be considered to provide an explanation for the trend of increasing organic matter richness in the rocks of these formations.

TABLE 5.7: CALCULATION OF SEDIMENTATION RATES FOR THE LOWER LIAS, THE OXFORD CLAY AND THE KIMMERIDGE CLAY IN S. ENGLAND

BOREHOLE	LOWER LIAS			OXFORD CLAY			KIMMERIDGE CLAY		
	Time Interval (m.y.)	Thick-ness (ft)	Sediment-ation Rate (ft/m.y.)	Time Interval (m.y.)	Thick-ness (ft)	Sediment-ation Rate (ft/m.y.)	Time Interval (m.y.)	Thick-ness (ft)	Sediment-ation Rate (ft/m.y.)
Arreton-2	21	858	40.9	5	434	86.8	4	1105	276.2
Winchester-1	"	968	46.1	"	480	96.0	"	1136	284.0
Penshurst	"	550	26.2	"	249	49.8	"	1242	310.5
Average Sedimentation Rate			37.7			77.5			290.2

CHAPTER VI

KEROGEN TYPES AND MATURITY-I: KEROGEN CHARACTERIZATION BY ELEMENTAL ANALYSIS, TRANSMITTED-LIGHT MICROSCOPY AND DENSITY FRACTIONATION

KEROGEN TYPES AND MATURITY - I:
KEROGEN CHARACTERIZATION BY ELEMENTAL ANALYSIS, TRANSMITTED-LIGHT MICROSCOPY AND DENSITY FRACTIONATION

6.1 ELEMENTAL COMPOSITION OF KEROGENS

6.1.1 Introduction

The term kerogen is used here to designate the disseminated organic matter of sedimentary rocks that is insoluble in non-oxidising mineral acids, bases, and organic solvents (Brooks, 1981). It is believed to be a three-dimensional macromolecule consisting of poly-aromatic nuclei cross-linked by various bridges which are hydrocarbon chains and functional groups such as esters, ketones, ethers or sulphides. Lipid molecules or geo-chemical fossils such as isoprenoid hydrocarbons can be entrapped within this three-dimensional kerogen matrix either physically or chemically - by weak absorption forces (Tissot and Welte, 1978; Kinghorn, 1983).

Following the work of Van Krevelen (1961) on thermal evolution of coal macerals, Tissot et al. (1974), on the basis of elemental composition (C, H, O) employing cross-plots of atomic $^{H}/_{C}$ and $^{O}/_{C}$ ratios, defined the first three types of kerogen (i.e. types I, II, and III). More recently, on the same basis, a fourth kerogen type has been identified and described (Bostick, 1979; Tissot et al., 1980, Brooks, 1981, Kinghorn, 1983) (Fig. 6.1). Type I refers to kerogen with a high initial hydrogen content (atomic $^{H}/_{C}$ ratio $\geq$ 1.5) but a low oxygen content (atomic O/C ratio $<$ 0.1). It comprises lipid material with a lot

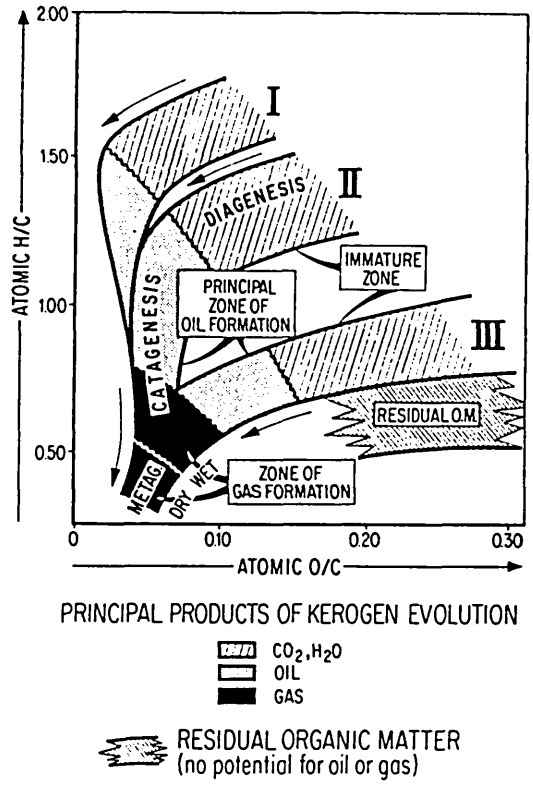


FIG.6.1-ELEMENTARY COMPOSITION OF KEROGENS SHOWING MAIN TYPES AND PRINCIPAL PRODUCTS GENERATED DURING THERMAL EVOLUTION OF KEROGEN TYPES I,II,AND III(Tissot et al, 1980).

of aliphatic chains but a low content of polyaromatic nuclei and hetero-atomic bonds. Its source is believed to be algal material which can be marine or lacustrine or it can originate from the remains of disseminated organic matter which has been extensively reworked by micro-organisms. This type of kerogen is said to have the greatest potential for oil generation with often up-to 80% convertibility (Tissot and Welte, 1978). Type II is described as the most commonly found oil-source kerogen with relatively high initial hydrogen content (atomic H/C ratio not quite as high as for Type I) and relatively low oxygen content (atomic $^{O}/C$ ratio slightly higher than for Type I). Compared to type I, it has more of the polyaromatic nuclei and hetero-atoms present plus more ketones and carboxylic acid groups. They however still contain abundant aliphatic chains of reasonable length as well as naphthenic rings and other cyclic structures. Type II kerogen is usually related to marine sediments in which an autochthonous organic matter derived from a mixture of phytoplankton, zooplankton and micro-organisms (like bacteria) together with lipid-rich residues of terrestrial spores, pollens and cuticles have been deposited in a reducing environment. Kinghorn (1983) pointed out that if this type of organic matter (as well as other types) is deposited in oxidising conditions, it may or may not be preserved. If preserved at all, its oil-generating potential may be greatly reduced or eliminated as a result of microbial degradation. Convertibilities of up to 60% have been quoted for Type II kerogens (Tissot & Welte, 1978). Type III kerogen has a relatively low initial

hydrogen content (atomic $^{H}/_{C}$ ratio < 1.0) and a high oxygen content (atomic $^{O}/_{C} \geq 0.2$). Compared to the first two, this kerogen type is believed to contain much smaller amounts of aliphatic chain material, mostly methyl and other short-chain species plus a few longer-chain alkyl groups originating from the waxes of higher terrestrial plants, but the proportion of polyaromatic nuclei and hetero-atomic bonds is much higher. It is believed to be derived mainly from allochthonous terrestrial higher plant material deposited in aquatic environments. Tissot et al. (1980) attributes the presence of type III kerogen in marine sediments largely to the transport of terrestrial organic matter into ocean where an oxic water column prevents the deposition of planktonic remains. Such conditions, they pointed out, lead to comparatively enhanced preservation of the more resistant, hydrogen-poor, terrestrial organic matter whereas the planktonic input is preferentially biodegraded. With an overall maximum convertibility of this Type III kerogen to hydrocarbons of about 35-40% (Kinghorn, 1983), it is often described as gas-prone with the least potential for oil generation. Type IV kerogen is described as consisting mostly of residual organic matter derived from highly oxidised/altered material (like charcoal) or high rank material recycled from older sediments. Its initial hydrogen content is known to be lower than in type III while its oxygen content may be lower or higher than in type III. Described as inertinitic in nature, it is considered as "dead carbon" with very little or no potential for hydrocarbons (Tissot et al., 1980; Bostick, 1979).

Tissot and Welte (1978) and Kinghorn (1983) have pointed out that occurrences of pure kerogens of one type or another in sedimentary rocks are rare but rather, kerogens occur commonly as mixtures of two or three types and the relative amounts of each type in a source bed vary as the conditions of deposition varied. Kerogen type variations in a lithologic unit, as they noted, can be lateral or vertical or both due to the varying of the shoreline or the position of the oxic-anoxic boundary at the times of deposition. Because some type IV kerogen materials can be rich in carbon but almost totally devoid of hydrogen and oxygen, their admixture with other kerogens will increase the carbon content of the containing sediment without increasing that sediments hydrocarbon genetic potential. And thus the use of purely chemical assays to ascertain the genetic potential of sediments can be upset when significant amounts of these inertinitic materials are present (Kinghorn, 1983).

The process of kerogen degradation or transformation to petroleum hydrocarbons as a consequence of sediment burial is often described in three successive stages - diagenesis, catagenesis, and metagenesis (Tissot and Welte, 1978; Hunt, 1979; Brooks, 1981; Kinghorn, 1983). Each stage is known to result in important changes in the elemental composition of kerogen. Diagenesis is the first stage occuring at conditions of shallow burial and low temperatures (normally less than 60^{o}C) where the sediment usually becomes consolidated. A slight decrease in the hydrogen content is often associated with this stage but with a much larger and more important decrease

in the oxygen content (and also O/C), mainly due to the elimination of the carbonyl groups (C = O). In terms of petroleum exploration, this stage is known to correspond to an immature kerogen and little fluid hydrocarbon generation occurs in the potential source rocks, but biogenic methane can be produced by microbiological activity. Large quantities of carbon dioxide,water, and also some hetero-atomic (N,S,O) compounds are known to be produced during this stage. Catagenesis stage is marked by the onset of thermal degradation or maturation of kerogen in the deeper samples (temperature range of 60^{o} - 150^{o}C) with the resultant generation of the majority of petroleum hydrocarbons. In terms of elemental composition, an important decrease in the hydrogen content (and of the $^{H}/C$ ratio) of the kerogen results, and at the same time the residual carbonyl groups (C = O) are eliminated thus reducing the oxygen content (and hence $^{O}/C$ ratio) as well. The kerogen becomes more aromatic with the significant reduction in the $^{H}/C$ ratio. The main products often associated with this stage are liquid petroleum, condensates and wet gas, in that order as the depth of burial (or temperature) increases. Thus the first part of this stage is often referred to as the "principal zone of oil formation" (Vassoevich et al., 1974) or the "oil window" (van Gijzel, 1980). No general opinion exists on the boundaries of the "oil window" (Staplin, 1977; van Gijzel, 1980). Some authors accept a maximum vitrinite reflectance value in oil of 0.4% (e.g. Snowdon and Powell, 1982), others a value of 0.60% Ro (e.g. Dow, 1977) and still others

report an average value of 0.50% Ro (e.g. Heroux et al., 1979) as the maturation level that is needed for the onset of oil generation. However, recent works tend to associate the onset of the main phase of oil generation with vitrinite reflectance values of about 0.60% Ro (Waples 1980; Powell et al., 1982; Peters et al., 1983; Cercone, 1984). The maturity level at which peak oil generation occurs is usually reported at about 1.0% Ro (Vassoevich et al. 1974; Waples, 1980). The lower boundary of the principal zone of oil generation is commonly put in the vitrinite reflectance range of 1.2 to 1.35% Ro (Vassoevich et al., 1974; Dow, 1977; Waples, 1980). Vassoevich et al. (1974); Tissot and Welte (1978) and Snowdon and Powell (1982) have pointed out that the boundaries of the "oil window" can vary depending on such factors as the initial facies - genetic type of kerogen, its content, and the nature of the mineral part of the containing rock. The second half of the catagenesis stage ($\sim$1.3 - 2.0% Ro) is marked mainly by wet gas formation (Dow, 1977). The beginning of the metagenesis (or the dry gas) stage has been reported to correspond approximately with a vitrinite reflectance value of 2.0% Ro, and it is observed only in very deep samples or in locations with a high geothermal gradient (Tissot and Welte, 1978). Major restructuring of the kerogen occurs in the stage and methane (dry gas) is the only hydrocarbon formed from both the kerogen degradation as well as the cracking of previously generated hydrocarbons. The $^{H}/_{C}$ ratio of the kerogens decreases very slowly during this stage with the carbon content rising to about 90% and the virtinite reflectance

value reaching up to 4% Ro.

The evolution paths of kerogen types I - III together with their degradation products at the various stages of the maturation process are shown in Fig. 6.1.

In considering the petroleum generation from the Jurassic kerogens in southern England, while a maximum vitrinite reflectance value in oil of 0.50% will be regarded as the maturity level at the base of the diagenesis stage or the top of the catagenesis stage, a value of 0.60 % Ro will be considered to mark the onset of the main phase of oil generation. Kerogen samples in the range 0.50 - 0.59% Ro will be described as marginally mature.

6.1.2 Results and Interpretations of the Elemental Composition of the Jurassic Kerogens

The elemental compositions (C, H, N, O) of the kerogen concentrates from the Kimmeridge Clay (KC), the Oxford Clay (OC) and the Lower Lias (LL) samples from outcrops and all the sampled boreholes are presented in Table 6.1. The Van Krevelan diagrams (plots of $^{H}/_{C}$ against $^{O}/_{C}$ atomic ratios) for the kerogen samples from each sampled locality are shown in Fig. 6.2.

As noted from Table 6.1 and Fig. 6.2, the kerogen samples from each of the three Jurassic formations show wide variation in their elemental composition and they have been classified into four groups or types. These are type II, mixed type II/III, type III, and type IV. Types II, III and IV are as defined in the previous section (6.1.1). The mixed type II/III are considered as those kerogen samples plotting in between the fields of type II and type

III. The formation of this intermediate or mixed type could be due to massive terrestrial organic matter input into anoxic marine basins where lipid-rich marine plankton material also accumulates (Tissot et al., 1980), and can also be produced by partial biodegradation of type II kerogen precursors deposited in bottom waters which are not completely anoxic. Kerogen types II, II/III and III have been identified in the samples from the Lower Lias, the Oxford Clay and the Kimmeridge Clay Formations. Type IV kerogens have been identified in the Lower Lias (Samples WM/LL.4 and WM/LL.5 from the Warlingham Well) and in the Oxford Clay (Upper) (sample CN/OC.1 from the Cranborne -1 Well) Formations but not in the Kimmeridge Clay. Thus vertical/stratigraphic variations in the kerogen types occur in each of these three formations. In the Lower Lias as well as the Kimmeridge Clay, just like the lithologic variations, no single trend in the kerogen type variation with stratigraphy is noticed in the present study (refer to Section 6.3 for possible reasons). Rather, alternations of the identified types tend to occur at various stratigraphic levels. By contrast, in the Oxford Clay Formation, a single stratigraphic trend is observed in the kerogen type variation throughout southern England. Where the complete Oxford Clay section has been sampled (e.g. outcrops, Cranborne -1, Warlingham, Penshurst, and Arreton-2 Wells), the following vertical trend in the kerogen types is generally noticed from the base to the top of the formation: type II → mixed type II/III → type III → type IV. Such a vertical variation certainly implies that there was a single directional variation in the position of the oxic-anoxic

TABLE 6.1 - ELEMENTAL COMPOSITION AND TYPING OF THE JURASSIC KEROGEN SAMPLES

Locality	Sample Number	Depth	ELEMENTAL COMPOSITION						Kerogen Type
			Wt%				Atomic Ratios		
			C	H	N	O	H/C	O/C	
Ringstead Bay, Dorset	OSD/KC.1	Outcrop	52.09	5.92	1.38	11.93	1.35	0.172	II
	OSD/KC.2	"	61.59	6.98	1.85	11.05	1.35	0.135	II
	OSD/KC.3	"	58.31	6.64	2.31	9.92	1.35	0.128	II
Kimmeridge Bay - Chapman's Pool Area, Dorset	OSD/KC.4	"	69.97	5.20	3.34	10.69	0.90	0.115	Mixed II/III
	OSD/KC.5	"	67.55	5.21	3.55	10.24	0.92	0.114	"
	OSD/KC.6	"	59.33	6.21	1.50	8.60	1.25	0.109	II
	OSD/KC.7	"	65.20	6.90	3.44	9.73	1.26	0.112	II
	OSD/KC.8	"	65.56	6.85	3.07	9.27	1.24	0.106	II
	OSD/KC.9	"	69.51	6.56	3.68	8.76	1.12	0.095	II
	OSD/KC.10	"	60.84	6.35	1.74	8.09	1.24	0.100	II
	OSD/KC.11	"	67.26	6.10	3.44	7.94	1.08	0.089	Mixed II/III
	OSD/KC.12	"	65.35	6.69	3.37	8.36	1.22	0.096	II
Shortlake, Dorset	OSD/OC.1	"	64.70	4.80	1.91	12.70	0.88	0.147	Mixed II/III
Chickerell, Dorset (Brickyard)	OSD/OC.2	"	64.28	5.78	1.72	11.92	1.07	0.139	"
	OSD/OC.3	"	64.96	7.06	2.04	11.28	1.29	0.130	II
	OSD/OC.4	"	62.43	6.80	2.19	10.62	1.30	0.128	II
	OSD/OC.5	"	59.65	6.49	1.91	10.43	1.29	0.131	II
Charmouth, Dorset	OSD/LL.1	"	57.65	3.66	1.12	12.61	0.76	0.164	III
	OSD/LL.2	"	64.12	4.68	1.17	11.32	0.87	0.133	Mixed II/III
	OSD/LL.3	"	56.39	6.13	1.40	9.37	1.29	0.125	II
	OSD/LL.4	"	53.81	6.01	3.21	10.80	1.33	0.151	II
	OSD/LL.5	"	59.40	5.60	3.63	9.52	1.21	0.120	II
	OSD/LL.6	"	54.66	4.99	3.03	9.30	1.22	0.128	II

TABLE 6.1 - ELEMENTAL COMPOSITION AND TYPING OF THE JURASSIC KEROGEN SAMPLES (Cont.)

Locality	Sample Number	Depth (ft.)	ELEMENTAL COMPOSITION Wt% C	H	N	O	Atomic Ratios H/C	O/C	Kerogen Type
Lyme Regis	OSD/LL.7	Outcrop	58.69	4.99	1.36	11.09	1.01	0.142	Mixed II/III
	OSD/LL.8	"	58.26	6.36	1.95	10.07	1.30	0.130	II
Marchwood Well (Hampshire)	MD/OC.1	2950	57.34	4.92	2.53	12.92	1.02	0.164	Mixed II/III
	MD/OC.2	2960	63.02	4.79	4.44	12.66	0.90	0.151	"
	MD/OC.3	2966	57.43	4.92	2.58	11.55	1.00	0.151	"
	MD/OC.4	2970	53.65	4.45	2.58	11.81	0.99	0.165	"
	MD/LL.1	4501	66.73	4.36	2.61	12.29	0.78	0.138	III
	MD/LL.2	4505	58.16	5.61	1.76	10.73	0.98	0.118	Mixed II/III
	MD/LL.3	4515	66.95	5.49	3.53	10.34	0.97	0.116	"
	MD/LL.4	4519	65.62	4.40	2.54	11.12	0.80	0.127	III
	MD/LL.5	4525	61.21	4.39	4.01	10.09	0.85	0.124	Mixed II/III
	MD/LL.6	4533	68.19	4.93	4.33	11.03	0.86	0.121	"
Winchester No. 1 Well (Hampshire)	WCH/KC.1	2342-2345	60.59	4.32	2.06	13.11	0.85	0.162	III
	WCH/KC.2	3218-3221	60.03	4.17	1.35	11.80	0.83	0.147	III
	WCH/KC.3	3230	56.81	3.98	0.90	11.04	0.83	0.146	III
	WCH/OC.1	3914	59.97	6.54	1.54	8.01	1.30	0.100	II
	WCH/OC.2	3942-3944	61.97	6.72	1.94	7.65	1.29	0.093	II
	WCH/OC.3	3977	62.41	6.57	1.74	8.08	1.25	0.097	II
	WCH/OC14	4004-4008	58.91	6.07	1.85	8.10	1.21	0.103	II
	WCH/LL.1	5814	71.30	6.04	2.61	7.93	1.01	0.083	II
	WCH/LL.2	5825-5826	65.19	5.50	1.66	7.53	1.00	0.087	Mixed II/III
	WCH/LL.3	5837	72.50	6.30	1.34	7.80	1.03	0.081	II

TABLE 6.1 - ELEMENTAL COMPOSITION AND TYPING OF THE JURASSIC KEROGEN SAMPLES (Cont.)

Locality	Sample Number	Depth (ft.)	ELEMENTAL COMPOSITION						Kerogen Type
			Wt%				Atomic Ratios		
			C	H	N	O	H/C	O/C	
Arreton No. 2 Well (Isle of Wight)	AR/KC.1	2700-2800	58.79	4.71	0.84	8.69	0.95	0.111	Mixed II/III
	AR/KC.3	2900-3000	57.32	5.74	2.30	7.44	1.19	0.097	II
	AR/KC.5	3100-3200	61.47	6.29	0.98	7.37	1.22	0.090	II
	AR/KC.7	3300-3400	61.10	6.20	1.56	6.92	1.21	0.085	II
	AR/KC.9	3500-3600	61.34	5.76	2.25	7.84	1.12	0.096	II
	AR/OC.2	4100-4200	58.01	4.82	1.43	8.50	0.99	0.110	Mixed II/III
	AR/OC.4	4300-4400	58.39	6.06	1.32	5.99	1.23	0.077	II
	AR/LL.1	5500-5600	67.48	5.53	1.69	6.92	0.97	0.077	II
	AR/LL.3	5700-5800	63.13	5.67	1.56	6.58	1.07	0.078	II
	AR/LL.5	5900-6000	61.43	5.71	1.66	6.55	1.10	0.080	II
	AR/LL.7	6100-6200	65.07	5.45	1.51	6.44	1.00	0.074	II
	AR.LL.9	6300-6400	59.47	4.90	1.44	6.34	0.98	0.080	II
Winterborne Kingston Well (Dorset)	WK/KC.1	1148	66.42	5.61	2.33	13.37	1.00	0.151	Mixed II/III
	WK/KC.2	1164.9	61.84	6.19	3.03	12.85	1.19	0.156	"
	WK/KC.3	1179.3	65.70	5.79	3.43	13.43	1.05	0.153	"
	WK/LL.1	4150	61.94	5.60	2.24	9.04	1.07	0.109	"
	WK/LL.2	4165.6	67.10	6.01	4.40	9.52	1.06	0.106	"
	WK/LL.3	4198.4	64.23	5.39	3.84	9.93	1.00	0.116	"
	WK/LL.4	4208.2	64.47	5.27	3.74	9.91	0.97	0.115	"
	WK/LL.5	5100.4	53.68	3.24	2.91	7.23	0.72	0.101	III
	WK/LL.6	5116.8	59.63	4.66	0.47	7.29	0.93	0.092	Mixed II/III
	WK/LL.7	5143	53.11	5.32	2.06	6.23	1.19	0.088	II
	WK/LL.8	5149.6	43.21	4.50	0.72	4.32	1.24	0.075	II

TABLE 6.1 - ELEMENTAL COMPOSITION AND TYPING OF THE JURASSIC KEROGEN SAMPLES (Cont.)

Locality	Sample Number	Depth (Ft.)	ELEMENTAL COMPOSITION Wt% C	H	N	O	Atomic Ratios H/C	O/C	Kerogen Type
Cranborne No. 1 Well (Dorset)	CN/KC.1	1718.7	63.22	6.13	1.68	12.04	1.15	0.143	Mixed II/III
	CN/OC.1	1974.6	63.38	3.31	1.30	12.42	0.62	0.147	IV
	CN/OC.2	2105.8 - 2112.3	58.63	4.52	1.64	12.92	0.92	0.165	Mixed II/III
	CN/OC.3	2230.4 - 2243.5	51.77	4.46	1.88	12.75	1.02	0.185	"
	CN/OC.4	2361.6 - 2374.7	59.60	6.54	0.37	10.03	1.31	0.126	II
	CN/OC.5	2466.6	57.51	6.17	1.10	10.87	1.28	0.142	II
	CN/LL.1	3568.6 - 3575	53.14	4.18	2.14	12.11	0.79	0.171	III
	CN/LL.2	3673.6 - 3680	41.68	3.92	2.21	8.76	1.12	0.158	Mixed II/III
	CN/LL.3	3739.2 - 3745.8	61.43	5.55	2.23	9.34	1.07	0.114	"
	CN/LL.4	3804.8 - 3824.5	56.87	5.29	2.08	9.53	1.11	0.126	"
	CN/LL.5	3936 - 3941.1	57.39	5.40	2.85	9.25	1.12	0.121	"
	CN/LL.6	4001.6 - 4014.7	54.70	5.02	2.75	8.85	1.08	0.121	"
Burton Row Well (Somerset)	BR/LL.1	122	57.73	5.07	1.70	9.38	1.04	0.122	Mixed II/III
	BR/LL.2	214.3	68.99	5.11	1.22	9.11	0.88	0.099	"
	BR/LL.3	360.7	58.09	5.88	1.53	7.52	1.20	0.097	II
	BR/LL.4	419.8	65.88	4.12	1.01	8.25	0.74	0.094	III
	BR/LL.5	503.5	59.57	5.70	0.86	8.68	1.14	0.109	II
	BR/LL.6	588.3	69.59	4.73	1.47	7.49	0.81	0.081	Mixed II/III
	BR/LL.7	759.9	72.46	4.79	1.34	8.82	0.79	0.091	"
	BR/LL.8	969.2	60.00	4.57	0.98	11.36	0.91	0.142	"
	BR/LL.9	1227.6	43.90	3.72	1.31	6.58	1.01	0.113	"
	BR/LL.10	1317.7	51.12	5.95	1.33	7.10	1.38	0.104	II
	BR/LL.11	1342.2	44.62	4.93	1.07	6.72	1.31	0.113	II

TABLE 6.1 - ELEMENTAL COMPOSITION AND TYPING OF THE JURASSIC KEROGEN

(Cont.) SAMPLES

Locality	Sample Number	Depth (ft.)	ELEMENTAL COMPOSITION						Kerogen Type
			Wt%				Atomic Ratios		
			C	H	N	O	H/C	O/C	
Cooles-Farm No. 1 Well	CF/LL.1	1000	67.98	5.06	2.67	14.21	0.89	0.156	Mixed II/III
	CF/LL.2	1200	56.77	5.05	2.23	12.17	1.06	0.161	"
	CF/LL.3	1400	71.49	5.74	0.90	10.62	0.96	0.112	"
	CF/LL.4	1500	64.04	5.54	1.60	10.47	1.03	1.23	"
	CF/LL.5	1700	59.86	4.11	0.11	13.16	0.82	0.165	III
	CF/LL.6	1800	64.97	5.88	1.78	11.47	1.08	0.133	Mixed II/III
	CF/LL.7	1900	62.98	5.61	1.81	10.70	1.06	0.128	"
Warlingham Well (Surrey)	WM/KC.1	2279.5	57.67	4.65	1.13	9.58	0.96	0.125	Mixed II/III
	WM/KC.2	2379.5	64.79	6.42	2.18	11.82	1.18	0.137	II
	WM/KC.3	2480.5	65.14	6.61	0.99	11.42	1.21	0.132	II
	WM/KC.4	2520	64.25	5.65	1.48	11.57	1.05	0.135	Mixed II/III
	WM/KC.5	2580	63.58	6.77	1.47	11.01	1.27	0.130	II
	WM/KC.6	2680	58.86	6.22	1.38	11.24	1.26	0.143	II
	WM/KC.7	2779.5	61.55	5.96	1.94	10.02	1.15	0.122	II
	WM/KC.8	2880	52.12	4.34	1.30	12.19	0.99	0.176	Mixed II/III
	WM/KC.9	2982	66.36	4.86	1.30	10.33	0.87	0.117	"
	WM/OC.1	3162.5	58.70	4.04	1.97	12.28	0.82	0.157	III
	WM/OC.2	3202	58.27	4.39	1.92	10.99	0.90	0.142	Mixed II/III
	WM/OC.3	3400.3	61.45	6.58	1.73	10.31	1.27	0.126	II
	WM/OC.4	3430	60.69	6.51	1.31	9.99	1.28	0.124	II
	WM/OC.5	3466	61.30	6.72	1.23	9.64	1.30	0.118	II
	WM/LL.1	4200	66.37	4.71	1.81	11.72	0.84	0.133	III
	WM/LL.2	4300	71.00	5.69	2.18	10.43	0.95	0.110	Mixed II/III

TABLE 6.1 - ELEMENTAL COMPOSITION AND TYPING OF THE JURASSIC KEROGEN (Cont.) SAMPLES

Locality	Sample Number	Depth (Ft.)	ELEMENTAL COMPOSITION						Kerogen Type
			Wt%				Atomic Ratios		
			C	H	N	O	H/C	O/C	
Warlingham Well (Cont.)	WM/LL.3	4350	44.54	3.29	1.80	7.82	0.88	0.132	Mixed II/III
	WM/LL.4	4400	67.99	2.87	2.07	11.28	0.50	0.125	IV
	WM/LL.5	4460.5	56.88	2.52	0.70	11.81	0.53	0.153	IV
	WM/LL.6	4480	67.18	3.32	1.75	10.66	0.59	0.116	III
Penshurst Well (Kent)	PH/KC.1	1174	66.72	6.38	1.91	9.24	1.14	0.104	II
	PH/KC.2	2242	59.71	5.16	1.35	9.03	1.03	0.113	Mixed II/III
	PH/KC.3	2308 - 2325	48.87	3.91	1.07	7.62	0.95	0.117	"
	PH/KC.4	2409 - 2412	67.40	6.22	1.75	8.98	1.10	0.100	II
	PH/OC.1	2928	44.02	3.51	1.32	6.74	0.94	0.115	Mixed II/III
	PH/OC.2	3005	46.84	4.37	1.49	5.62	1.11	0.090	II
	PH/OC.3	3139	57.91	5.84	1.42	5.17	1.20	0.067	II
	PH/LL.1	4105 - 4135	60.32	5.12	1.62	7.07	1.01	0.088	Mixed II/III
	PH/LL.2	4200 - 4233	59.97	4.89	1.38	7.27	0.97	0.091	"
	PH/LL.3	4304 - 4335	54.83	4.89	1.49	4.75	1.06	0.065	II
	PH/LL.4	4407 - 4438	52.67	4.52	1.42	4.77	1.02	0.068	II
	PH/LL.5	4518 - 4550	53.70	4.05	1.31	6.80	0.90	0.095	Mixed II/III
Henfield Well (West Sussex)	HN/KC.1	1585 - 1587	55.31	4.06	1.49	11.74	0.87	0.159	III
	HN/KC.2	2092 - 2094	65.16	6.86	1.61	11.51	1.25	0.133	II
	HN/KC.3	2102	65.19	5.71	1.94	11.53	1.04	0.133	Mixed II/III
	HN/LL.1	4416	60.85	4.82	1.05	9.22	0.94	0.114	"
	HN/LL.2	4698	63.11	3.92	0.89	8.37	0.74	0.099	III
	HN/LL.3	4707	65.19	3.80	1.25	7.47	0.69	0.086	III
	HN/LL.4	4838	57.50	4.63	1.36	7.99	0.96	0.104	Mixed II/III
	HN/LL.5	4843.5	55.54	3.65	1.05	7.52	0.78	0.102	III

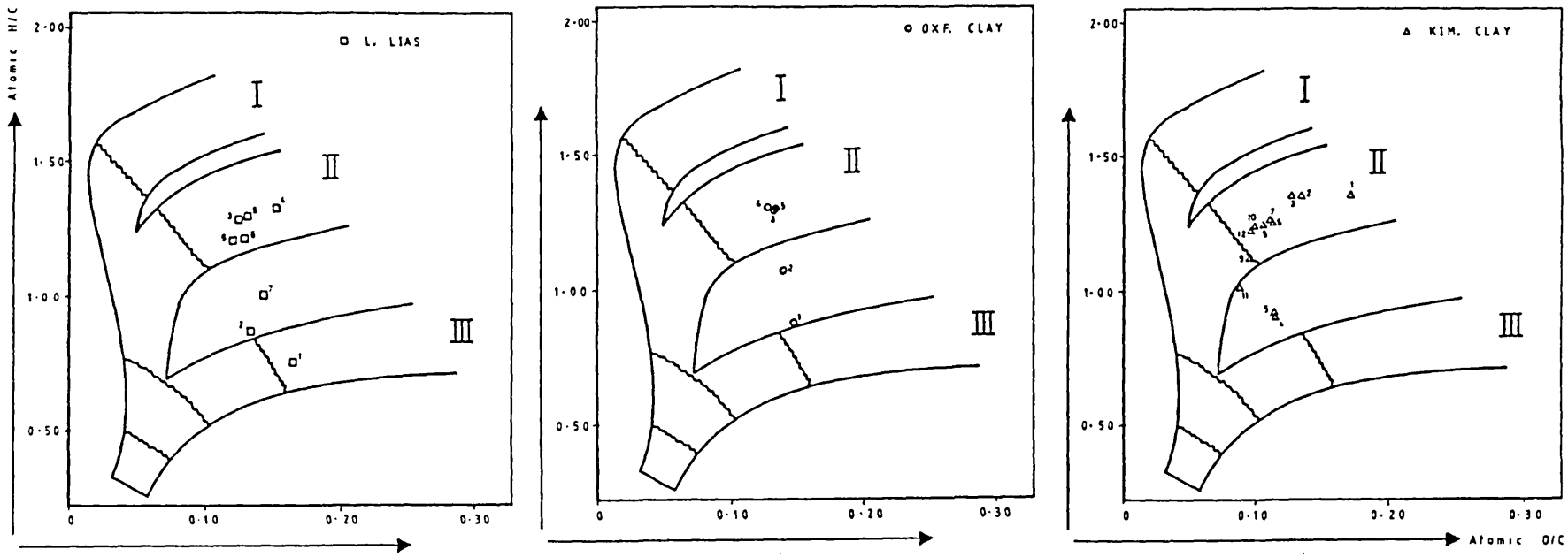


FIG. 6.2(a) VAN KREVELEN DIAGRAMS FOR OUTCROP SAMPLES FROM DORSET

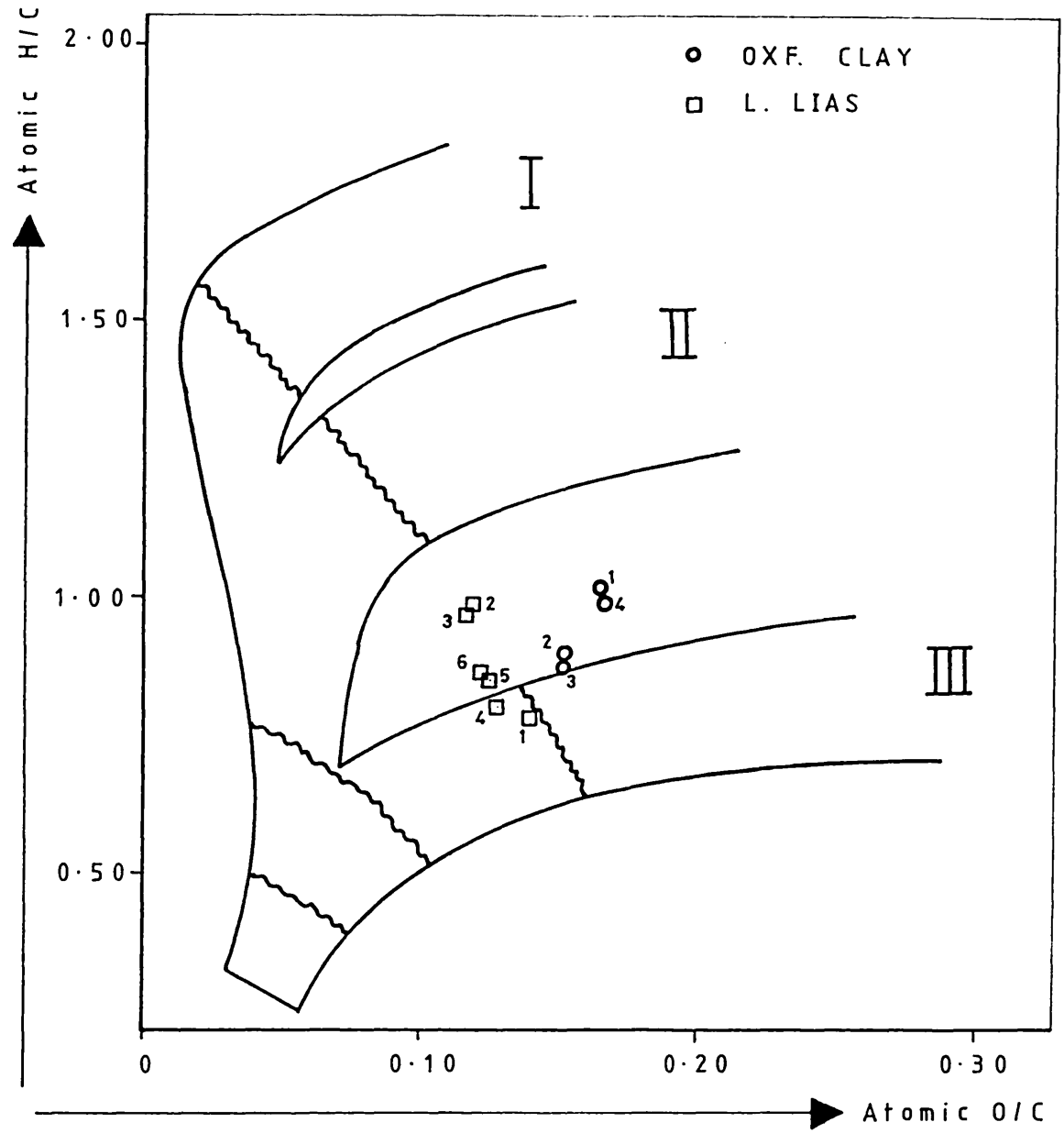


FIG. 6.2(b) VAN KREVELEN DIAGRAM: MARCHWOOD WELL

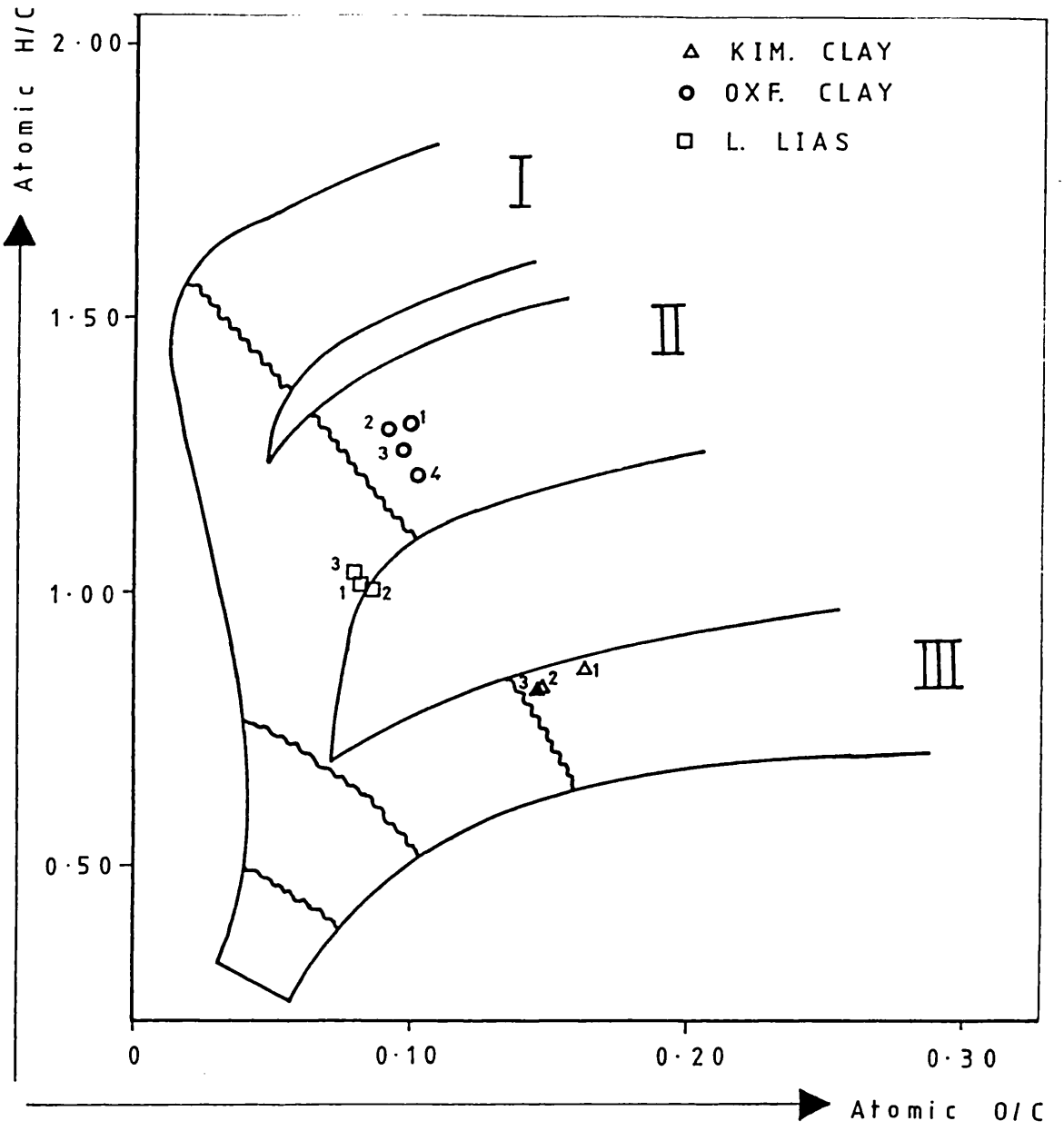


FIG. 6.2(c) VAN KREVELEN DIAGRAM: WINCHESTER-1 WELL

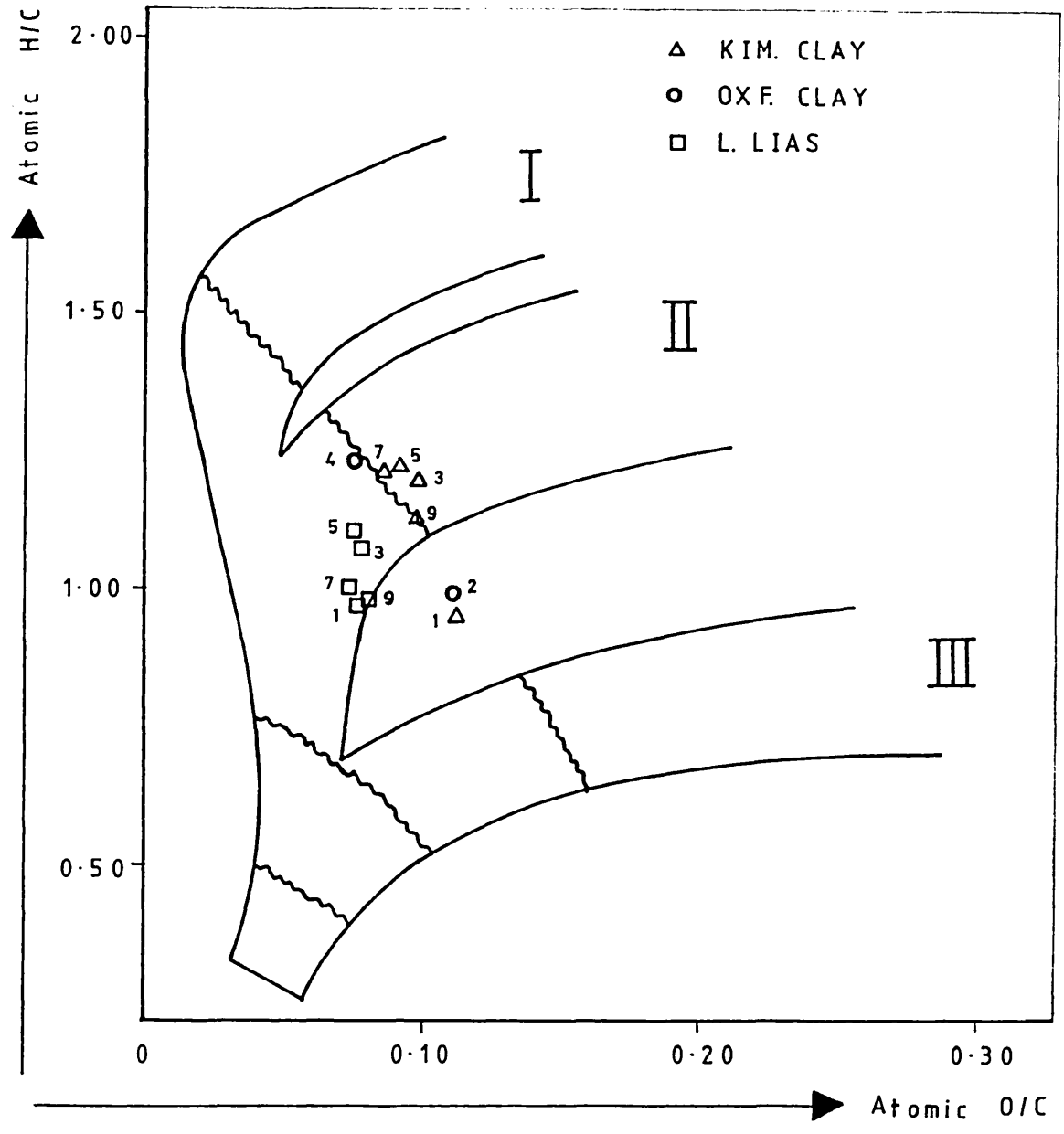


FIG. 6.2(d) VAN KREVELEN DIAGRAM: ARRETON-2 WELL

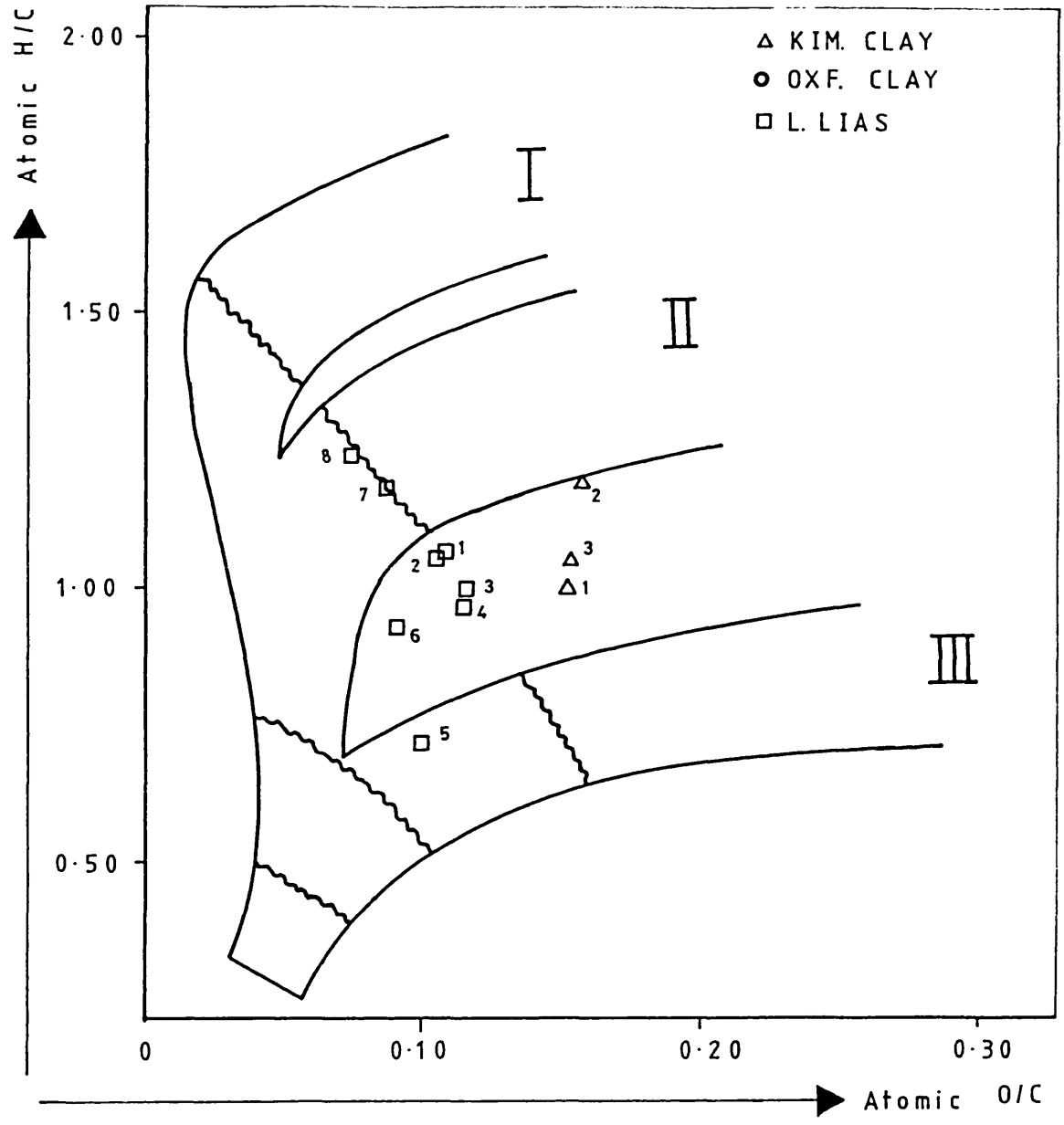


FIG. 6.2(e) VAN KREVELEN DIAGRAM: WINTERBORNE KINGSTON WELL

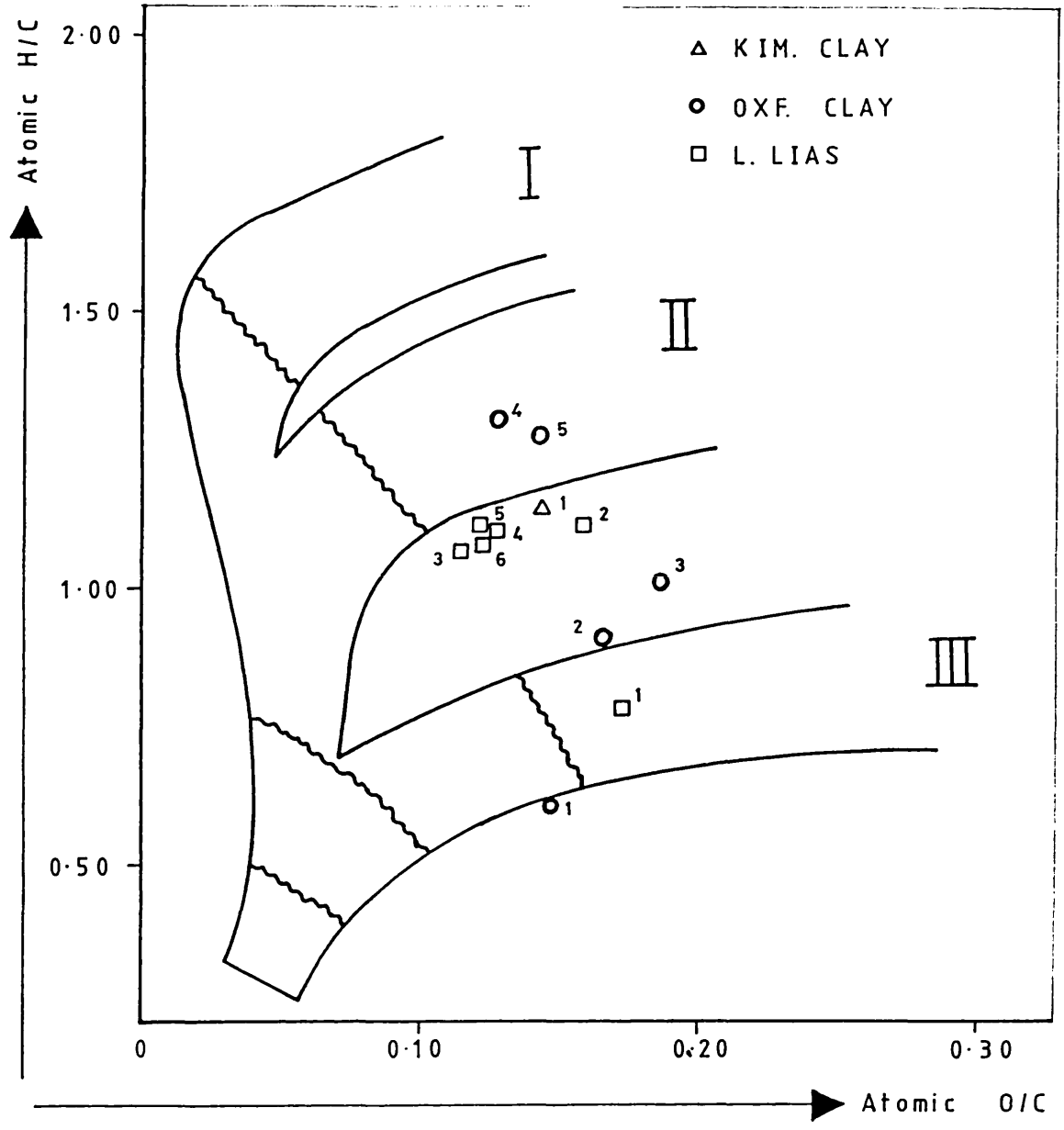


FIG. 6.2(f) VAN KREVELEN DIAGRAM: CRANBORNE-1 WELL

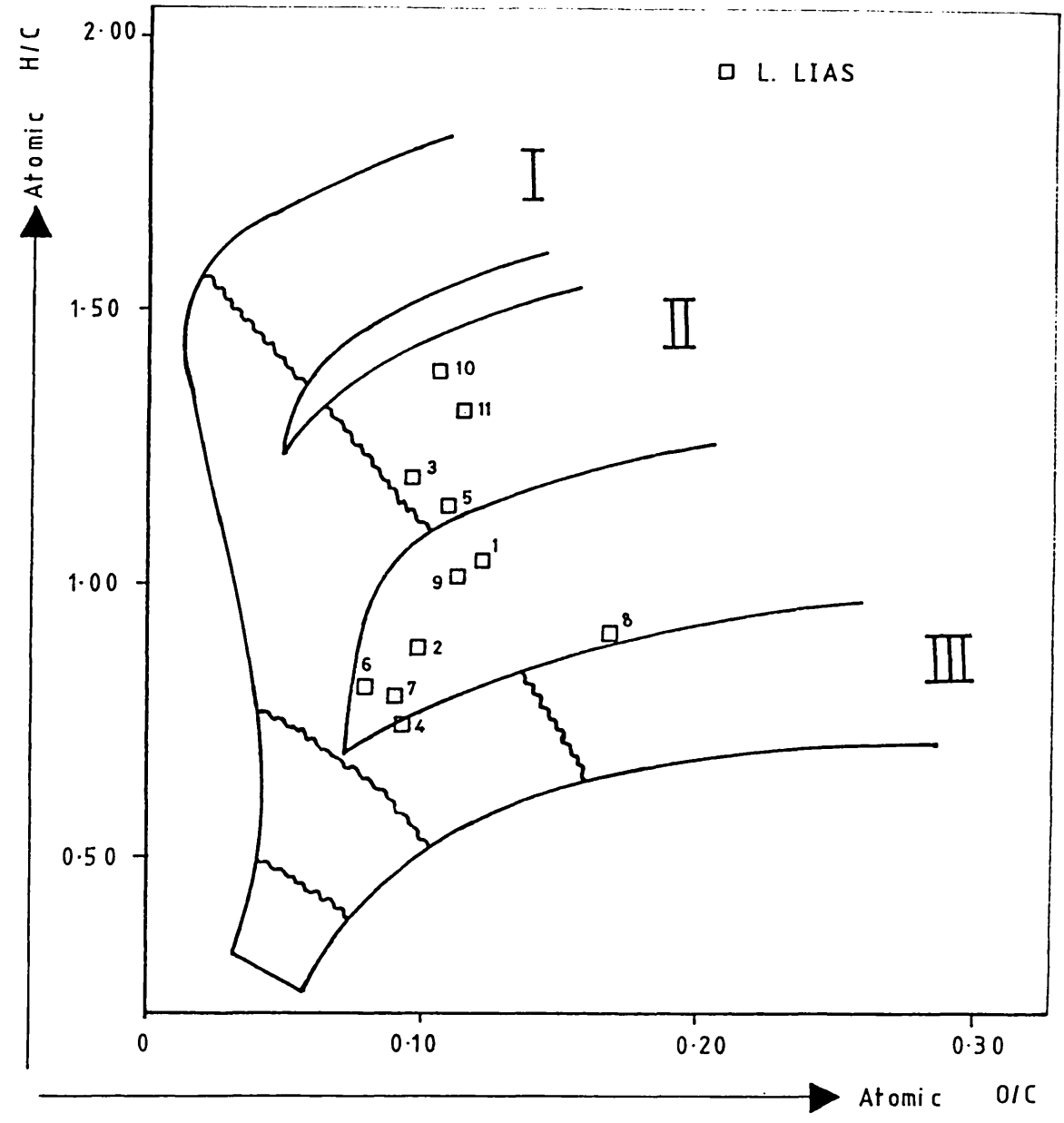


FIG. 6.2(g) VAN KREVELEN DIAGRAM: BURTON ROW WELL

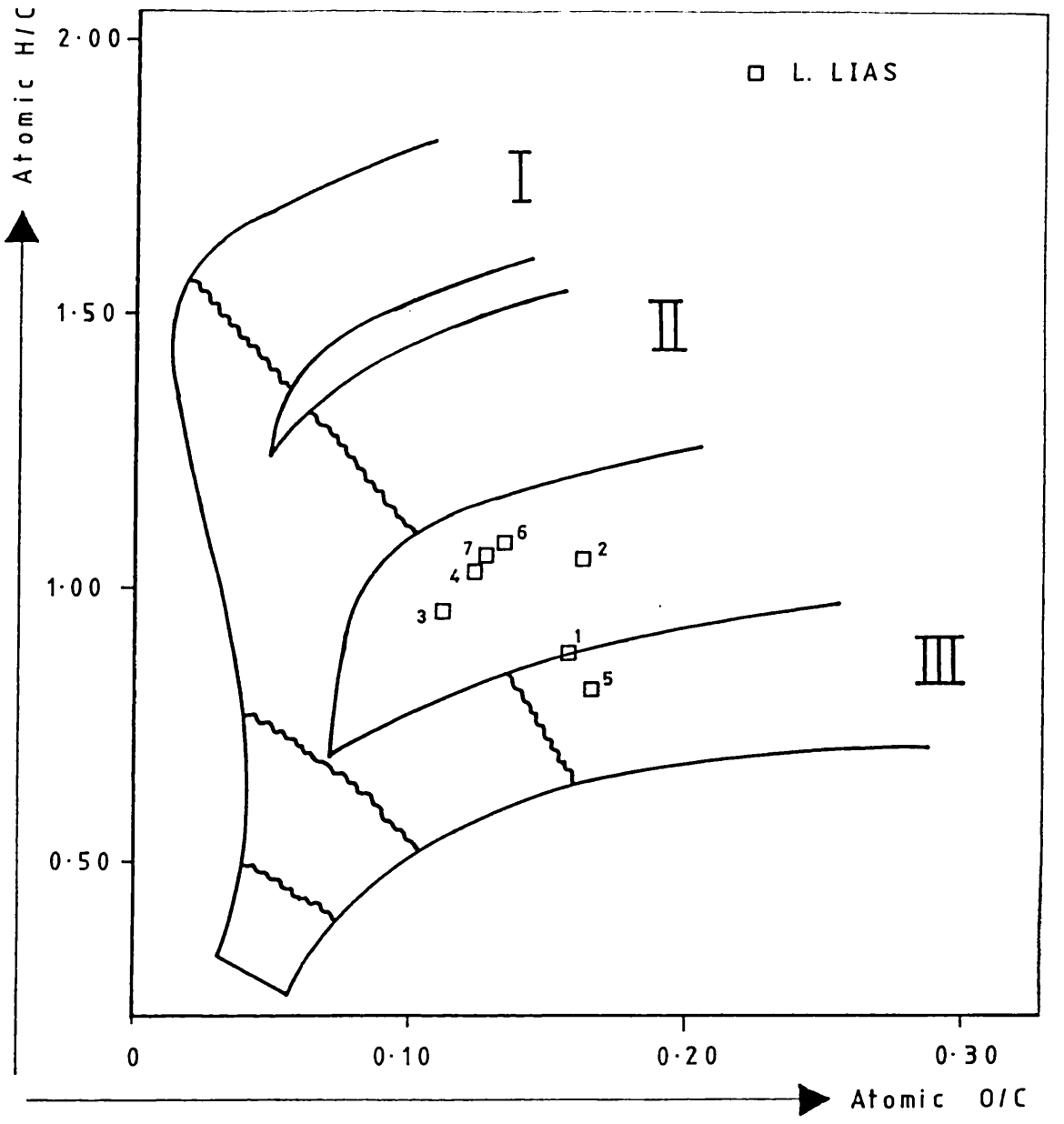


FIG. 6.2 (h) VAN KREVELEN DIAGRAM: COOLES-FARM-1 WELL

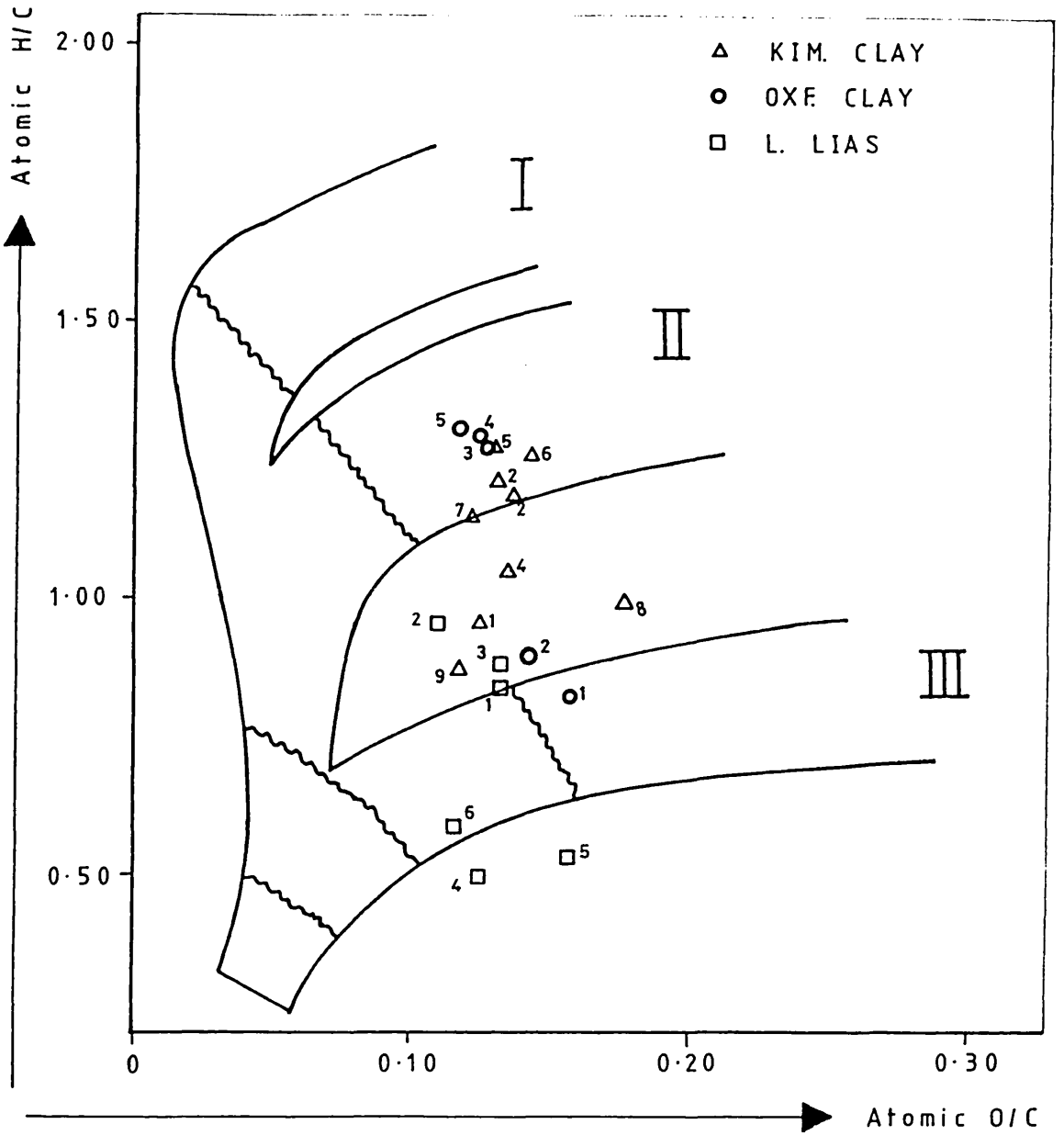


FIG. 6.2(i) VAN KREVELEN DIAGRAM: WARLINGHAM WELL

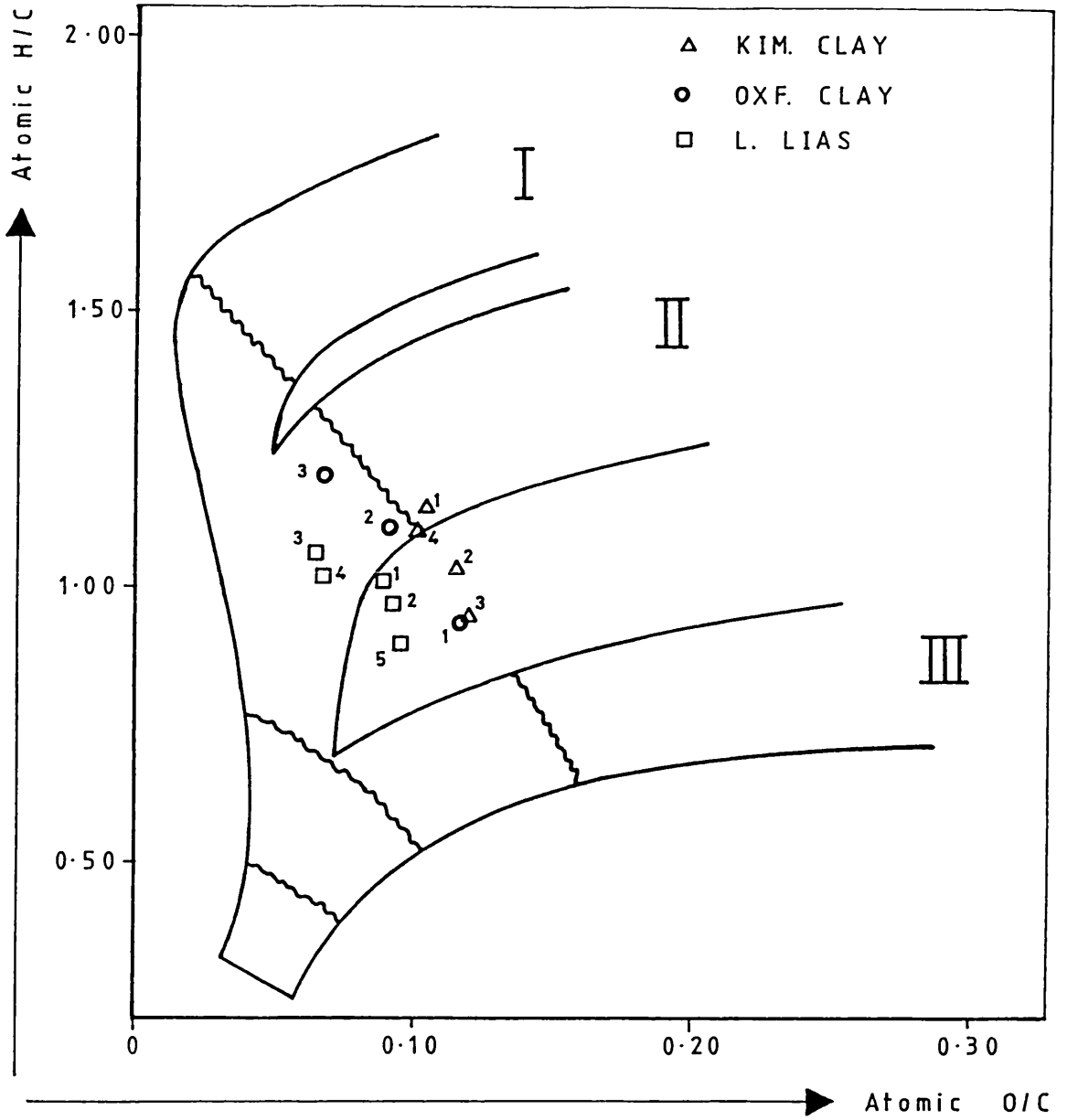


FIG. 6.2(j) VAN KREVELEN DIAGRAM: PENSHURST WELL

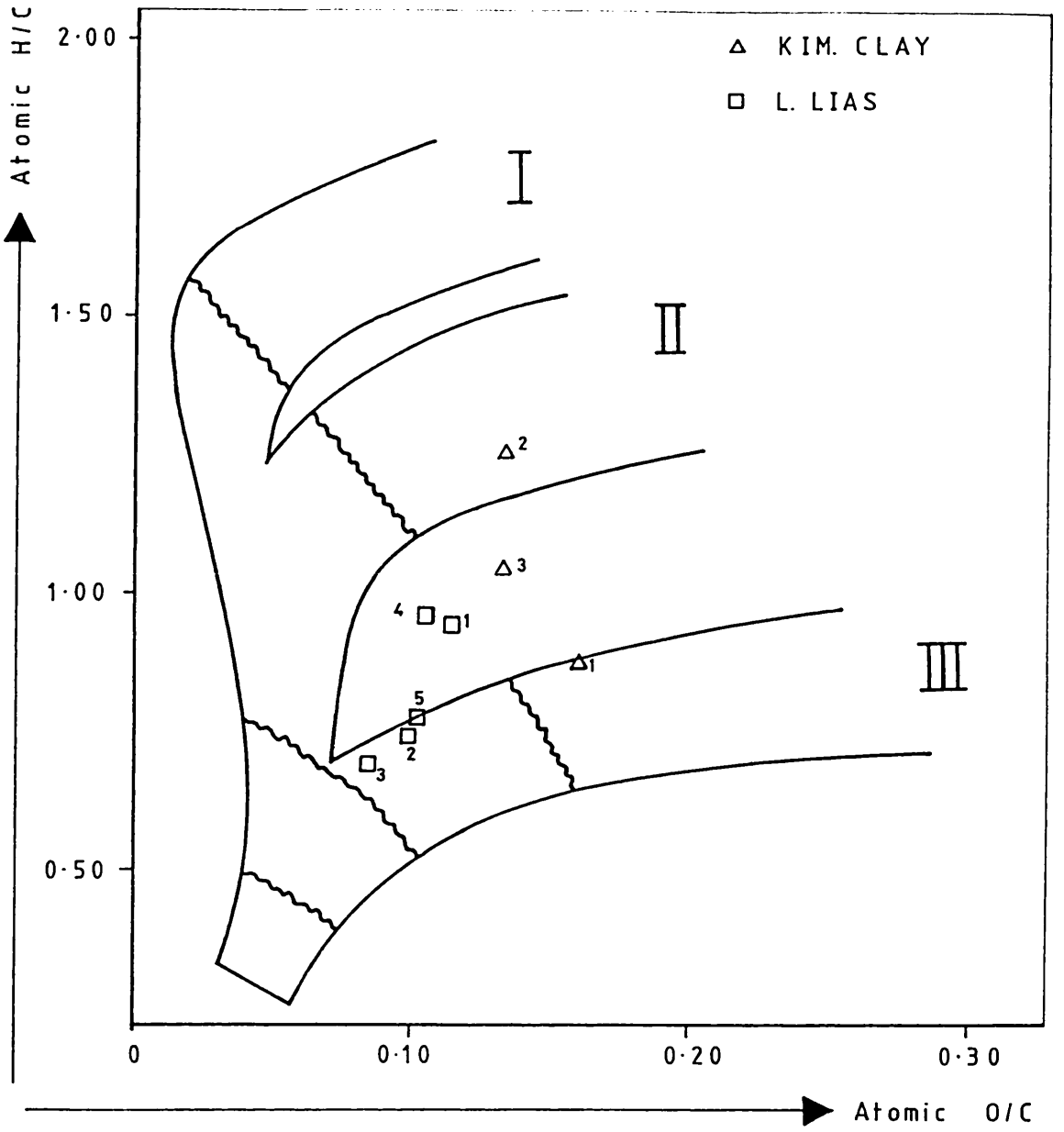


FIG. 6.2(K) VAN KREVELEN DIAGRAM: HENFIELD WELL

boundary during the deposition of the Oxford Clay sediments.

A very complicated picture on the levels of maturity of the Jurassic kerogens is presented by their elemental analytical data. In the previous section (6.1.1), it was noted that kerogen samples normally become more mature with increased depth of burial, and this maturity trend was noted to result in a progressive change in the kerogen elemental composition - generally towards an increased carbon content relative to hydrogen or oxygen. Many shallow immature Jurassic kerogens, particularly those with low $^{H}/_{C}$ atomic ratios belonging to types II/III, III and IV, show elemental compositions characteristic of deep, mature samples. In many Jurassic sections, for example in the Burton Row and the Henfield Wells (see Figs. 6.2 g and k), shallower samples are noticed to show maturity levels higher than the deeper ones. A possible explanation of this complicated trend could be the result of various admixtures of carbon-rich inertinitic type IV kerogen materials almost completely devoid of hydrogen and oxygen in the samples. This would result in relatively low $^{H}/_{C}$ and $^{O}/_{C}$ atomic ratios for the kerogen mixtures. Therefore, the assessment of the levels of maturity of these Jurassic kerogens based essentially on elemental composition of the bulk concentrates is made difficult by the possible kerogen type mixtures. However, it is observed that in most cases the elemental compositions of the type II kerogen samples tend to be the least influenced by these admixed inertinitic

macerals. This is most probably due to the fact that these type IV materials account for a minor proportion of these oil prone kerogens. Thus, the maturity levels indicated by the elemental composition of the type II samples are considered to be fairly representative of the actual levels attained by primary contemporaneous organic materials. It can, therefore, be reasoned that the kerogens from the lower part of the Kimmeridge Clay and the whole of the Oxford Clay Formations have (probably) entered the catagenesis stage in the Arreton-2 (Isle of Wight, Fig. 6.2d) and Penshurst (Kent, Fig. 6.2j) Wells whereas those from either part or the whole of the Lower Lias Formation are in this mature stage in the Winterborne Kingston (Dorset), Arreton-2, Winchester-1 (Hampshire), and Penshurst Wells (Figs. 6.2e, d, c, & j).

6.2 CHARACTERIZATION OF THE KEROGENS BY TRANSMITTED-LIGHT MICROSCOPY AND DENSITY FRACTIONATION

6.2.1 Introduction

Four categories of organic materials commonly identified in transmitted-light microscopic examination of kerogen samples (Staplin, 1969; Correia, 1971; Burgess, 1974) are: amorphous, consisting of unorganized, structureless organic debris which may be finely disseminated or coagulated into fluffy masses; herbaceous, comprising of all non-opaque recognizable plant matter that is not of woody origin and includes plant cuticles, spores, pollens, and dinoflagellate cysts; woody, consisting of elongate

fibrous material of woody origin ranging in colour from pale yellow to brown; and coaly, consisting of black, opaque, usually angular particles. Conford (1977 in Tissot and Welte, 1978) and Brooks (1981) have attempted a correlation of these four categories of organic matter with the known chemical kerogen types. The coaly material is regarded as inertinitic with very little or no hydrocarbon potential and in terms of chemical classification, corresponds to kerogen type IV. The woody fragments correspond to the vitrinite coal maceral and belong to the kerogen type III. Both the woody and the coaly organic debris are grouped together by these authors as humic, terrestrially derived organic materials. The amorphous and the herbaceous kerogen materials are regarded as lipid-rich (classed together as liptinites by Tissot and Welte, 1978; Bostick, 1979) and have been matched mainly with type II kerogen with some contribution to the type I kerogens. According to Staplin (1969), herbaceous constituents are very resistant materials, and in areas where the pattern of erosion and deposition is constantly shifting, some of these materials which have been relatively stabilized in composition can be reworked from older cycles of deposition and incorporated in subsequent depositional layers. The hydrocarbon potential of such harbaceous components will certainly be low. Powell et al. (1982) and Kinghorn and Rahman (1983) have pointed out that not all amorphous organic matter is lipid-rich, and they have identified both the hydrogen-rich (or oil-prone) and the hydrogen-lean (or gas-prone) varieties. The hydrogen-rich amorphous is

believed to be derived from algal material deposited in reducing environments (and therefore sapropelic) whereas the hydrogen-lean variety is regarded as the result of microbial degradation of marine or terrestrially derived organic materials. At low levels of organic maturation, the sapropelic, oil-prone amorphous material (classified as kerogen types I and II) are noted to occur commonly as unorganized fluffy to semi-coherent masses whereas the gas-prone amorphous (classified as type III kerogen) tend to be finely dispersed in texture (Kinghorn and Rahman, 1983).

Based on the findings of Stach et al. (1975) and Flenely (1971) that maceral components of the various types of sedimentary organic matter (i.e. exinites, vitrinites, inertinites etc.) each have a characteristic density, Kinghorn and Rahman (1980, 1983) using the method of density separation in heavy liquid (zinc bromide) have characterized the various kerogen materials (particularly the amorphous), in terms of their type and maturity. They have shown that the hydrogen-rich amorphous is characteristically light with a specific gravity range of < 1.45 to 1.65 whereas the hydrogen-lean amorphous is heavy with a specific gravity range of 1.53 to 2.2. In both cases, the specific gravities have been shown to increase with increasing level of organic maturity. They have associated the humic fragments (i.e. vitrinites and inertinites) with the same specific gravity range as the gas-prone amorphous material.

It has been shown that the thermal alteration of sedimentary organic matter as a result of burial or

increased temperature is usually reflected in the progressive darkening and structural alteration of kerogen constituents such as plant pollens, spores, non-woody cuticles and sapropelic amorphous material (Gutjahr, 1966; Correia, 1967; Staplin, 1969; Peters et al. 1977). Based on the microscopic observations of both colour and structural alteration of these organic debris, Staplin (1969) expressed this gradual organic metamorphism in a TAI scale (Thermal Alteration Index), with values ranging from 1 to 5 (see Table 6.2). Staplin (1977) correlated the TAI scale with vitrinite reflectance values, hydrocarbon facies, and coal rank (Fig. 6.3).

In this study, the organic constituents of the kerogen samples are classified into four easily recognizable categories of sedimentary organic matter by transmitted-light microscopy. These are the amorphous (described as sapropelic or fine-grained), the palynormorphs (include pollens, spores, dinoflagellates and acritarchs), humic (- brown to opaque woody and coaly fragments), and the "cuticles" (- any thin, translucent, tissue-like fragments). The relative abundances of these four organic groups were visually estimated and expressed as "Dominant" (symbol ◆ : > 75%), "Abundant" (symbol ● : 50 - 75%), "Very Common" (symbol ■ : 35-49%), "Common" (symbol □ : 20-34%); "Minor" (symbol ▲ : 5 - 19%), and "Rare" (symbol x : < 5%). The colour scale of Staplin (1977) was used to obtain the TAI values for the Jurassic kerogens, and by using the conversion curve shown in Fig. 6.4 based on the TAI - R_o chart of Waples (1980), the estimated TAI values were converted to maximum vitrinite reflectance values in

TABLE 6.2

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

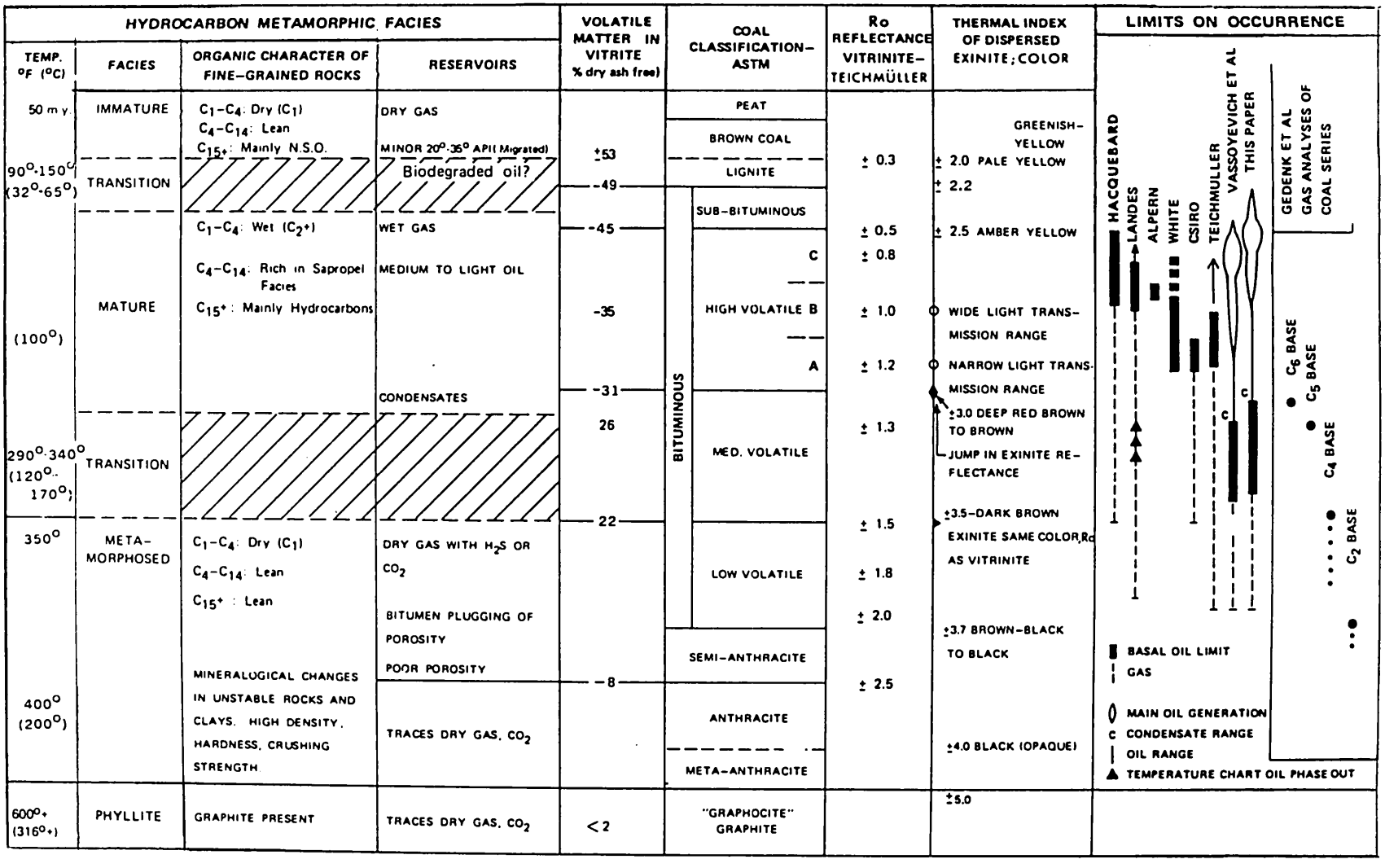


FIG. 6.3 CORRELATION OF HYDROCARBON FACIES, COAL RANK, AND THERMAL ALTERATION INDEX (TAI) (AFTER STAPLIN, 1977)

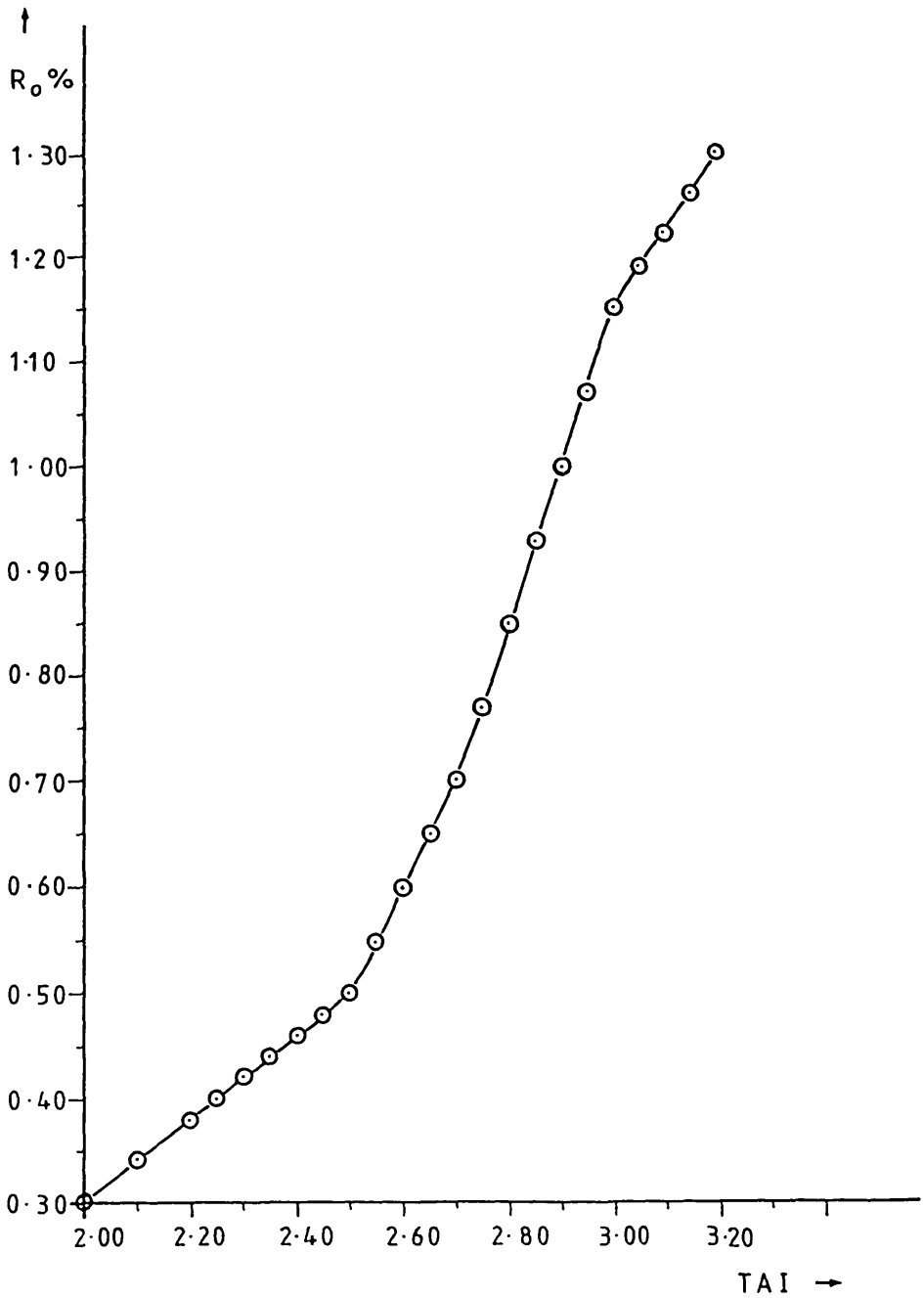


FIG. 6.4 CONVERSION CURVE: PLOT OF VITRINITE REFLECTANCE VALUES (Ro%) AGAINST TAI VALUES (DATA FROM WAPLES, 1980)

oil (R_o%). Subject to the fact that only contemporaneous kerogen constituents were considered in this optical maturity assessment, the levels of maturation arrived at for all the kerogen samples were considered to be indicative of the actual evolutionary stages attained by these Jurassic organic matter.

6.2.2 Results and Interpretation of the Optical Assessment and Density Fractionation of the Jurassic Kerogens

Table 6.3 shows the results of the transmitted-light microscopic assessment of all the kerogen samples as well as the density separation ranges for the amorphous and the humic fractions of these kerogens. The chemical kerogen type is indicated for each sample on the table for ease of compositional comparison between the various types.

As with the elemental compositions, variations are noted in the relative abundances of the four organic matter categories in samples within each kerogen type. But some significant differences are observed in the compositions of the four identified kerogen types (i.e. II, Mixed II/III, III and IV). In the type II group, the most abundant material is the yellow to pale brown sapropelic amorphous with specific gravity mostly in the range of < 1.45 to 1.65, and therefore regarded as light (see Plate 6.1). However, a few type II kerogen samples at low maturity levels are noted to contain a mixture of sapropelic and finely dispersed amorphous material (see Plate 6.1 F). This is probably indicative of cases of an early arrested biodegradation of the deposited marine

planktons with a possible accumulation of the bacterial biomass. Also noted is the fact that the sapropelic amorphous matter of some samples have specific gravities ranging up to 2.2. The heaviness is most probably explained by the unique abundance of opaque particles - most probably pyrite - in the fluffy masses (see Plate 6.1 G). "Cuticular fragments" tend to be quite common (5-49%) in these type II kerogens whereas the humic fragments are rare to minor (i.e.< 20%) in content. The palymorphs constitute less than 35% in all type II kerogens. The humic particles in this Jurassic kerogen group tend to be very light (specific gravity range: <1.45 to 1.65) compared to the heavy vitrinites and inertinites (specific gravity: ≥ 1.65) reported by Kinghorn & Rahman, (1980). This may be interpreted to indicate that light inertinitic materials like charcoal are the major constituents of the humic fraction of the Jurassic type II kerogens. By using reflected light microscopic technique, Douglas and Williams (1981) reported that the particulate sedimentary organic matter in the Kimmeridge Oil Shale (from the Blackstone or "Kimmeridge Coal" band) samples from outcrops and shallow boreholes in England are mainly composed of structureless, very low reflecting amorphous sapropel (bituminite) whilst recognisable coal macerals are not generally abundant. And of these, inertinite was observed to be predominant with secondary and primary vitrinites being subordinate and locally rare. This finding by Douglas and Williams agrees very well with the composition of the type II kerogens in the three Jurassic formations described above based on transmitted-light microscopy and density fractionation. In the type III kerogen

samples, the amorphous material is again the most abundant organic constituent (> 50%) but here, it is the heavy (specific gravity: 1.53 - 2.2), hydrogen-lean, fine-grained type described by Kinghorn and Rahman (1983) (see Plate 6.2). It is commonly greyish to greyish brown in colour. The humic fragments of wide specific gravity range (< 1.45 to 2.2) constitute the next most abundant material in this kerogen group and make up 20-49% in most samples. This indicates a relatively high terrestrial influence compared to the type II situation with the inclusion of a wide variety of humic material ranging from the very light fusinitic ones (like charcoal) to the very heavy, high rank, recycled ones. The palynomorphs constitute less than 20% in all the type III samples whereas the "cuticles" are rare (< 5%) to just common (20 - 34%) in abundance. The mixed type II/III kerogens occupy an intermediate position between types II and III with regards to the relative abundance and form of the four organic matter categories. The amorphous material is still the most abundant, being either wholly finely dispersed or made up of relatively few sapropelic masses in a fine-grained groundmass. In many type II/III samples, the humic particles of wide density range (specific gravity:< 1.45 – 2.2) constitute the next most abundant material, and form 5-49% of all samples in this group. In the type IV kerogen group, the heavy, fine-grained, greyish amorphous material constitute over 50% of the total concentrate and is again the most abundant component; and like the type III kerogens, the humic fragments (specific gravity:< 1.45 to 2.2) are the next in abundance forming 35 to 49% in all

TABLE 6.3 OPTICAL ASSESSMENT AND DENSITY FRACTIONATION DATA FOR THE JURASSIC KEROGENS

Locality /Borehole	Sample Number	Kerogen Type	Composition of Insoluble Organic Matter				Density Separation		Spore/Pollen Colour	Thermal Alteration Index (TAI)	Estimated Vitrinite Reflectance(Ro%)
			Amorphous	Palynomorphs	Humic	"Cuticles"	Specific gravity Range for most of Amorphous matter	Specific gravity range for the Humic fragments			
Ringstead Bay, Dorset	OSD/KC.1	II	◆ (s)	▲	▲	▲	1.45-2.2*	1.53-2.2	Pale yellow	2.00	0.30
"	OSD/KC.2	II	● (s)	x	▲	□	1.45-1.53	1.45-2.2	" "	2.15	0.36
"	OSD/KC.3	II	● (s)	▲	▲	□	1.45-2.2*	1.45-1.53	" "	"	0.36
Kimmeridge Bay — Chapman's Pool, Dorset	OSD/KC.4	Mixed II/III	● (FG)	▲	▲	□	1.53-1.65	1.45-2.2	" "	2.33	0.43
	OSD/KC.5	"	◆ (FG)	▲	▲	▲	1.65-2.2	1.45-1.65	" "	"	0.43
"	OSD/KC.6	II	● (s)	▲	▲	□	1.45-1.65	1.45-1.53	" "	2.35	0.44
"	OSD/KC.7	II	● (s)	▲	x	□	<1.45-1.53	1.53-1.65	" "	"	0.44
"	OSD/KC.8	II	● (s)	x	▲	□	1.45-1.53	1.53-1.65	" "	2.38	0.45
"	OSD/KC.9	II	● (S+FG)	▲	▲	□	1.45-2.2	1.45-1.65	" "	"	0.45
"	OSD/KC.10	II	● (s)	▲	▲	□	1.45-1.53	1.53-1.65	" "	2.40	0.46
"	OSD/KC.11	Mixed II/III	● (s+FG)	▲	▲	□	1.53-1.65	1.45-2.2	" "	2.42	0.47
"	OSD/KC.12	II	● (s+FG)	□	▲	□	1.45-1.65	1.45-1.65	Yellow	2.45	0.48
Short lake Dorset	OSD/OC.1	Mixed II/III	● (FG)	□	□	▲	1.65-2.2	1.45-2.2	Pale yellow	2.25	0.40

(a) - Outcrop Samples

◆ = Dominant (>75%); ● = Abundant (50-75%); ■ = Very Common (35-49%); □ = Common (20-34%);
▲ = Minor (5-19%); x = Rare (5%); * = Presence of Pyrite; S = Sapropelic; FG = Fine Grained

TABLE 6.3 (Cont.) OPTICAL ASSESSMENT AND DENSITY FRACTIONATION DATA FOR THE JURASSIC KEROGENS

Locality /Borehole	Sample Number	Kerogen Type	Composition of Insoluble Organic Matter				Density Separation		Spore/Pollen Colour	Thermal Alteration Index (TAI)	Estimated Vitrinite Reflectance(Ro%)
			Amorphous	Palynomorphs	Humic	"Cuticles"	Specific gravity Range for most of Amorphous matter	Specific gravity range for the Humic fragments			
Chickerell, Dorset	OSD/OC.2	Mixed II/III	● (FG+S)	▲	□	□	1.65 - 2.2	1.53 - 2.2	Pale yellow	2.30	0.42
"	OSD/OC.3	II	● (S)	▲	x	□	1.45 - 1.65	1.53 - 1.65	"	"	0.42
"	OSD/OC.4	II	● (S)	▲	▲	□	1.45 - 1.65	1.53 - 1.65	"	2.35	0.44
"	OSD/OC.5	II	● (S+FG)	▲	x	■	1.53 - 1.65	1.53 - 2.2	"	"	0.44
Charmouth, Dorset	OSD/LL.1	III	● (FG)	▲	■	▲	1.65 - 2.2	<1.45 - 2.2	"	2.12	0.35
"	OSD/LL.2	Mixed II/III	● (FG)	▲	□	▲	1.53 - 2.2	1.45 - 2.2	"	"	0.35
"	OSD/LL.3	II	● (S)	x	x	□	1.53 - 1.65	1.53 - 1.65	"	2.15	0.36
"	OSD/LL.4	II	● (S)	▲	x	□	1.45 - 1.65	1.65 - 2.2	"	2.10	0.34
"	OSD/LL.5	II	● (S)	x	▲	■	1.45 - 2.2*	1.45 - 1.65	"	2.15	0.36
"	OSD/LL.6	II	● (S)	x	x	■	1.45 - 2.2*	1.45 - 1.65	"	"	0.36
Lyme Regis, Dorset	OSD/LL.7	Mixed II/III	◆ (FG)	▲	▲	x	1.65 - 2.2	<1.45 - 2.2	"	2.05	0.32
"	OSD/LL.8	II	● (S)	x	▲	■	1.53 - 2.2*	<1.45 - 1.65	"	"	0.32

Table 6.3(a) (Cont.)

TABLE 6.3 (Cont.) OPTICAL ASSESSMENT AND DENSITY FRACTIONATION DATA FOR THE JURASSIC KEROGENS

Locality /Borehole	Sample Number	Kerogen Type	Composition of Insoluble Organic Matter				Density Separation		Spore/Pollen Colour	Thermal Alteration Index (TAI)	Estimated Vitrinite Reflectance(Ro%)
			Amorphous	Palynomorphs	Humic	"Cuticles"	Specific gravity Range for most of Amorphous matter	Specific gravity range for the Humic fragments			
Marchwood Well	MD/OC.1	Mixed II/III	● (FG+S)	□	□	x	1.65 - 2.2	1.53 - 2.2	Pale yellow	2.30	0.42
	MD/OC.2	"	● (FG)	▲	□	▲	1.65 - 2.2	1.53 - 2.2	" "	"	0.42
	MD/OC.3	"	● (FG+S)	▲	□	x	1.65 - 2.2	1.45 - 2.2	" "	"	0.42
	MD/OC.4	"	● (FG+S)	▲	□	x	1.65 - 2.2	1.45 - 2.2	" "	"	0.42
	MD/LL.1	III	◆ (FG)	x	▲	x	1.65 - 2.2	< 1.45 - 2.2	Yellow	2.50	0.50
	MD/LL.2	Mixed II/III	◆ (FG+S)	x	▲	x	1.53 - 2.2	1.53 - 2.2	"	"	0.50
	MD/LL.3	"	◆ (FG+S)	x	▲	x	1.65 - 2.2	< 1.45 - 2.2	"	"	0.50
	MD/LL.4	III	● (FG)	x	■	x	1.53 - 2.2	< 1.45 - 2.2	"	"	0.50
	MD/LL.5	Mixed II/III	● (FG)	x	□	x	1.65 - 2.2	< 1.45 - 2.2	"	"	0.50
	MD/LL.6	"	● (FG)	x	□	x	1.53 - 2.2	< 1.45 - 2.2	"	"	0.50

Table 6.3(b): Marchwood Well

TABLE 6.3 (Cont.) OPTICAL ASSESSMENT AND DENSITY FRACTIONATION DATA FOR THE JURASSIC KEROGENS

Locality /Borehole	Sample Number	Kerogen Type	Composition of Insoluble Organic Matter				Density Separation		Spore/Pollen Colour	Thermal Alteration Index (TAI)	Estimated Vitrinite Reflectance(Ro%)
			Amorphous	Palynomorphs	Humic	"Cuticles"	Specific gravity Range for most of Amorphous matter	Specific gravity range for the Humic fragments			
Winchester No. 1 Well	WCH/KC.1	III	● (FG)	▲	□	□	1.65 - 2.2	1.53 - 2.2	Pale yellow	2.25	0.40
	WCH/KC.2	III	● (FG)	▲	□	▲	1.65 - 2.2	1.45 - 1.65	" "	2.30	0.42
	WCH/KC.3	III	● (FG)	▲	▲	▲	1.65 - 2.2	1.45 - 1.65	" "	"	0.42
	WCH/OC.1	II	● (S)	▲	x	■	1.45 - 2.2*	1.53 - 1.65	" "	2.40	0.46
	WCH/OC.2	II	● (S)	▲	▲	■	1.45 - 1.65	1.53 - 1.65	" "	"	0.46
	WCH/OC.3	II	● (S)	▲	▲	■	1.45 - 1.65	1.45 - 2.2	Yellow	2.45	0.48
	WCH/OC.4	II	● (S+FG)	▲	▲	□	1.65 - 2.2*	1.45 - 2.2	"	"	0.48
	WCH/LL.1	II	● (FG)	▲	▲	□	1.65 - 2.2	<1.45 - 2.2	"		0.66
	WCH/LL.2	Mixed II/III	● (FG)	▲	▲	□	1.65 - 2.2	<1.45 - 2.2	"	"	0.66
	WCH/LL.3	II	● (FG)	▲	▲	□	1.65 - 2.2	<1.45 - 2.2	"	"	0.66

Table 6.3(c): Winchester-1 Well

TABLE 6.3 (Cont.) OPTICAL ASSESSMENT AND DENSITY FRACTIONATION DATA FOR THE JURASSIC KEROGENS

Locality /Borehole	Sample Number	Kerogen Type	Composition of Insoluble Organic Matter				Density Separation		Spore/Pollen Colour	Thermal Alteration Index (TAI)	Estimated Vitrinite Reflectance(Ro%)
			Amorphous	Palynomorphs	Humic	"Cuticles"	Specific gravity Range for most of Amorphous matter	Specific gravity range for the Humic fragments			
Arreton No. 2 Well	AR/KC.1	Mixed II/III	● (S+FG)	▲	□	▲	<1.45 - 2.2	<1.45 - 1.65	Pale yellow	2.38	0.45
	AR/KC.3	II	● (S)	▲	▲	□	1.45 - 2.2*	1.45 - 1.53	" "	2.40	0.46
	AR/KC.5	II	● (S)	▲	x	□	<1.45 - 1.53	1.45 - 1.65	Yellow	2.45	0.48
	AR/KC.7	II	● (S)	▲	▲	□	<1.45 - 1.65	1.45 - 1.53	"	2.50	0.50
	AR/KC.9	II	● (S)	▲	▲	□	<1.45 - 1.65	<1.45 - 1.65	"	2.52	0.52
	AR/OC.2	Mixed II/III	● (FG+S)	▲	□	□	1.53 - 2.2	<1.45 - 1.65	"	2.54	0.54
	AR/OC.4	II	● (S)	x	▲	□	1.45 - 1.65	1.53 - 1.65	"	2.58	0·58
	AR/LL.1	II	● (S+FG)	▲	□	▲	1.45 - 2.2	<1.45 - 1.65	Dark yellow	2.70	0.70
	AR/LL.3	II	◆ (S)	▲	▲	▲	1.45 - 2.2*	<1.45 - 1.65	"	2.73	0.74
	AR/LL.5	II	● (S+FG)	▲	▲	□	<1.45 - 2.2*	<1.45 - 1.53	Orange	2.77	0.80
	AR/LL.7	II	● (S+FG)	x	▲	□	1.45 - 2.2*	<1.45 - 1.65	"	2.79	0.84
	AR/LL.9	II	◆ (S+FG)	x	▲	▲	1.53 - 2.2*	<1.45 - 1.53	"	2.83	0.90

Table 6.3(d): Arreton-2 Well

TABLE 6.3 (Cont.) OPTICAL ASSESSMENT AND DENSITY FRACTIONATION DATA FOR THE JURASSIC KEROGENS

Locality /Borehole	Sample Number	Kerogen Type	Composition of Insoluble Organic Matter				Density Separation		Spore/Pollen Colour	Thermal Alteration Index (TAI)	Estimated Vitrinite Reflectance(Ro%)
			Amorphous	Palynomorphs	Humic	"Cuticles"	Specific gravity Range for most of Amorphous matter	Specific gravity range for the Humic fragments			
Winterborne Kingston Well	WK/KC.1	Mixed II/III	● (FG+S)	■	▲	▲	1.53 - 1.65	1.45 - 2.2	Pale yellow	2.05	0.32
	WK/KC.2	"	● (FG+S)	□	▲	□	1.53 - 2.2	1.45 - 2.2	"	"	0.32
	WK/KC.3	"	● (FG+S)	□	▲	□	1.53 - 2.2	1.45 - 2.2	"	"	0.32
	WK/LL.1	"	● (FG+S)	▲	▲	▲	1.53 - 2.2	< 1.45 - 2.2	Yellow	2.45	0.48
	WK/LL.2	"	● (FG)	▲	▲	▲	1.53 - 2.2	1.45 - 2.2	"	"	0.48
	WK/LL.3	"	● (FG)	▲	▲	▲	1.65 - 2.2	1.45 - 2.2	"	"	0.48
	WK/LL.4	"	● (FG)	▲	▲	▲	1.65 - 2.2	1.45 - 2.2	"	"	0.48
	WK/LL.5	III	◆ (FG)	x	▲	x	1.65 - 2.2	< 1.45 - 2.2	"	2.55	0.55
	WK/LL.6	Mixed II/III	◆ (FG+S)	▲	▲	x	1.65 - 2.2	< 1.45 - 2.2	"	"	0.55
	WK/LL.7	II	◆ (S)	x	▲	x	<1.45 - 2.2*	1.45 - 1.65	"	"	0.55
	WK/LL.8	II	◆ (S)	x	▲	▲	<1.45 - 2.2*	1.53 - 1.65	"	2.56	0.56

Table 6.3(e): Winterborne Kingston Well

TABLE 6.3 (Cont.) OPTICAL ASSESSMENT AND DENSITY FRACTIONATION DATA FOR THE JURASSIC KEROGENS

Locality /Borehole	Sample Number	Kerogen Type	Composition of Insoluble Organic Matter				Density Separation		Spore/Pollen Colour	Thermal Alteration Index (TAI)	Estimated Vitrinite Reflectance(Ro%)
			Amorphous	Palynomorphs	Humic	"Cuticles"	Specific gravity Range for most of Amorphous matter	Specific gravity range for the Humic fragments			
Cranbourne No. 1 Well	CN/KC.1	Mixed II/III	● (FG+S)	▲	▲	□	1.53 - 1.65	1.45 - 2.2	Pale Yellow	2.15	0.36
	CN/OC.1	IV	● (FG)	▲	■	▲	1.65 - 2.2	<1.45 - 2.2	" "	2.20	0.38
	CN/OC.2	Mixed II/III	● (FG)	□	□	▲	1.65 - 2.2	1.45 - 2.2	" "	"	0.38
	CN/OC.3	"	● (FG)	▲	▲	□	1.65 - 2.2	1.45 - 2.2	" "	2.25	0.40
	CN/OC.4	II	● (S+FG)	▲	x	■	1.45 - 1.53	1.53 - 1.65	" "	"	0.40
	CN/OC.5	II	● (S)	▲	▲	■	1.53 - 2.2*	1.45 - 1.65	" "	2.30	0.42
	CN/LL.1	III	◆ (FG)	▲	▲	▲	1.65 - 2.2	<1.45 - 1.65	" "	2.38	0.45
	CN/LL.2	Mixed II/III	◆ (FG+S)	▲	▲	▲	1.65 - 2.2	1.45 - 1.65	" "	"	0.45
	CN/LL.3	"	● (FG+S)	▲	▲	□	1.65 - 2.2	1.45 - 1.65	" "	2.40	0.46
	CN/LL.4	"	● (FG+S)	▲	▲	□	1.65 - 2.2	1.45 - 1.65	" "	"	0.46
	CN/LL.5	"	● (FG+S)	▲	▲	□	1.65 - 2.2	1.45 - 1.65	Yellow	2.45	0.48
	CN/LL.6	"	● (FG+S)	▲	▲	□	1.65 - 2.2	1.45 - 1.65	"	"	0.48

Table 6.3(f): Cranborne-1 Well

TABLE 6.3 (Cont.) OPTICAL ASSESSMENT AND DENSITY FRACTIONATION DATA FOR THE JURASSIC KEROGENS

Locality /Borehole	Sample Number	Kerogen Type	Composition of Insoluble Organic Matter				Density Separation		Spore/Pollen Colour	Thermal Alteration Index (TAI)	Estimated Vitrinite Reflectance(Ro%)
			Amorphous	Palynomorphs	Humic	"Cuticles"	Specific gravity Range for most of Amorphous matter	Specific gravity range for the Humic fragments			
Burton Row Well	BR/LL.1	Mixed II/III	● (FG+S)	▲	■	▲	1.65 - 2.2	1.45 - 2.2	Pale Yellow	2.20	0.38
	BR/LL.2	"	● (FG)	▲	■	▲	1.65 - 2.2	1.45 - 2.2	" "	"	0.38
	BR/LL.3	II	● (S+FG)	x	□	□	1.53 - 2.2	1.45 - 2.2	" "	2.25	0.40
	BR/LL.4	III	● (FG)	x	□	▲	1.65 - 2.2	1.45 - 2.2	" "	"	0.40
	BR/LL.5	II	● (S+FG)	▲	▲	□	1.53 - 2.2	1.53 - 2.2	" "	2.30	0.42
	BR/LL.6	Mixed II/III	● (FG)	▲	□	▲	1.65 - 2.2	1.45 - 2.2	" "	"	0.42
	BR/LL.7	"	● (FG)	▲	□	▲	1.53 - 2.2	1.45 - 2.2	" "	2.32	0.43
	BR/LL.8	"	● (FG)	x	□	▲	1.65 - 2.2	<1.45 - 2.2	" "	"	0.43
	BR/LL.9	"	● (FG+S)	▲	■	▲	1.53 - 2.2	<1.45 - 2.2	" "	2.35	0.44
	BR/LL.10	II	◆ (S)	x	x	▲	<1.45 - 2.2*	1.53 - 1.65	" "	2.38	0.45
	BR/LL.11	II	◆ (S)	x	▲	▲	<1.45 - 2.2*	1.53 - 1.65	" "	"	0.45

Table 6.3(g): Burton Row Well

TABLE 6.3 (Cont.) OPTICAL ASSESSMENT AND DENSITY FRACTIONATION DATA FOR THE JURASSIC KEROGENS

Locality /Borehole	Sample Number	Kerogen Type	Composition of Insoluble Organic Matter				Density Separation		Spore/Pollen Colour	Thermal Alteration Index (TAI)	Estimated Vitrinite Reflectance(Ro%)
			Amorphous	Palynomorphs	Humic	"Cuticles"	Specific gravity Range for most of Amorphous matter	Specific gravity range for the Humic fragments			
Cooles Farm No. 1 Well	CF/LL.1	Mixed II/III	● (FG+S)	▲	□	□	1.65 - 2.2	1.45 - 2.2	Pale yellow	2.20	0.38
	CF/LL.2	"	● (FG+S)	▲	□	□	1.53 - 2.2	1.45 - 2.2	" "	"	0.38
	CF/LL.3	"	● (FG+S)	▲	□	▲	1.65 - 2.2	1.45 - 2.2	" "	"	0.38
	CF/LL.4	"	● (FG+S)	▲	▲	□	1.53 - 2.2	1.53 - 2.2	" "	2.25	0.40
	CF/LL.5	III	● (FG)	▲	□	□	1.65 - 2.2	1.45 - 2.2	" "	"	0.40
	CF/LL.6	Mixed II/III	● (FG+S)	▲	▲	□	1.53 - 2.2	1.45 - 2.2	" "	2.30	0.42
	CF/LL.7	"	● (FG+S)	▲	▲	□	1.65 - 2.2	1.45 - 2.2	" "	"	0.42

Table 6.3(h): Cooles Farm-1 Well

TABLE 6.3 (Cont.) OPTICAL ASSESSMENT AND DENSITY FRACTIONATION DATA FOR THE JURASSIC KEROGENS

Locality /Borehole	Sample Number	Kerogen Type	Composition of Insoluble Organic Matter				Density Separation		Spore/Pollen Colour	Thermal Alteration Index (TAI)	Estimated Vitrinite Reflectance(Ro%)
			Amorphous	Palynomorphs	Humic	"Cuticles"	Specific gravity Range for most of Amorphous matter	Specific gravity range for the Humic fragments			
Warlingham Well	WM/KC.1	Mixed II/III	● (FG+S)	▲	□	▲	1.53 - 2.2	1.45 - 1.65	Pale Yellow	2.12	0.35
	WM/KC.2	II	● (S+FG)	▲	▲	■	1.53 - 1.65	1.53 - 1.65	" "	2.15	0.36
	WM/KC.3	II	● (S+FG)	x	▲	□	1.53 - 1.65	1.65 - 2.2	" "	"	0.36
	WM/KC.4	Mixed II/III	● (FG+S)	▲	□	x	1.65 - 2.2	1.45 - 2.2	" "	2.17	0.37
	WM/KC.5	II	● (S)	▲	▲	□	1.53 - 1.65	1.45 - 1.65	" "	"	0.37
	WM/KC.6	II	◆ (S+FG)	▲	▲	x	1.45 - 1.65	1.53 - 1.65	" "	2.20	0.38
	WM/KC.7	II	● (S+FG)	▲	□	□	1.53 - 2.2	1.45 - 2.2	" "	"	0.38
	WM/KC.8	Mixed II/III	◆ (FG)	▲	▲	▲	1.65 - 2.2	< 1.45 - 1.65	" "	2.25	0.40
	WM/KC.9	"	● (FG)	▲	■	x	1.65 - 2.2	< 1.45 - 2.2	" "	"	0.40
	WM/OC.1	III	● (FG)	▲	□	▲	1.65 - 2.2	1.45 - 2.2	" "	2.30	0.42
	WM/OC.2	Mixed II/III	● (FG+S)	▲	□	▲	1.65 - 2.2	1.45 - 2.2	" "	"	0.42
	WM/OC.3	II	● (S)	▲	▲	□	1.53 - 1.65	1.45 - 1.65	" "	2.35	0.44
	WM/OC.4	II	● (FG+S)	▲	▲	□	1.53 - 1.65	< 1.45 - 1.53	" "	"	0.44

Table 6.3(i): Warlingham Well

TABLE 6.3 (Cont.) OPTICAL ASSESSMENT AND DENSITY FRACTIONATION DATA FOR THE JURASSIC KEROGENS

Locality /Borehole	Sample Number	Kerogen Type	Composition of Insoluble Organic Matter				Density Separation		Spore/Pollen Colour	Thermal Alteration Index (TAI)	Estimated Vitrinite Reflectance(Ro%)
			Amorphous	Palynomorphs	Humic	"Cuticles"	Specific gravity Range for most of Amorphous matter	Specific gravity range for the Humic fragments			
Warlingham Well (Cont.)	WM/OC.5	II	● (S)	▲	▲	□	< 1.45 - 1.53	< 1.45 - 1.53	Pale yellow	2.38	0.45
	WM/LL.1	III	● (FG)	▲	□	□	1.53 - 2.2	1.45 - 2.2	Yellow	2.45	0.48
	WM/LL.2	Mixed II/III	● (FG)	▲	□	□	1.53 - 2.2*	1.45 - 1.65	"	2.50	0.50
	WM/LL.3	Mixed II/III	● (FG)	▲	□	x	1.65 - 2.2	<1.45 - 2.2	"	"	0.50
	WM/LL.4	IV	● (FG)	▲	■	x	1.65 - 2.2	< 1.45 - 2.2	"	2.52	0.52
	WM/LL.5	IV	● (FG)	x	■	▲	1.65 - 2.2	< 1.45 - 2.2	"	2.54	0.54
	WM/LL.6	III	● (FG)	x	■	x	1.65 - 2.2	1.45 - 2.2	"	"	0.54

Table 6.3(i) (Cont.): Warlingham Well

TABLE 6.3 OPTICAL ASSESSMENT AND DENSITY FRACTIONATION DATA FOR THE JURASSIC KEROGENS

Locality /Borehole	Sample Number	Kerogen Type	Composition of Insoluble Organic Matter				Density Separation		Spore/Pollen Colour	Thermal Alteration Index (TAI)	Estimated Vitrinite Reflectance (Ro%)
			Amorphous	Palynomorphs	Humic	"Cuticles"	Specific gravity Range for most of Amorphous matter	Specific gravity range for the Humic fragments			
Penshurst Well	PH/KC.1	II	● (S)	□	▲	■	1.45 - 2.2*	1.45 - 1.65	Yellow	2.45	0.48
	PH/KC.2	Mixed II/III	● (FG+S)	▲	▲	□	1.65 - 2.2	1.45 - 2.2	"	2.54	0.54
	PH/KC.3	"	● (FG)	▲	□	□	1.65 - 2.2	1.45 - 2.2	"	2.58	0.58
	PH/KC.4	II	● (S)	▲	▲	■	1.53 - 1.65	1.45 - 1.53	"	2.62	0.62
	PH/OC.1	Mixed II/III	● (FG)	▲	▲	□	1.65 - 2.2	1.45 - 1.65	"	2.68	0.68
	PH/OC.2	II	◆ (FG+S)	▲	▲	▲	1.65 - 2.2	1.45 - 2.2	Dark yellow	2.70	0.70
	PH/OC.3	II	● (S)	▲	x	■	1.45 - 1.65	<1.45 - 1.53	"	2.73	0.74
	PH/LL.1	Mixed II/III	● (FG+S)	▲	▲	■	1.53 - 2.2	1.45 - 1.65	"	2.76	0.78
	PH/LL.2	"	● (FG+S)	▲	▲	□	1.65 - 2.2	1.45 - 2.2	Orange	2.77	0.80
	PH/LL.3	II	● (S+FG)	▲	▲	□	1.53 - 2.2*	1.45 - 1.53	"	2.78	0.82
	PH/LL.4	II	● (FG+S)	▲	▲	□	1.53 - 2.2	1.45 - 1.65	"	2.79	0.84
	PH/LL.5	Mixed II/III	● (FG+S)	▲	□	□	1.53 - 2.2	<1.45 - 2.2	"	2.80	0.85

Table 6.3(j): Penshurst Well

TABLE 6.3 OPTICAL ASSESSMENT AND DENSITY FRACTIONATION DATA FOR THE JURASSIC KEROGENS

Locality /Borehole	Sample Number	Kerogen Type	Composition of Insoluble Organic Matter				Density Separation		Spore/Pollen Colour	Thermal Alteration Index (TAI)	Estimated Vitrinite Reflectance(Ro%)
			Amorphous	Palynomorphs	Humic	"Cuticles"	Specific gravity Range for most of Amorphous matter	Specific gravity range for the Humic fragments			
Henfield Well	HN/KC.1	III	● (FG)	▲	▲	▲	1.53 - 2.2	1.45 - 1.53	Pale yellow	2.15	0.36
	HN/KC.2	II	● (S+FG)	▲	x	□	1.45 - 1.65	1.53 - 1.65	"	2.25	0.40
	HN/KC.3	Mixed II/III	● (FG)	▲	▲	▲	1.65 - 2.2	1.45 - 1.65	"	2.25	0.40
	HN/LL.1	"	● (FG+S)	▲	▲	□	1.53 - 2.2	1.45 - 1.65	Yellow	2.55	0.55
	HN/LL.2	III	● (FG)	▲	□	□	1.65 - 2.2	< 1.45 - 1.65	"	2.58	0.58
	HN/LL.3	III	● (FG)	▲	□	▲	1.65 - 2.2	< 1.45 - 2.2	"	2.60	0.60
	HN/LL.4	Mixed II/III	● (FG+S)	x	▲	□	1.53 - 2.2	1.45 - 2.2	"	2.62	0.62
	HN/LL.5	III	● (FG)	▲	□	▲	1.65 - 2.2	1.45 - 2.2	"	"	0.62

Table 6.3(k): Henfield Well

the samples. Both the palynomorphs and the "cuticles" are rare to minor in content (see Plate 6.3). Some of the organic fragments described as "cuticles", particularly in the kerogen type II and Mixed type II/III, are likely to be incompletely altered algal fragments as judged from their fibrous nature (Batten, 1983) (see Plate 6.1 H).

The maturity levels arrived at for these Jurassic kerogens based on the TAI scale (see Table 6.3) are fairly consistent with the levels of maturation portrayed by the type II samples on the van Krevelen type - plots shown on Fig. 6.2. Kerogens from all the outcrop samples of the Lower Lias, the Oxford Clay and the Kimmeridge Clay are immature (Vitrinite reflectance values < 0.50% Ro) (Plate 6.4). Of particular interest is the observation that in Dorset, the kerogens in the outcrop samples of the Kimmeridge Clay to the south of the Purbeck - Isle of Wight Line of Disturbance (i.e. in the Kimmeridge Bay - Chapman's Pool area) are relatively more mature than to the north of that line (i.e. in Ringstead Bay area) (see Fig. 6.2a, Table 6.3a and Plate 6.4). This maturity difference was implied in the organic geochemical data of outcrop samples for the Kimmeridge Oil Shale in Dorset reported by Douglas and Williams (1981). Measured vitrinite reflectance values of 0.39 to 0.43% Ro, similar to the estimated values reported here, were obtained by these authors for the Upper Kimmeridgian Blackstone samples from the Kimmeridge Bay - Chapman's Pool area. Kerogen samples from the lower part of the Kimmeridge Clay Formation and those from the whole of the Oxford Clay Formation obtained from the Arreton No. 2 Well in the Isle

of Wight (see Table 6.3d and Plate 6.7) are marginally mature (Ro: 0.50% to less than 0.60%) but those from the Penshurst Well in the central part of Weald (see Table 6.3k and Plate 6.6) have entered the main phase of oil generation (i.e. $R_o \geq 0.60\%$). Thus mature contemporaneous organic matter in these two formations are identified only in two localities in southern England: Isle of Wight and central Weald (Fig. 6.5). By contrast, there is a wider distribution of mature sections of the Lower Lias Formation. The kerogen samples in the lower part or the whole of the Lower Lias are in the catagenesis stage in Arreton-2, Winterborne Kingston, Marchwood, Winchester-1, Henfield, Warlingham and Penshurst Wells (see Tables 6.3b, c, d, e, i, j, k; Fig. 6.5), however, samples in the main phase of oil generation are encountered only in Arreton-2, Henfield, Winchester-1, and Penshurst Wells (see Plates 6.5 - 6.7). The most mature Lower Lias sections occur in Arreton No. 2 (R_o values up to 0.90%) and Penshurst (R_o values up to 0.85%) Wells - the same localities where the most mature Kimmeridge Clay and Oxford Clay samples are identified in this study. In the Penshurst Well, the thickness of the Jurassic is about 4,130 feet (1,259 metres). In areas of the central Weald where the Jurassic attains thicknesses of over 5,000 feet (1,524 metres) (in northern West Sussex - southern Surrey, Fig. 6.6) it is very likely the organic matter in these three Jurassic formations have attained higher maturity levels than those reported here for the Penshurst Well.

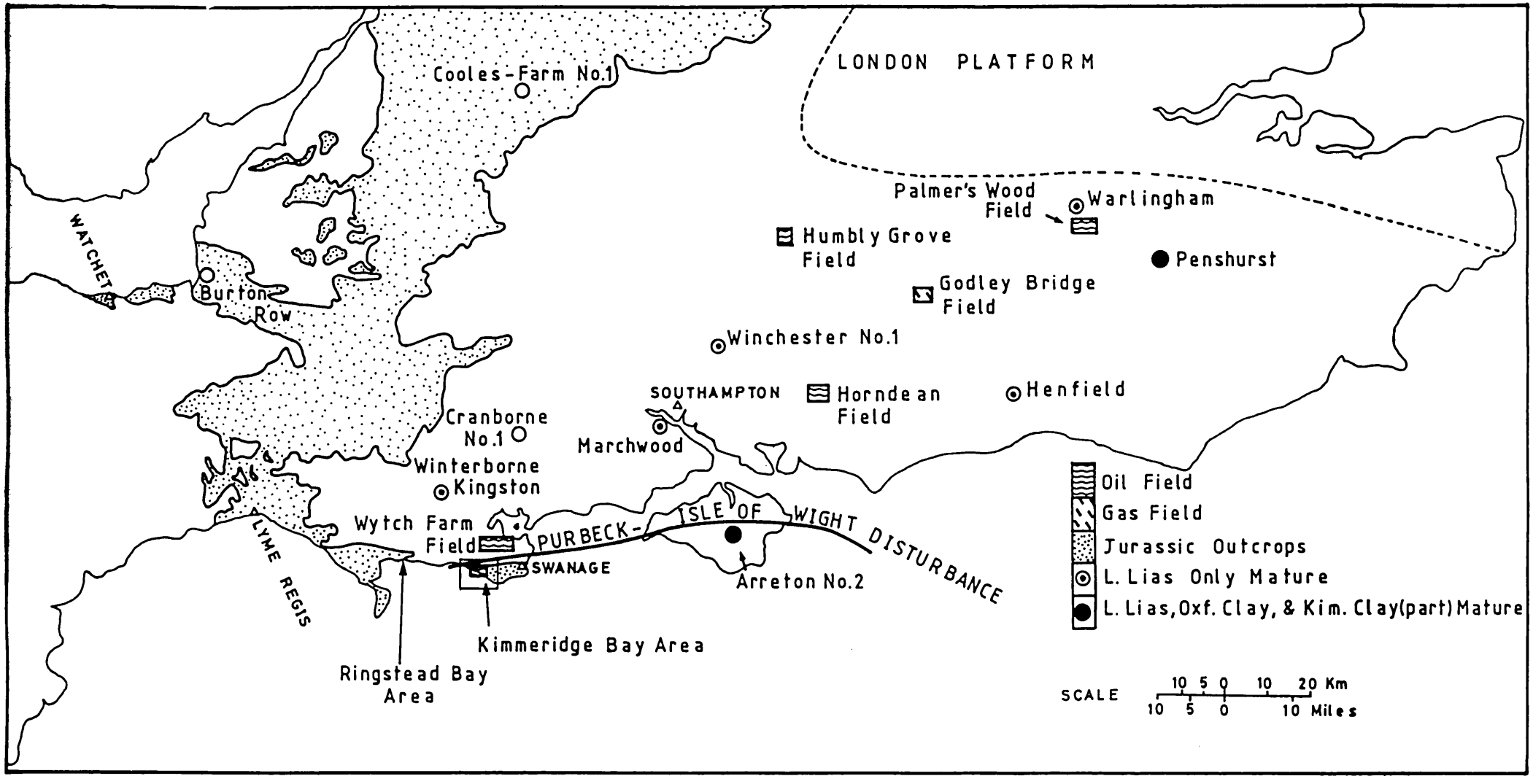


FIG. 6.5 MAP SHOWING KNOWN OIL AND GAS ACCUMULATIONS AND LOCALITIES WHERE THE KIMMERIDGE CLAY, THE OXFORD CLAY AND THE LOWER LIAS KEROGENS ARE FOUND MATURE IN S. ENGLAND (i.e. AT Ro $\geq$ 0.50%)

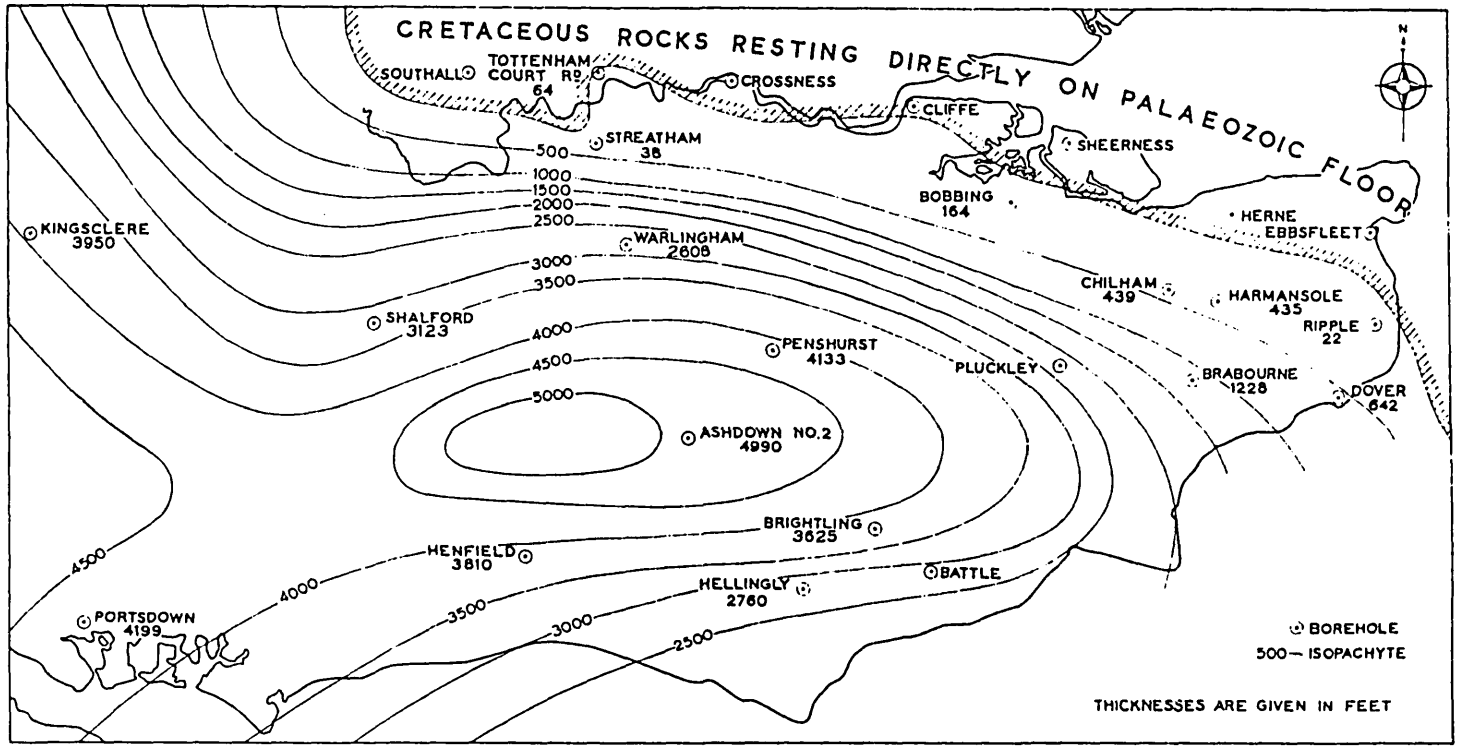


FIG. 6.6 ISOPACHYTE MAP OF THE JURASSIC ROCKS OF SOUTH-EAST ENGLAND SHOWING THE DEPTH OF THE JURASSIC SEDIMENTARY BASIN (AFTER GALLOIS, 1965)

PLATE 6.1: KEROGEN TYPE II

A - The 1.45 Density Fraction of Sample WM/OC.5

This fraction accounts for about 38 vol.% of the total kerogen concentrate, and consists mainly of yellowish sapropelic amorphous matter. "Cuticles", Humic matter, and Palynomorphs are relatively minor in contents (Magnification x 45).

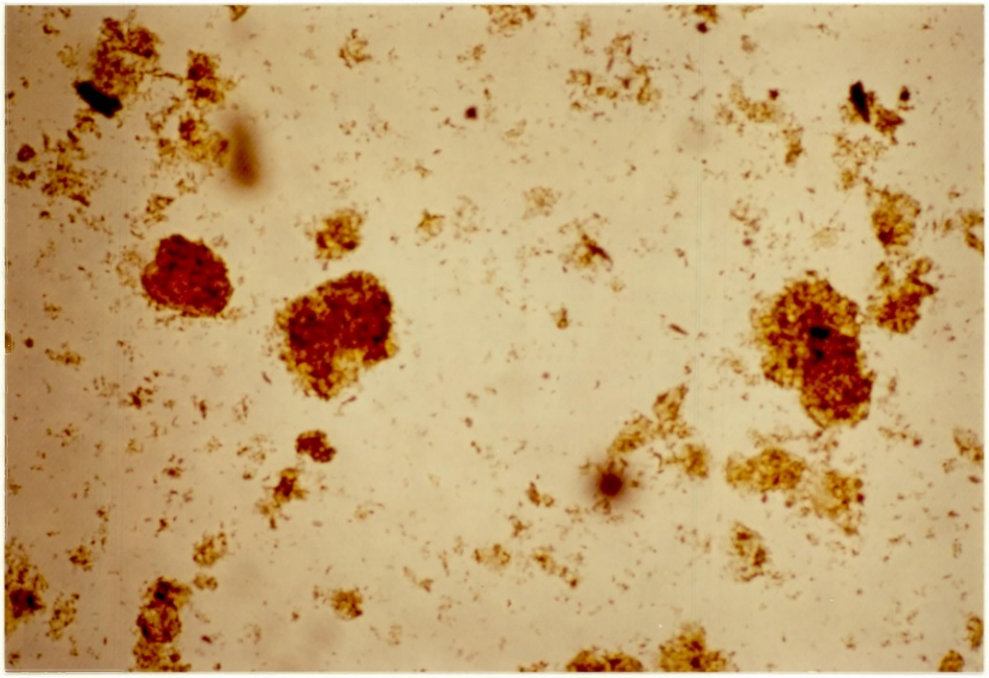
B - The 1.45 - 1.53 Density Fraction of Sample WM/OC.5

This fraction accounts for about 38 vol.% of the total kerogen concentrate, consisting mainly of yellowish sapropelic amorphous matter and "Cuticular" fragments. Humic matter is minor, and Palynomorphs are rare (Magnification x 45).

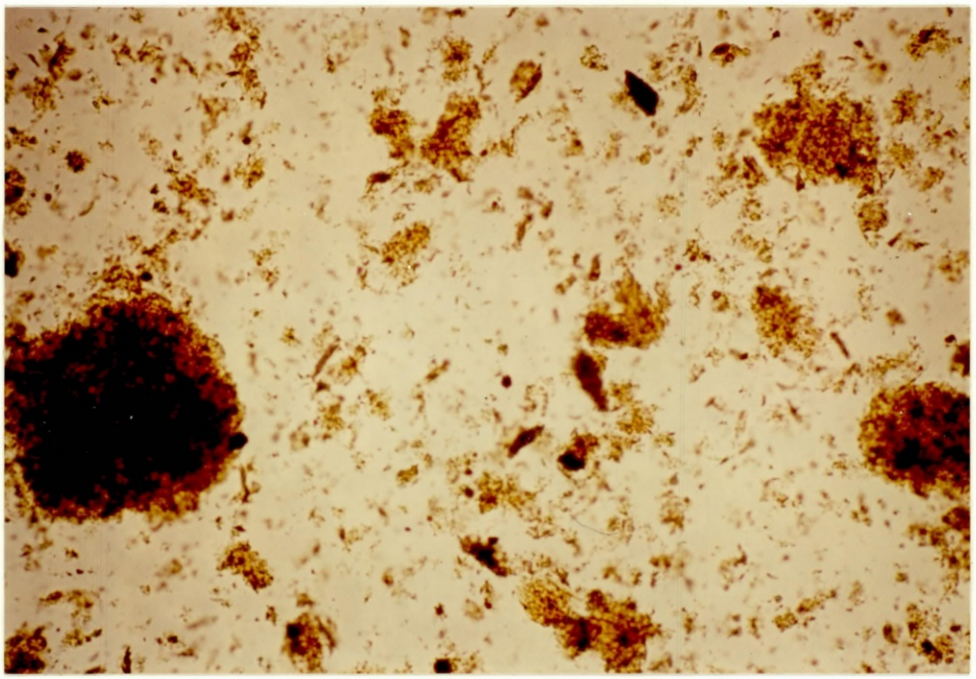
C - The 1.53 - 1.65 Density Fraction of Sample WM/OC.5

This fraction forms about 14 vol.% of the total kerogen concentrate, consisting mainly of yellowish sapropelic amorphous matter and "cuticles". Humic matter and Palynomorphs are rare (Magnification x 45).

A



B



D

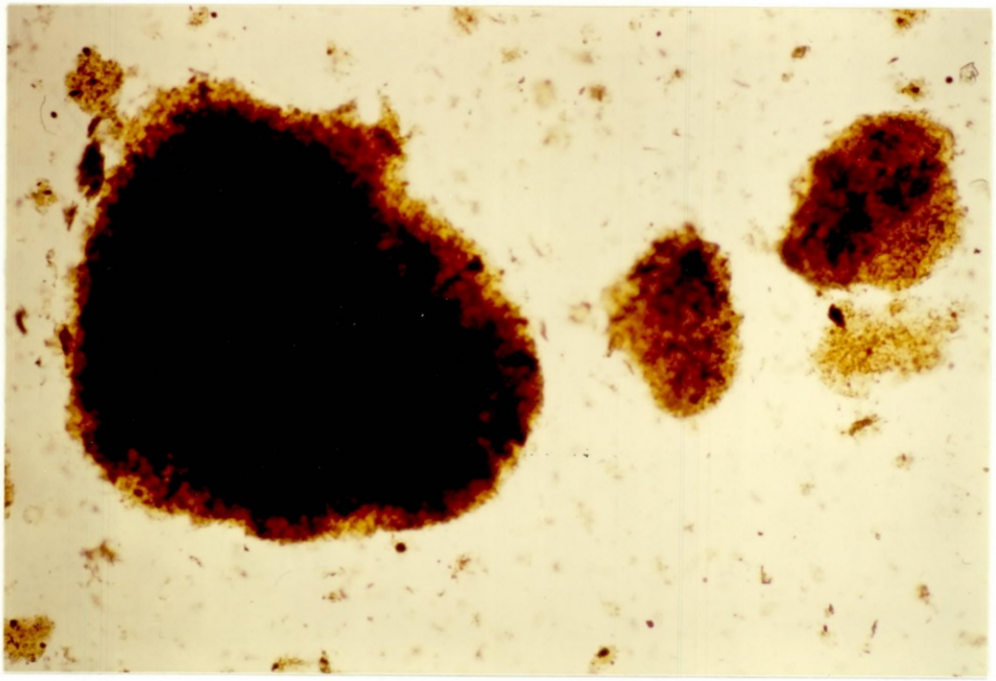


PLATE 6.1 - KEROGEN TYPE II (Contd.)

D - The 1.65 - 2.2 Density Fraction of Sample WM/OC.5

This fraction accounts for about 10 vol.% of the total kerogen concentrate, and consists dominantly of sapropelic amorphous masses and some palynomorphs both containing plenty of opaque particles - probably pyrite (Magnification x 45).

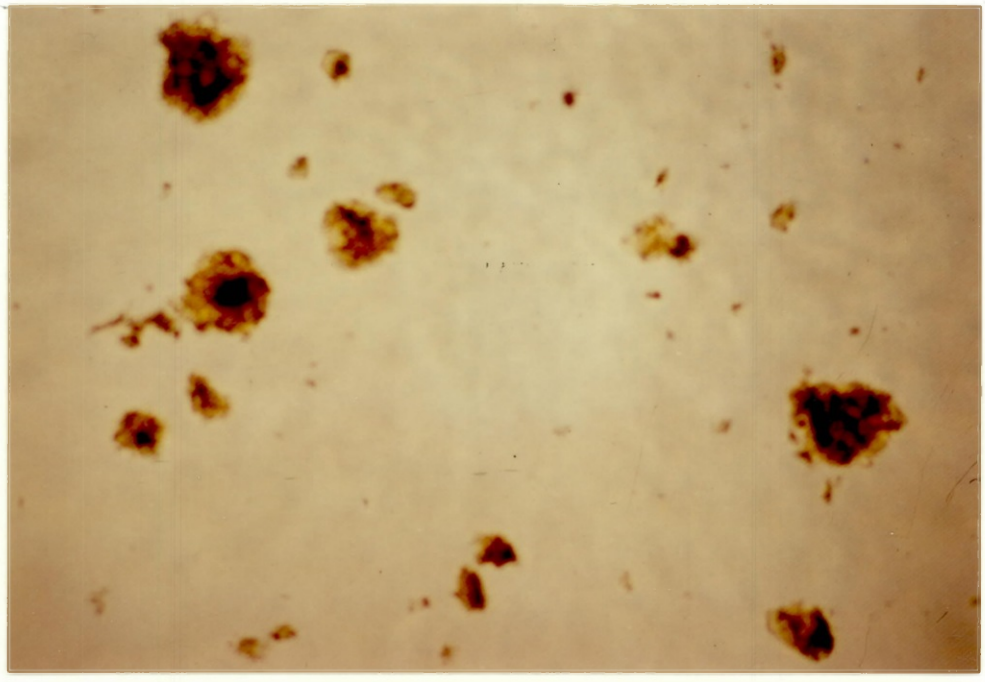
E - The Total Insoluble Organic Matter:
Sample WM/OC.5

Consists mainly of yellowish sapropelic masses and "Cuticular" fragments. Humic fragments and Paynomorphs are quite minor in contents (Magnification x 45).

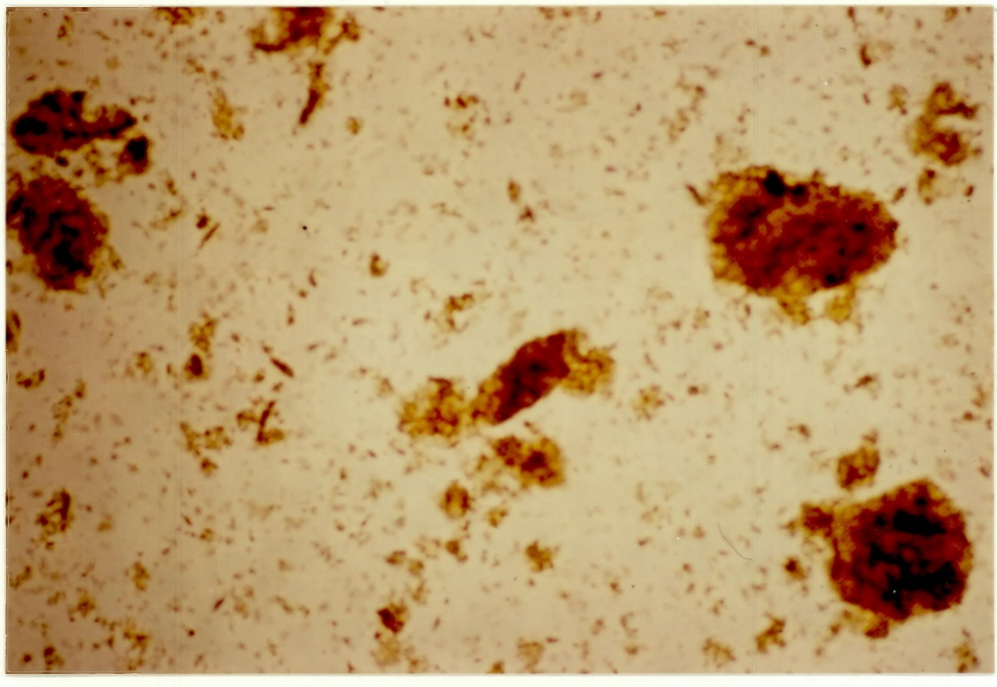
F - The Total Insoluble Organic Matter:
Sample WM/KC.3

Consists mainly of yellowish brown sapropelic amorphous masses and dispersed greyish brown amorphous fines. "Cuticles" are fairly common, Humic matter is minor, and Palynomorphs are rare (Magnification x 45).

D



E



F

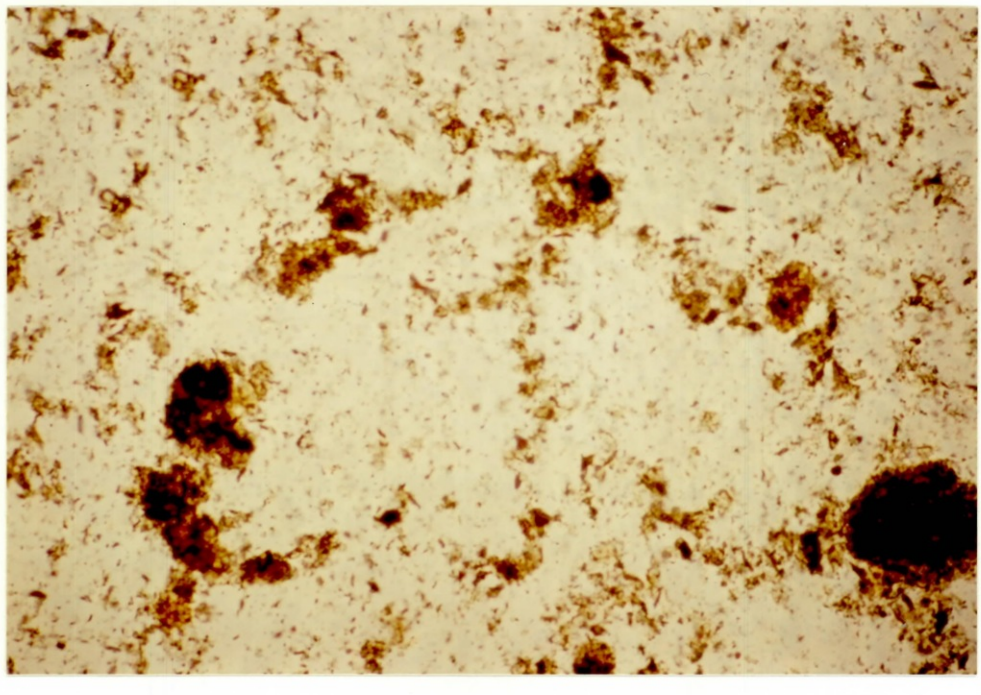


PLATE 6.1: KEROGEN TYPE II (Contd.)

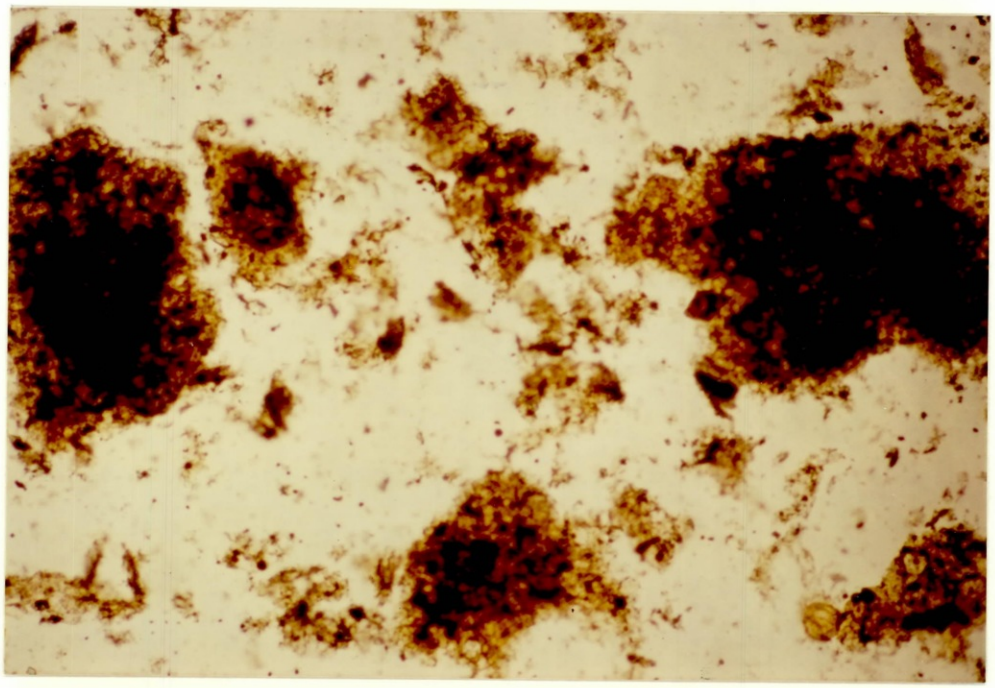
G - The 1.65 - 2.2 Density Fraction of Sample BR/LL.11

This highest density fraction accounts for about 75 vol.% of the total kerogen concentrate of this sample, and consists dominantly of sapropelic amorphous masses heavily infested with opaque, ?heavy mineral grains - most probably pyrite (Magnification x 45).

H - Highly Magnified "Cuticular" Fragments in a Type II Kerogen Sample (Sample: WM/OC.5)

The fibrous nature of these fragments is suggestive of incompletely altered algal material (Batten, 1983) (Magnification x 180).

G



H

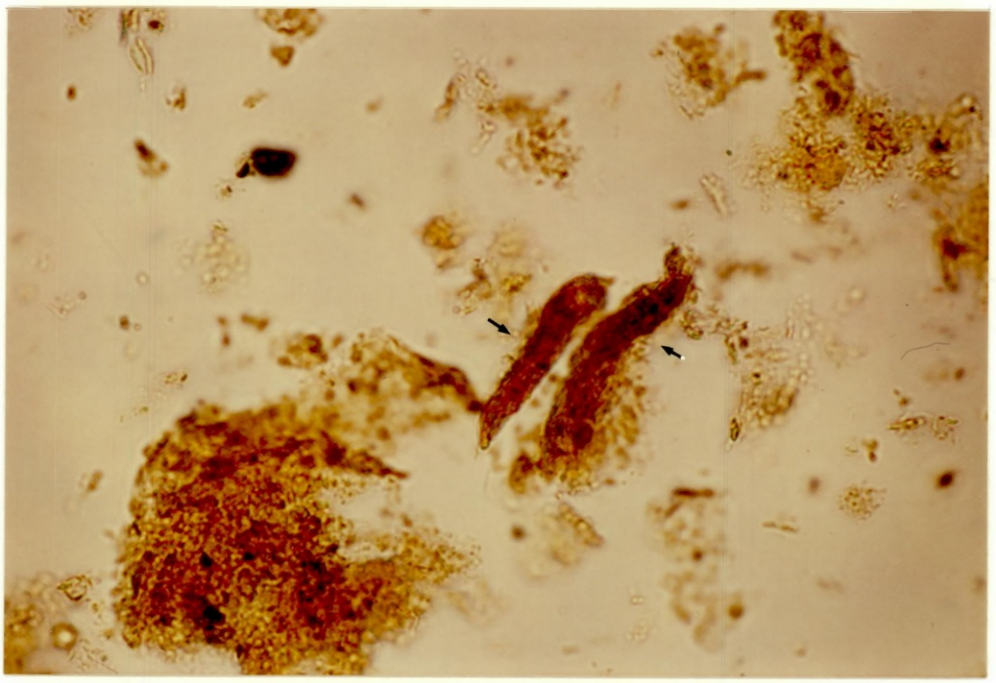


PLATE 6.2: KEROGEN TYPE III

A - The 1.45 Density Fraction of Sample OSD/LL.1

This fraction accounts for about 5 vol.% of the total kerogen concentrate and consists mainly of greyish Amorphous fines, Humic fragments and Palynomorphs. "Cuticles" are rare (Magnification x 45).

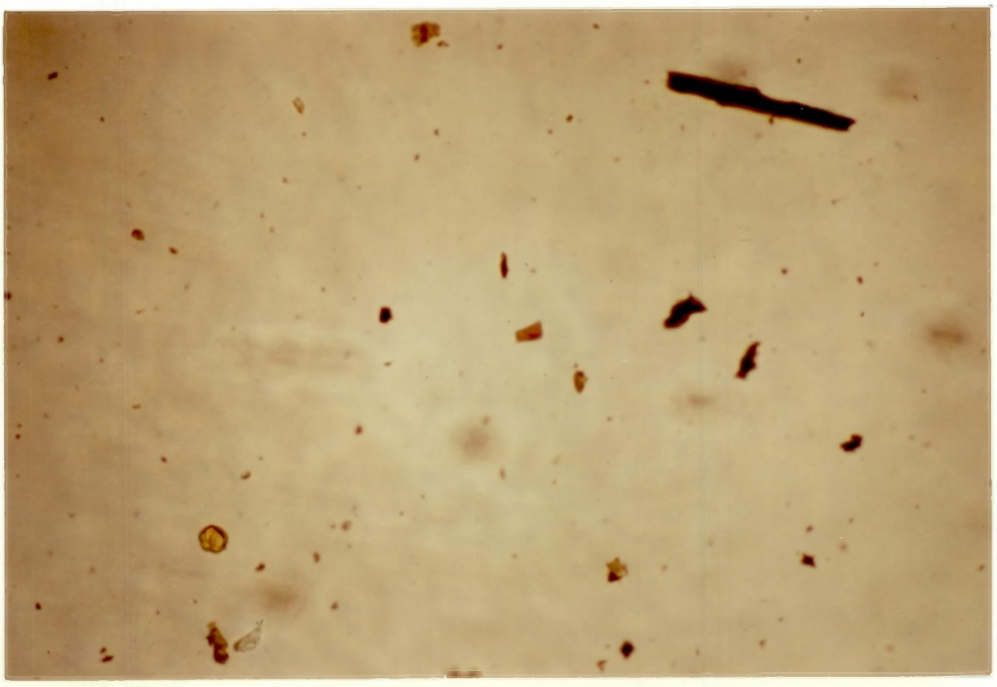
B - The 1.45 - 1.53 Density Fraction of Sample OSD/LL.1

This fraction accounts for about 10 vol.% of the total kerogen concentrate, consisting mainly of Humic matter. Palynomorphs, "Cuticles" and fine-grained Amorphous matter, in that order, are relatively minor in contents (Magnification x 45).

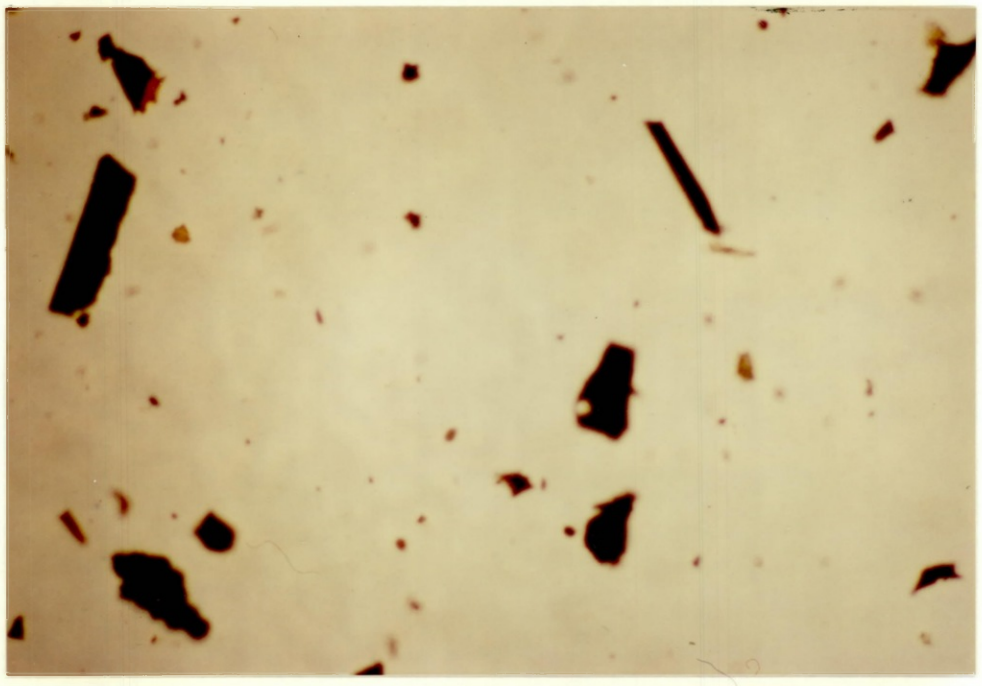
C - The 1.53 - 1.65 Density Fraction of Sample OSD/LL.1

This fraction accounts for about 25 vol.% of the total kerogen concentrate, and consists mainly of greyish fine-grained Amorphous matter and Humic fragments. Palynomorphs and "Cuticles" occur in minor amounts. (Magnification x 45).

A



B



C

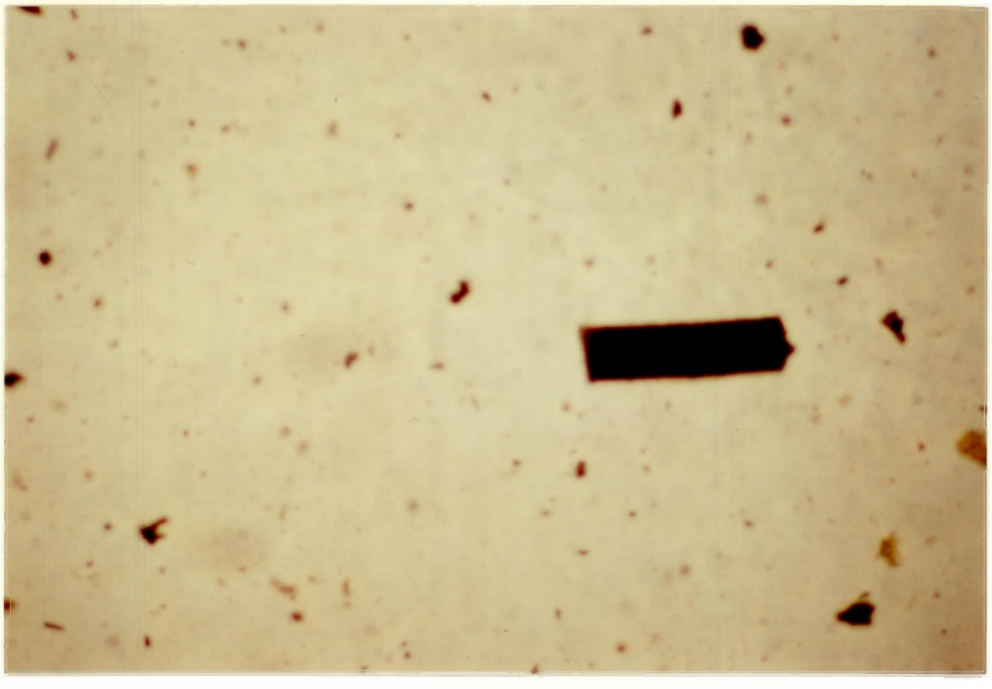


PLATE 6.2: KEROGEN TYPE III (Contd.)

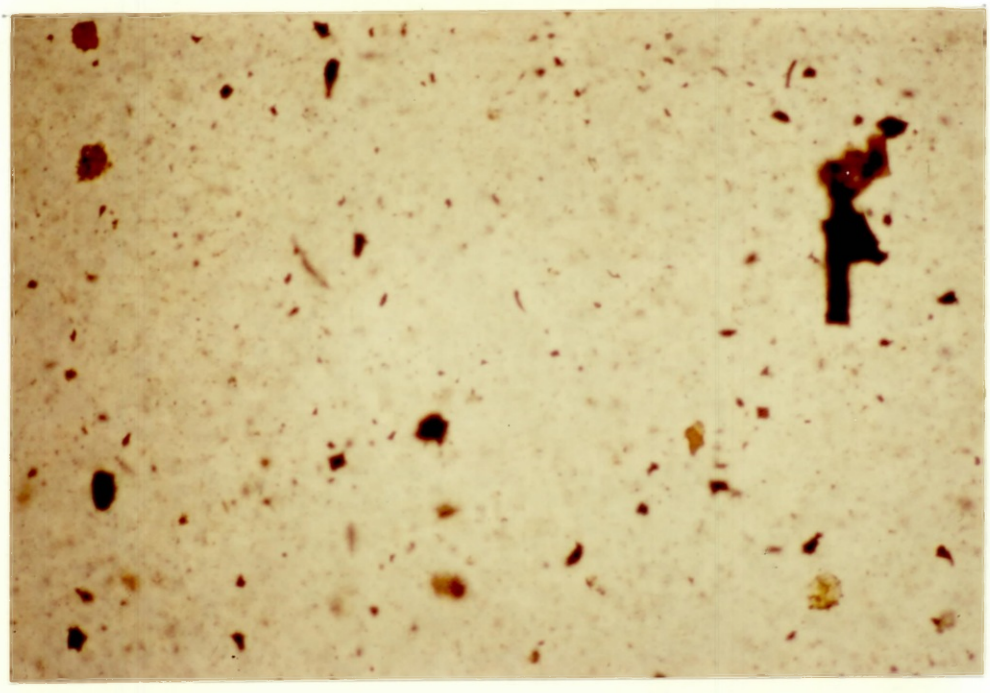
D - The 1.65 - 2.2 Density Fraction of Sample OSD/LL.1

This fraction accounts for about 60 vol.% of the total kerogen concentrate, consisting mainly of greyish granular Amorphous matter and Humic matter. "Cuticles" are minor in content while Palynomorphs are rare (Magnification x 45).

E - The Total Insoluble Organic Matter: Sample OSD/LL.1

Consists mainly of greyish granular Amorphous material and Humic fragments. "Cuticles" and Palynomorphs are minor components (Magnification x 45).

D



E

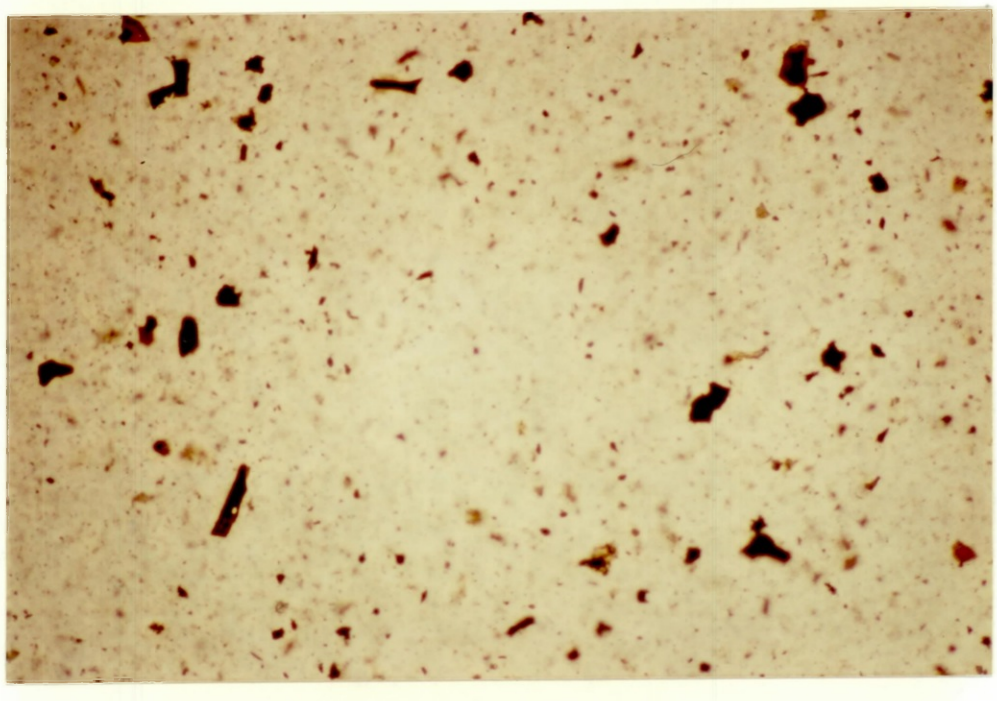


PLATE 6.3: KEROGEN TYPE IV

A - The 1.45 Density Fraction of Sample WM/LL.5

This fraction accounts for about 1 vol.% of the total kerogen concentrate, and consists of Humic matter, Palynomorphs, "Cuticles" and altered structred materials ("Amorphous" matter) (Magnification x 45).

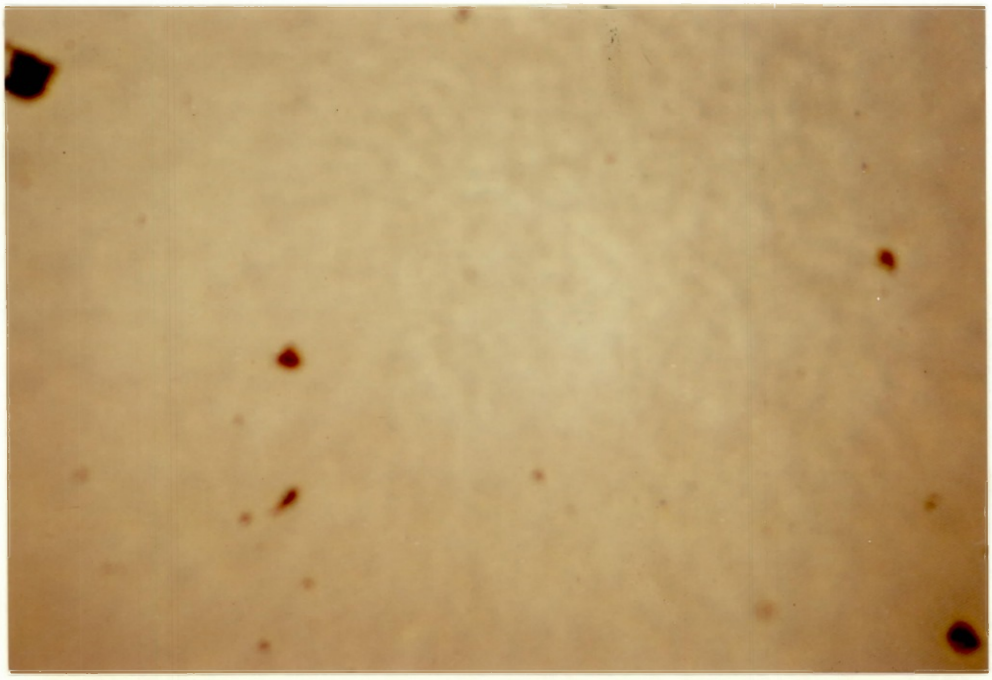
B - The 1.45 - 1.53 Density Fraction of Sample WM/LL.5

This fraction accounts for about 3 vol.% of the total kerogen concentrate, consisting mainly of Humic matter with Palynomorphs and "Cuticles" being fairly common. Amorphous matter is very rare (Magnification x 45).

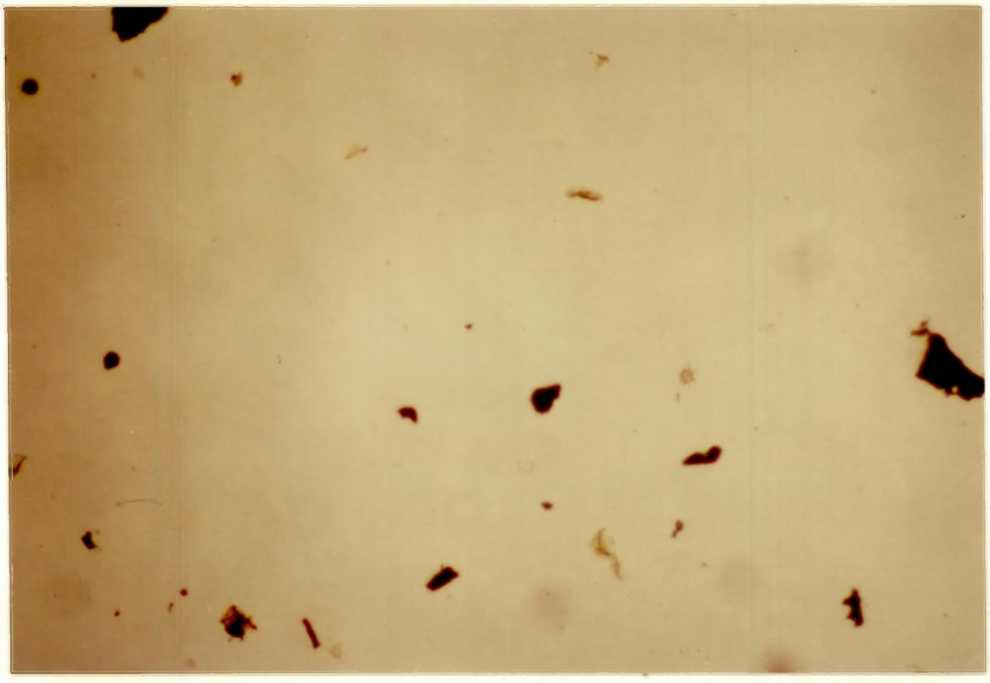
C - The 1.53 - 1.65 Density Fraction Sample WM/LL.5

This accounts for about 19 vol.% of the total kerogen concentrate, and consists essentially of the Humic matter. Other organic components are minor to rare (Magnification x 45).

A



B



C

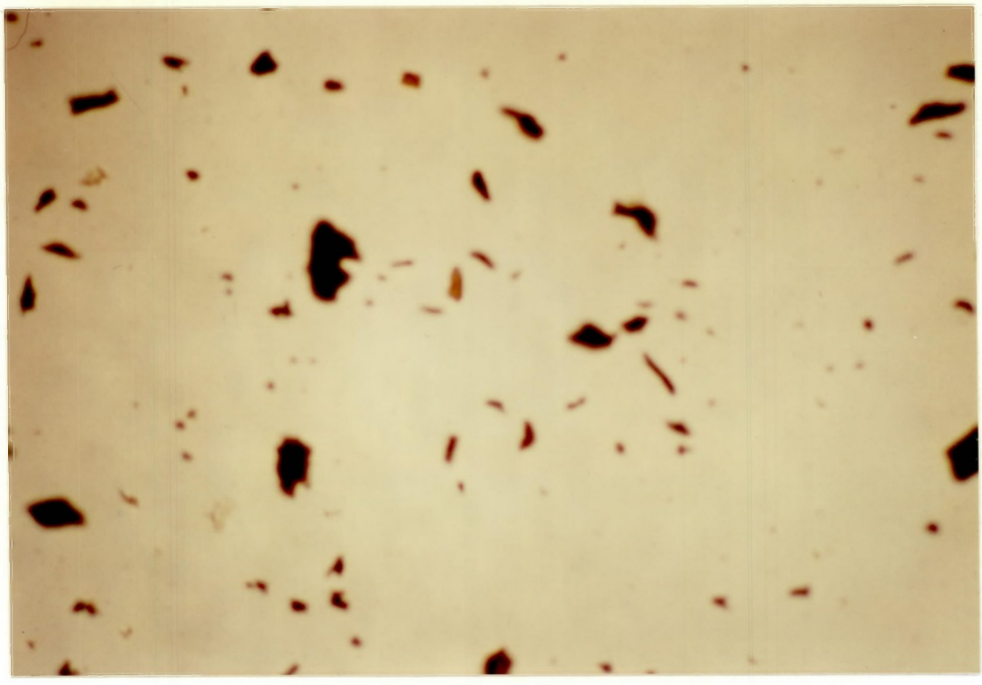


PLATE 6.3: KEROGEN TYPE IV (Contd.)

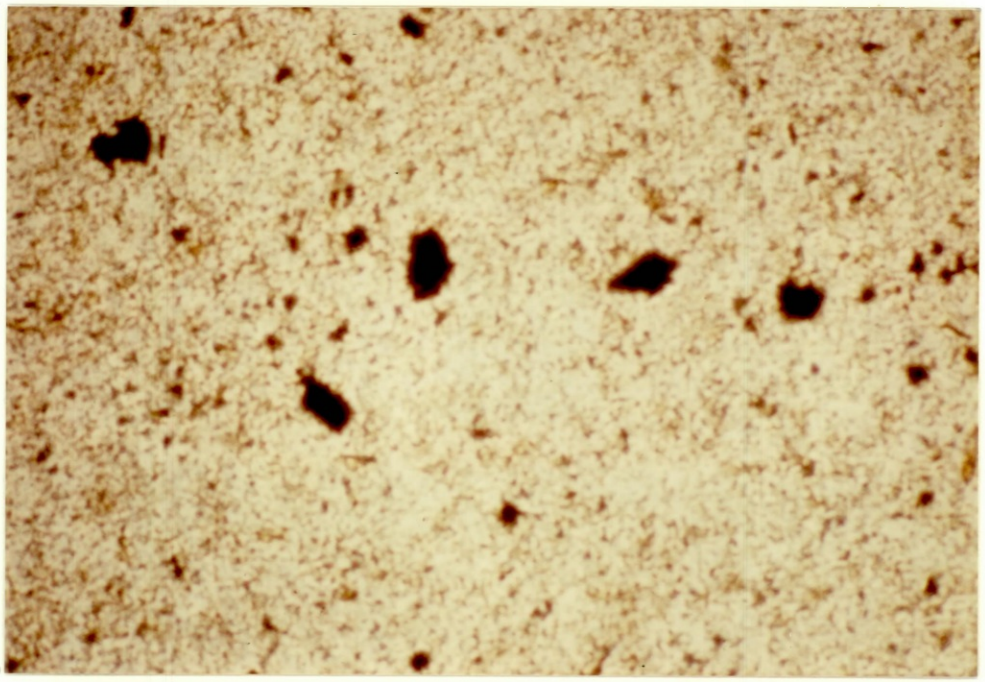
D - The 1.65 - 2.2 Density Fraction of Sample WM/LL.5

This accounts for about 77 vol.% of the total kerogen concentrate, consisting mainly of greyish granular Amorphous matter. Humic fragments are fairly common while Palynomorphs and "Cuticles" are minor to rare (Magnification x 45).

E - The Total Insoluble Organic Matter: Sample WM/LL.5

Consists mainly of fine-grained Amorphous matter and Humic fragments. Palynomorphs and "Cuticles" are very minor in contents (Magnification x 45).

D



E

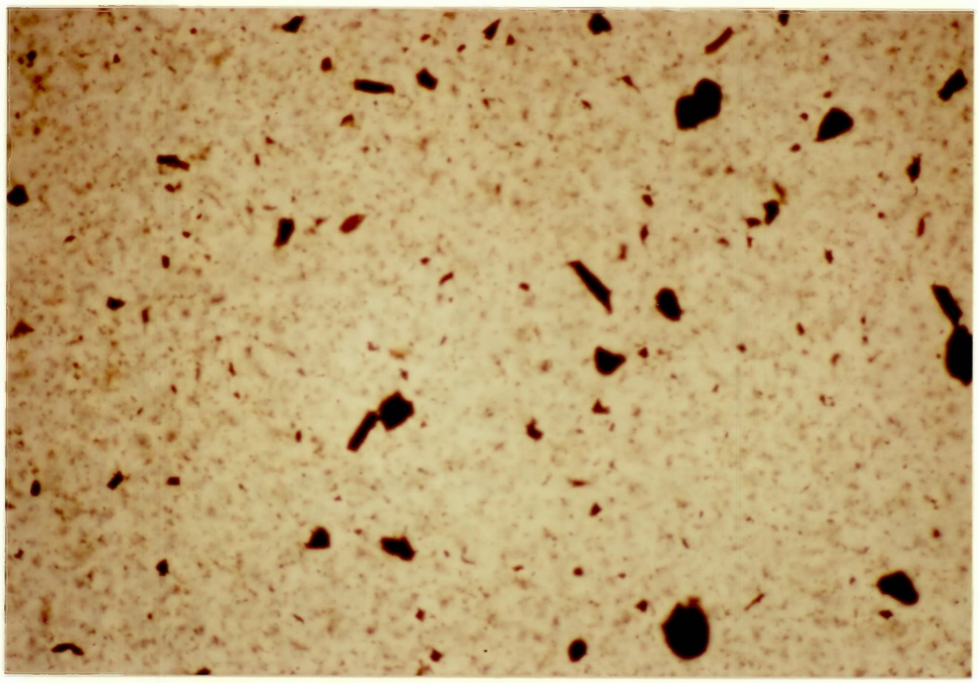


PLATE 6.4: OUTCROP SAMPLES (DORSET)

A - Kimmeridge Clay Sample - OSD/KC.1 (Ringstead Bay Area)
A pollen in the diagenesis stage: colour = very pale yellow; TAI = 2.00; estimated R_o = 0.30%. Magnification x 450.

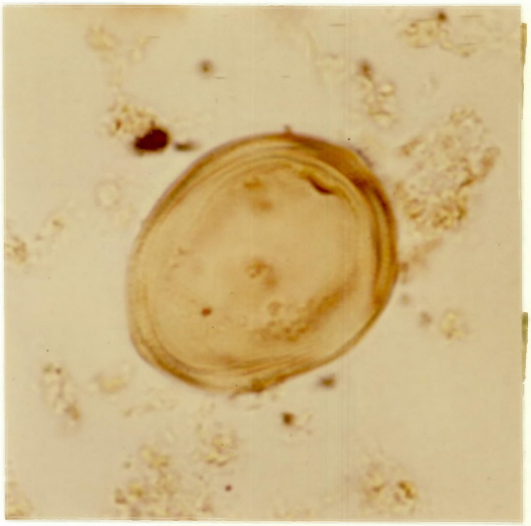
B - Kimmeridge Clay Sample - OSD/KC.4 (Kimmeridge Bay - Chapman's Pool Area; Rotunda Ammonite Zone)
A pollen in the diagenesis stage: colour = pale yellow; TAI = 2.33; estimated R_o = 0.43%. Magnification x 450.

C - Kimmeridge Clay Sample - OSD/KC.12 (Kimmeridge Bay - Chapman's Pool Area; Euxodus Ammonite Zone)
A pollen in the late diagenesis stage: colour = yellow; TAI = 2.45; estimated R_o = 0.48%. Magnification x 450.

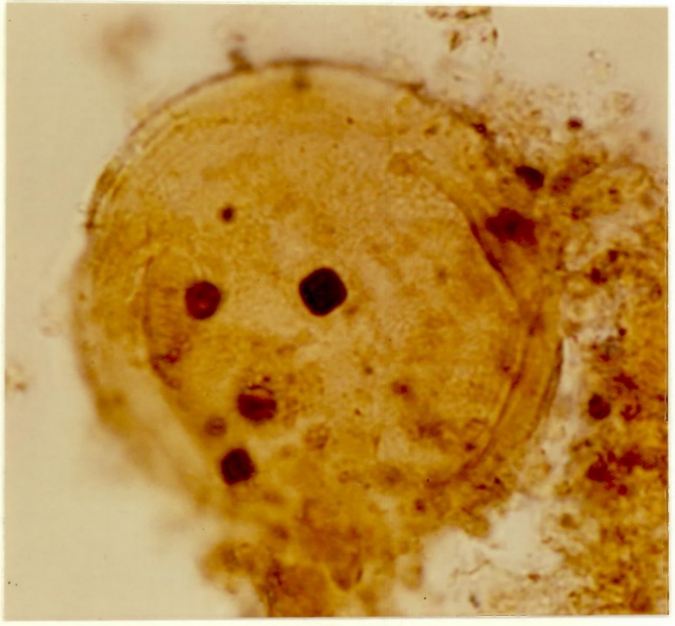
D - Lower Oxford Clay Sample - OSD/OC.4 Chickerell; Coronatum Ammonite Zone)
A pollen in the diagenesis stage: colour = pale yellow; TAI = 2.35; estimated R_o = 0.44%. Magnification x 450.

E - Lower Lias Sample - OSD/LL.8 (Lyme Regis; The Blue Lias)
A pollen (Classopolis) in the diagenesis stage: colour = very pale yellow; TAI = 2.05; estimated R_o = 0.32%. Magnification x 450.

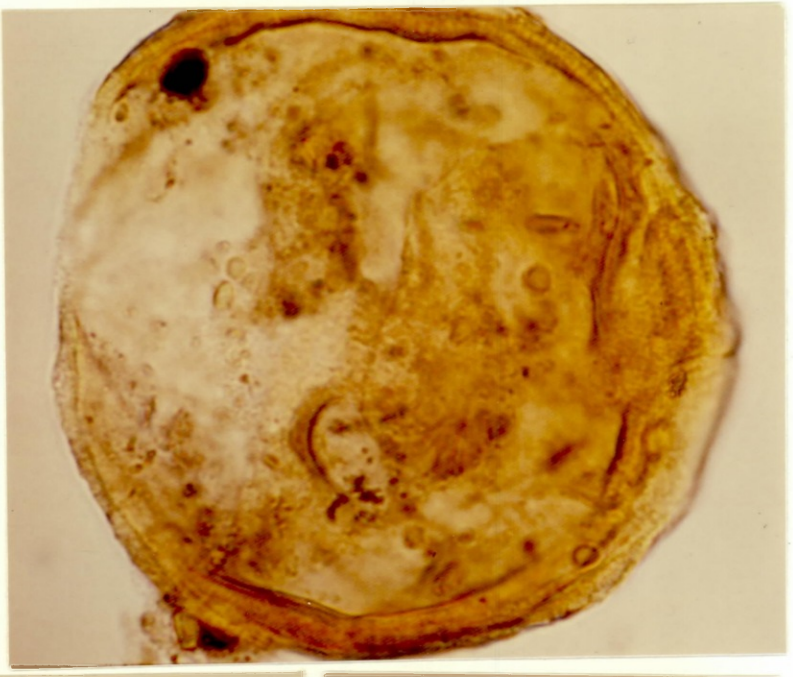
A

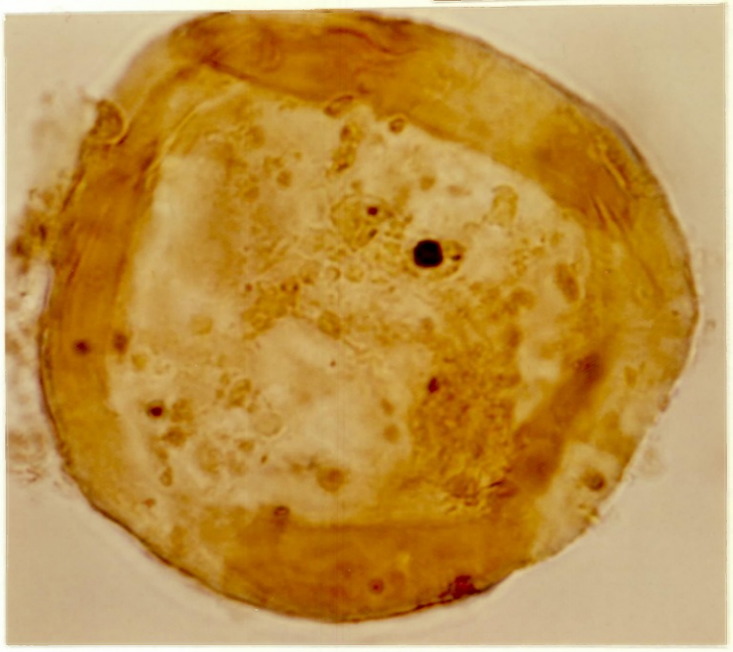


B



C





D



E

PLATE 6.5: BOREHOLE SAMPLES - WINTERBORNE KINGSTON, HENFIELD AND WINCHESTER NO. 1 WELLS

A - Sample: WK/LL.8 (Lower Lias, Winterborne Kingston Well):
A pollen in the early catagenesis stage: colour = yellow; TAI = 2.56; estimated R_o = 0.56%.
Magnification x 450.

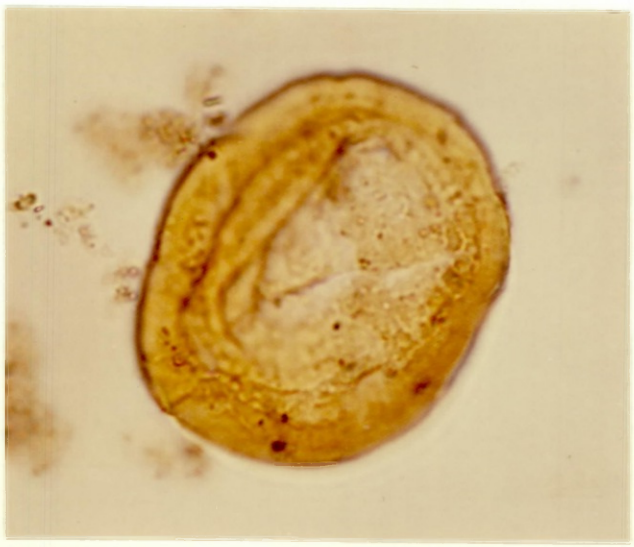
B(i) Sample: HN/KC.2 (Kimmeridge Clay, Henfield Well)
A pollen in the diagenesis stage: colour = pale yellow; TAI = 2.25; estimated R_o = 0.40%.
Magnification x 450.

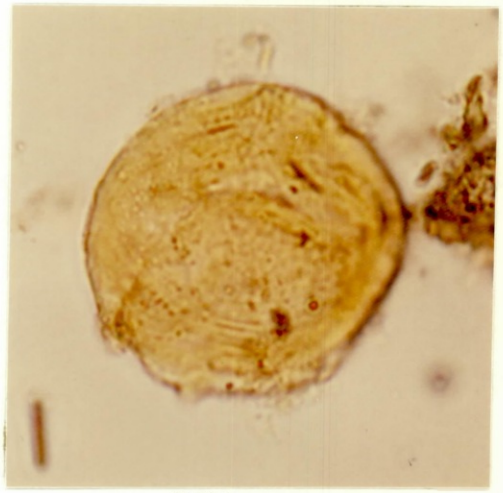
B(ii) Sample: HN/LL.4 (Lower Lias, Henfield Well)
A pollen in the catagenesis stage: colour = yellow; TAI = 2.62, estimated R_o = 0.62%.
Magnification x 450.

C(i) Sample: WCH/OC.2 (Oxford Clay, Winchester-1 Well)
A pollen in the diagenesis stage: colour = pale yellow; TAI = 2.40; estimated R_o = 0.46%.
Magnification x 450.

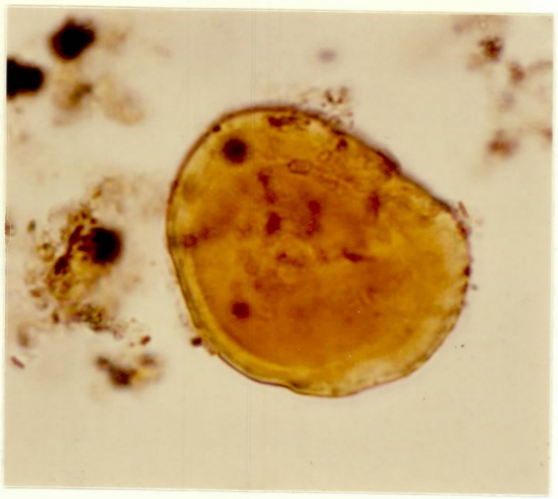
C(ii) Sample: WCH/LL.3 (Lower Lias, Winchester-1 Well)
A pollen in the catagenesis stage: colour = yellow; TAI = 2.66; estimated R_o = 0.66%.
Magnification x 450.

A

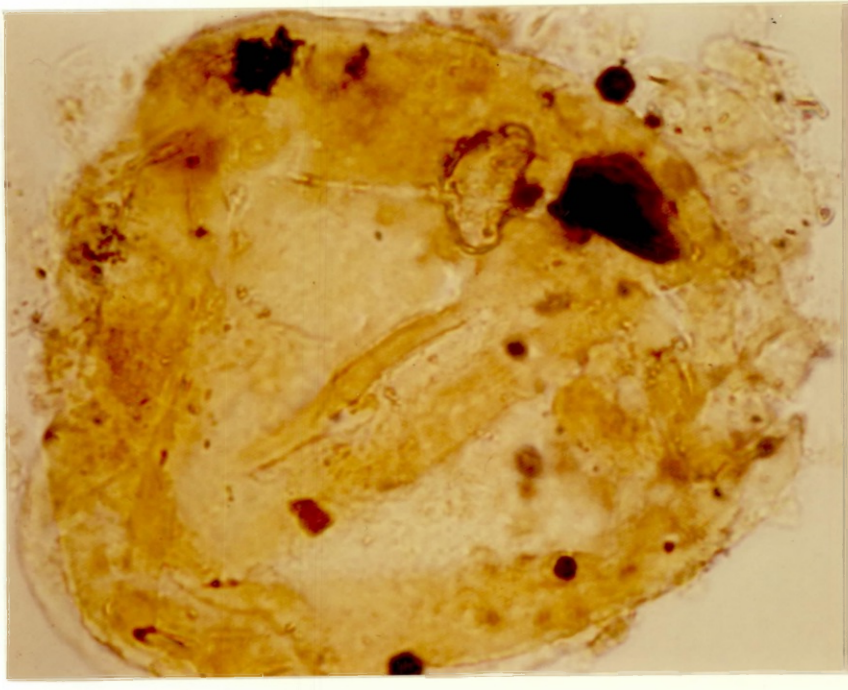




B(i)



B(ii)



C(i)



C(ii)

PLATE 6.6: BOREHOLE SAMPLES - PENSHURST WELL

A - Sample: PH/KC.4 (Lower Kimmeridge Clay)

A pollen in the catagenesis stage: colour = yellow; TAI = 2.62; estimated R_o = 0.62%. Magnification x 450.

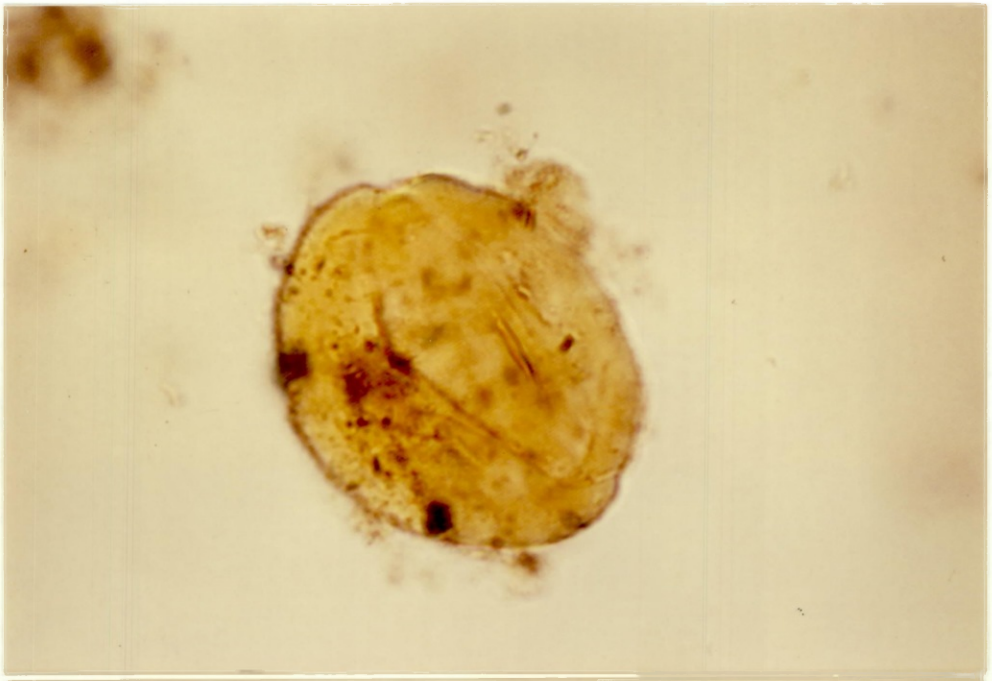
B - Sample: PH/OC.3 (Lower Oxford Clay)

A pollen in the catagenesis stage: colour = dark yellow; TAI = 2.73; estimated R_o = 0.74%. Magnification x 450.

C - Sample: PH/LL.5 (Lower Lias)

A pollen in the catagenesis stage: colour = orange; TAI = 2.80; estimated R_o = 0.85%. Magnification x 450.

A



B



C

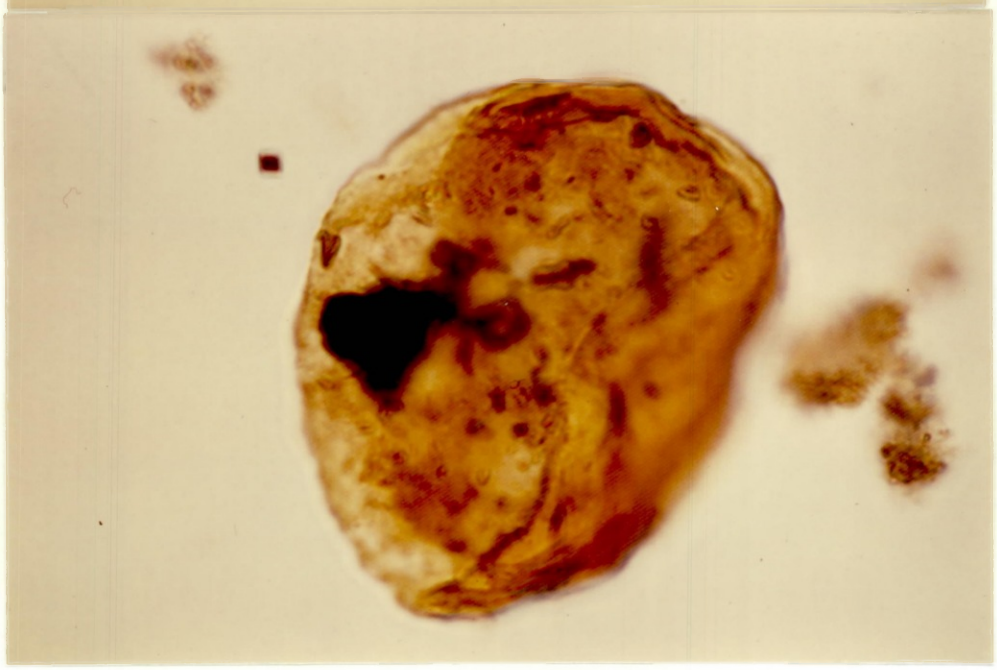


PLATE 6.7: BOREHOLE SAMPLES - ARRETON NO. 2 WELL

A - Sample: AR/KC.1 (Upper Kimmeridge Clay)

A pollen in the diagenesis stage: colour = pale yellow; TAI = 2.38; estimated R_o = 0.45%. Magnification x 450.

B - Sample: AR/KC.9 (Lower Kimmeridge Clay)

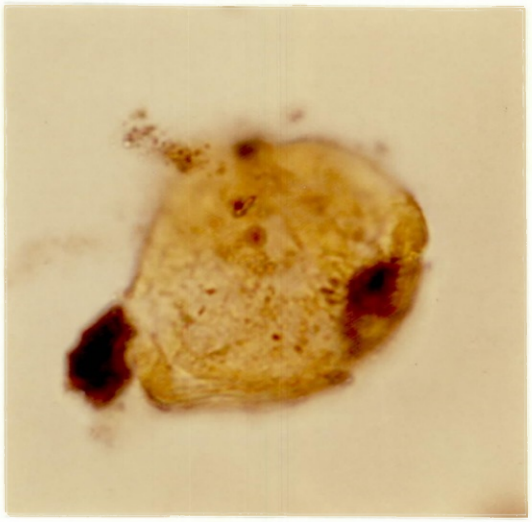
A pollen in the early catagenesis stage: colour = yellow; TAI = 2.52, estimated R_o = 0.52%. Magnification x 450.

C - Sample: AR/OC.4 (Lower Oxford Clay)

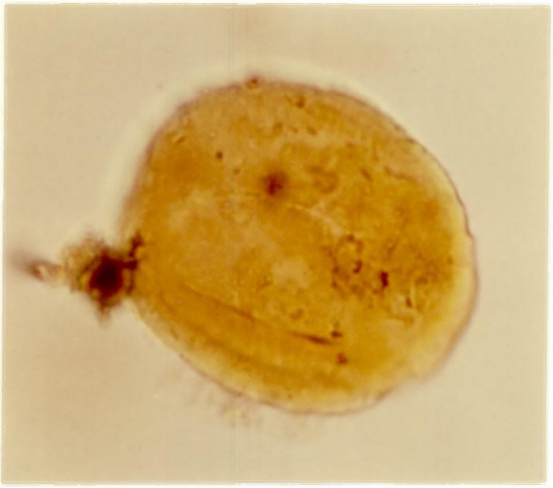
A pollen in the catagenesis stage: colour = yellow; TAI = 2.58; estimated R_o = 0.58%. Magnification x 450.

D - Sample: AR/LL.7 (Lower Lias)

A pollen in the catagenesis stage: colour = orange; TAI = 2.79; estimated R_o = 0.84%. Magnification x 450.

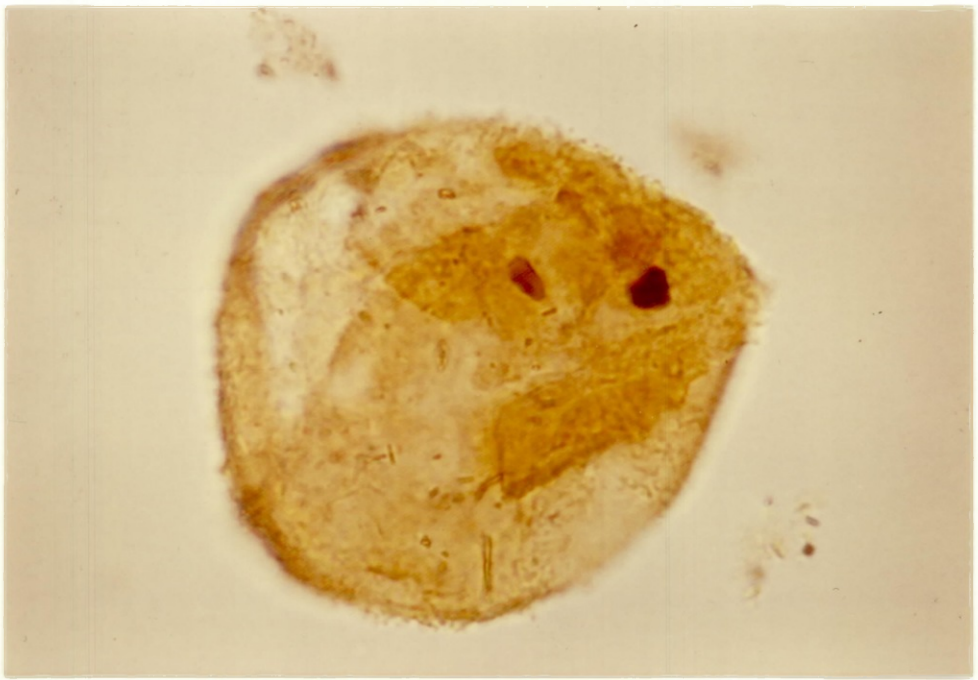


A

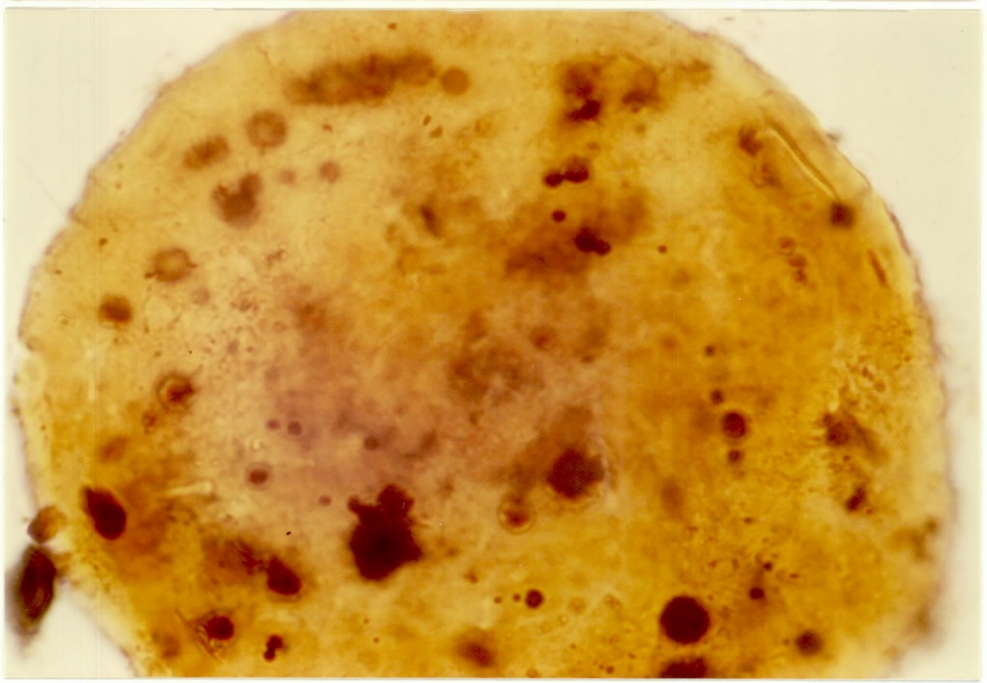


B

C



D



6.3 RELATIONSHIPS BETWEEN KEROGEN TYPE, DEPOSITIONAL ENVIRONMENT, LITHOLOGY AND ORGANIC RICHNESS OF THE JURASSIC MUDROCK SAMPLES

Based on transmitted-light microscopic study, it is noted that the main differences in the four Jurassic kerogen types are in the nature and relative abundance of mainly two organic matter categories: the amorphous and the humic. Palaeogeographic reconstructions based on fossil content, lithology and mineralogy of the Jurassic (Wills, 1951; Arkell, 1933; Wall, 1965; Hallam, 1975; Mebradu, 1975; Ionnides et al., 1976; and others) indicate that marine conditions prevailed in southern England throughout this Mesozoic Period. The observation of the content of sapropelic, hydrogen-rich amorphous material in association with mainly relatively light humic matter in the type II kerogens seems to indicate that the precursors of this kerogen group in the Jurassic were deposited in deep water conditions, far removed from the shoreline, where the environment was reducing and quiet and only the very light land-derived organic matter (humic and herbaceous) could be transported to these deep depo-sites. By contrast, the compositions of the mixed type II/III, type III and type IV tend to reflect, in that order, increasingly shallower depositional conditions where the bottom waters were more oxidising and less quiet, and being shallow, were in closer proximity to the shore-line or land and hence the incorporation of larger amounts of terrestrially derived organic matter of wide density range. Under such oxidising bottom conditions, the marine planktons would have been preferentially biodegraded

resulting in increasing preservation of the more resistant, diverse humic fragments as is noted in this study.

A comparative study of Table 6.1 and Table 5.1 (in Chapter 5) shows that there is no simple relationship between kerogen types and the associated lithologies in the three Jurassic mudrock - formations. The various kerogen types occur both in the argillaceous as well as in the carbonate rocks. Shales (argillaceous rocks) are normally considered in a sedimentary sequence to suggest deeper water phases while the limestones (carbonate rocks) should indicate periods of shallower and clearer water (Perkins, 1977; Selley, 1978). But there seems to be a relationship between the kerogen types and the organic richness of the rock samples. Kerogen type II is noted to be mainly associated with the very organic-rich samples whereas the other kerogen types occur in rock samples with moderate to low total organic carbon contents. It was noted in Chapter 5 (Section 5.3.2) that the mudshales, the clayshales and the laminated limestones are the most organic-rich lithologic types in the three Jurassic formations. Since these lithologies are considered to represent anoxic depositional bottom environments, it thus implies that the Jurassic type II kerogen precursors were mainly deposited and preserved in oxygen-deficient bottom waters. It may be suggested that it was this unfavourable condition for the benthic fauna and flora that resulted in the increased preservation of the deposited marine phytoplankton. It thus seems that the nature or compositions of the mixed type II/III, type III and type IV kerogens as well as the relatively low TOC values

of their associated lithologies are due to the oxidising nature of their depositional environments and not necessarily on the organic input. Oxic bottom conditions would have favoured significant destruction of the deposited organic matter and in particular, the preferential degradation of the marine planktons with a resulting increase in the relative contents of the more resistant humic materials. This line of reasoning seems to correlate fairly well with the observation on the nature and composition of the identified kerogen types: the humic matter is subordinate to the amorphous matter in all the kerogen types.

The fluctuating anoxic - oxic depositional conditions during the Jurassic therefore appear to have been the major factor controlling the distribution of the kerogen types as well as the organic matter richness of the associated lithologies in the Lower Lias, the Oxford Clay and the Kimmeridge Formations. This general conclusion is supported by the observation by Melville and Freshney (1982) that these major Jurassic mudrock formations were probably laid down in water of practically the same, if moderate, depth and sluggish circulation, and that the variation in the facies of these formations were produced by the enhanced importance of quite small depth fluctuations of the generally shallow Jurassic Sea in response to continent-wide small-scale epeirogenic movements (of amplitudes generally less than 30 metres or 98 feet) of the time.

CHAPTER VII

KEROGEN TYPES AND MATURITY-II: KEROGEN CHARACTERIZATION BY STABLE ISOTOPIC COMPOSITIONS, PYROLYSIS AND INFRA-RED SPECTROSCOPY

KEROGEN TYPES AND MATURITY-II: KEROGEN CHARACTERIZATION BY STABLE ISOTOPIC COMPOSITIONS, PYROYLSIS AND INFRA-RED SPECTROSCOPY

7.1 STABLE CARBON AND HYDROGEN ISOTOPIC COMPOSITIONS OF KEROGENS

7.1 Introduction

Many previous workers have demonstrated or proposed the idea that the $\delta^{13}C$ and δD values of sedimentary organic matter (kerogens, bitumen and oils) are influenced by the primary sources of these materials (Silverman and Epstein, 1958; Degens, 1969; Tissot and Welte, 1978; Redding et al., 1979; Roger, 1980; Yeh and Epstein, 1981 and others). On the basis of carbon isotope analysis, terrestrially derived organic matter are believed to be isotopically lighter than their marine counterparts - mainly as a result of their respective sources of carbon. Commonly, the difference in the isotopic compositions of marine and non-marine sedimentary organic matter is explained by the difference in the form of carbon dioxide (CO_2) used by their photosynthesizing organic precursors: terrestrial plants utilize the ^{13}C - depleted molecular CO_2 from the atmosphere whereas marine organisms use bicarbonate molecules which are relatively enriched in the heavy carbon isotope - ^{13}C (Silverman and Epstein, 1958; Degens, 1969; Kinghorn, 1983). Sofer (1984) has pointed out that this explanation suffers from several over-simplifications and that these previous authors

have not considered factors like the different photosynthetic pathways, the difference between lacustrine phytoplankton and land plants, availability of CO_2 or bicarbonate, species variation and temperature variation, which may be crucial in determining the isotopic compositions of the organic precursors. Deines (1980) doubted that a distinction between the marine and non-marine organic matter could be made in general based on their carbon isotopic compositions. Yeh and Epstein (1981) also suggested that this conclusion need to be revised because they found marine oils that are isotopically more negative (i.e. light) than non-marine oils. Data on carbon and hydrogen isotopic compositions of type kerogens from Uinta Basin (type I, non-marine), Paris Basin and Posidonia Shale of N.W. Germany (type II, marine), and Douala Basin (type III, non-marine) published by Redding et al. (1980) failed to distinguish marine and non-marine organic matter.

Although the isotope ratios of sedimentary organic matter are known to show considerable variations with geological time, a single trend of enrichment of the light carbon isotope, ^{12}C, has been noted with increasing age (Welte, 1970; Welte et al., 1975a, 1975b; Stahl, 1976; 1977b; Degens, 1969; Galimov, 1980). This trend is suspected to be caused by variations in the intensity of photosynthesis, which could change the isotopic composition of the atmospheric CO_2 (Welte, 1970, Welte et al., 1975a). The known age trend in $\delta^{13}C$ values of sedimentary organic matter is illustrated in Figs. 7.1 and 7.2 from Stahl, (1977b) (based on crude oil analysis)

and Galimov (1980) (based on kerogen and bitumen analyses) respectively.

Redding et al. (1980) have noted that during coalification or organic matter maturation, carbon- and hydrogen-bearing gaseous constituents which are depleted in ^{13}C and deuterium (D) with respect to their parent material are released, and thus the residue should be continuously enriched in both heavy isotopes with increasing maturity. Laboratory simulations of organic maturation by pyrolysis have shown methane to be the only product evolved in significant quantities during heating that produces important isotopic fractionation both in carbon and hydrogen (Sackett, 1978; Peters et al., 1981). Stahl (1977b) and Simoneit et al. (1981) have reported trends of increasing $\delta^{13}C$ and δD values of kerogen with increasing organic maturity produced by igneous intrusions. Similar isotopic trends were observed by Peters et al. (1981) during their laboratory-simulated thermal maturation experiments. But Ishiwatari et al. (1978) did not observe any significant differences in the $\delta^{13}C$ values for kerogen samples prior to and after heating in their pyrolysis experiments. They thus concluded that kerogen in sediments maintains its initial $\delta^{13}C$ value during early catagenesis, particularly when methane expulsion represents a small proportion of carbon loss. In their investigations of isotopic compositions (carbon and hydrogen) of type kerogens and coals in the 0.3 to about 2.8% Ro maturity range from various parts of the world, Redding et al. (1980) failed to find any appreciable isotopic effect which could be

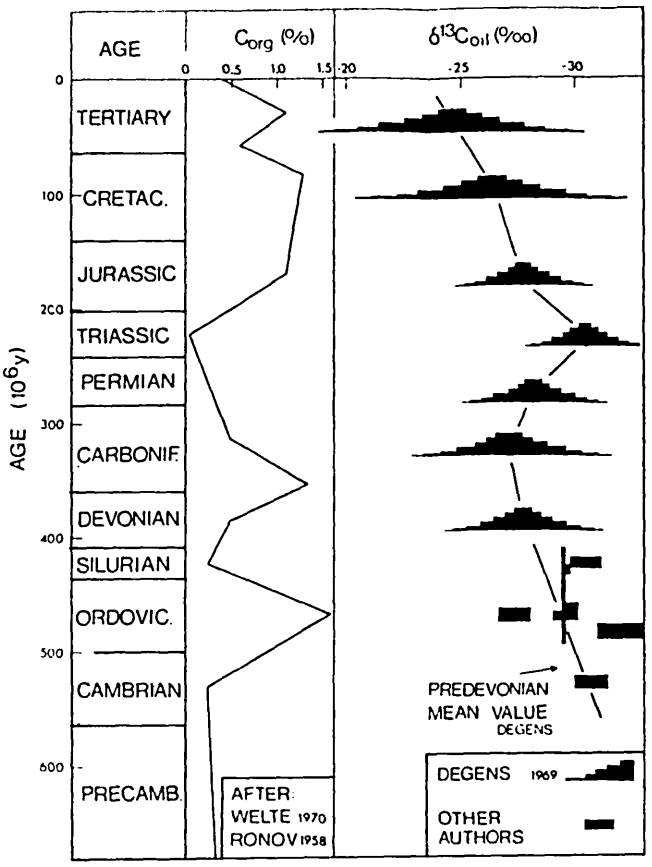


Fig.7.1- Compilation of $^{13}C/^{12}C$ measurement of crude oils of different geologic ages (From Stahl, 1977b).

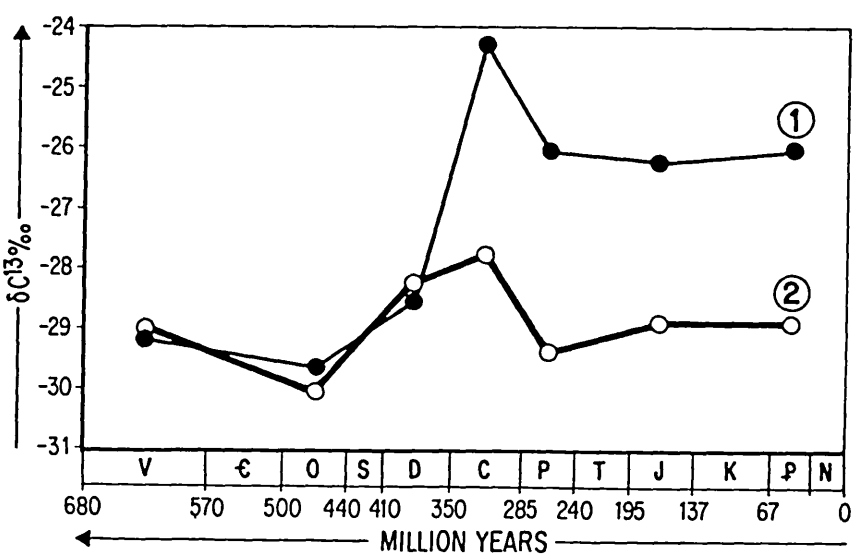


Fig. 7·2 – Dependence of the mean isotopic composition of carbon in:

1. Kerogen. 2. Chloroform-extracted bitumen on geologic age of rocks in the Phanerozoic sequence of the Russian Platform (From Galimov, 1980)

equated to the increasing maturity of the organic materials. They attributed any observed variations in the $\delta^{13}C$ and δD values for the kerogens and coals to primary source variability. The authors pointed out that isotopic effects due to the thermal alteration of kerogens and coals can only be expected from late stage metagenic and metamorphic processes (at $R_o > 4\%$) as have been demonstrated by McKirdy and Powell (1974) and Hoefs and Frey (1976) in regionally metamorphosed sediments. According to Redding et al. (1980), it is at this very high maturity level that methane generation from kerogens and coals occurs in a single step process resulting in a major isotope fractionation in the residue. Simoneit et al. (1981) however claimed to have noticed thermal or maturity effect on the kerogen isotopic compositions at lower maturity levels ($R_o < 2.0\%$). But the considerable scatter of points in their plots of $\delta^{13}C$ values against maturity indicators (R_o and atomic $^{H}/_{C}$ ratios) and also in their plot of R_o against $^{H}/_{C}$ is suggestive of a significant organic source influence on their isotope data.

In the present study, stable isotope analysis of the Jurassic kerogens of southern England were carried out to (i) investigate any variations in the isotopic compositions with the identified kerogen types (ii) to investigate any possible age trend(s) in the isotope data, and (iii) to check for any variation in the isotopic compositions with organic maturity. To achieve these objectives, selected type II, mixed type II/III, type III, and type IV kerogen samples were analysed for their stable carbon isotopes. Only selected

TABLE 7.1 STABLE ISOTOPE DATA FOR SELECTED LOWER LIAS KEROGEN SAMPLES

Kerogen Type	Sample Number	Borehole/ Locality	Atomic H/C	Estimated Ro(%)	$\delta^{13}C_{PDB}$ (‰)	δD_{SMOW} (‰)
II	OSD/LL.4	Outcrop, Dorset	1.33	0.34	-26.11	-121.7
	OSD/LL.5	" "	1.21	0.36	-27.09	-
	BR/LL.3	Burton Row	1.20	0.40	-29.69	-98.5
	BR/LL.5	" "	1.14	0.42	-27.83	-122.9
	BR/LL.10	" "	1.38	0.45	-29.81	-101.9
	WK/LL.8	Winterborne Kingston	1.24	0.56	-29.23	-
	WCH/LL.3	Winchester-1	1.03	0.66	-26.42	-96.3
	AR/LL.5	Arreton-2	1.10	0.80	-25.83	-101.0
	PH/LL.3	Penshurst	1.06	0.82	-25.75	-91.6
	AR/LL.9	Arreton-2	0.98	0.90	-26.68	-
II/III	OSD/LL.2	Outcrop, Dorset	0.87	0.35	-26.16	
	BR/LL.2	Burton Row	0.88	0.38	-26.15	
	BR/LL.6	" "	0.81	0.42	-24.46	
	WM/LL.2	Warlingham	0.95	0.50	-26.02	
	WK/LL.3	Winterborne Kingston	1.00	0.48	-26.33	
	WK/LL.6	" "	0.93	0.55	-28.45	
	HN/LL.4	Henfield	0.96	0.62	-28.25	
	PH/LL.5	Penshurst	0.90	0.85	-24.95	
III	HN/LL.3	Henfield	0.69	0.60	-26.12	
	HN/LL.5	"	0.78	0.62	-26.72	
IV	WM/LL.5	Warlingham	0.53	0.54	-24.27	

TABLE 7.2 - STABLE ISOTOPE DATA FOR SELECTED OXFORD CLAY KEROGEN SAMPLES

Kerogen Type	Sample Number	Borehole/ Locality	Atomic H/C	Estimated Ro(%)	$\delta^{13}C_{PDB}$ (‰)	δD_{SMOW} (‰)
II	WM/OC.4	Warlingham	1.28	0.44	-27.08	-
	OSD/OC.4	Outcrop, Dorset	1.30	0.44	-26.25	-117.9
	WCH/OC.2	Winchester-1	1.29	0.46	-26.45	-
	AR/OC.4	Arreton-2	1.23	0.58	-26.16	-160.5
	PH/OC.3	Penshurst	1.20	0.74	-26.70	-103.6
II/III	OSC/OC.1	Outcrop, Dorset	0.88	0.40	-23.74	
	WM/OC.2	Warlingham	0.90	0.42	-20.72	
	AR/OC.2	Arreton-2	0.99	0.54	-24.89	
	PH/OC.1	Penshurst	0.94	0.68	-24.51	

TABLE 7.3 STABLE ISOTOPE DATA FOR SELECTED KIMMERIDGE CLAY KEROGEN SAMPLES

Kerogen Samples	Sample Number	Borehole/ Locality	Atomic H/C	Estimated Ro(%)	$\delta^{13}C_{PDB}$ (‰)	δD_{SMOW} (‰)
II	OSD/KC.2	Outcrop, Dorset	1.35	0.36	-24.50	-145.1
	WM/KC.6	Warlingham	1.26	0.38	-24.77	-
	HN/KC.2	Henfield	1.25	0.40	-25.02	-
	OSD/KC.7	Outcrop, Dorset	1.26	0.44	-25.45	-108.7
	PH/KC.1	Penshurst	1.14	0.48	-24.34	-113.2
	AR/KC.5	Arreton-2	1.22	0.48	-24.56	-
	AR/KC.9	"	1.12	0.52	-25.54	-113.6
II/III	WM/KC.9	Warlingham	0.87	0.40	-25.11	
	OSD/KC.4	Outcrop, Dorset	0.90	0.43	-25.77	
	AR/KC.1	Arreton-2	0.95	0.45	-26.07	
	PH/KC.3	Penshurst	0.95	0.58	-25.24	
III	HN/KC.1	Henfield	0.87	0.36	-26.27	
	WCH/KC.3	Winchester-1	0.83	0.42	-24.76	

type II kerogen samples were subjected to the hydrogen isotopic analysis. The estimated vitrinite reflectance values and the atomic $^{H}/_{C}$ ratios were used as kerogen maturity indicators for the purpose of data analysis and interpretations.

7.1.2 Results and Interpretations of the Carbon and Hydrogen Isotope Data

The $\delta^{13}C_{PDB}$ and δD_{SMOW} values in parts per mil (‰) obtained for the selected kerogen samples from the Lower Lias, the Oxford Clay, and the Kimmeridge Clay Formations together with the kerogen maturity indicators are presented in Tables 7.1, 7.2, and 7.3 respectively.

7.1.2.1 Interpretations of the Carbon Isotope ($\delta^{13}C$) data

Fig. 7.3 is a histogram of the $\delta^{13}C$ values for all the samples analysed showing the distribution for the four identified kerogen types in the three Jurassic formations. Although it shows overlaps in the ranges of values, certain trends seem apparent in the distribution. The type II samples tend to be isotopically the lightest ($\delta^{13}C$: -30 to -24‰) while the types III and IV kerogens tend to be the heaviest ($\delta^{13}C$: -27 to -24‰). The isotope values for the mixed type II/III occupy the intermediate range of -29 to -20‰. The mode of the $\delta^{13}C$ values for type II, type II/III, and type III kerogen samples is in the range of -27 to -26‰. This modal range is similar to the average $\delta^{13}C$ value indicated by Galimov (1980) for the Jurassic kerogens from the

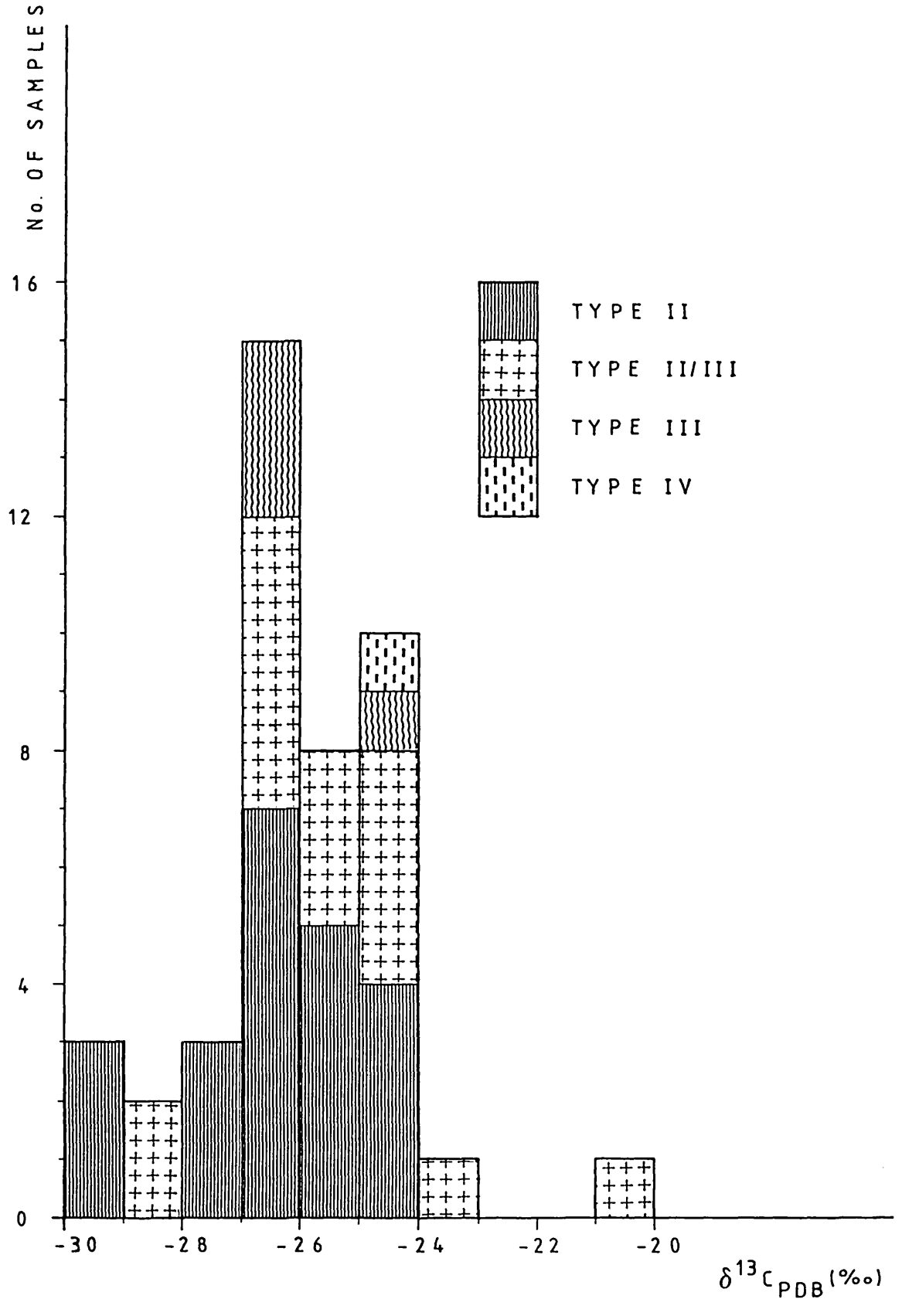


FIG. 7.3 DISTRIBUTION OF $\delta^{13}C$ VALUES FOR JURASSIC KEROGENS FROM S. ENGLAND

Phanerozoic sequence of the Russian Platform (see Fig. 7.2).

In order to check for any age influence on the $\delta^{13}C$ values for these Jurassic kerogen samples, histograms of the carbon isotope ratios for the Lower Lias, the Oxford Clay, and the Kimmeridge Clay samples have been separately drawn, and these are shown in Fig. 7.4. When the isotope ratios for the kerogen type II samples are considered, a single trend of increasing enrichment in the ^{13}C (i.e. increasing positiveness $\delta^{13}C$ values) with decreasing age of the containing formation is noticed - the Kimmeridge Clay type II kerogens being isotopically the heaviest ($\delta^{13}C$: -26 to -24‰) and the Lower Lias samples the lightest ($\delta^{13}C$: -30 to -25‰). A poorly defined trend of increasing $\delta^{13}C$ values with decreasing age is again noted for the mixed type II/III kerogens. An illustration of this possible age trend in the $\delta^{13}C$ values for the Jurassic kerogens is shown in Fig. 7.5. Though no definite age-trend could be associated with the $\delta^{13}C$ values for the types III and IV kerogens as a result of the limited number of samples analysed, but based on the few isotope data obtained for the type III kerogens, the Kimmeridge Clay samples tend to be isotopically heavier than the Lower Lias samples (see Fig. 7.4).

Some differences seem apparent in the distribution patterns of $\delta^{13}C$ values for the various kerogen groups from the three stratigraphic units. In the Lower Lias, type II samples tend to be isotopically the lightest ($\delta^{13}C$: -30 to -25‰) and the type III and type IV samples being the heaviest ($\delta^{13}C$: -27 to -24‰) with the mixed

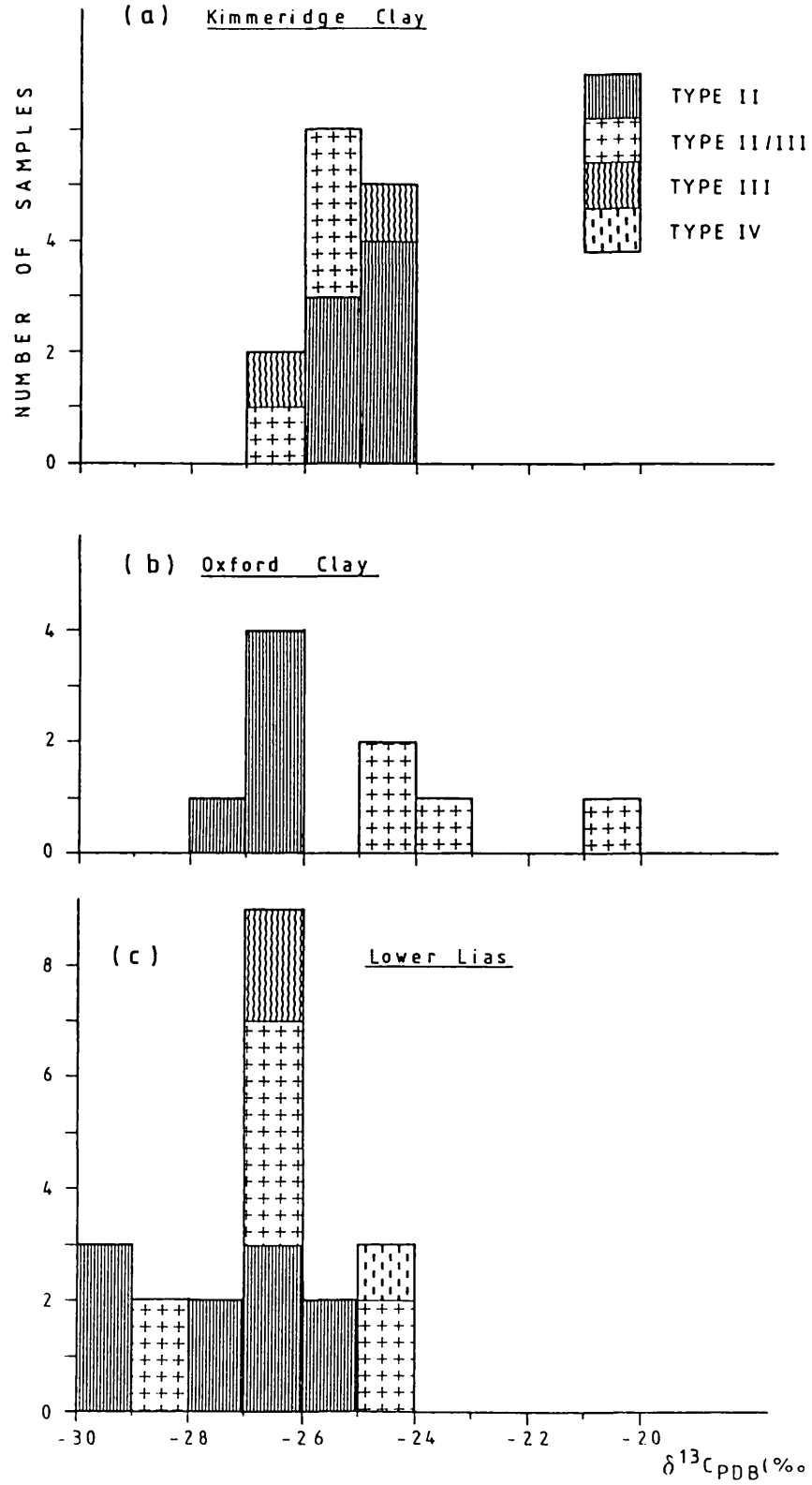


FIG. 7.4 HISTOGRAMS OF $\delta^{13}C$ VALUES FOR KEROGEN SAMPLES FROM (a) THE KIMMERIDGE CLAY (b) THE OXFORD CLAY AND (c) THE LOWER LIAS

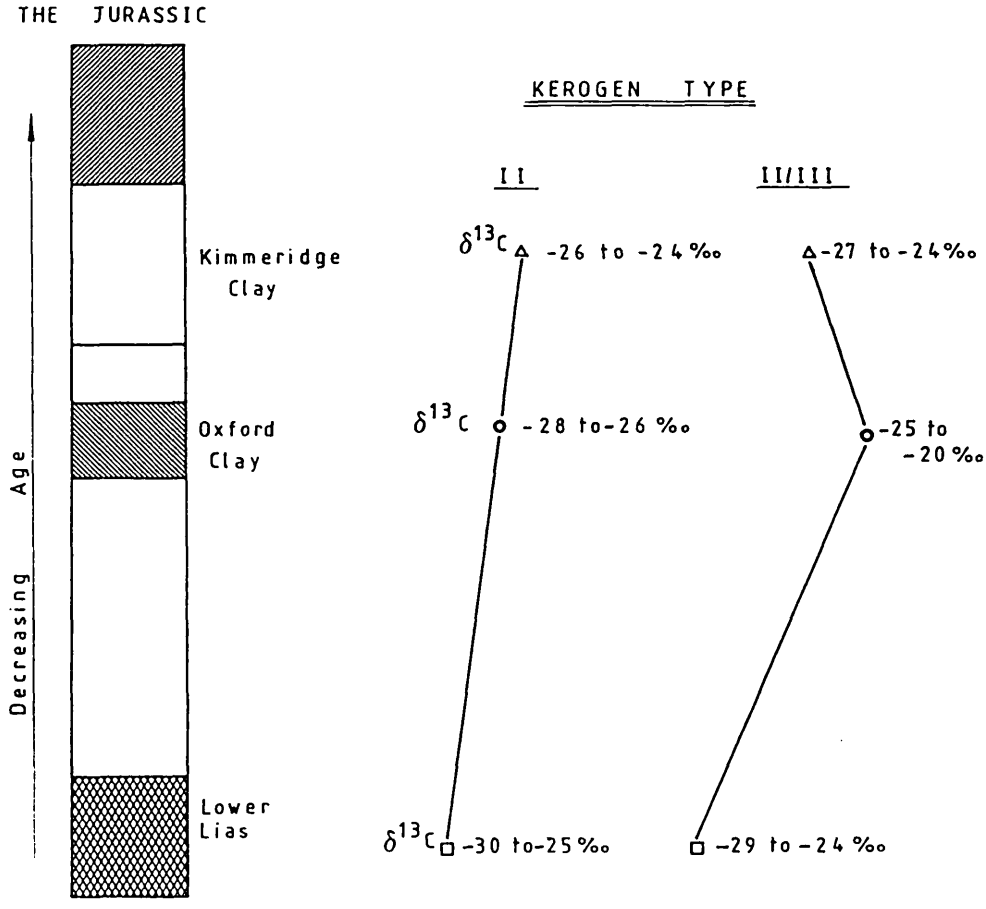


FIG. 7.5 A DIAGRAMATIC ILLUSTRATION OF THE POSSIBLE AGE-TEND IN $\delta^{13}C$ VALUES FOR THE JURASSIC KEROGEN SAMPLES

type II/III isotope values occupying the middle range ($\delta^{13}C$: -29 to -24‰). The distribution pattern of the $\delta^{13}C$ data for the Oxford Clay samples is similar to that of the Lower Lias: the type II samples are isotopically lighter ($\delta^{13}C$: -28 to -26‰) than the mixed type II/III kerogens ($\delta^{13}C$: -25 to -20‰). No pure type III kerogen sample from the Oxford Clay Formation was analysed in this study. Since, as already noted in Chapter 6, the type II kerogens are restricted in occurrence to the lower parts while the mixed type II/III kerogens are present in the higher parts of the Oxford Clay Formation, there is by implication, an age/stratigraphic trend in the organic carbon isotopic composition within this lithologic unit. The Oxford Clay mixed type II/III are isotopically more diverse than their type II counterparts - probably due to the higher contribution of recycled or non-contemporaneous organic materials to the former kerogen group, thus resulting in significant variations in the kerogen composition. The distribution of the $\delta^{13}C$ values for the Kimmeridge Clay kerogens indicates a trend which appears contrasting to that observed above for either the Lower Lias or the Oxford Clay organic matter. Here, the type II kerogens tend to be isotopically heavier ($\delta^{13}C$: -26 to -24‰) than either the mixed type II/III ($\delta^{13}C$: -27 to -25‰) or the type III ($\delta^{13}C$: -27 to -24‰) samples.

To investigate the presence of any trend in the carbon isotope data with maturity, plots of $\delta^{13}C$ values against the maturity indicators, atomic $^{H}/_{C}$ ratios and estimated Ro values, have been made for type II, mixed

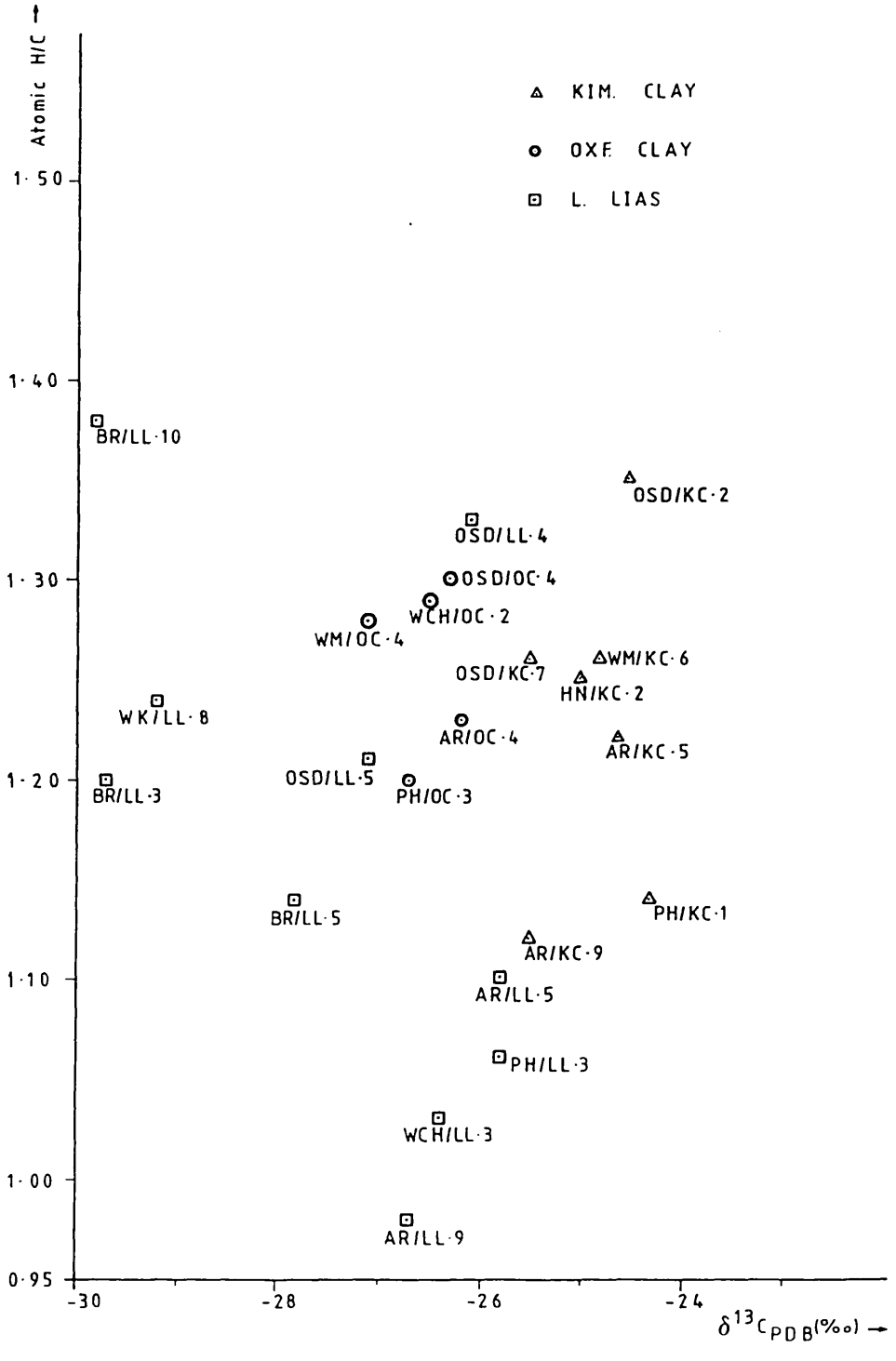


FIG. 7.6(a) PLOT OF ATOMIC $^{H}/C$ RATIOS AGAINST $\delta^{13}C$ VALUES: TYPE II KEROGEN SAMPLES

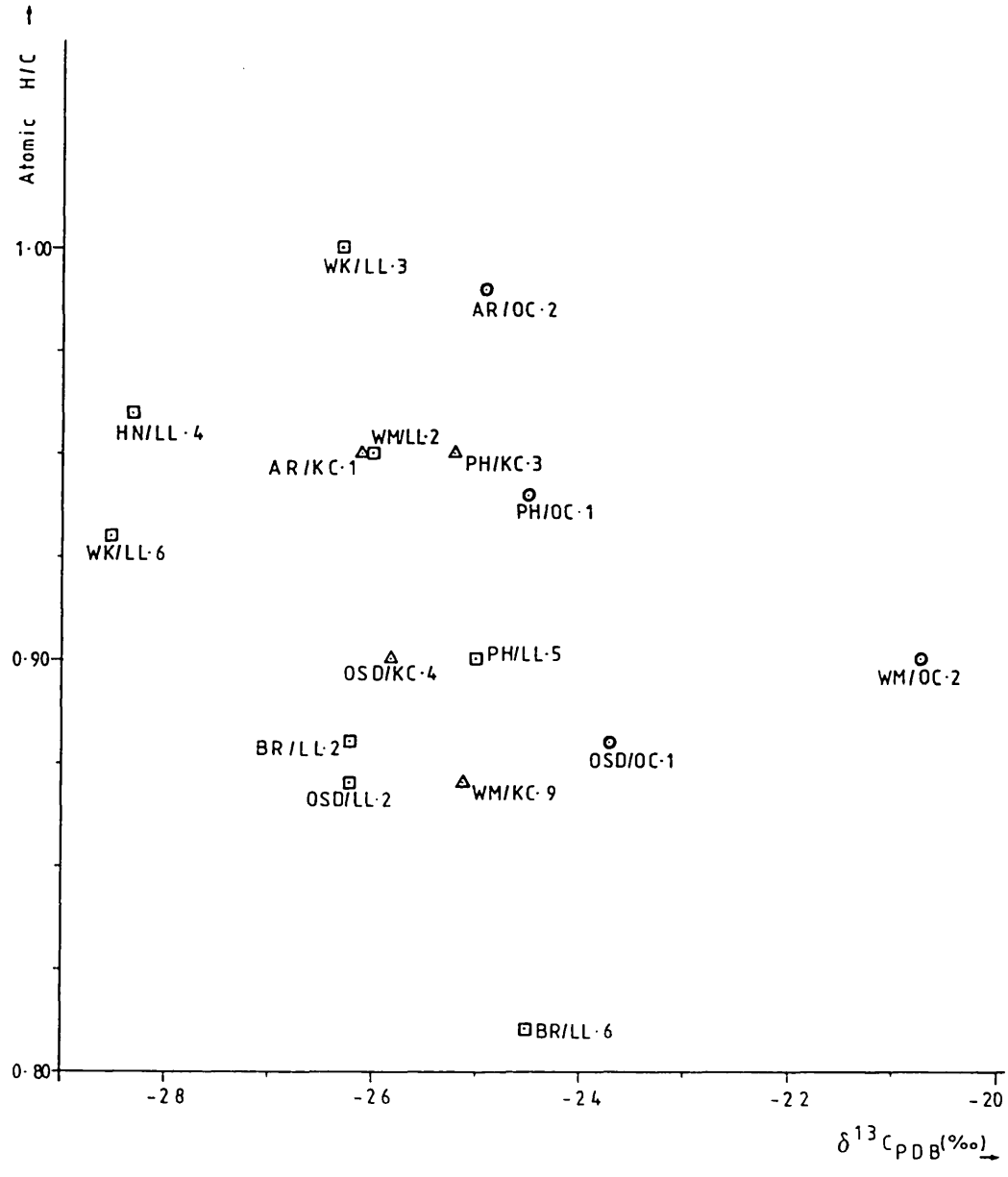


FIG. 7.6(b) PLOT OF ATOMIC $^{H}/C$ RATIOS AGAINST $\delta^{13}C$ VALUES: MIXED TYPE II/III KEROGEN SAMPLES

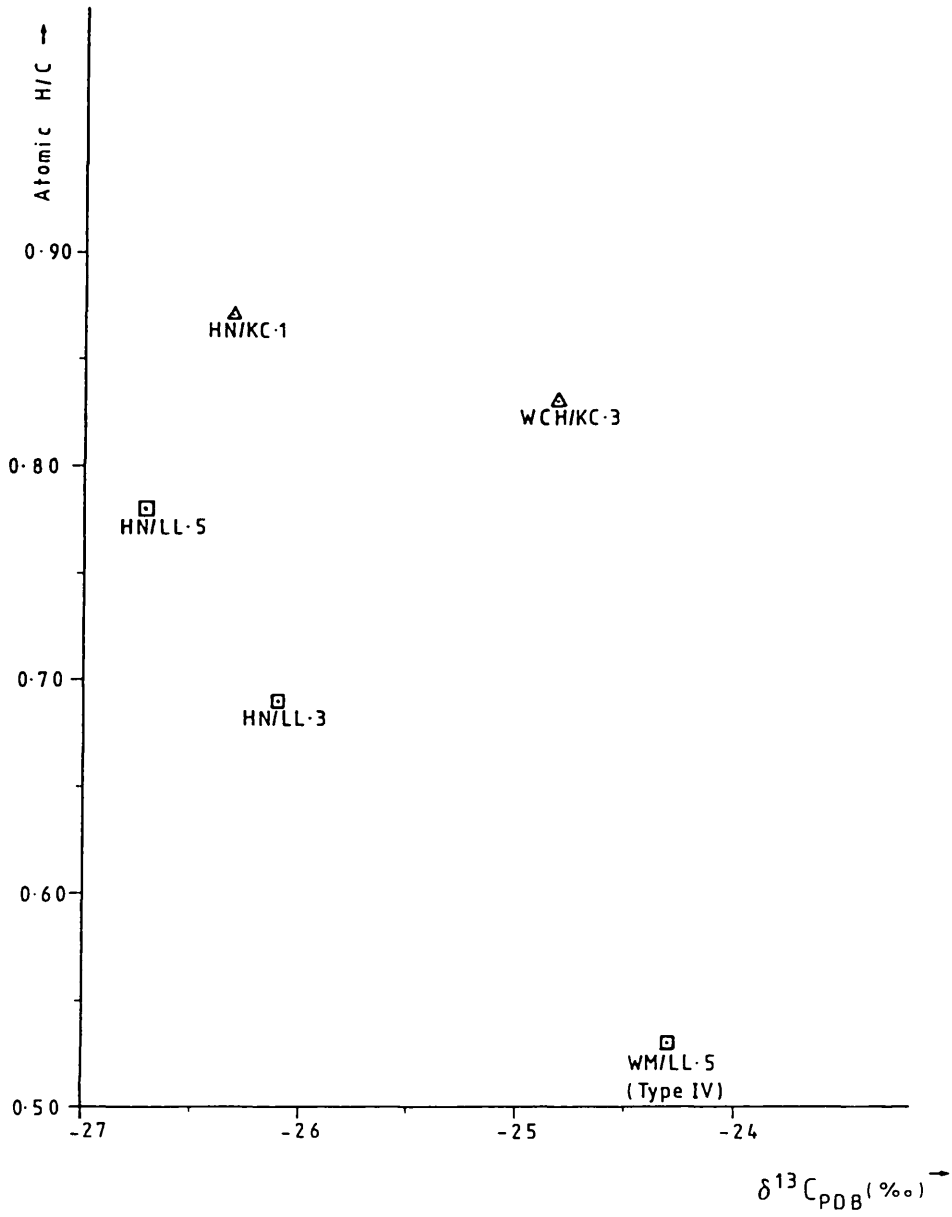


FIG. 7.6(C) PLOT OF ATOMIC $^{H}/C$ RATIOS AGAINST $\delta^{13}C$ VALUES: TIPE III KEROGEN SAMPLES

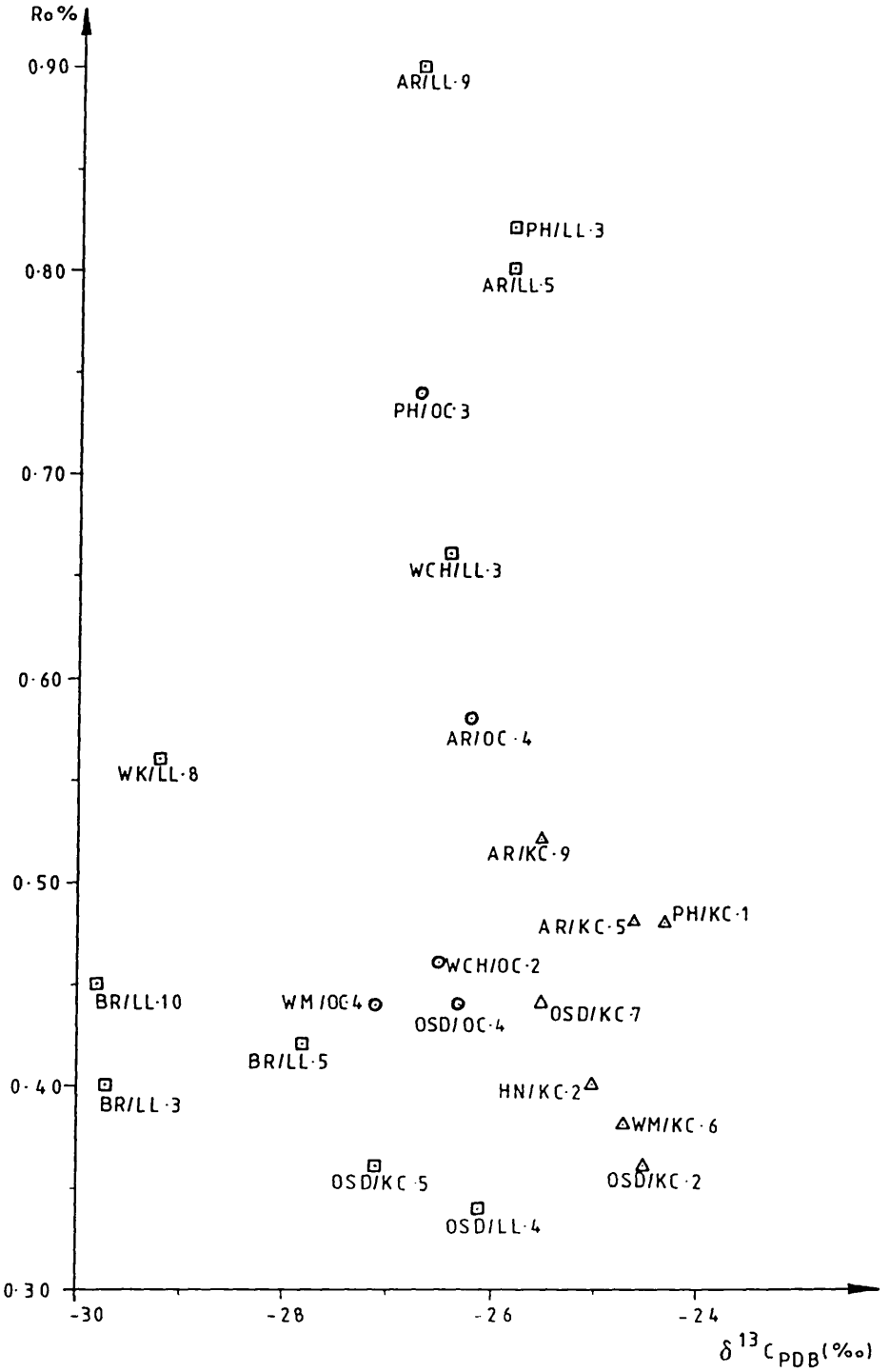


FIG. 7.7(a) PLOT OF Ro VALUES (ESTIMATED) AGAINST $\delta^{13}C$ VALUES: TYPE II KEROGEN SAMPLES

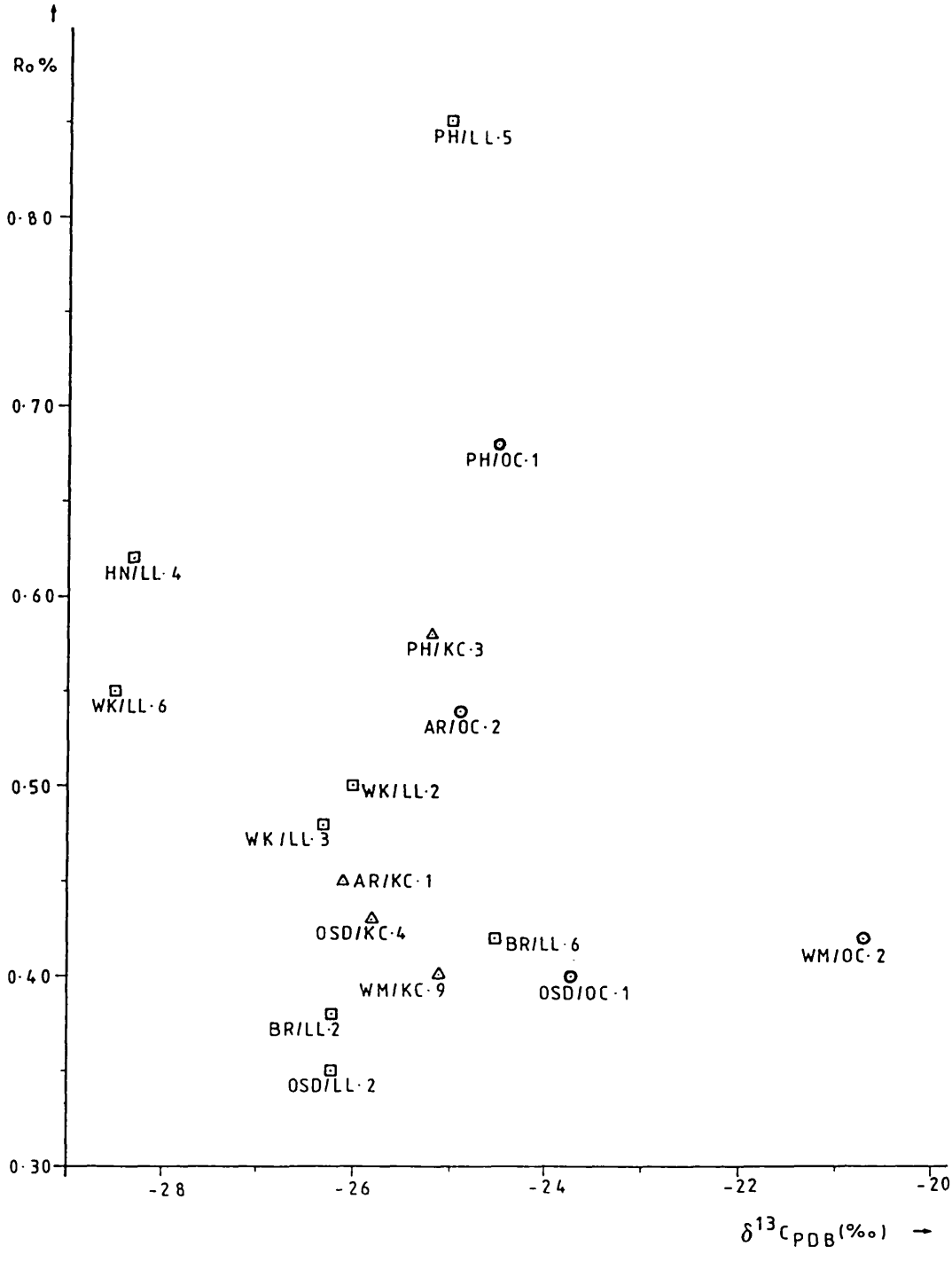


FIG. 7.7(b) PLOT OF Ro VALUES (ESTIMATED) AGAINST $\delta^{13}C$ VALUES: TYPE II/III KEROGEN SAMPLES

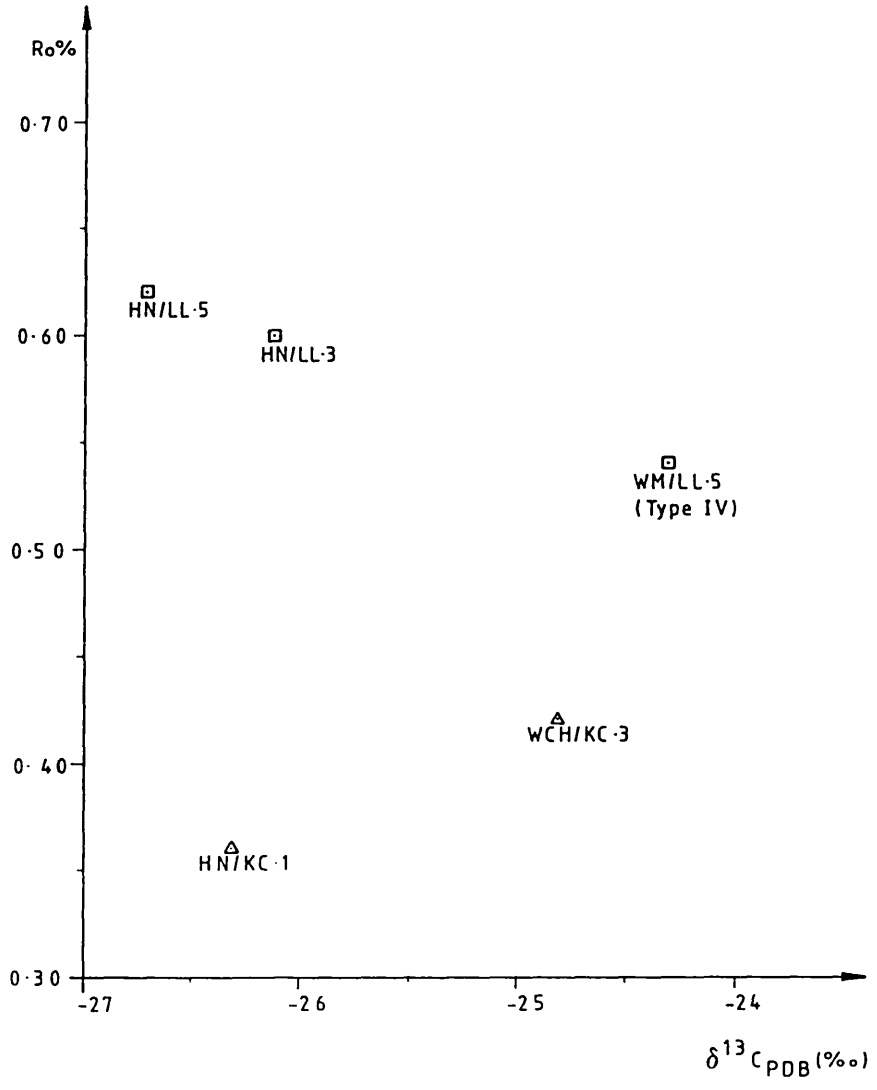


FIG. 7.7(c) PLOT OF Ro VALUES (ESTIMATED) AGAINST $\delta^{13}C$ VALUES: TYPE III KEROGEN SAMPLES

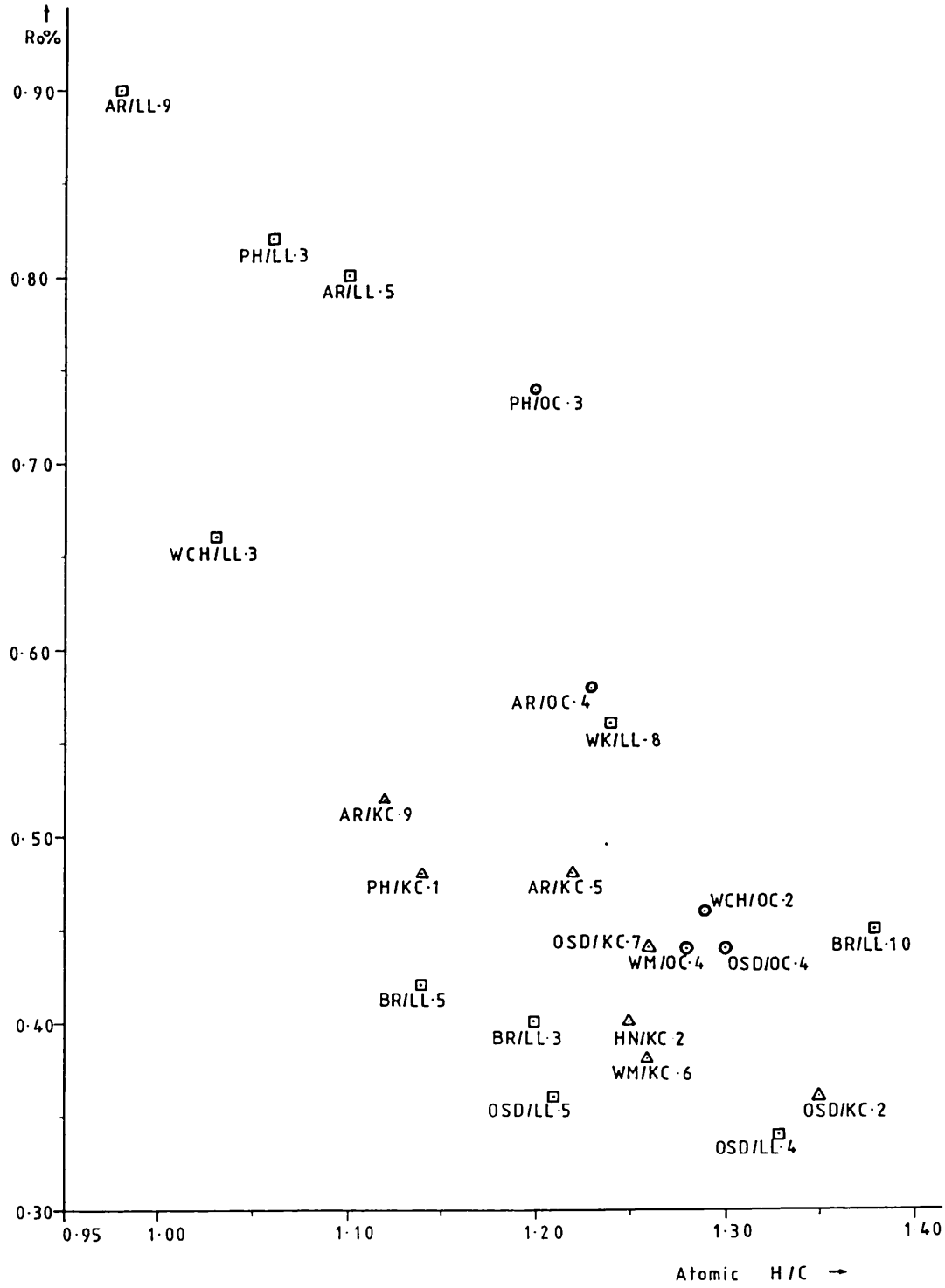


FIG. 7.8(a) PLOT OF Ro VALUES (ESTIMATED) AGAINST ATOMIC $^{H}/_{C}$ RATIOS: TYPE II KEROGEN SAMPLES

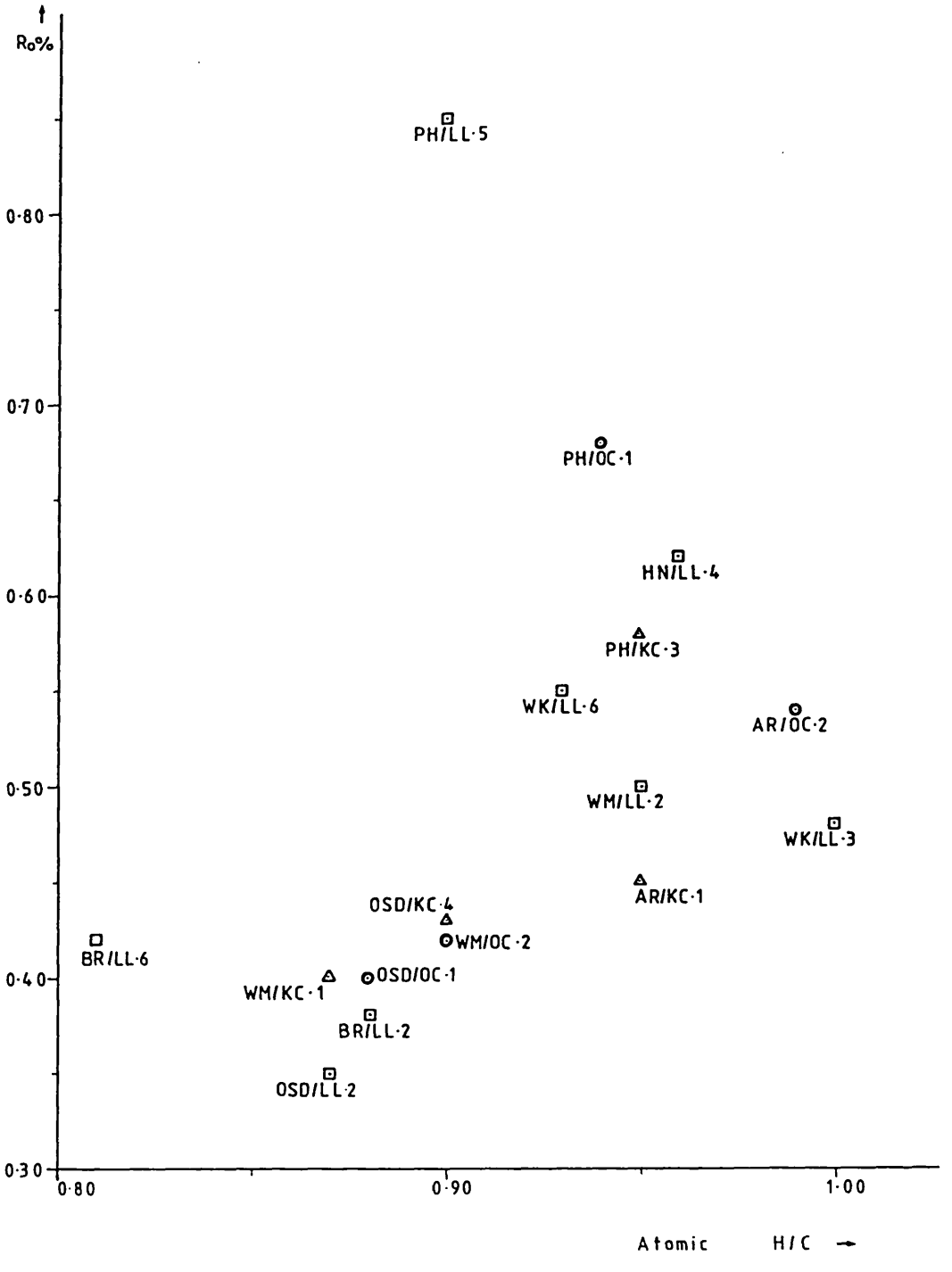


FIG. 7.8(b) PLOT OF Ro VALUES (ESTIMATED) AGAINST ATOMIC H/C RATIOS: MIXED TYPE II/III KEROGEN SAMPLES

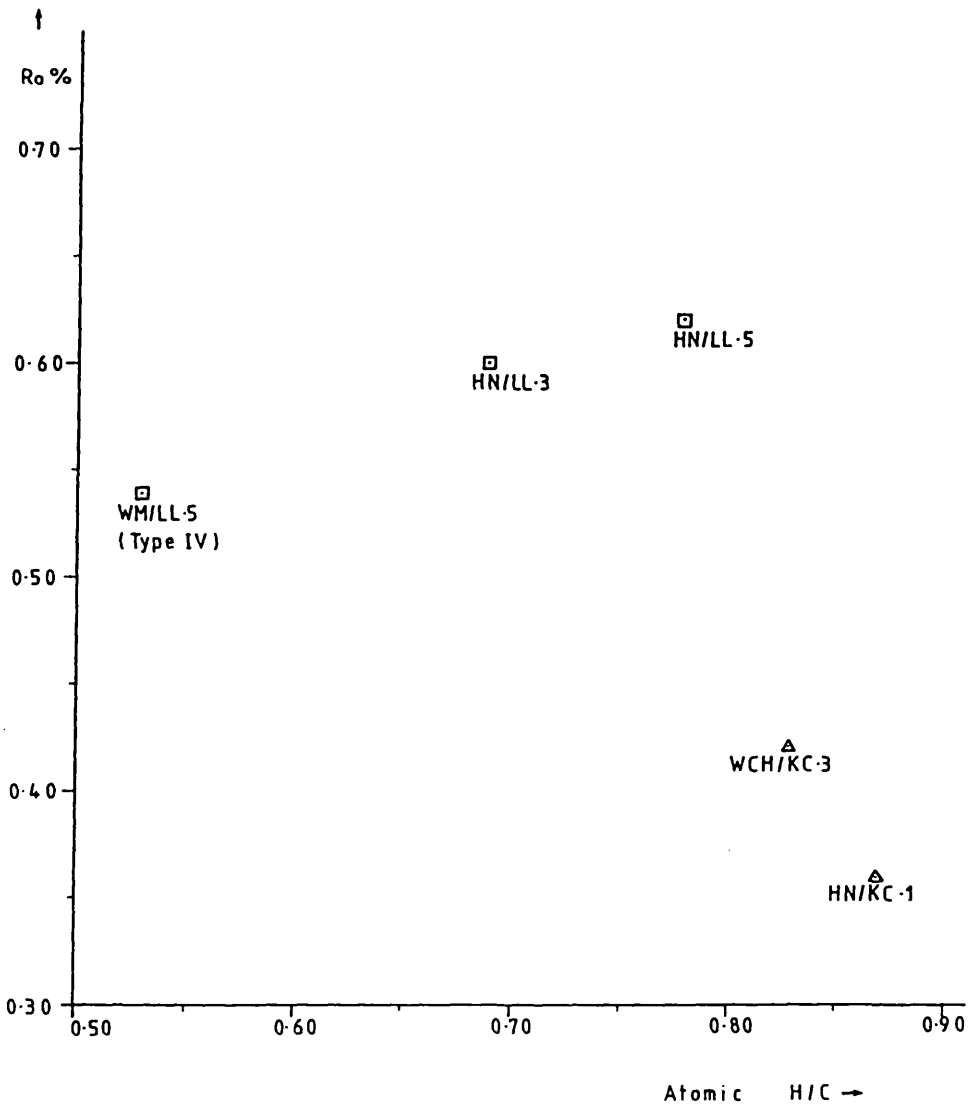


FIG. 7.8(c) PLOT OF Ro VALUES (ESTIMATED) AGAINST ATOMIC H/C RATIOS: TYPE III KEROGEN SAMPLES

type II/III, and type III samples as shown in Figs. 7.6 and 7.7. The single type IV kerogen sample from the Lower Lias, WM/LL.5, is grouped with the type III samples for the purpose of these plots. Judging from the wide scatter of points in these plots, no clear definition of a maturity effect on the $\delta^{13}C$ values is observed for the Jurassic kerogens in southern England. This lack of expected trend in the carbon isotope values with maturity is most likely due to the compositional variations of the organic matter inflicted by the primary source, and the relatively low maturity levels attained by these Jurassic kerogens are hardly sufficient to overshadow the influence due to source variability. The poor reliability of the kerogen elemental composition as a maturity indicator in the Jurassic of southern England was mentioned and illustrated in Chapter 6. This finding is further demonstrated here by the poor or lack of correlation of the atomic $^{H}/_{C}$ ratios with the estimated vitrinite reflectance values (Ro) shown in Fig. 7.8.

7.1.2.2 Interpretation of the Hydrogen Isotope (δD) Data

A histogram showing the distribution of the δD values for the selected Type II kerogen samples from the three litho-stratigraphic units is shown in Fig. 7.9. From this construction, it is clearly noticed that the Jurassic type II kerogens show a very wide range in their δD values (-180 to -60‰) and this reflects the chemical heterogeneity of this single kerogen type. Broad overlaps occur in the

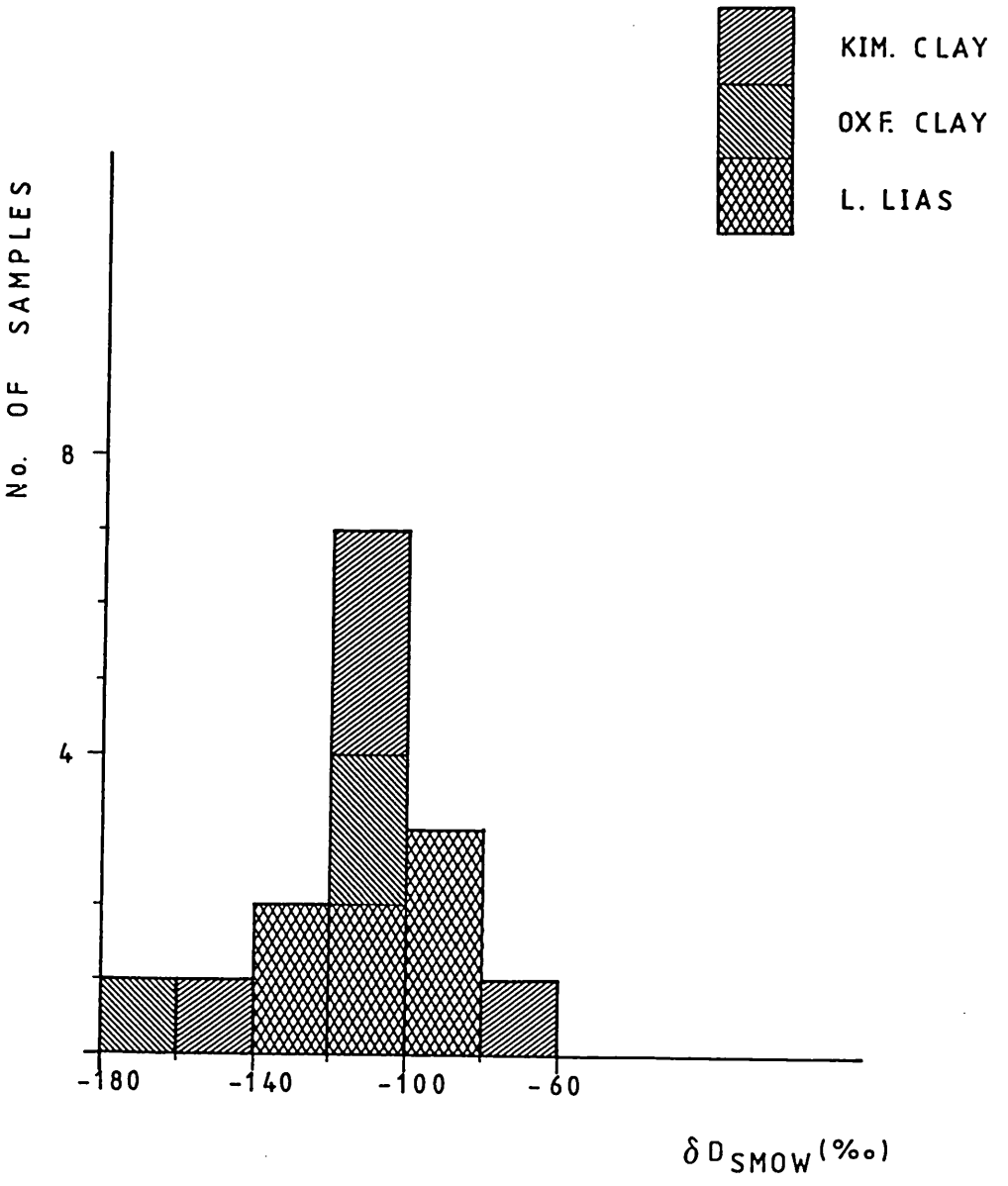


FIG. 7.9 DISTRIBUTION OF δD VALUES FOR SELECTED JURASSIC TYPE II KEROGEN SAMPLES FROM S. ENGLAND

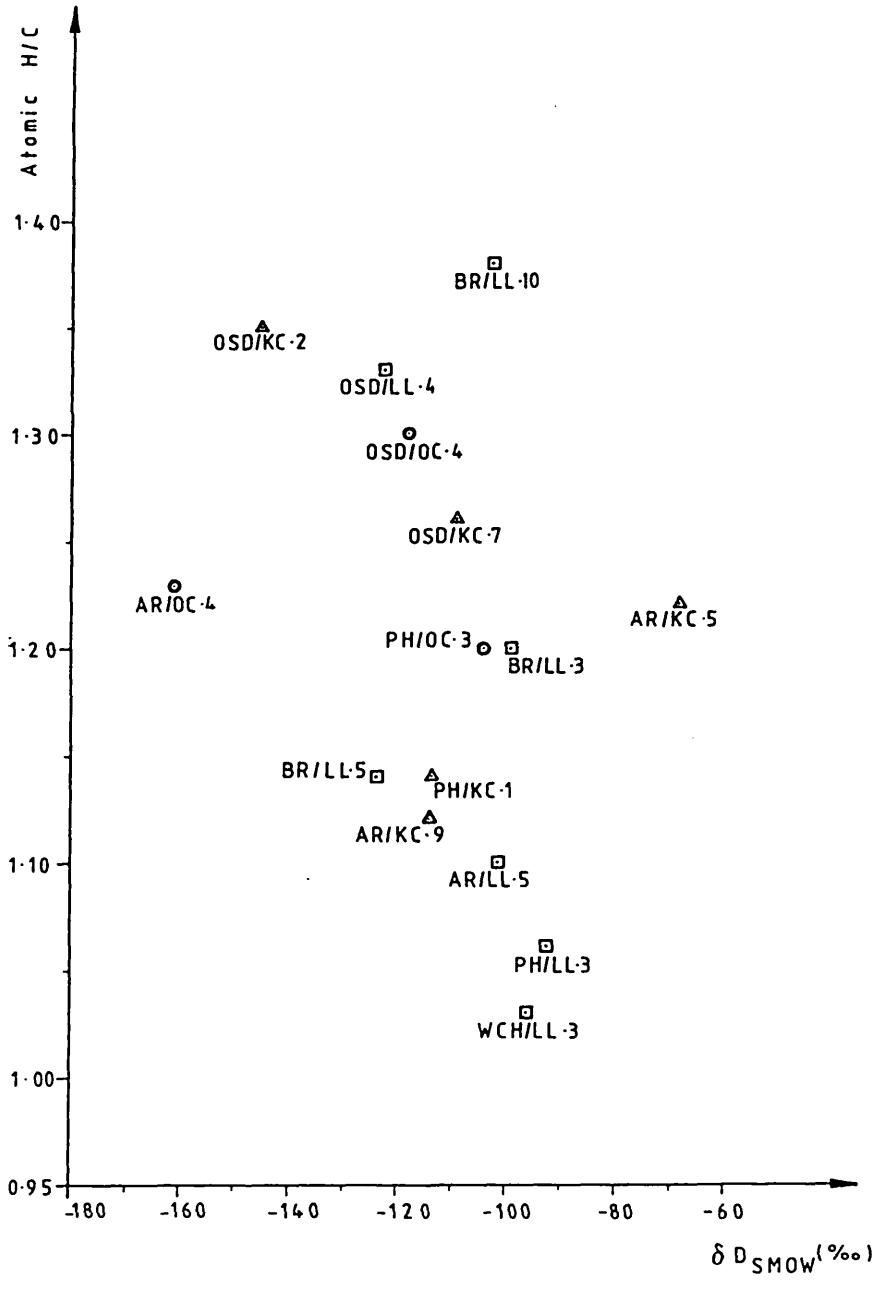


FIG. 7.10 PLOT OF ATOMIC $^{H}/_{C}$ RATIOS AGAINST δD VALUES FOR THE TYPE II KEROGEN SAMPLES

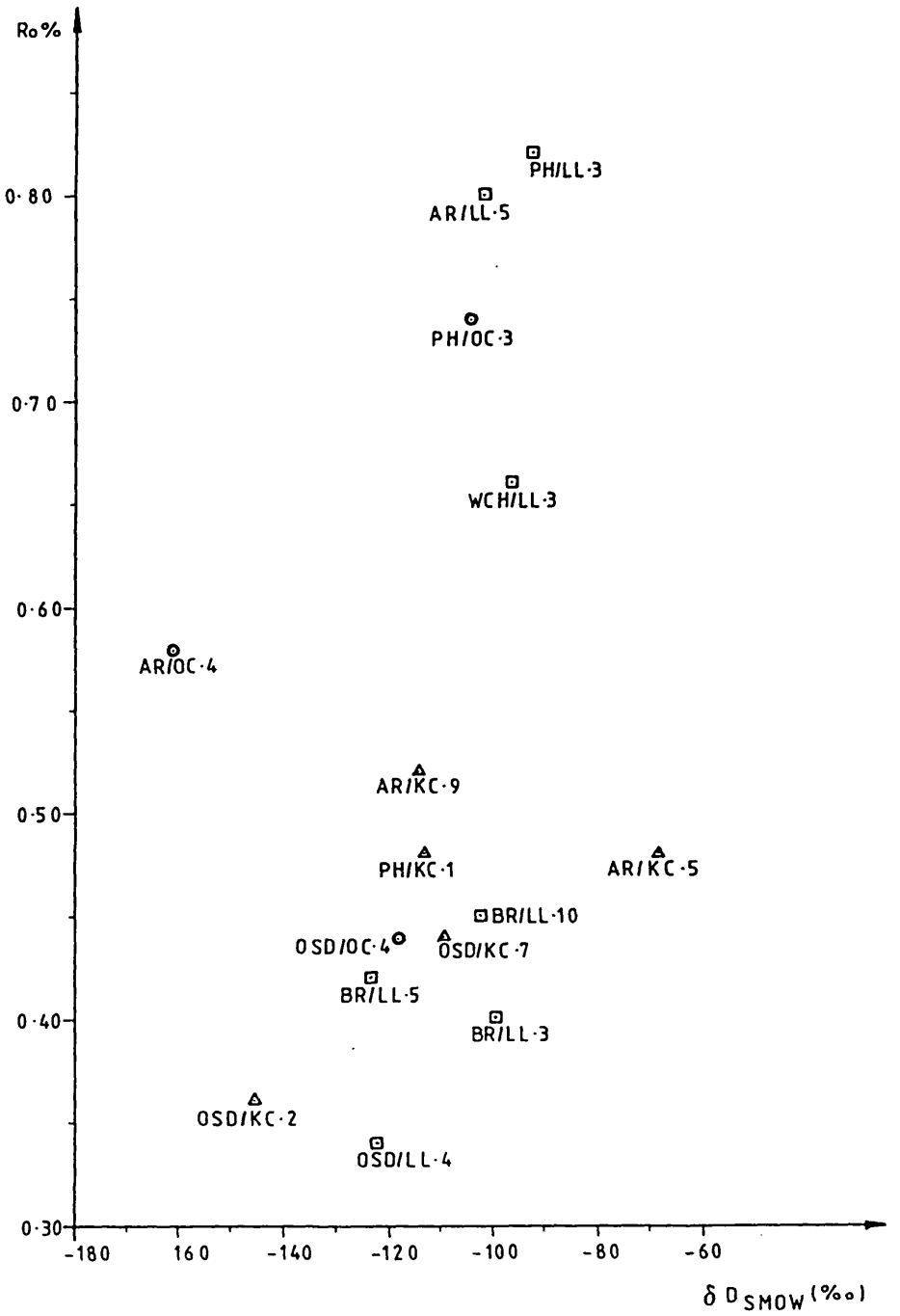


FIG. 7.11 PLOT OF Ro (ESTIMATED) VALUES AGAINST δD VALUES FOR THE TYPE II KEROGEN SAMPLES

ranges of δD values for samples from the three formations. However, the Oxford Clay samples tend to be the lightest (δD: -180 to -100‰ while the Kimmeridge Clay samples appear to be the heaviest (δD: -160 to -60‰). An intermediate range -140 to -80‰ is shown by the Lower Lias samples.

No trend in the δD values with atomic $^{H}/_{C}$ ratios or with the estimated vitrinite reflectance values (Ro) is observed (see Figs. 7.10 and 7.11).

This isotopically diverse nature of the Jurassic kerogens noted in this study supports the view expressed by Bailey (1981) that it is difficult to understand why Tissot et al. (1974) classified kerogen into three distinctly different chemical types, as sedimentary organic matter should vary in composition as a function of species, environment, and diagenesis thus resulting in a chemical continuum.

7.2 PYROLYSIS

7.2.1 Pyrolysis - Gas Chromatographic Analysis of Kerogens

Recently gas chromatograms of kerogen pyrolysates have been used by a number of workers to assess both type and hydrocarbon potential of insoluble sedimentary organic matter (Larter and Douglas, 1978; 1980; Van de Meent et al., 1980; Bailey, 1981; Dembicki et al., 1983). The pyrolysis products from woody kerogen material derived from terrestrial higher plants have been shown by these authors to consist dominantly of aromatic and phenolic

species with only minor contributions from the normal alkenes and normal alkanes, and most of these compounds characteristically occur in the less than C_{12} range. The normal alkenes and normal alkanes, which are believed to be produced during kerogen pyrolysis by way of a free radical cracking mechanism (Burnham and Ward, 1980), normally occur as doublets with the alkenes eluted first. Herbaceous organic matter derived from land plants (spores, pollens and cuticles) are typified by pyrolysates which are not only paraffinic but waxy - their chromatograms being characterized by well developed n-alkene - alkane doublets extending out to the heavy ends (C_{25} to C_{30} range). Chromatograms of pyrolysates from the hydrogen-rich algal and amorphous kerogen materials derived from aquatic precursors have been documented to show mainly aliphatic structures with more branched-chain hydrocarbons than found in the aforementioned land derived organic matter pyrolysates. Relatively minor contributions from aromatic compounds have been noted in the pyrolysates of these aquatic derived materials. Another known characteristic of the pyrolysates of algal and sapropelic amorphous materials is their non-waxy nature with most of the generated compounds in the carbon number range of less than twenty four ($< C_{24}$). Oil-prone types I and II kerogens are known to consist mainly of algal and sapropelic amorphous materials with some admixtures of herbaceous materials, whereas type III kerogens, often described as mainly gas-prone, consist of woody materials as well as oxidised or biodegraded aquatic and terrestrially derived organic materials. According to Bailey (1981), a kerogen sample

is judged to be non-oil prone if its pyrolysate consists almost exclusively of materials lighter than approximately C_{15} due to the fact that about half of a typical crude oil consists of the missing C_{15+} fraction.

In the present work, kerogen pyrolysis-gas chromatographic analysis was carried out to further characterize the various kerogen types identified in the three Jurassic formations in southern England in terms of their nature and hydrocarbon generating potentials. Fig. 7.12 shows typical chromatograms of pyrolysates from Jurassic type II kerogens - consisting mainly of sapropelic, hydrogen-rich amorphous material. As shown by the chromatograms, the pyrolysates consist mainly of normal alkene - alkane doublets in the C_{9+} range with a high doublet peak to background ratio. The background components represent contributions from branched and cyclic alkenes and alkanes and aromatic compounds. The chemical nature of these Jurassic type II kerogens portrayed by the pyrolysate chromatograms in Fig. 12 is at variance with the results of similar analysis on type II kerogen concentrates from the Kimmeridge Clay (sampled in the Kimmeridge Bay) published by Williams and Douglas (1980) which showed the pyrolysates to consist mostly of aromatic hydrocarbons with only subordinate amounts of aliphatic hydrocarbons. The presence of components extending into the C_{24+} range in the pyrolysates on these type II kerogens confirms the oil-prone nature of this kerogen type and indicates some contributions of terrestirally derived herbaceous materials to the kerogen composition. Thus, some waxiness in the oils sourced by this kerogen type in southern England may not be unexpected.

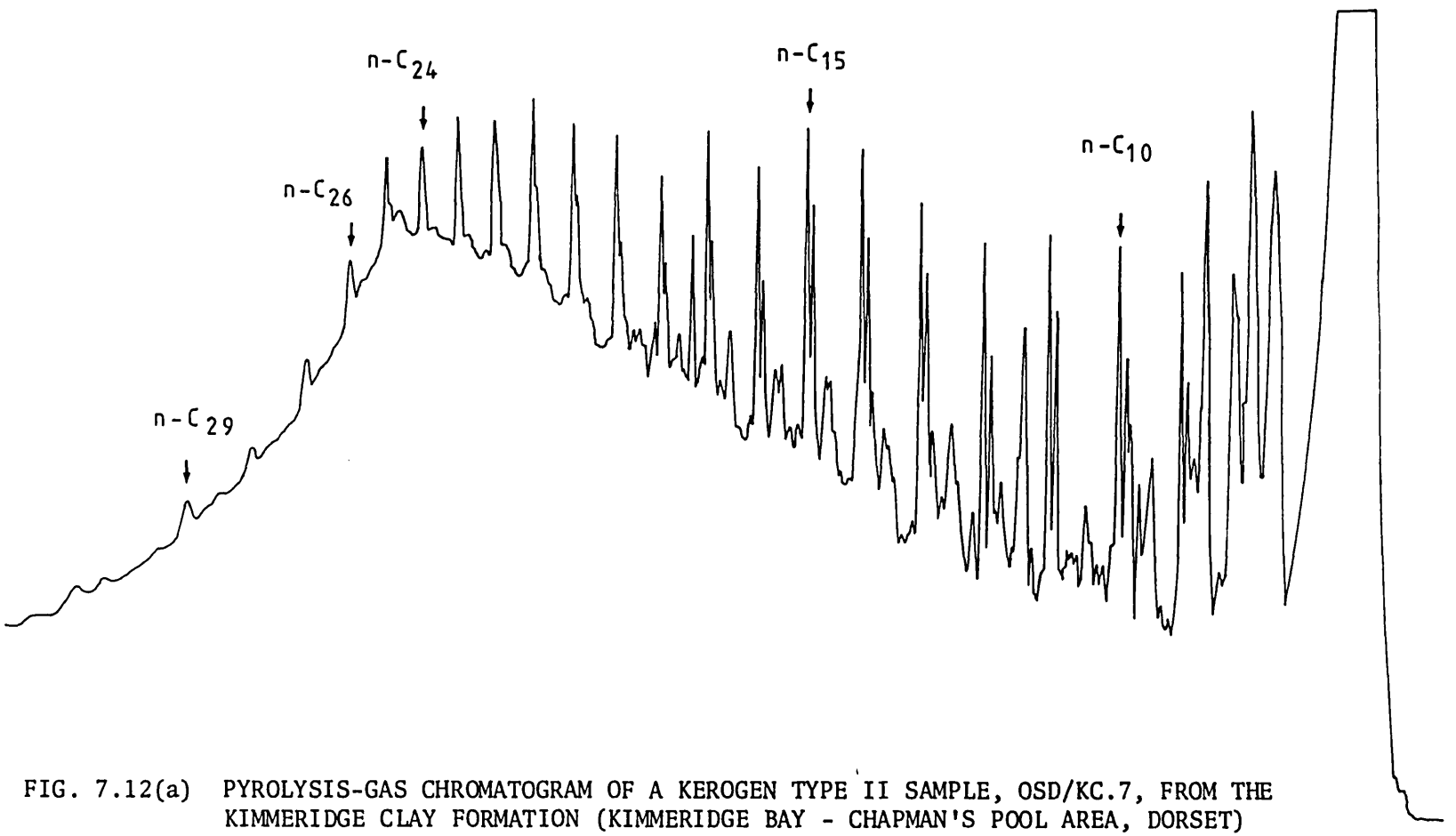


FIG. 7.12(a) PYROLYSIS-GAS CHROMATOGRAM OF A KEROGEN TYPE II SAMPLE, OSD/KC.7, FROM THE KIMMERIDGE CLAY FORMATION (KIMMERIDGE BAY - CHAPMAN'S POOL AREA, DORSET)

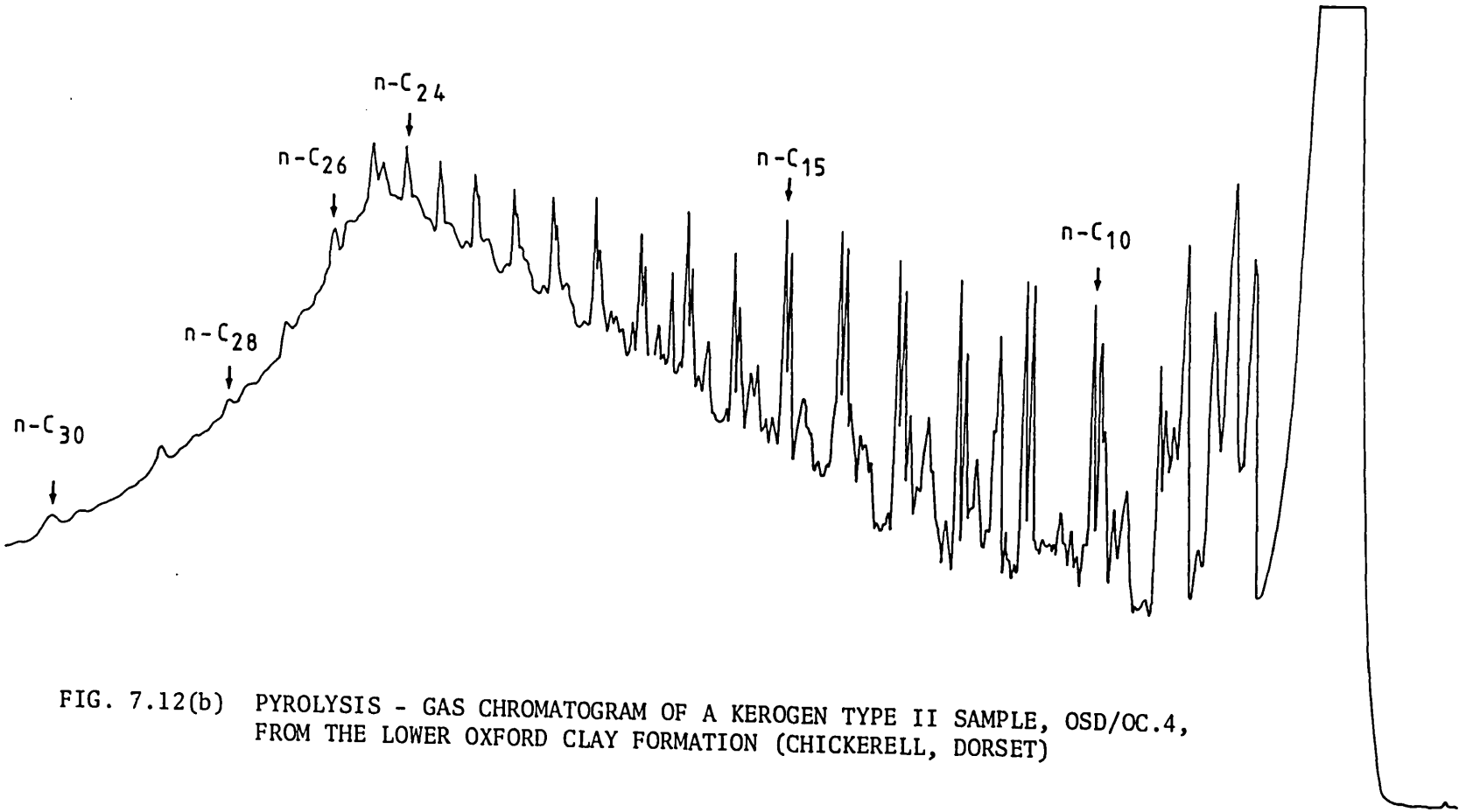


FIG. 7.12(b) PYROLYSIS - GAS CHROMATOGRAM OF A KEROGEN TYPE II SAMPLE, OSD/OC.4, FROM THE LOWER OXFORD CLAY FORMATION (CHICKERELL, DORSET)

Typical chromatograms of mixed type II/III kerogen pyrolysates are shown in Fig. 7.13. They appear similar to the kerogen type II pyrolysate chromatograms with a slightly lower aliphatic hydrocarbon doublet peak to background ratio in some cases - probably reflecting the higher humic matter contents as well as the partially oxidised nature of the amorphous material in this mixed kerogen facies compared to the pure type II. Fig. 7.14 is a Lower Lias type III kerogen pyrolysate chromatogram showing the aliphatic hydrocarbons as constituting a significant proportion of the pyrolysis yield, and components are noted to extend to the heavy end (C_{25}+ range) with an increased peak strength in the C_{24} - C_{26} range. Also noted is the higher contributions of the background components in the C_{9+} fraction compared to the cases of the first two kerogen groups. Based on this chromatogram (Fig. 7.14), it may be argued that the Jurassic type III kerogens identified in the present work as consisting mainly of hydrogen-lean amorphous material with some admixtures of humic and herbaceous organic matter, have both gas and oil generating capabilities. Of particular interest is the chromatogram of a Lower Lias type IV kerogen pyrolysate shown in Fig. 7.15. Normal alkene - alkane doublets as well as other organic compounds are present up to C_{30}. The result of this analysis thus shows that the identified kerogen type IV samples in the Jurassic of Southern England do have some potential for gaseous and oil-range hydrocarbon generation. This finding is contradictory to the general notion that hydrogen-lean

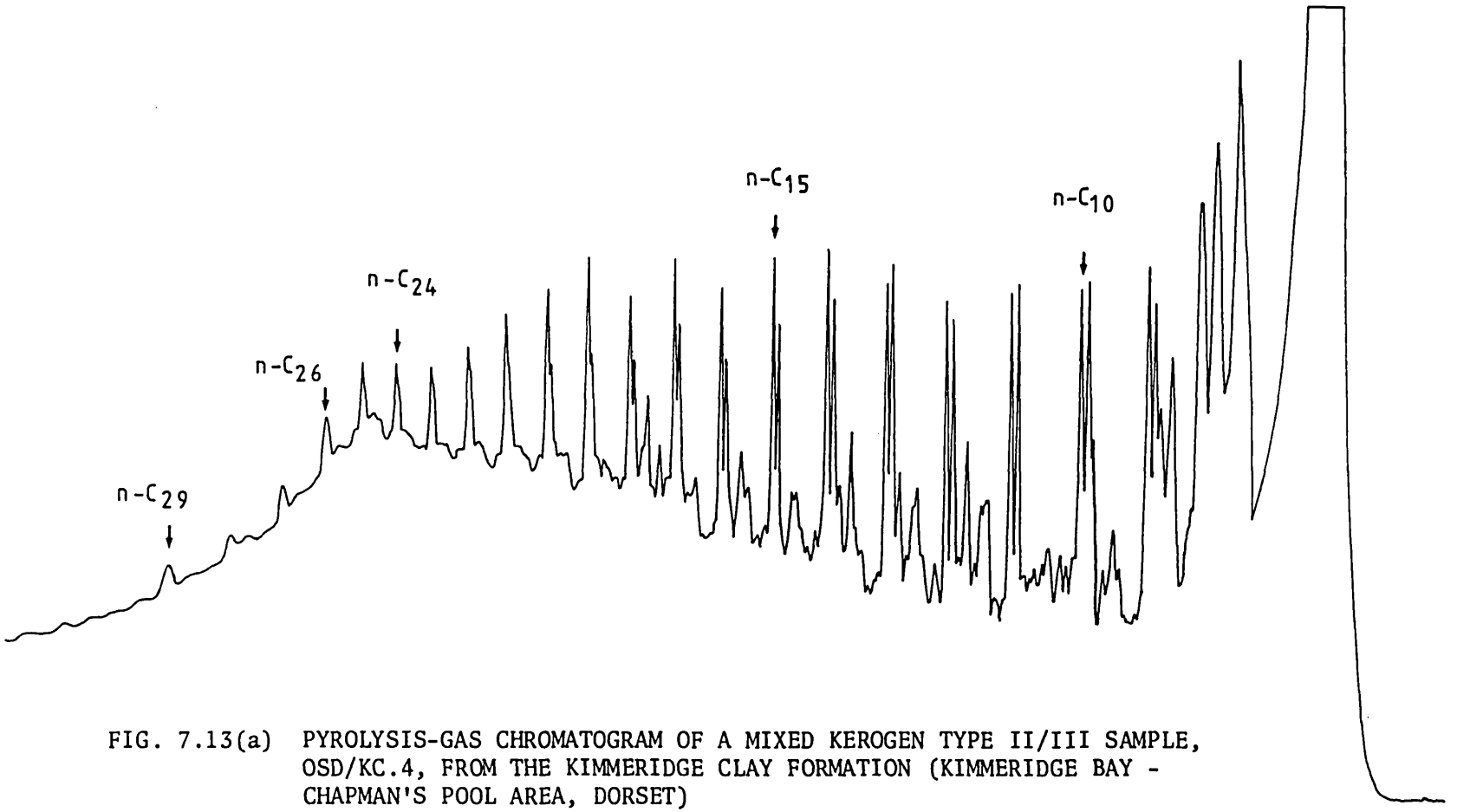


FIG. 7.13(a) PYROLYSIS-GAS CHROMATOGRAM OF A MIXED KEROGEN TYPE II/III SAMPLE, OSD/KC.4, FROM THE KIMMERIDGE CLAY FORMATION (KIMMERIDGE BAY - CHAPMAN'S POOL AREA, DORSET)

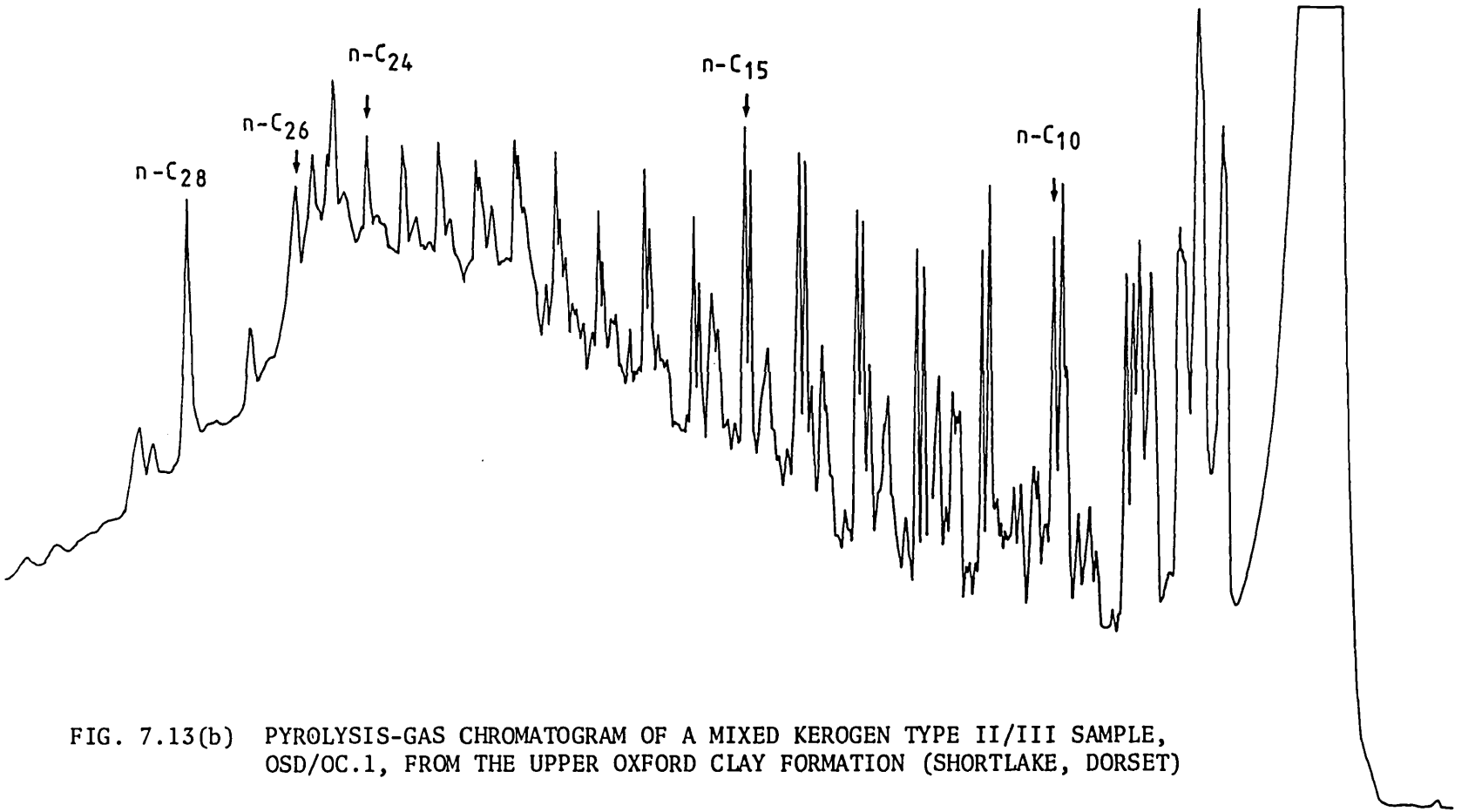


FIG. 7.13(b) PYROLYSIS-GAS CHROMATOGRAM OF A MIXED KEROGEN TYPE II/III SAMPLE, OSD/OC.1, FROM THE UPPER OXFORD CLAY FORMATION (SHORTLAKE, DORSET)

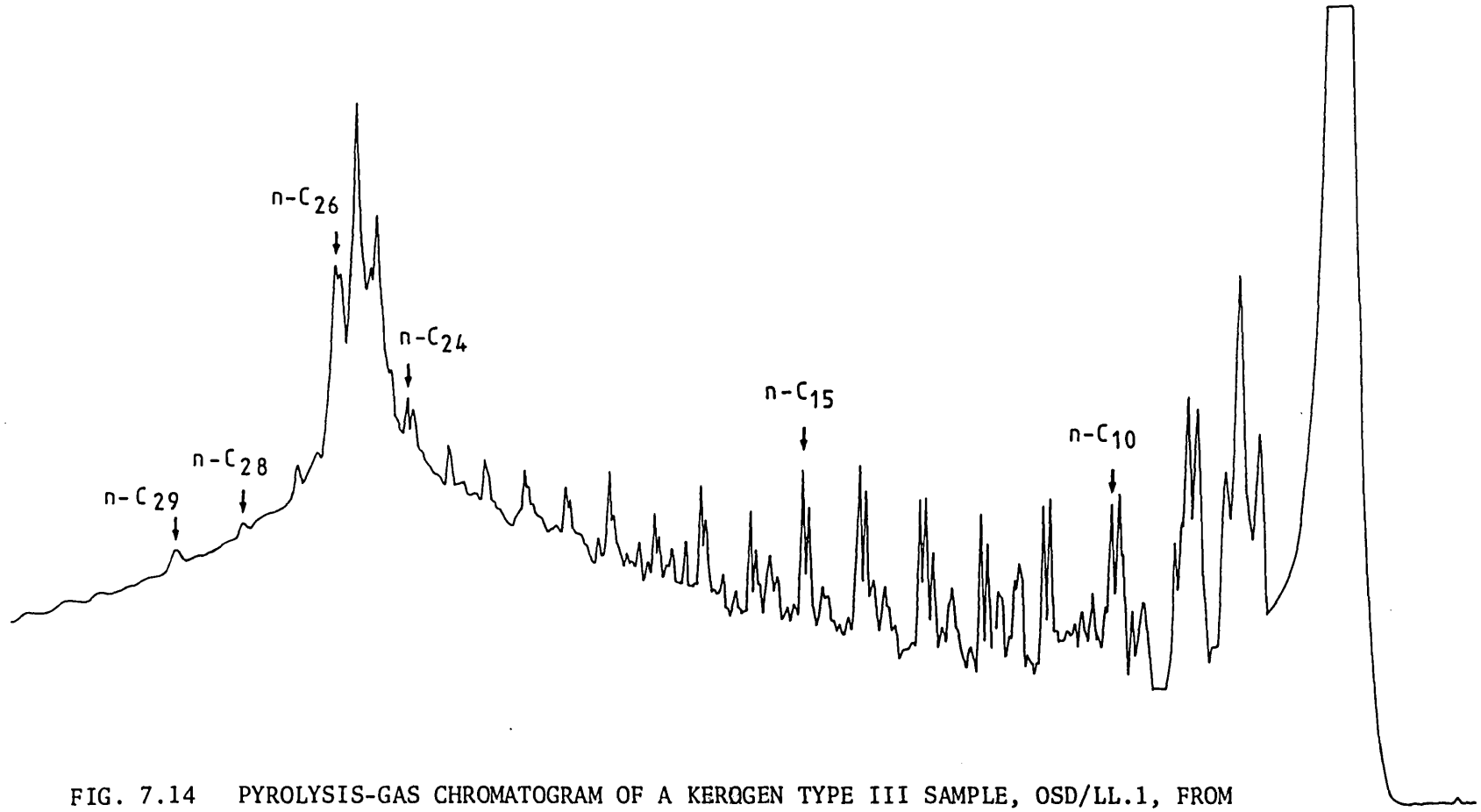


FIG. 7.14 PYROLYSIS-GAS CHROMATOGRAM OF A KEROGEN TYPE III SAMPLE, OSD/LL.1, FROM THE LOWER LIAS FORMATION (CHARMOUTH, DORSET)

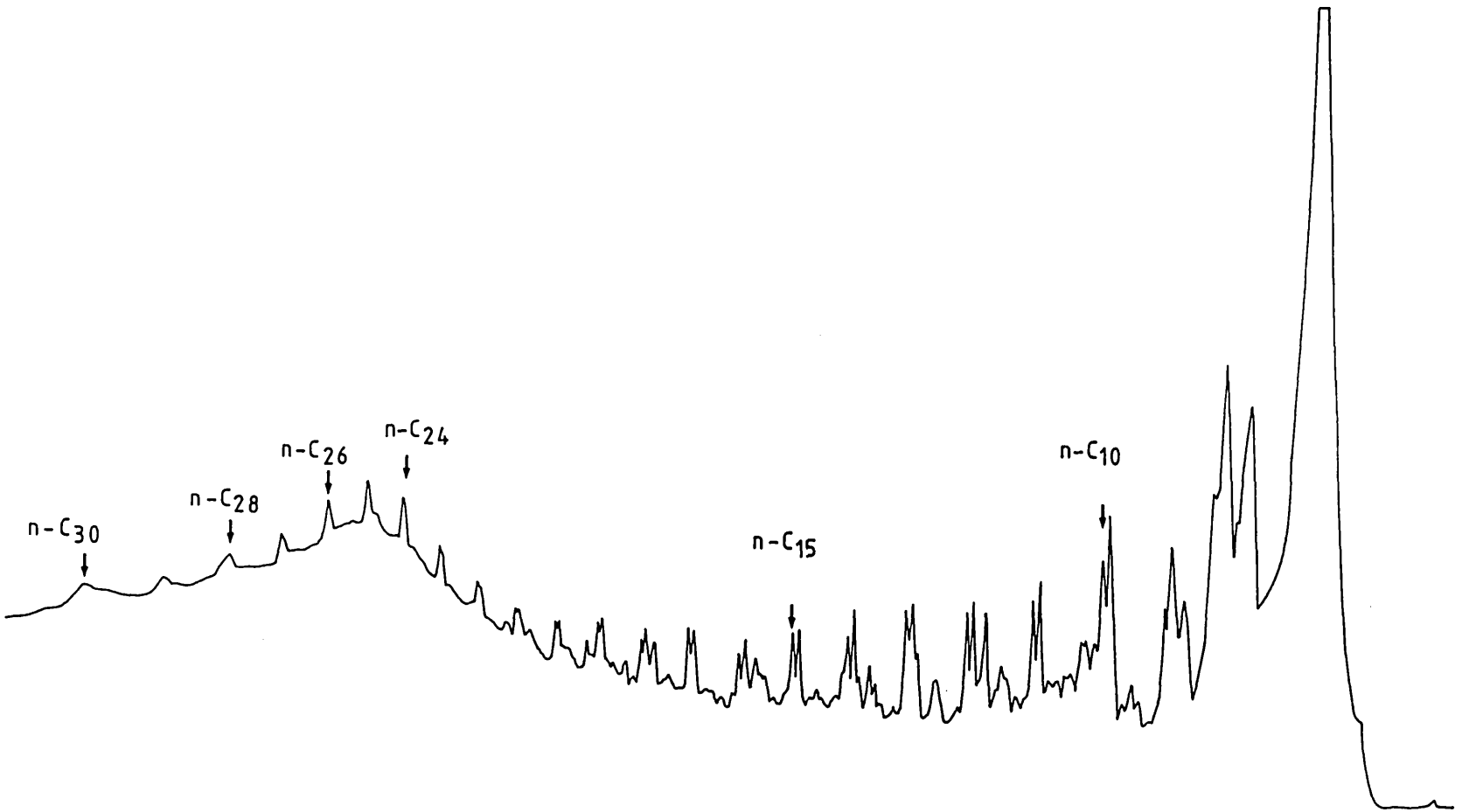


FIG. 7.15 PYROLYSIS-GAS CHROMATOGRAM OF A KEROGEN TYPE IV SAMPLE, WM/LL.5, FROM THE LOWER LIAS FORMATION (WARLINGHAM BOREHOLE)

inertinitic materials have no potential for hydrocarbon generation. Though this study has proved this very hydrogen-poor kerogen to have some hydrocarbon potential, to function as a commercial oil-source, quite a high concentration of this kerogen type material will be required in a rock - as judged from the comparatively large quantity of this kerogen material that was needed to generate the chromatogram shown in Fig. 7.15. Recently, Smyth (1983) proposed the dispersed inertinite in the Gidgealpa Group sediments as one of the sources for the liquid and gaseous hydrocarbons in the Cooper Basin in Australia based on the results of organic petrographic analyses. The finding in the present organic geochemical investigation of the Jurassic mudrocks in southern England supports Smyth's suggestion that inertinite should be considered as a source or potential source material for liquid hydrocarbons.

7.2.2 Programmed-Temperature Pyrolysis of Some Whole-Rock Samples

The principles and applications of this analytical method were outlined in Chapter 4. The two detector peak responses commonly produced in the course of programmed pyrolysis of a potential hydrocarbon source-rock sample are: P_1 - due to thermal distillation of already generated bitumen in the rock, and P_2 - due to hydrocarbons generated by the pyrolytic degradation of the contained kerogen. The pyrolysis temperature at which the second peak reaches maximum detector response is the T_{max}. The main objective for employing this study technique was to further assess

the maturity of organic matter in the three Jurassic potential hydrocarbon source formations. As already mentioned in Chapter 4, both the Transformation Ratios (= $P_1/P_1 + P_2$) as well as the T_{max} values are known to increase with increasing maturity of the samples. Also mentioned is the fact that due to the bulk nature of these chemical maturity indicators, significant variations can occur depending on the kerogen type or the relative concentrations of the various kerogen components. According to Dembicki et al. (1983), for a given level of maturity and heating rate, the vitrinites show a higher T_{max} value than the sporinite (herbaceous organic matter) and thus their kerogen analogs - types III and II respectively. Migration effect is another factor which can affect the Transformation Ratio and therefore its reliability as a maturity index. A recently documented work by Leythaeuser et al. (1984) on hydrocarbon migration has shown that expulsion efficiencies of the total C_{15+} soluble organic matter from well depleted sections of mature source-rock shales can be as high as 23%. Numerous faults associated with basin formation as well as the Cretaceous and Tertiary earth movements in southern England are known to occur in the Jurassic System (Chapter 2). And since faults in proximity to mature fine-grained rocks provide easy and efficient primary migration pathways for generated bitumen, the unreliability of this maturity indicator is not unlikely in parts of the Jurassic of southern England.

The results of the programmed-temperature pyrolysis of selected whole-rock samples are presented in Table 7.4. Based on four repeated analysis of the laboratory

TABLE 7.4 RESULTS OF PROGRAMMED-TEMPERATURE PYROLYSIS OF SELECTED WHOLE-ROCK SAMPLES

Sample Locality	Sample Number	Total Organic Carbon (Wt.%)	Kerogen Type	Kerogen Maturity (Estimated Ro)	Transformation Ratio ($P1_{/P_1+P_2}$)	T_{max} (°C)
Outcrops, Dorset	OSD/KC.2	16.34	II	0.36	0.011	423
	OSD/KC.8	20.48	II	0.45	0.018	430
	OSD/KC.12	6.16	II	0.48	0.021	435
	OSD/OC.4	8.14	II	0.44	0.021	429
	OSD/LL.5	7.36	II	0.36	0.007	425
	OSD/LL.8	5.98	II	0.32	0.004	437
Burton Row Well (Somerset)	BR/LL.3	4.54	II	0.40	0.026	434
	BR/LL.5	3.54	II	0.42	0.039	440
	BR/LL.10	5.43	II	0.45	0.054	440
Cranborne-1 Well (Dorset)	CN/OC.5	3.66	II	0.42	0.032	439
	CN/LL.5	3.10	Mixed II/III	0.48	0.031	437
Marchwood Well (Hampshire)	MD/LL.2	1.45	Mixed II/III	0.50	0.055	440
Winterborne Kingston Well (Dorset)	WK/KC.2	3.94	Mixed II/III	0.32	0.010	437
	WK/LL.8	1.91	II	0.56	0.084	440
Winchester-1 Well (Hampshire)	WCH/OC.2	9.43	II	0.46	0.022	435
	WCH/OC.4	2.31	II	0.48	0.038	436
	WCH/LL.3	2.92	II	0.66	0.048	451
Henfield Well (W. Sussex)	HN/KC.2	10.02	II	0.40	0.029	437
	HN/LL.4	1.27	Mixed II/III	0.62	0.089	447
Arreton-2 Well (Isle of Wight)	AR/KC.2	3.02	n.d.	0.45 - 0.46	0.023	443
	AR/KC.8	4.59	"	0.50 - 0.52	0.026	437
	AR/OC.1	1.30	"	0.52 - 0.54	0.040	444
	AR/LL.4	1.87	"	0.74 - 0.80	0.064	447
	AR/LL.8	2.79	"	0.84 - 0.90	0.105	456
Penshurst Well (Kent)	PH/KC.1	8.38	II	0.48	0.039	435
	PH/OC.3	4.19	II	0.74	0.058	440
	PH/LL.3	1.52	II	0.82	0.093	444

n.d. = not determined

standard sample, the T_{max} values and the calculated transformation ratios are correct to within $\pm$ 3°C and $\pm$ 0.008 respectively. As noted from the results, some variations in the T_{max} as well as the transformation ratios occur due probably to variations in the kerogen compositions in the rock samples. Some effect on these parameters due to mineralogic variations in the samples may not be entirely ruled out despite organic carbon contents in excess of 1.0% in all samples (Espitalie et al., 1980). But desipte these variations, some trends are noticed in these parameters with increasing maturity (Fig. 7.16). Most of the samples at maturity levels of 0.5% Ro and above tend to show T_{max} values of $\geq$ 440°C and transformation ratios of $\geq$ 0.040. The highest transformation ratio of 0.105 is associated with the most mature sample analysed - a Lower Lias sample, AR/LL.8, from the Arreton-2 borehole at an estimated vitrinite reflectance value of between 0.84 to 0.90% (Ro) (see Fig. 7.16). The relatively high ratio of 0.054 recorded for the immature, organic-rich sample, BR/LL.10 (estimated R_o = 0.45%) from the Burton Row Well (Somerset), is indicative of a high content of already generated but non-migrated bitumen in that sample. Peters et al. (1983) recorded transformation ratios of 0.03 and 0.15 for samples of thermally altered Cretaceous black shales containing type II kerogen at maturity levels of 0.50% Ro and about 1.0% Ro respectively.

On a broad consideration, the results of this programmed whole-rock pyrolysis support the levels of maturation already arrived at for the analysed samples based on transmitted light microscopic examination of

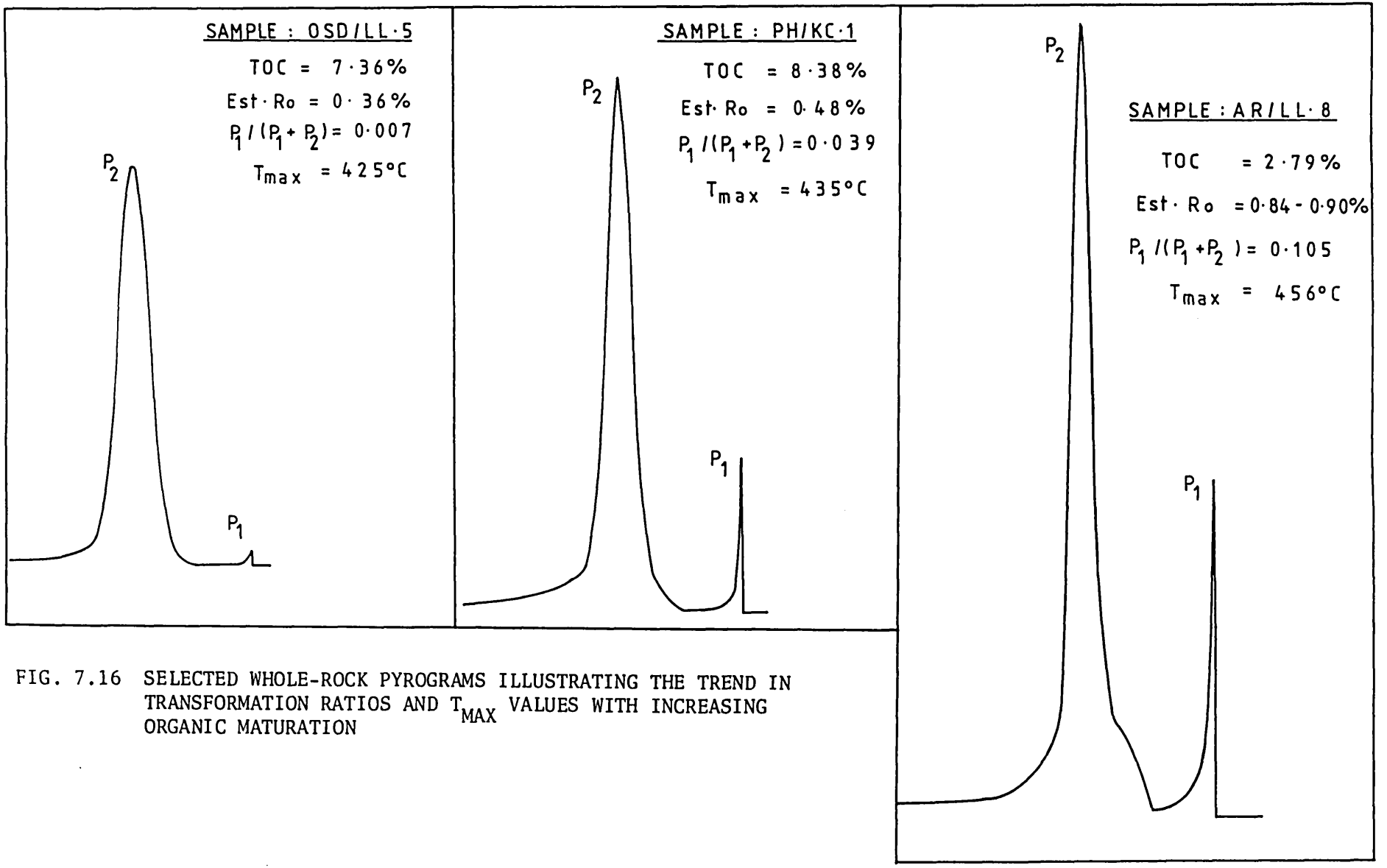


FIG. 7.16 SELECTED WHOLE-ROCK PYROGRAMS ILLUSTRATING THE TREND IN TRANSFORMATION RATIOS AND T_{MAX} VALUES WITH INCREASING ORGANIC MATURATION

kerogen concentrates. The relatively low transformation ratios recorded for the Jurassic samples in this study are indicative of the fact that the degrees of maturation which have been attained by organic matter in this system in most parts of southern England are relatively low.

7.3 INFRA-RED (IR) SPECTROSCOPIC ANALYSIS OF KEROGENS

This method has been used by some workers to examine concentrates of insoluble sedimentary organic matter for clues to both type and degree of maturation of these materials (Tissot et al. 1974; Durand and Espitalie, 1976; Vandenbroucke et al., 1976; Tissot and Welte, 1978; Rouxhet et al., 1980; Dypvik et al., 1979). The IR spectra of shallow, immature kerogens have been shown to reflect the differences of elemental composition due to the origin of the material. Kerogens of types I and II categories which are characterized by high $^{H}/_{C}$ ratios (the parent materials of which contained important contributions of aquatic phyto-planktons and herbaceous plant materials) give intense C-H bands due to aliphatic compounds.

By contrast, the hydrogen-lean type III kerogens, mainly originating from higher plants, give less intense aliphatic C-H bands but very intense C = O and mostly aromatic C = C bands (Fig. 7.17). The application of infra-red technique to kerogen maturation studies is based on the progressive changes in the abundances of these functional groups with increasing kerogen evolution (Fig. 7.18). The first step of kerogen evolution (diagenesis) often

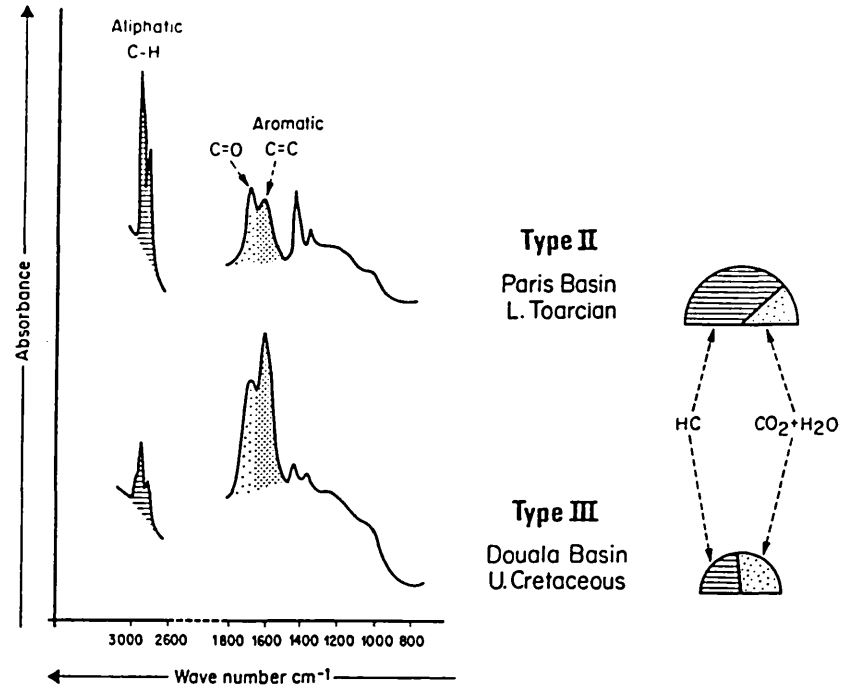


Fig. 7.17—Comparison of the petroleum potential of two different kerogens: type II, Paris Basin; type III, Douala Basin. *Left:* IR spectra recorded on shallow samples show that type II contains more aliphatic material, and type III more aromatic and carbonyl groups. *Right:* the areas of the *half circles* represent the amounts of products yielded upon experimental heating. The respective proportions of hydrocarbons (HC) and carbon dioxide plus water ($CO_2 + H_2O$) are also shown (Tissot et al., 1974)

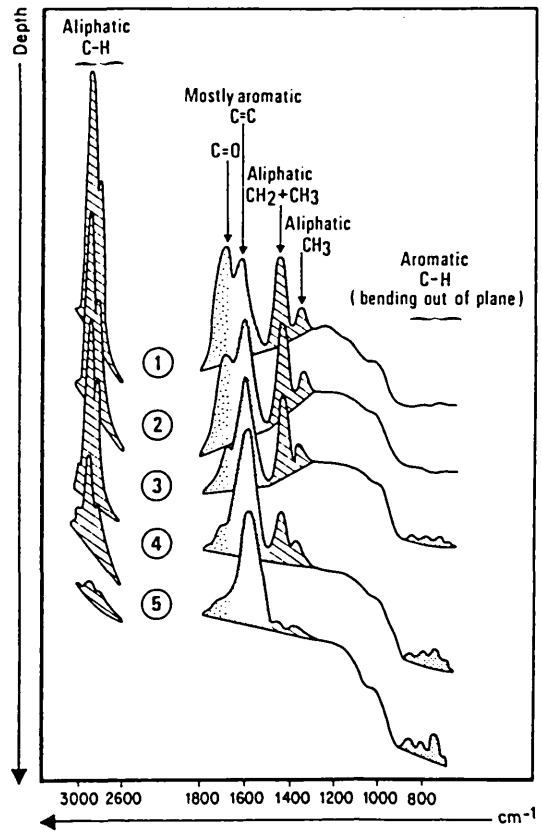


Fig. 7.18— Infrared spectra showing evolution of type-II kerogen during burial (Lower Toarcian, Paris Basin; Silurian, Sahara) (Tissot & Welte, 1978)

marked by an important decrease of the kerogen $^{O}/_{C}$ ratio corresponds to a strong reduction of the C = O band and of the O-H stretching band. During the catagenesis stage, the main known features on the kerogen IR spectra are a progressive reduction of the aliphatic bands correlative to the atomic $^{H}/_{C}$ lowering, rapid completion of the elimination of the residual $^{O}/_{C}$ ratios, and the appearance of aromatic C-H bands from 930 to 700 cm^{-1}. The appearance of these aromatic bands is believed to be due to a desubstitution on aromatic nuclei and possibly to an increasing aromatization of naphthenic rings (Tissot and Welte, 1978).

Infra-red spectroscopy was employed in this study to attempt a differention of some of the kerogen facies identified as well as investigate its use as a maturity indicator. Kerogen samples in both diagenesis (immature) and catagenesis (mature) stages from two wells, Winchester-1 and Arreton-2, were studied by this technique. IR spectra of one type III and two type II samples from Winchester-1 Well are shown in Fig. 7.19. A clear distinction is observed between the spectrum of the immature type III (WCH/KC.2) sample and that of the immature type II (WCH/OC.2) sample in terms of the relative intensities of their aliphatic C-H, C=O, and aromatic C=C bands. A marked reduction in the C=O band relative to the C=C band is noted in the mature Lower Lias type II sample (WCH/LL.3); and the presence of intense aliphatic C-H bands in the spectrum of this sample (i.e. WCH/LL.3) is indicative of the fact that the sample is still at an early mature stage. A similar trend of decreasing intensity of the C=O

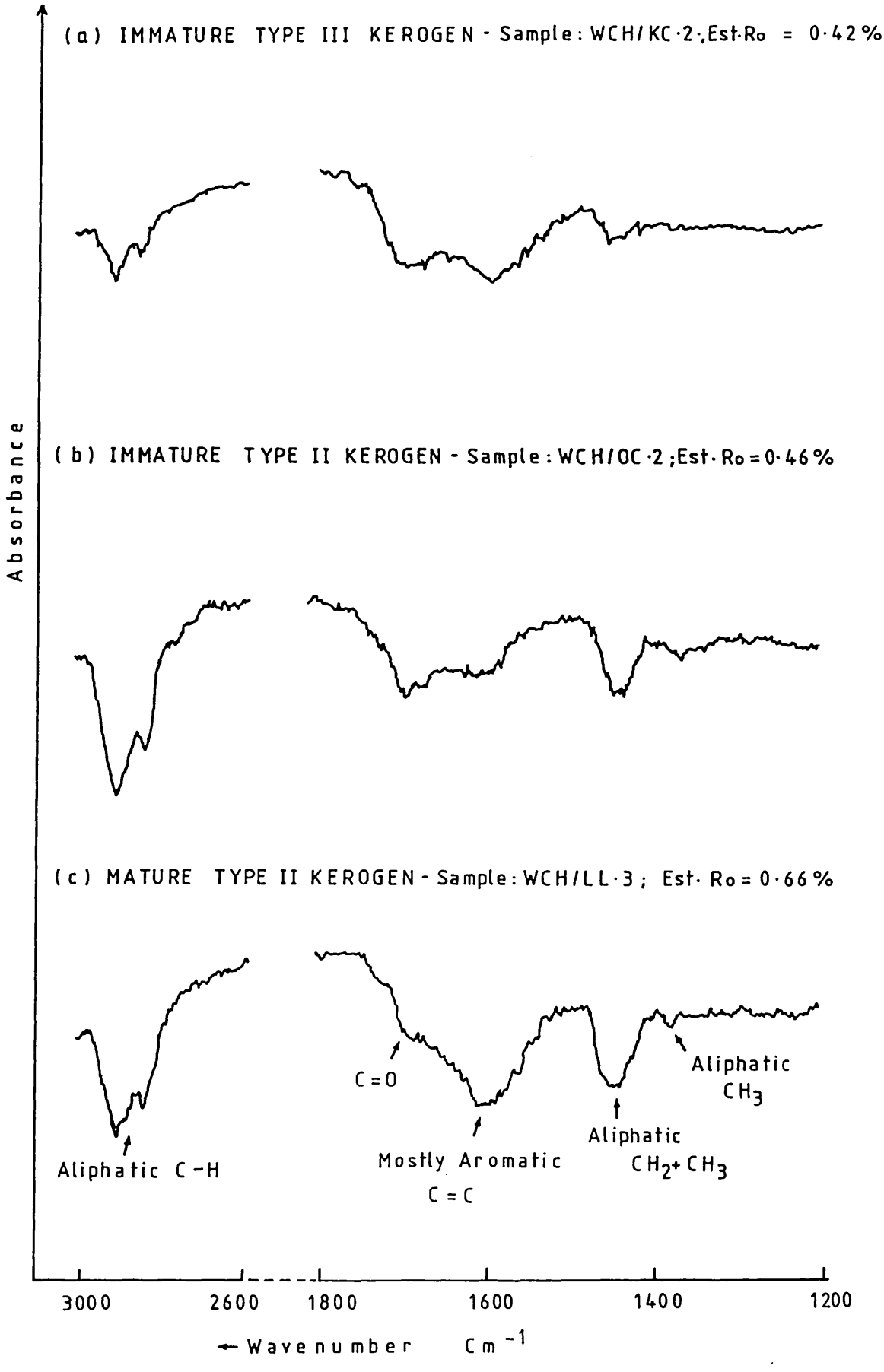


FIG. 7.19 INFRA-RED SPECTRA OF SELECTED KEROGEN SAMPLES FROM WINCHESTER-1 WELL ILLUSTRATING THE STRUCTURAL DIFFERENCES BETWEEN TYPES II AND III AND SHOWING THE EVOLUTION OF TYPE II KEROGENS DUE TO BURIAL

band relative to the aromatic C = C band with increasing maturity is again observed in the spectra of type II kerogen samples from Arreton-2 Well (Fig. 7.20). The presence of a significant residual hydrocarbon potential in the deep, mature Lower Lias sample, AR/LL.7, can be judged from the occurrence of intense aliphatic C-H bands in its IR spectrum.

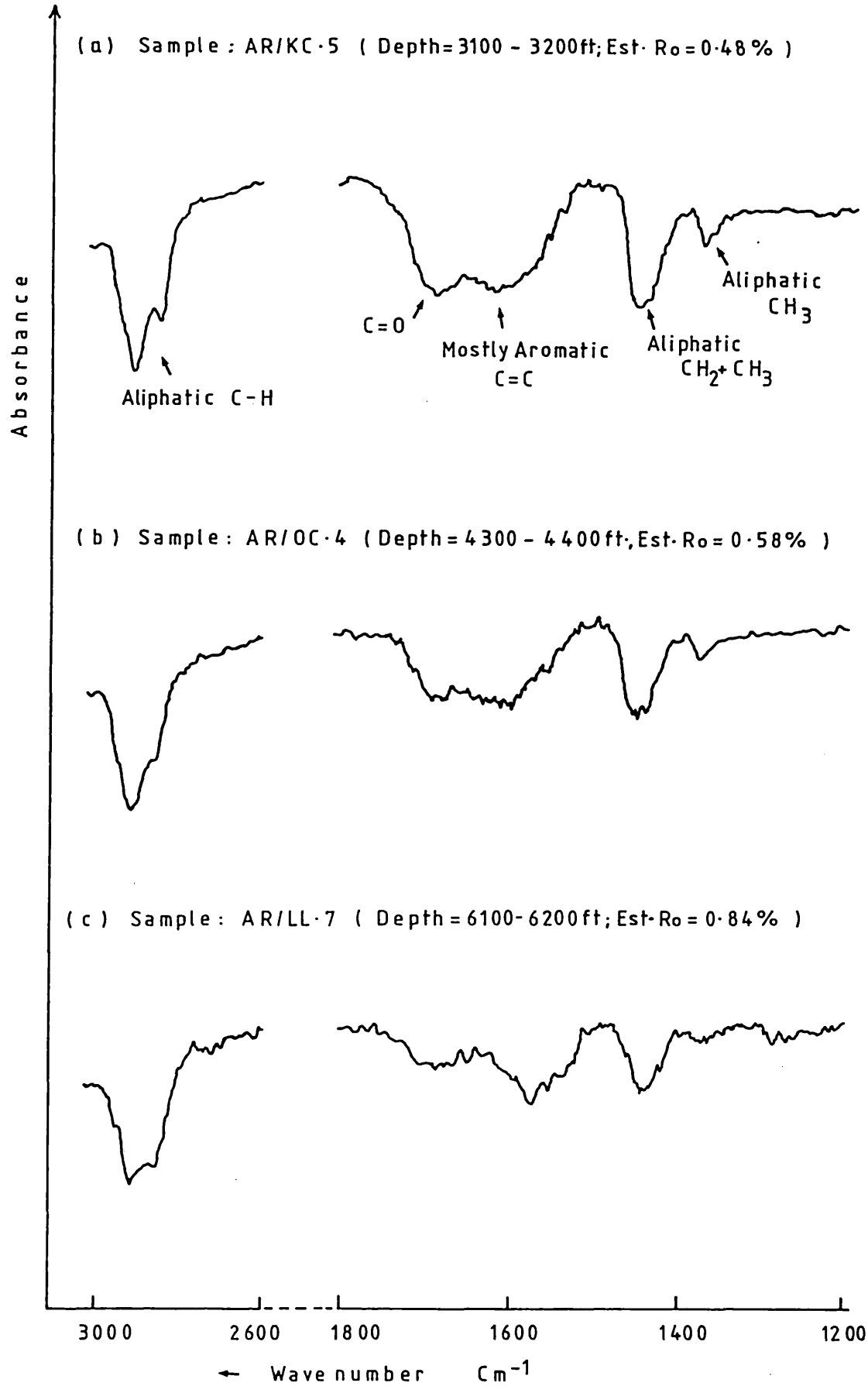


FIG. 7.20 INFRA-RED SPECTRA SHOWING THE EVOLUTION OF JURASSIC TYPE II KEROGENS IN ARRETON NO. 2 WELL

CHAPTER VIII

ORGANIC GEOCHEMISTRY OF SOLUBLE ORGANIC EXTRACTS (BITUMEN) AND SOME DORSET RESERVOIRED OILS

ORGANIC GEOCHEMISTRY OF SOLUBLE ORGANIC EXTRACTS (BITUMEN) AND SOME DORSET RESERVOIRED OILS

8.1 RESULTS AND INTERPRETATION OF BITUMEN ANALYSES

Table 8.1 shows the results of solvent extraction, bitumen de-asphalting, liquid and gas chromatographic analyses. Only selected rock samples from outcrops, Burton Row Well (north Somerset), Winterborne Kingston Well (Dorset), Arreton No. 2 Well (Isle of Wight) Winchester No. 1 Well (Hampshire), Henfield Well (West Sussex) and Penshurst Well (Kent) were analysed for their bitumen contents. The total organic extract (TOE) from each sample is expressed in milligrams/gram organic carbon (mg/g C_{org}). The organic maturity of each sample based on kerogen analysis is also indicated in the table.

8.1.1 Quantity and Composition of Soluble Organic Matter in the Jurassic Samples

Most of the rock samples subjected to solvent extraction are associated with type II kerogens (see Chapter 6). But inspite of the known oil-prone nature of this kerogen type, the total extractable soluble organic matter indicated for these samples in Table 8.1 appears low compared to the values recorded by Tissot et al. (1971) for samples of Early Toarsian shales from the Paris Basin containing similar kerogen type at similar maturity levels. Values close to 200 mg/g C_{org} were reported by these authors for samples at maturity levels below the peak oil generation whereas in the present work no value greater than 100 mg/g

TABLE 8.1 RESULTS OF BITUMEN ANALYSES

Borehole/ Locality	Sample Number	Organic Maturity (est. Ro%)	Total Extract mg/g C org.	De-asphaltening & HPLC					Alkane Ratios				
				Sat. %	Arom. %	Resins %	Asph. %	Sat./ Arom.	Pri/ Phy.	Pri./ $n\text{-}C_{17}$	Phy./ $n\text{-}C_{18}$	$\frac{(Pr.+Phy.)}{n\text{-}C_{17}+n\text{-}C_{18}}$	CPI $(C_{24}\text{-}C_{30})$
Outcrops, Dorset	OSD/KC.2	0.36	14.7	4.1	3.4	66.2	26.3	1.2	0.54	1.87	5.63	3.30	1.68
	OSD/KC.7	0.44	33.3	-	-	-	-	-	-	-	-	-	-
	OSD/KC.12	0.48	25.2	28.4	11.1	36.8	23.7	2.5	1.02	1.37	1.77	1.54	1.03
	OSD/OC.4	0.44	21.0	-	-	-	-	-	0.81	1.44	2.44	1.86	1.31
	OSD/LL.5	0.36	14.5	3.2	4.4	65.6	26.8	0.7	<0.67	2.74	5.82	4.01	2.08
Burton Row Well, North Somerset	BR/LL.3	0.40	37.4	-	-	-	-	-	0.85	-	6.67	-	1.15
	BR/LL.5	0.42	35.0	-	-	-	-	-	0.94	-	4.90	-	1.00
	BR/LL.10	0.45	79.2	51.7	19.2	27.4	1.7	2.7	0.85	1.12	1.40	1.26	1.10
Winterborne Kingston Well, Dorset	WK/KC.2	0.32	5.6	-	-	-	-	-	-	-	-	-	-
	WK/LL.8	0.56	41.9	-	-	-	-	-	1.30	0.59	0.47	0.53	0.97
Winchester-1 Well, Hampshire	WCH/OC.2	0.46	26.2	29.7	14.0	42.0	14.3	2.1	1.75	2.98	2.31	2.70	1.02
	WCH/OC.4	0.48	30.7	-	-	-	-	-	-	-	-	-	-
	WCH/LL.3	0.66	20.0	30.6	19.5	25.7	24.2	1.6	2.59	1.40	0.49	0.92	1.33
Henfield Well, West Sussex.	HN/KC.2	0.40	25.1	20.7	14.7	50.6	14.0	1.4	1.20	1.81	2.14	1.94	1.79
	HN/LL.4	0.62	34.7	21.6	5.7	47.6	25.1	3.8	1.81	1.13	0.63	0.88	1.22

- Not determined

TABLE 8.1 (Cont.) RESULTS OF BITUMEN ANALYSES

Borehole/ Locality	Sample Number	Organic Maturity (est. Ro%)	Total Extract mg/g C org.	De-asphaltening & HPLC					Alkane Ratios				
				Sat. %	Arom. %	Resins %	Asph. %	Sat./ Arom.	Pri/ Phy.	Pri./ $n\text{-}C_{17}$	Phy./ $n\text{-}C_{18}$	$\frac{(Pr.+Phy.)}{n\text{-}C_{17}+n\text{-}C_{18}}$	CPI $(C_{24}\text{-}C_{30})$
Arreton-2 Well, Isle of Wight	AR/KC.2	0.45-0.46	29.8	-	-	-	-	-	0.68	1.21	2.32	1.69	1.37
	AR/KC.4	0.46-0.48	27.9	-	-	-	-	-	-	-	-	-	-
	AR/KC.8	0.50-0.52	36.6	32.0	16.1	47.7	4.2	2.00	1.21	1.44	1.20	1.32	1.35
	AR/OC.1	0.52-0.54	15.6	-	-	-	-	-	-	-	-	-	-
	AR/OC.3	0.54-0.58	33.8	-	-	-	-	-	1.10	-	0.92	-	1.19
	AR/LL.2	0.70-0.74	43.0	-	-	-	-	-	-	-	-	-	-
	AR/LL.4	0.74-0.80	36.4	-	-	-	-	-	-	-	-	-	-
	AR/LL.6	0.80-0.84	57.6	-	-	-	-	-	1.21	0.65	0.57	0.61	1.12
	AR/LL.8	0.84-0.90	38.0	37.7	11.2	39.2	11.9	3.4	1.20	0.79	0.80	0.80	0.95
Penshurst Well, Kent	PH/KC.1	0.48	41.0	-	-	-	-	-	1.09	1.51	1.71	1.60	0.97
	PH/KC.4	0.62	24.8	-	-	-	-	1.3	1.82	0.76	0.64	0.71	1.18
	PH/OC.3	0.74	61.1	36.8	18.1	40.1	5.0	2.0	1.66	0.99	0.70	0.86	0.99
	PH/LL.3	0.82	24.3	35.8	12.4	40.5	11.3	2.9	1.76	1.03	0.67	0.86	1.08

C_{org} was obtained. A number of factors may be responsible for the low bitumen yields noted here for the Jurassic mudrock samples from southern England. The efficiency of extraction is an important factor and this depends on both the extraction method employed as well as the solvent used - the more polar the solvent the better the extract yield (Albrecht et al. 1976). In this project, dichloromethane was the solvent used and the extraction procedure was by stirring the rock powder in 75 ml of solvent for 30 minutes. Sampling and storage of the rock samples can also account for the low extract yields. Rock samples analysed in this study were outcrop samples which may have suffered some weathering, and borehole samples (cores and cuttings) some of which have been in open storage for over 40 years. According to Ekweozor and Gormly (1983), such long sample storage may result in hydrocarbon loss with a concomitant reduction in the amount of extracted bitumen.

Modern theories of petroleum genesis require that petroleum hydrocarbons be generated from kerogen in sediments at depth, under the influence of an increased temperature, mainly from lipid components of organisms incorporated in the sediments during deposition (Jurg and Eisma, 1967; Erdman, 1967; Tissot and Welte, 1978; Hunt, 1979; Kinghorn, 1983). This process should be reflected in a number of changes undergone by sedimentary organic material with increasing depth of burial or thermal maturity such as an increase in TOE, an increase in the ratio of saturated hydrocarbons to total organic carbon and also an increase in the ratio of saturated to aromatic hydrocarbons (Tissot et al. 1971; Albrecht et al.

1976; Claypool, 1978). But as pointed out by Albrecht et al. (1976) and Waples (1980), the above expected evolutionary trends in the soluble organic matter with maturity may not be clearly observable in a lithologic series where there are variations in properties of the insoluble organic matter (kerogen) as well as mineralogy. No regular trends with maturity are noted in the TOE, percentage of saturates and the saturates/aromatics ratio in many of the Jurassic sections considered in Table 8.1. In Chapters 5, 6 and 7 the variations in the mineralogy of the Lower Lias, the Oxford Clay and the Kimmeridge Clay Formations as well as the chemistry of their contained kerogens were highlighted. These factors as well as the possible migration effect in the mature sections are most likely the reasons for the lack of consistent trends in the above named bitumen parameters with maturity. McKirdy and Cook (1980) reported aliphatic/aromatic hydrocarbon ratios of 0.4 to 8.3 for immature samples from Pliocene - Pleistocene calcareous sediments in DSDP Site 262 (Trimor Trough) and the values of this ratio were noted to vary non-uniformly down the borehole. They attributed the variations in the ratio to varying sources of organic matter in the sediments. According to Leythaeuser et al. (1984), the expulsion efficiency of C_{15+} total extract from well depleted sections of early mature source-rock shales (such as along margins of open fractures) can be as high as 23%. Therefore, hydrocarbon migration can constitute an important factor affecting the expected trends in the bitumen parameters.

8.1.2 Aliphatic Hydrocarbon Patterns

Figs. 8.1 - 8.7 are gas chromatograms of some bitumen samples showing n-alkane distributions and the proportions of the isoprenoid hydrocarbons (pristane and pytane) relative to the n-alkanes. Some differences are noted in the alphatic hydrocarbon patterns between the immature and mature bitumen samples. According to Williams and Douglas (1980), the distribution patterns of n-alkanes found in the soluble organic matter of shallow, immature sediments are governed by the nature of the primary organic input to the sediment and as maturity increases, the initial fingerprints are masked by hydrocarbons generated from the thermal degradation of kerogen materials. Two n-alkane maxima in the C_{17} - C_{19} and C_{21} - C_{23} ranges are clearly observable in the chromatograms of most immature samples. A similar observation was made by Williams and Douglas (1980) in the gas chromatograms of saturated hydrocarbon fractions of bitumen extracted from Kimmeridge Oil Shales sampled in the Kimmeridge Bay area. Another observable feature in the gas chromatograms of these immature samples is the presence of an odd-carbon-number predominance in the C_{15} - C_{24} n-alkane range. Studies of hydrocarbons in algae and bacteria suggest that the C_{15} - C_{22} alkanes found in recent marine sediments originate largely from marine phytoplankton and possibly also photosynthetic bacteria, and depending on the composition of the microbiota in the water columnm the principal hydrocarbon contributed to the underlying sediment is likely to be the C_{15}, C_{17}, C_{19}, or C_{21} n-alkanes (or an equivalent alkene)

(cf. McKirdy and Cook, 1980). In the case of blue-green and green algae, the most commonly associated alkane (and/or alkene) is n-C_{17} (Han et al., 1968a; Winters et al., 1969; Gelpi et al., 1970) whereas in the case of photosynthetic diatoms and dinoflagellates it is the n-$C_{21:6}$ alkene (Lee and Loeblich, 1971; Blummer et al., 1971) which upon hydrogenation in the sediment (Rhead et al., 1971) would yield the corresponding alkane. Based on these findings, McKirdy and Cook (1980) concluded that a marked predominance of odd over even carbon-numbered n-alkanes in the range C_{15} to C_{22} is to be expected in young thermally unaltered marine sediments as observed in the present study. The absence of this feature in some immature marine samples is thought to be due to the post-depositional consumption of the odd-carbon-numbered n-alkanes in that range by non-photosynthetic bacteria which convert them into hydrocarbons of higher molecular weight (Han et al., 1968b; Dembicki et al., 1976). The n-alkane maximum observed at n-C_{23} in some immature Jurassic samples is harder to explain. However, Williams and Douglas (1980) are of the opinion that the input of lower land plants may be responsible for this n-alkane maximum based on the finding that n-C_{23} is the major n-alkane associated with peat waxes of sphagnum moss (Corrigan et al., 1973) and phragmites (Morrison and Bick, 1967).

The Carbon Preference Index (CPI) values shown in Table 8.1 range from 2.08 to 0.97 for immature samples (estimated $Ro < 0.5\%$) and from 1.33 to 0.95 for marginally mature and mature samples (estimated $Ro \geq 0.5\%$). Although

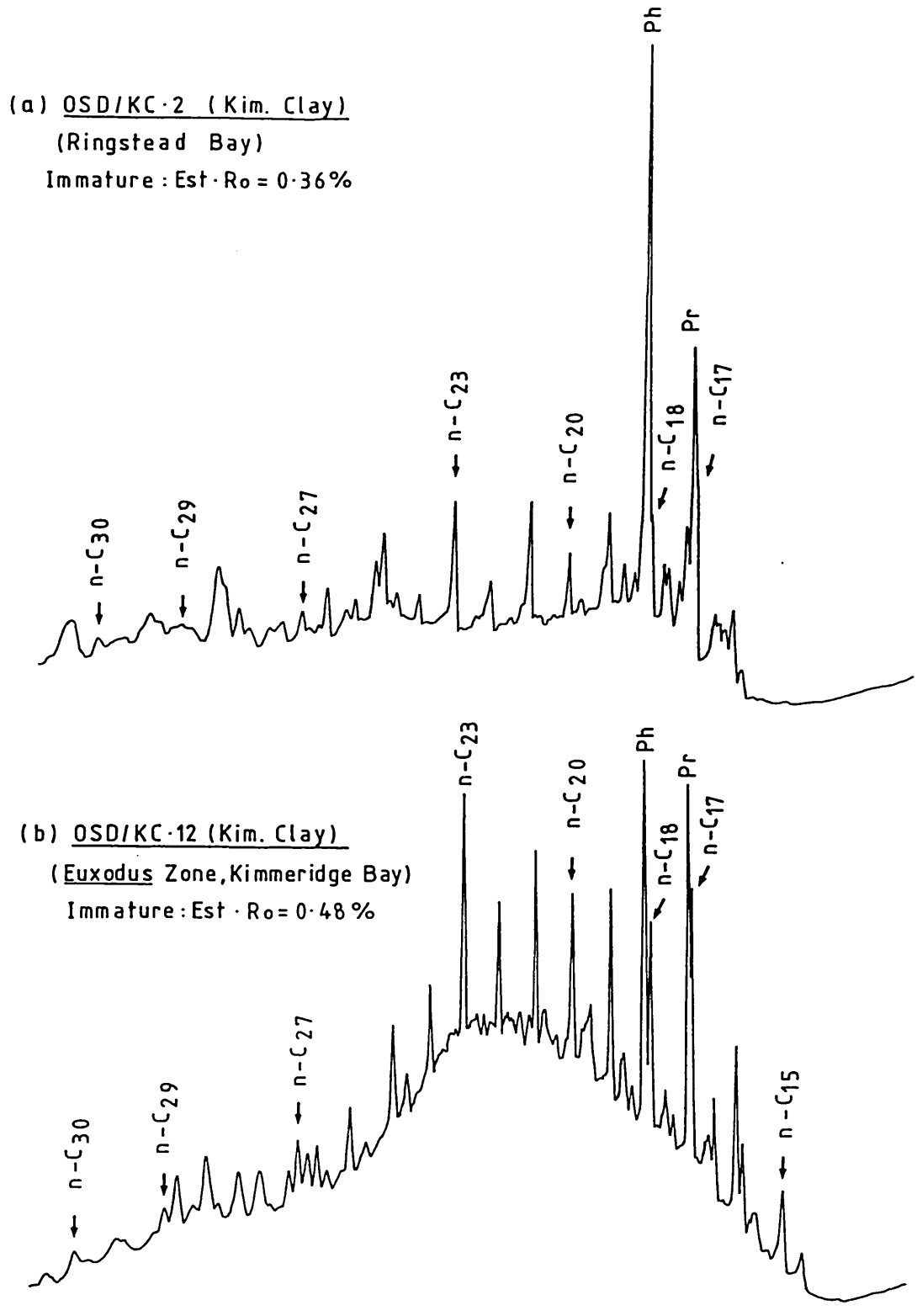


FIG. 8.1 GAS CHROMATOGRAMS OF BITUMEN FRACTIONS OF SOME OUTCROP SAMPLES FROM DORSET [(a), (b), & (d) ARE HYDROCARBON FRACTIONS WHILE (c) IS A DE-ASPHALTED BITUMEN SAMPLE]

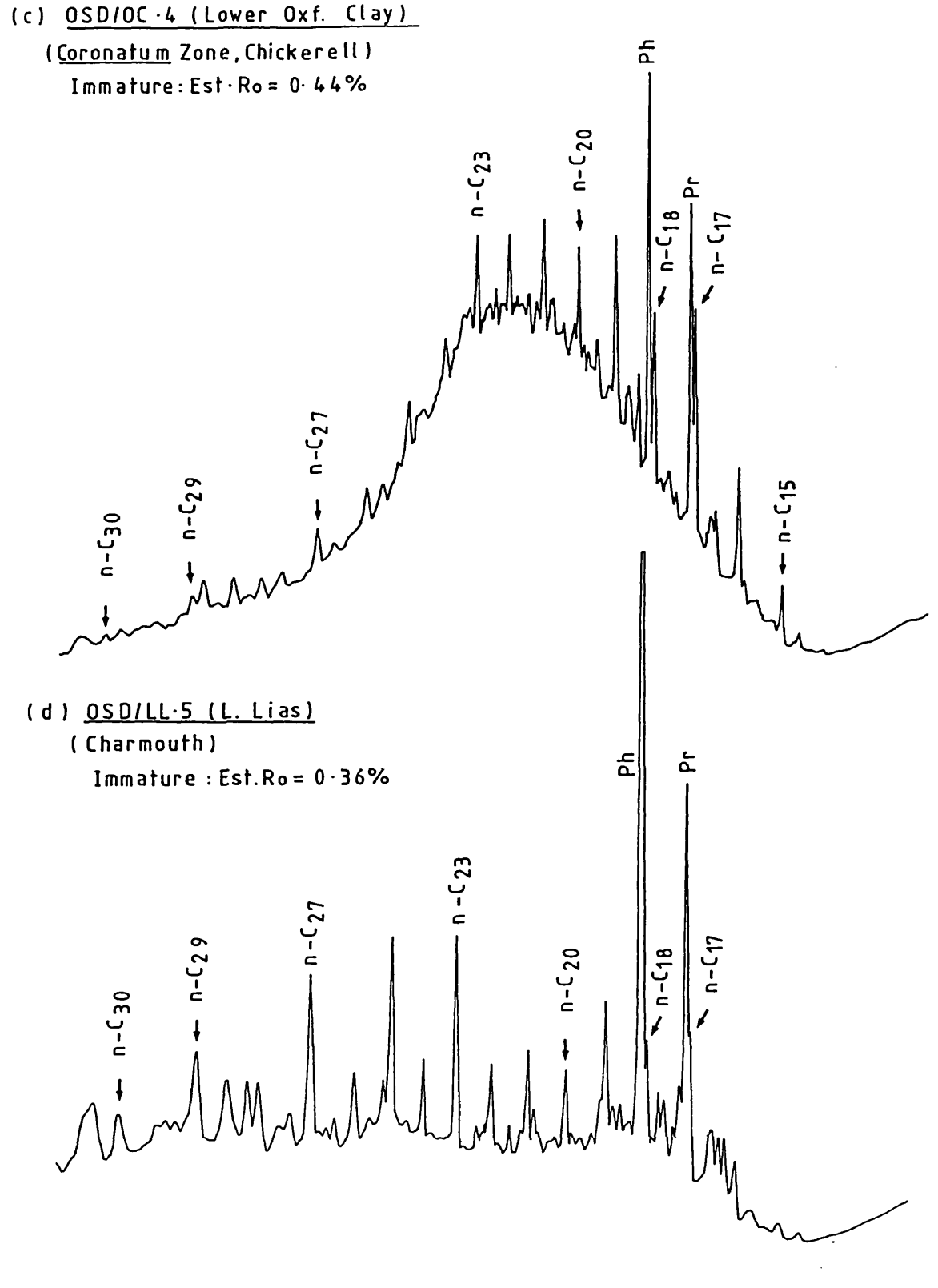


FIG. 8.1 (Cont.): OUTCROP SAMPLES

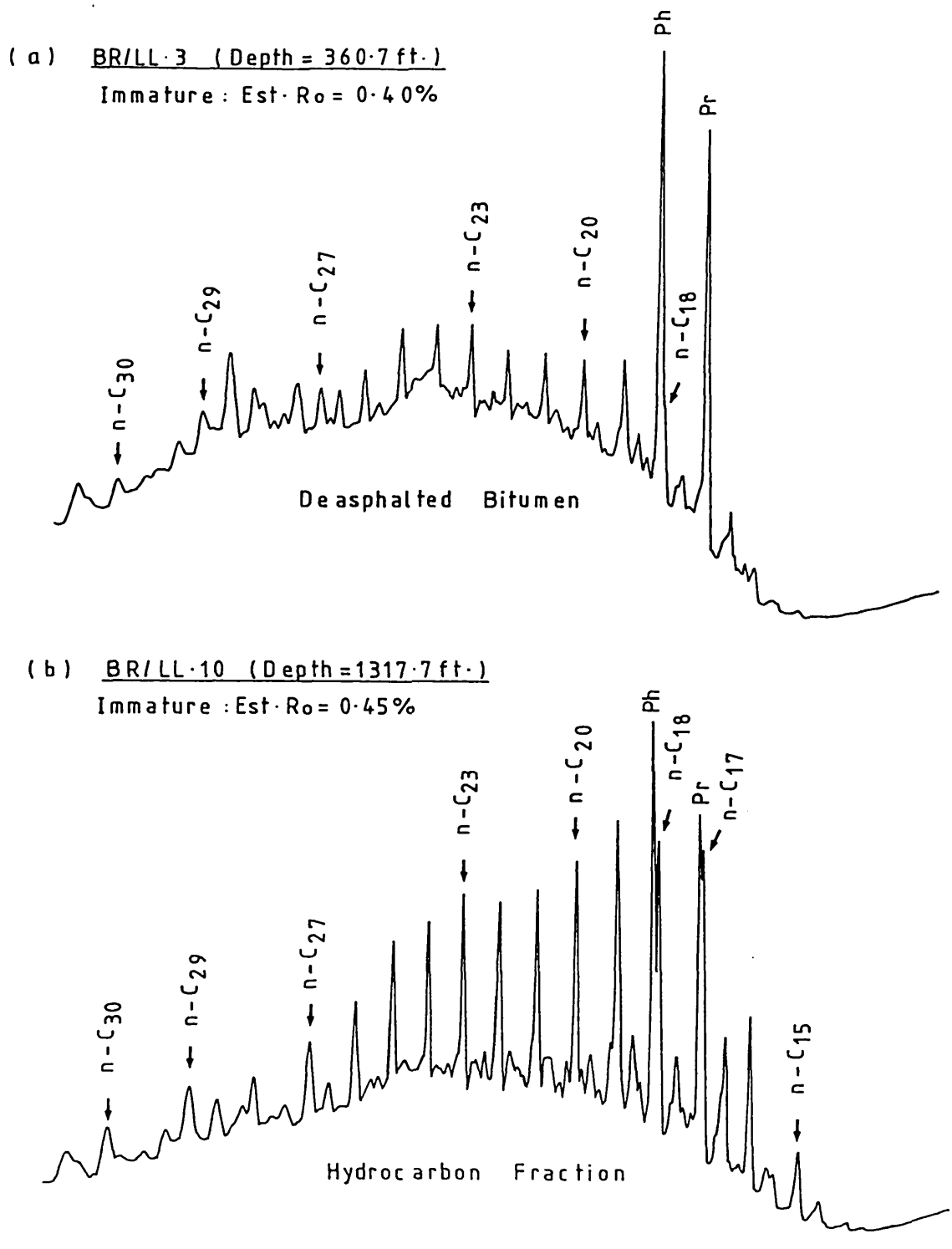


FIG. 8.2 GAS CHROMATOGRAMS OF BITUMEN FRACTIONS OF SOME LOWER LIAS SAMPLES FROM THE BURTON ROW WELL (NORTH SOMERSET)

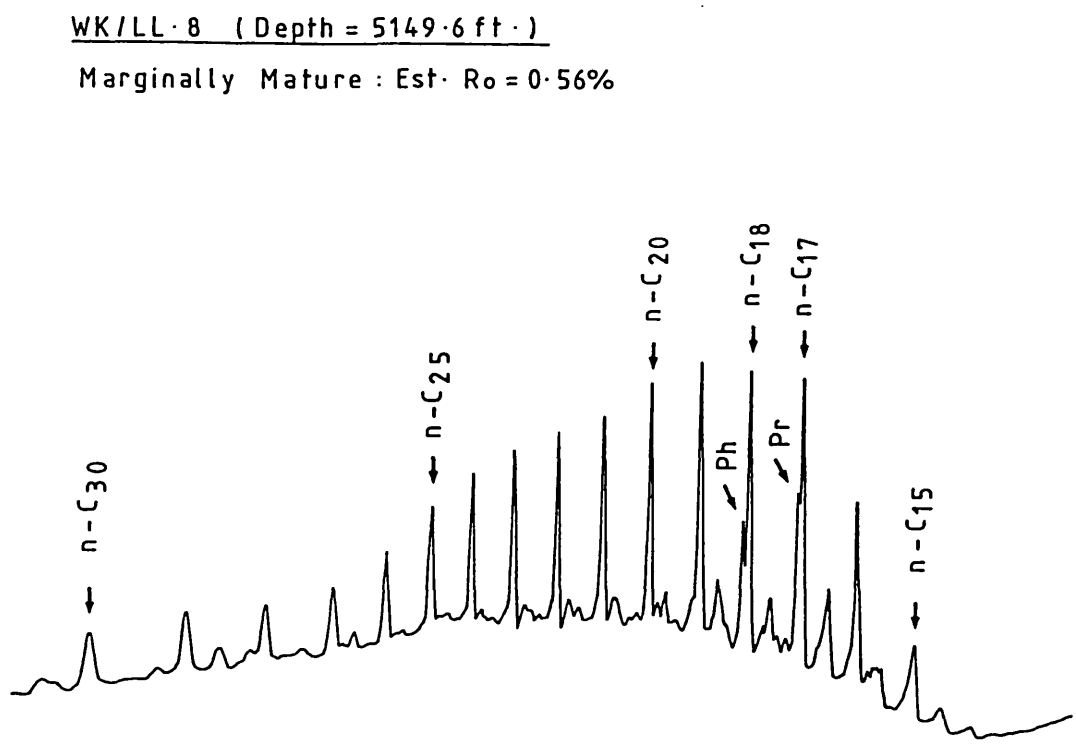


FIG. 8.3 GAS CHROMATOGRAM OF THE DE-ASPHALTED BITUMEN OF A BASAL LOWER LIAS SAMPLE FROM THE WINTERBORNE KINGSTON WELL (DORSET)

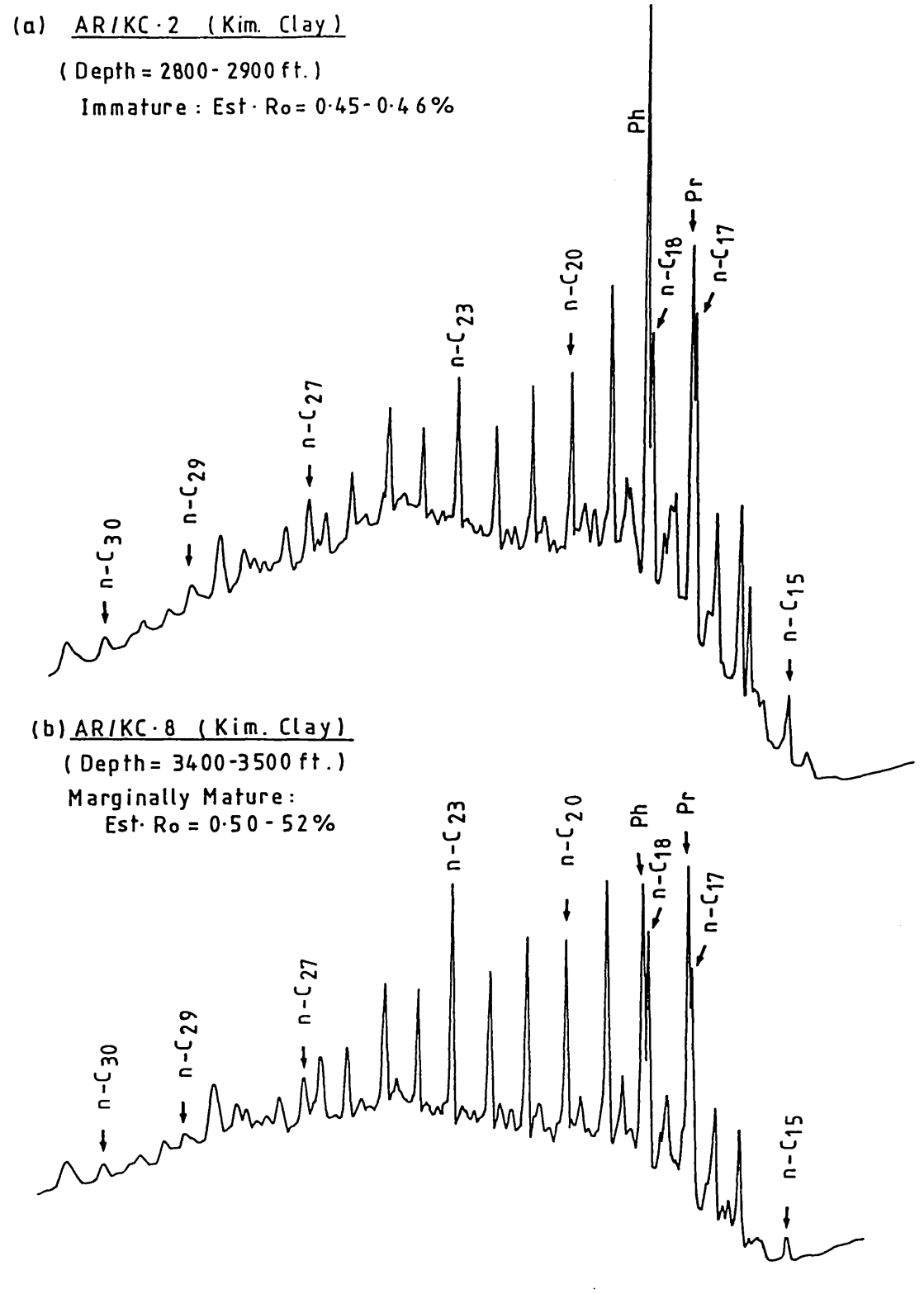
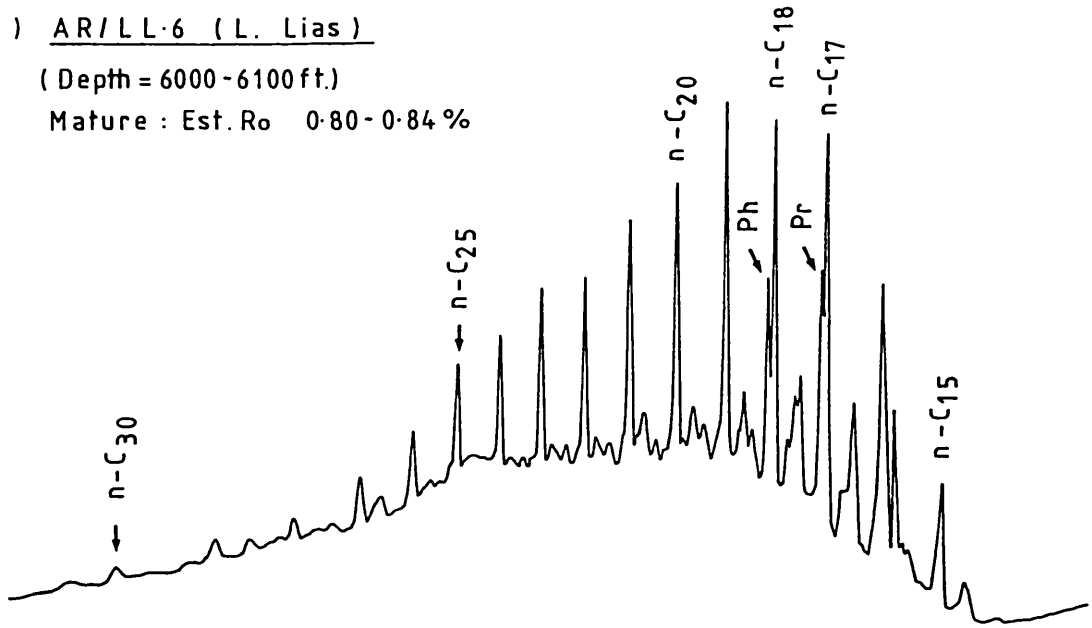


FIG. 8.4 GAS CHROMATOGRAMS OF BITUMEN FRACTIONS OF SOME SAMPLES FROM THE ARRETON NO. 2 WELL (ISLE OF WIGHT) [(a) & (c) ARE DE-ASPHALTED BITUMEN SAMPLES and (b) & (d) ARE HYDROCARBON FRACTIONS]

(c) AR/LL·6 (L. Lias)

(Depth = 6000 - 6100 ft.)

Mature : Est. Ro 0·80 - 0·84 %



(d) AR/LL·8 (L. Lias)

(Depth = 6200 - 6300 ft.)

Mature : Est. Ro 0·84 - 0·90 %

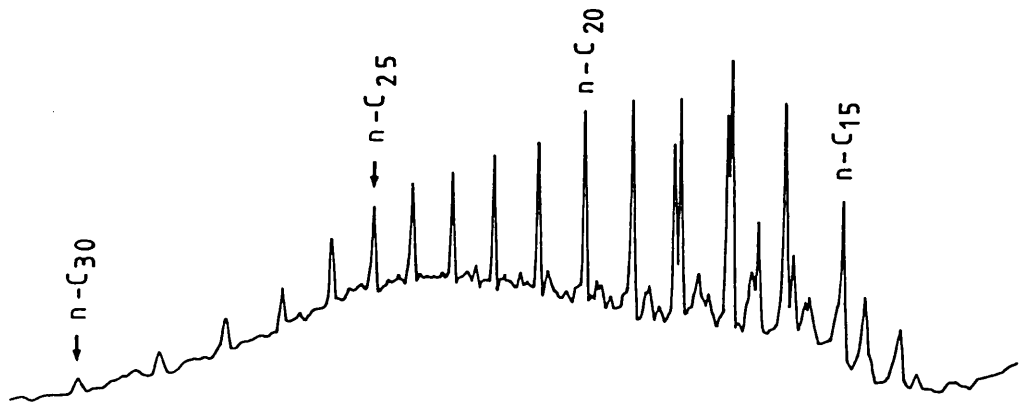


FIG. 8.4 (Cont.): ARRETON NO. 2 WELL

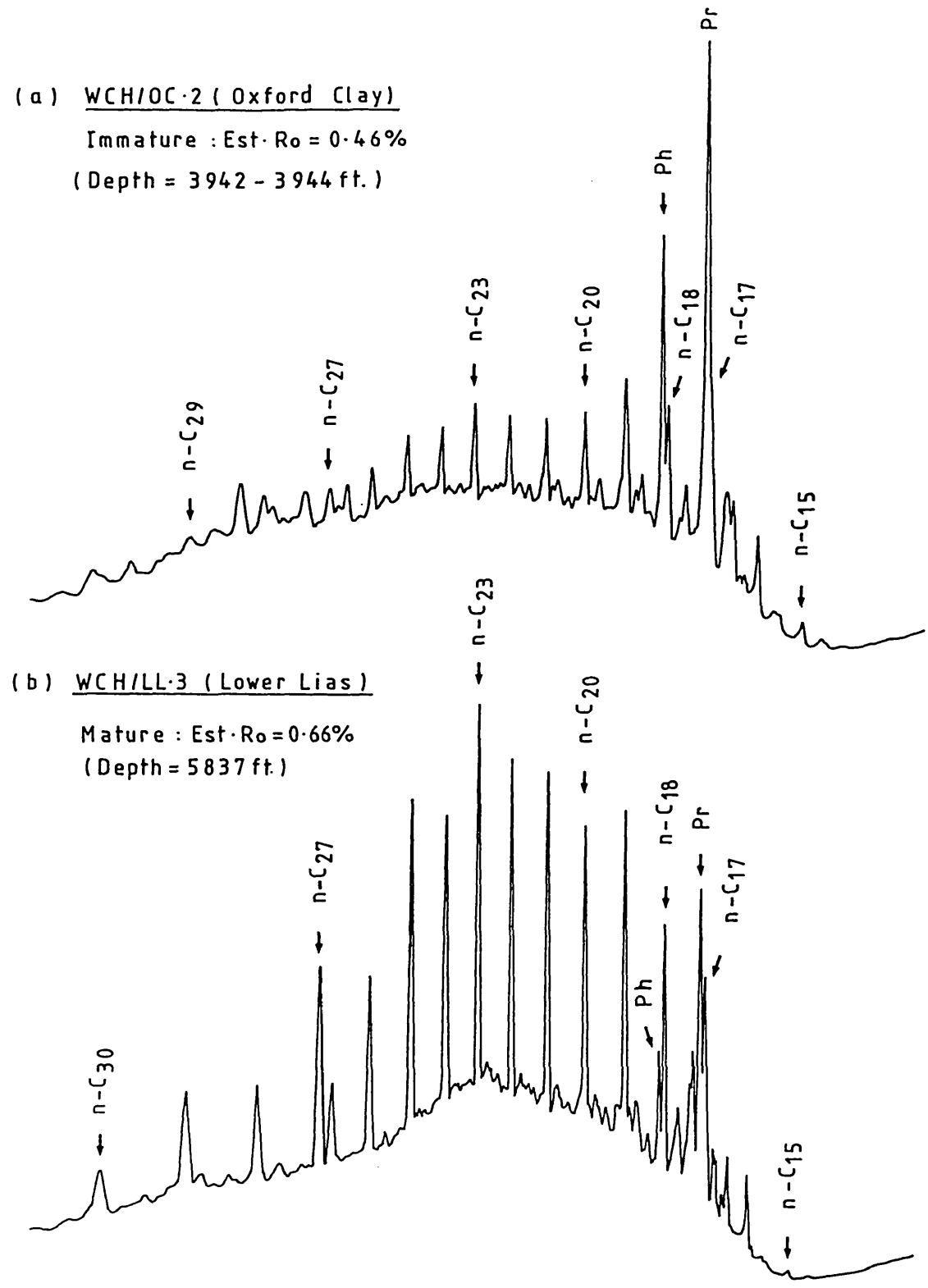


FIG. 8.5 GAS CHROMATOGRAMS OF THE HYDROCARBON FRACTIONS OF SOME BITUMEN SAMPLES FROM THE WINCHESTER NO. 1 WELL (HAMPSHIRE)

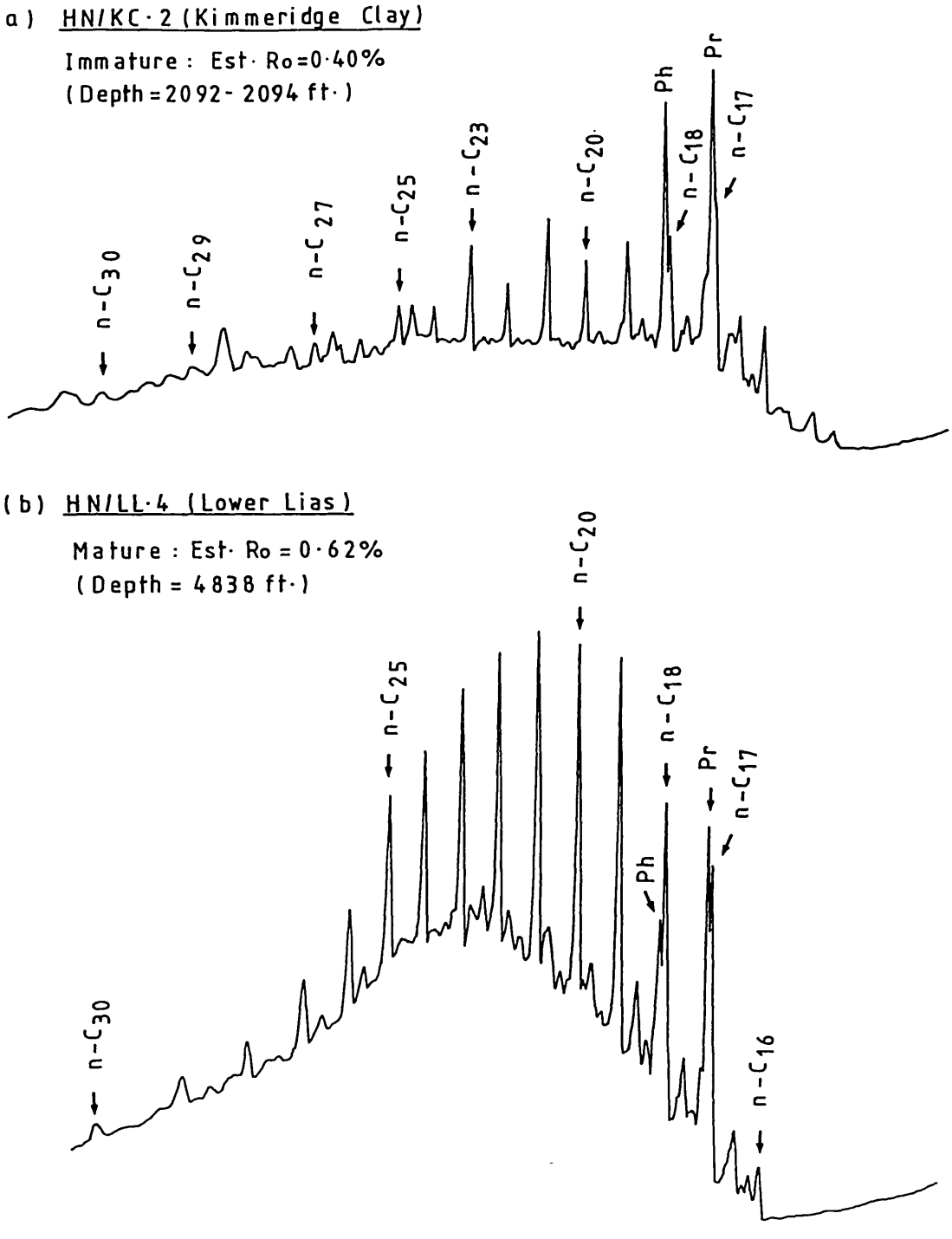


FIG. 8.6 GAS CHROMATOGRAMS OF THE HYDROCARBON FRACTIONS OF SOME BITUMEN SAMPLES FROM THE HENFIELD WELL (WEST SUSSEX)

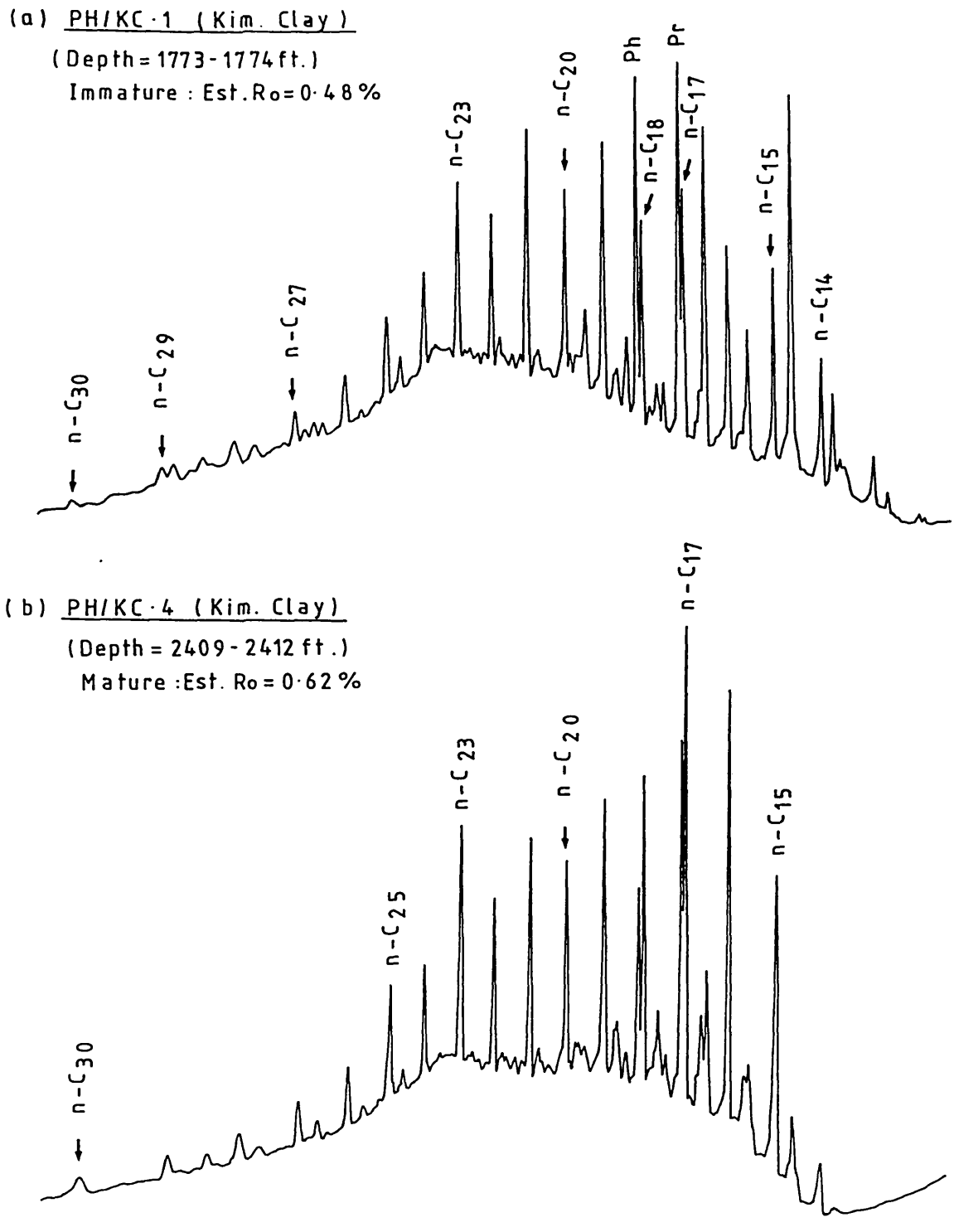


FIG. 8.7 GAS CHROMATOGRAMS OF BITUMEN FRACTIONS OF SOME SAMPLES FROM THE PENSHURST WELL (KENT) [(a) = DE-ASPHALTED BITUMEN; (b)-(d) = HYDROCARBON FRACTIONS]

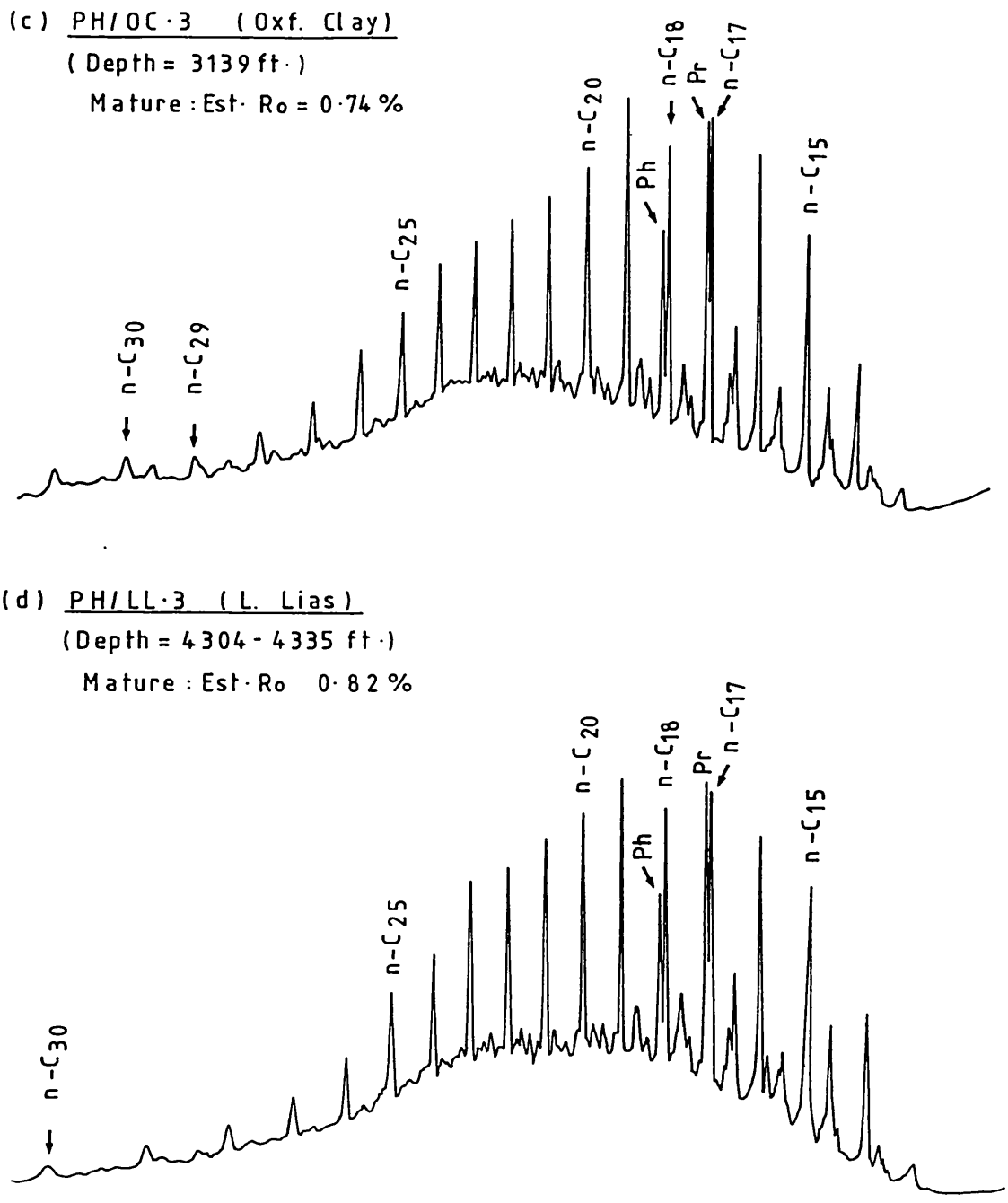


FIG. 8.7 (CONT.): PENSHURST WELL

there is only a small difference in the n-alkane distribution in the C_{24} - C_{30} range between immature and mature samples, the CPI values for all the mature samples are close to unity. CPI values can give an indication of the level of organic maturity within sedimentary rocks where the original organic matter had important contribution from the higher land plant waxes and resins. Bray and Evans (1961) and Philippi (1965) examined the CPI values of the n-alkanes from recent sediments, ancient shales and crude oils, and found that the predominance of odd-carbon-numbered n-alkanes in the C_{24} - C_{33} range decreased from high values in recent sediments to values around 1.0 for crude oils. CPI values approaching unity have been used by Tissot et al. (1971) to indicate increasing maturity of sedimentary organic matter. But as pointed out by Tissot and Welte (1978), the absence of a moderate to strong odd-carbon preference is not necessarily a consequence of catagenesis. Some young and shallow sediments with little or no contribution from terrestrial higher plants have been found to show a distribution of n-alkanes containing many low to medium molecular weight molecules and few n-alkanes beyond C_{25} with a slight or no odd-carbon preference (Powell and McKirdy, 1973; Vandenbroucke et al., 1976; Tissot et al., 1977). This may explain the observation of the small or lack of odd-carbon-numbered n-alkane predominance in the C_{24} - C_{30} range of the immature Jurassic samples from southern England, and since most of the bitumen samples analysed in this study are associated with type II kerogens, this finding confirms the point already mentioned

in Chapter 6 that the Jurassic type II kerogens were derived mainly from marine precursors with little contribution from the terrestrial higher plants.

The isoprenoid alkanes - pristane and phytane - are noted to make important contributions to the total hydrocarbon fractions of all immature samples (see Figs. 8.1 - 8.7). In these immature samples, the n-alkanes are observed to be subordinate to pristane and phytane whereas in the mature samples the n-alkanes are comparable to or slightly predominant over these isoprenoids. A similar observation was made by Claypool et al. (1978) for samples of Black Shale Members of the Phosphoria Formation of Western Interior U.S.A. The pristane/phytane (^{Pr}/Ph) ratios for these kerogen type II - associated immature bitumen samples vary from less than to slightly higher than 1.0 (see Table 8.1). ^{Pr}/Ph ratios lower than unity in immature samples are known to be indicative of a reducing environment of organic deposition whereas values higher than 1.0 have been shown to indicate oxidising depositional environment (Brooks et al., 1969; Didyk et al., 1978). Thus the range of values of this ratio noted for the immature samples in this study is indicative of the fact that the depositional environment for the Jurassic type II kerogen precursors was not entirely uniform but varied from very reducing to slightly oxidising. The ^{Pr}/Ph ratio of sedimentary organic matter has been shown to increase with increasing thermal maturity, (Brooks et al., 1969, Leythaeuser and Welte 1969; Simoneit et al., 1981).

However, with increasing thermal maturity the geochemical fossils such as pristane and phytane become increasingly diluted by the newly formed alkanes resulting from kerogen degradation. This is reflected in the progressive reduction with maturity in the ratios of these isoprenoid hydrocarbons to their associated n-alkanes (Tissot et al. 1971; Tissot and Welte, 1978; Connan and Cassou, 1980). Values of $^{Pr}/n\text{-}C_{17}$, $^{Ph}/n\text{-}C_{18}$, and $^{(Pr+Ph)}/(n\text{-}C_{17}+n\text{-}C_{18})$ ratios for the samples analysed by gas chromatography are given in Table 8.1. It is noted that these ratios are lower in the mature samples than in the immature ones although their reductions with maturity are not consistent. This observation of the apparent absence of a uniform reduction in these ratios with increasing maturity may be due to variations in the depositional environment as well as the nature of the organic precursors (Lijmbach, 1975). Leythaeuser et al. (1984) have also pointed out that these ratios, particularly the $^{Pr}/n\text{-}C_{17}$, may be affected by the degree of hydrocarbon expulsion from mature sequences since pristane and phytane have approximately half the expulsion efficiencies of their straight-chain isomers - $n\text{-}C_{19}$ and $n\text{-}C_{20}$ respectively.

The above aliphatic hydrocarbon patterns displayed by the Jurassic bitumen samples seem to correlate well with the maturation levels of their associated kerogens thus supporting the conclusions, given in Chapter 6, on the maturity of organic matter in the three Jurassic formations across southern England.

8.2 ANALYSES OF SOME DORSET OILS AND THEIR CORRELATION

Table 8.2 shows the results of some organic geochemical analyses of three Dorset reservoired oils namely the Cornbrash Oil from the Kimmeridge Bay, the Bridport Oil and the Sherwood Oil both from the Wytch Farm Oilfield. The three oils are shown to be high in saturated hydrocarbons and low in asphaltenes contents. But they are noted to vary in their saturates to aromatics ratios with the Cornbrash Oil showing the highest value of 8.5 followed by the Sherwood Oil with a value of 5.9 and then the Bridport Oil with the least value of 3.1. The three oils thus seem to differ on compositional basis. Genetically related oils can vary in their compositions as a result of numerous factors including source bed variation and maturity, degree of hydrocarbon expulsion, migration, and thermal alteration of pooled oils (Connan et al. 1975; Fuex, 1979; Kinghorn, 1983, Sofer, 1984; Leythaeuser et al. 1984). Migration and thermal alteration are known to improve oil quality by reducing the concentration of polar as well as high molecular weight compounds with a resulting increase in the saturates/aromatics ratio. The depths of occurrences of the three oils range from 1,791 ft to 5,594 ft. (546 - 1,705 metres) (see Table 8.2) and based on the present-day average geothermal gradient of $30^{o}C/km$ (J. Wheildon, pers. comm.) in Southern England, the temperature range of the reservoirs is 20^{o}-$60^{o}C$. No significant differential thermal alterations of the crude oils are feasible within such a temperature interval.

TABLE 8.2 ORGANIC GEOCHEMICAL ANALYSES OF THE DORSET CRUDE OILS

Depth of Reservoir (Ft.)	Sample	API* Gravity	De-asphaltening & HPLC					Alkane Ratios						Isotope Ratios	
			Sat. %	Arom. %	Resins %	Asph. %	Sat./ Arom.	Pri/ Phy.	Pri/ n-C_{17}	Phy./ n-C_{18}	$\frac{(Pri+Phy)}{n\text{-}C_{17}+n\text{-}C_{18}}$	$\frac{n\text{-}C_{21}+n\text{-}C_{22}}{n\text{-}C_{28}+n\text{-}C_{29}}$	CPI $\frac{(n\text{-}C_{24}-C_{30})}{}$	$\delta^{13}C_{PDB}$ (‰)	δD_{SMOW} (‰)
1791	Cornbrash Oil (Kimmeridge Bay)	-	82.2	9.7	6.7	1.5	8.5	1.41	0.58	0.49	0.54	4.15	1.02	-29.8	-68
3038-3225	Bridport Oil (Wytch Farm Field)	35-37°	56.6	18.1	23.2	2.1	3.1	1.45	0.69	0.56	0.63	3.54	1.04	-28.5	-133
5156-5594	Sherwood Oil (Wytch Farm Field)	38-42°	67.5	11.4	17.8	3.3	5.9	1.30	0.61	0.52	0.56	4.21	0.98	-29.5	-108

* API gravity data from Colter and Havard, 1981.

The API gravity of the Bridport Oil (= 35 - 37°) is lower than that of the deeper Wytch Farm Oil in the Sherwood Sandstone Group (= 38 - 42°). The API gravity of oils have been used by some workers as a maturity indicator with values increasing with increasing thermal alteration (e.g. Waples, 1980; Evans et al. 1971). But Evans et al. (1971) also pointed out that the API gravity of original oils can vary depending on the source materials and the environments from which the oils evolved. Clastic environments composed of sands and shales tend to yield an original oil of medium gravity and low sulphur content, whereas carbonate and evaporite environments yield an original oil that is considerably heavier and richer in sulphur. Migration can also influence the API gravity of pooled oils depending on the type of rocks which provided the migration fairways and the distance over which migration occurred: heavy polar compounds are removed by adsorption on clay minerals resulting in a tendency for the migrating oil to become lighter (Kinghorn, 1983).

The infra-red spectra of the 3 oils shown in Fig. 8.8 seem to conform with the results of liquid chromatography. The spectra show the aromatic fractions of the oils to be subordinate in proportion to that of the aliphatic hydrocarbon fractions. The higher content of the aromatic compounds in the Bridport Oil compared to the other two oils is also portrayed by the infra-red spectra.

Fig. 8.9 shows the gas chromatograms of the hydrocarbon fractions of the oils. The presence of the full range of n-alkanes in the C_{15} - C_{30} range with very similar

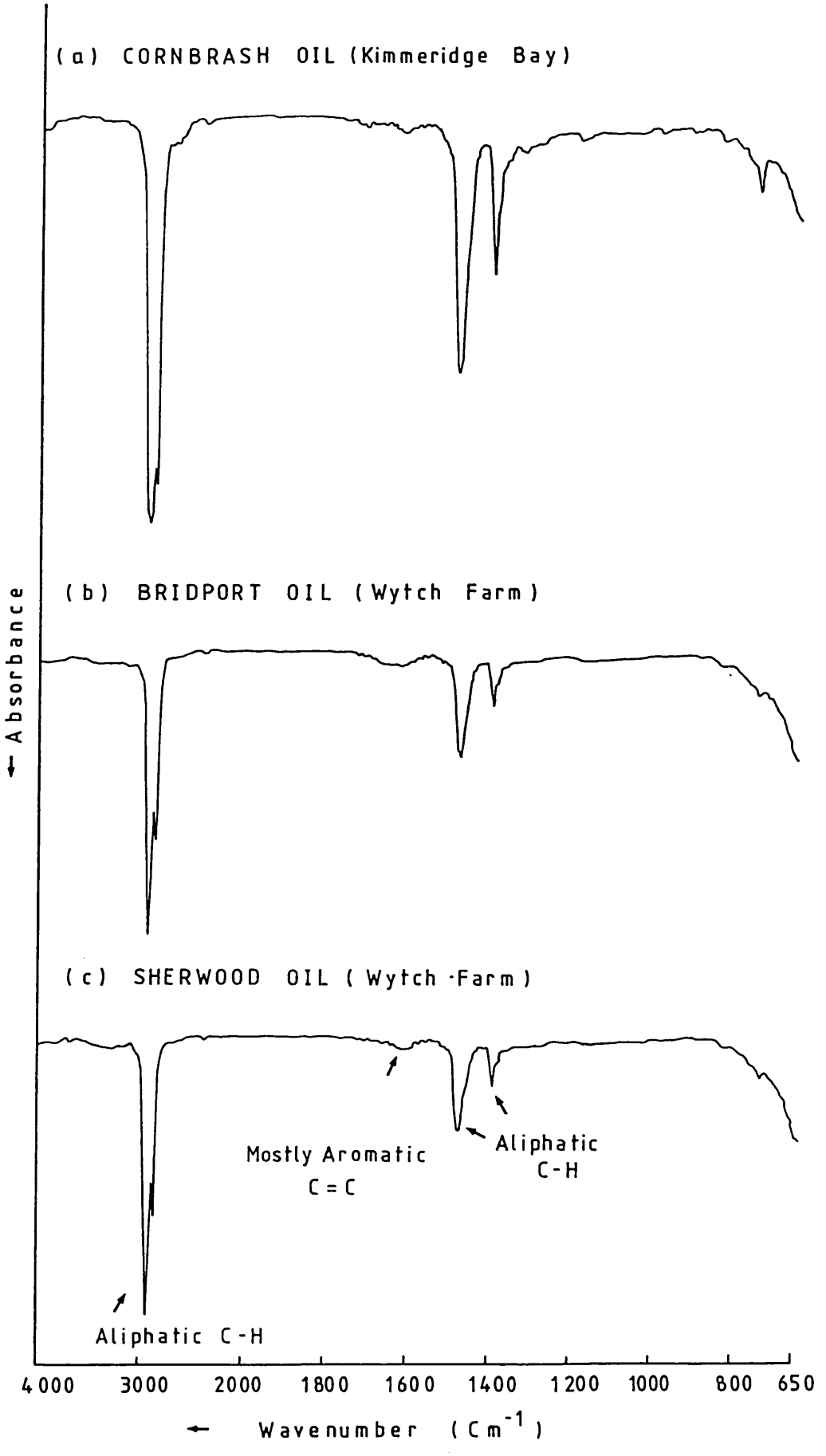


FIG. 8.8 INFRA-RED SPECTRA OF THE THREE DORSET CRUDE OILS

distribution shows that non of the oils has suffered biodegradation as well a significant differential thermal alteration, (William and Winters, 1969; Evans et al., 1971; Bailey et al., 1973; Connan et al., 1975). A single maximum at n-C_{17} is observed in the n-alkane distribution of each of the 3 oils. All the oils show very similar alkane ratios with CPI values of about 1.0. Their ^{Pr}/Ph ratios in the range 1.30 - 1.45 suggest that the oils have been sourced mainly by organic matter deposited in a slightly oxidising environment. That the oils are dominantly marine in origin is indicated by the high $(C_{21} + C_{22})/(C_{28} + C_{29})$ n-paraffins ratios of 3.54 to 4.21 - within the 1.5 - 5.0 range obtained by Philippi (1974).

The $\delta^{13}C_{PDB}$ and δD_{SMOW} values of the oils (topped) are also presented in Table 8.2. The $\delta^{13}C$ values show a narrow range of -28.5 to -29.8‰ for the 3 oils with a spread of 1.3‰ . According to Sofer (1984), such a spread is quite acceptable for genetically related oils taking into account the fact that isotopic variations in the source beds can result in isotopic variations in the oils of a magnitude larger than 2‰. The $\delta^{13}C$ values for the oils are noticed to vary very consistently with their saturates/aromatics ratios: the Cornbrash Oil with the highest ratio of 8.5 is isotopically the lightest ($\delta^{13}C$ = -29.8‰) and the Bridport Oil with the lowest ratio of 3.1 is the heaviest isotopically ($\delta^{13}C$= -28.5‰). The above results are consistent with the fact that the aromatic hydrocarbon fraction in petroleum is isotopically heavier ($\delta^{13}C$) than the associated saturated hydrocarbon fraction (Stahl, 1977a and b; Sofer, 1984). The hydrogen

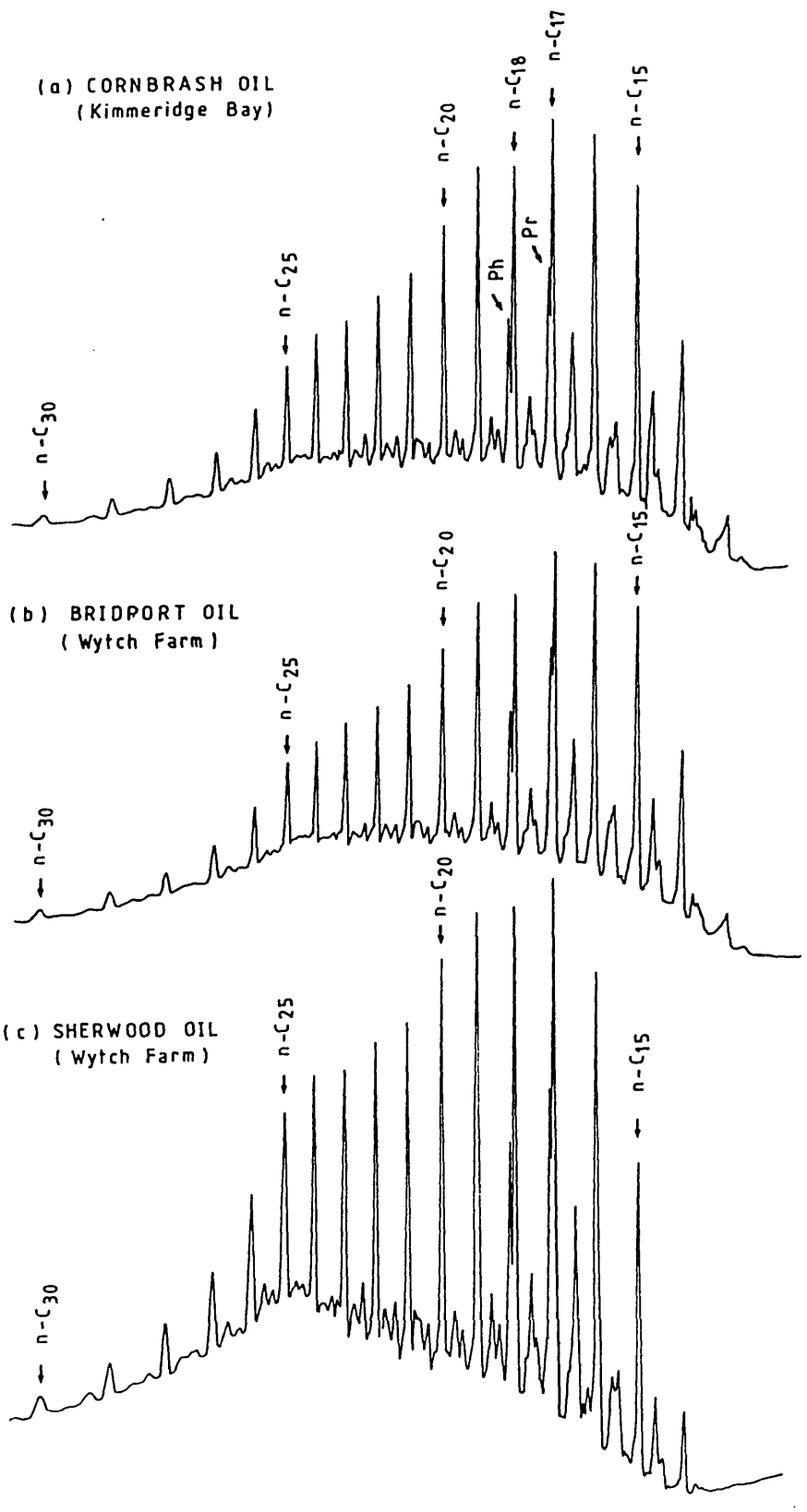


FIG. 8.9 GAS CHROMATOGRAMS OF THE HYDROCARBON FRACTIONS OF THE THREE DORSET CRUDE OILS

isotope ratios (δD) for the oils show a rather wide range as well as a trend contrasting to that of the $\delta^{13}C$ values: the Cornbrash Oil is the heaviest with δD value of -68‰ while the Bridport Oil is the lightest with a δD value of -133‰ . No clear distinction seems to have been made yet between the hydrogen isotopic compositions of the saturated and aromatic hydrocarbon fractions of crude oils (Yeh and Epstein, 1981).

Thus based on the very similar n-paraffin distributions and the alkane ratios as well as the very narrow range of topped oil $\delta^{13}C$ values (Fuex, 1977, Ross, 1980; Sofer, 1984), it may be concluded that the three Dorset oils appear to have been derived from the same source rock or similar source rocks.

8.3 OIL - SOURCE CORRELATION

Welte et al. (1975b) and Alexander et al. (1981) listed a number of prime parameters which can be used for oil - source rock correlations. These include investigation of steroid and triterpenoid hydrocarbons of the C_{27+} cyclic molecules, n-alkane distributions, CPI values, pristane/phytane ratios, isoprenoid/n-alkane ratios, and carbon isotope studies of both the whole oils/soluble organic extracts and their fractions. Yeh and Epstein (1981) have demonstrated the use of hydrogen isotope ratios (δD) in oil-source correlations. Kinghorn (1983) has pointed out that oil-source rock correlation can be problematic because one is comparing an unmigrated bitumen with a migrated hydrocarbon mixture which may have been altered. According

to Leythaeuser et al. (1984), primary migration of hydrocarbons from shale source rocks can occur with chromatographic fractionation depending on the level of maturation of organic matter and the degree of expulsion of the generated bitumen, and this chromatographic effect can result in pronounced compositional discrepancies between reservoired crude oils and the extracts of their associated source rocks. Their calculation of expulsion efficiences showed a strong decrease with increasing chain length of n-alkanes in well depleted early mature shales. More over, genetically related oils and source rocks may undergo differential levels of thermal maturation after separation of the oil from the source rock, giving differences in the pristane/phytane and isoprenoid/n-alkane ratios.

However, on the bases of n-alkane distributions and alkane ratios, the mature Lower Lias samples from Arreton No. 2 Well (Isle of Wight) (AR/LL.6 and AR/LL.8) and the marginally mature basal Lower Lias sample from the Winterborne Kingston Well (Dorset) (WK/LL.8) show good correlations with the three Dorset oils (see Tables 8.1 and 8.2; and Figs. 8.3, 8.4 and 8.9). Alexander et al. (1981) suggested that for good oil-source correlation the alkane ratios of the correlated source rock extract should be within the following limits of the oil:- $^{Pr}/Ph$ ratio $\pm$ 0.6; $^{Pr}/n\text{-}C_{17} \pm 0.8$; $^{Ph}/n\text{-}C_{18} \pm 0.8$; $^{(Pr+Ph)}/(n\text{-}C_{17} + n\text{-}C_{18}) \pm 0.6$; and CPI $\pm$ 0.05. The above selected samples are noted to satisfy most of these conditions. For a further test of the correlation of the Lower Lias bitumen from the two wells with the oils, some samples were subjected to carbon

and hydrogen isotopic analyses. The hypothesis of crude oil-source rock extract correlation by these stable isotopic measurements is based on the thinking that genetically related organic materials should be isotopically similar since there are no significant hydrogen and carbon isotopes fractionations during petroleum migration and maturation processes (Stahl, 1977b; Fuex, 1977; Yeh and Epstein 1981; Sofer, 1984). According to the existing theoretical considerations on the kinetics of petroleum generation, a crude oil should be similar to or isotopically lighter than its source rock extract and the extract isotopically lighter than the kerogen if the crude oil and the organic matter of the rock believed to be the source rock are genetically related. However, some exceptions from this rule have been noted (Welte et al., 1975b; Stahl, 1976). The $\delta^{13}C$ and δD values of selected Lower Lias extracts from Arreton-2 and Winterborne Kingston Wells are shown in Table 8.3. On the basis of these isotope data, it can be seen that the Lower Lias samples from Arreton No. 2 Well appear to correlate more with the 3 Dorset crude oils than the sample from Winterborne Kingston Well. The Lower Lias sample from the latter Well (WK/LL.8) is isotopically (both $\delta^{13}C$ and δD) lighter than the 3 oils, and the marginal maturity level (< 0.6% Ro) of kerogens in the basal parts of the Lower Lias Formation in this Well (Winterborne Kingston) suggests that expulsion of commercial quantities of hydrocarbons from this locality may not have commenced yet. Similarly, the low maturity levels of the Kimmeridge Clay and the Oxford Clay organic matter in Arreton No. 2 Well (i.e.< 0.6% Ro) show that little or no hydrocarbon expulsions from these Jurassic sections

TABLE 8.3 CARBON AND HYDROGEN ISOTOPE RATIOS OF BITUMEN OF SELECTED LOWER LIAS SAMPLES FROM WINTERBORNE KINGSTON AND ARRETON-2 WELLS

Well	Sample No.	Isotope Ratios	
		$\delta^{13}C_{PDB}$ (‰)	δD_{SMOW} (‰)
Winterborne Kingston	WK/LL.8	-30.0	-145
Arreton No. 2	AR/LL.2	-29.6	-96
	AR/LL.4	-30.5	-93
	AR/LL.8	-28.9	-103

have occurred yet.

It may thus be concluded that the mature Lower Lias Formation in the locality of Arreton No. 2 Well to the south of the Purbeck - Isle of Wight Disturbance (see Fig. 6.5) is the main source of the 3 Dorset crude oils.

The findings of the present work has clarified the statement by Colter and Havard (1981) that "geochemical analysis suggested that not only do the Kimmeridge Clay, the Oxford Clay and the Lias of Arreton No. 2 contain rich potential source rocks, but that they are at or close to maturity". The oil-source correlation discussed above is in favour of the migration model for the Wytch Farm Oils suggested by Colter and Havard (1981) which considers the oils to have migrated from the deep mature Jurassic source rocks in the downthrown southern block across the Purbeck-Isle of Wight fault zone into the Triassic and Jurassic reservoir rocks in the upthrown northern block.

CHAPTER IX

BURIAL-THERMAL HISTORY OF THE JURASSIC AND HYDROCARBON GENERATION IN SOUTHERN ENGLAND

BURIAL - THERMAL HISTORY OF THE JURASSIC AND HYDROCARBON GENERATION IN SOUTHERN ENGLAND

9.1 INTRODUCTION

Waples (1980) presented a method, originally introduced by Lopatin (1971), for estimating the effects of time and temperature in petroleum generation by utilizing burial and thermal history of a geologic section of interest. In order to estimate the present thermal maturity of organic matter in a given stratigraphic section, Lopatin calculated the time - temperature index of maturity (TTI). This index is calculated on the basis of the time of residence in a particular temperature interval by a specific geologic horizon. The Lopatin method assumes that the rate of chemical reactions involved in the maturation of sedimentary organic matter approximately doubles with each 10°C (18°F) increase in temperature. Waples (1980) correlated the TTI values with other maturity scales such as vitrinite reflectance (Ro) or Thermal Alteration Index (TAI) (see Table 9.1 and Fig. 9.1) and also with important stages of oil generation and preservation (see Table 9.2). According to his charts, the TTI value for the onset of oil generation, 15, is equivalent to Ro of 0.65% (TAI of 2.65) whereas the TTI value for peak oil generation, 75, is equivalent to Ro of 1.0% (TAI of 2.90). However, as already indicated in Chapter 6, a vitrinite reflectance value of 0.60% (Ro) is considered in the present work as the organic maturity level at the onset of main phase of oil generation and this is equivalent to a TTI value of 10.

TABLE 9.1 CORRELATION OF TIME-TEMPERATURE INDEX OF MATURITY (TTI) WITH VITRINITE REFLECTANCE (R_o) (After Waples, 1980)

R_o	TTI	R_o	TTI
0.30	< 1	1.36	180
0.40	< 1	1.39	200
0.50	3	1.46	260
0.55	7	1.50	300
0.60	10	1.62	370
0.65	15	1.75	500
0.70	20	1.87	650
0.77	30	2.00	900
0.85	40	2.25	1,600
0.93	56	2.50	2,700
1.00	75	2.75	4,000
1.07	92	3.00	6,000
1.15	110	3.25	9,000
1.19	120	3.50	12,000
1.22	130	4.00	23,000
1.26	140	4.50	42,000
1.30	160	5.00	85,000

TABLE 9.2 CORRELATION OF TTI WITH IMPORTANT STAGES OF OIL GENERATION AND PRESERVATION (After Waples, 1980)

Stage	TTI	R_o	TAI
Onset of oil generation	15	0.65	2.65
Peak oil generation	75	1.00	2.9
End of oil generation	160	1.30	3.2
Upper TTI limit for occurrence of oil with API gravity <40°	~500	1.75	3.6
Upper TTI limit for occurrence of oil with API gravity <50°	~1,000	2.0	3.7
Upper TTI limit for occurrence of wet gas	~1,500	2.2	3.75
Last known occurrence of dry gas	65,000	4.8	>4.0
Liquid sulfur in Lone Star Baden 1 (below dry gas limit)	972,000	>5.0	>4.0

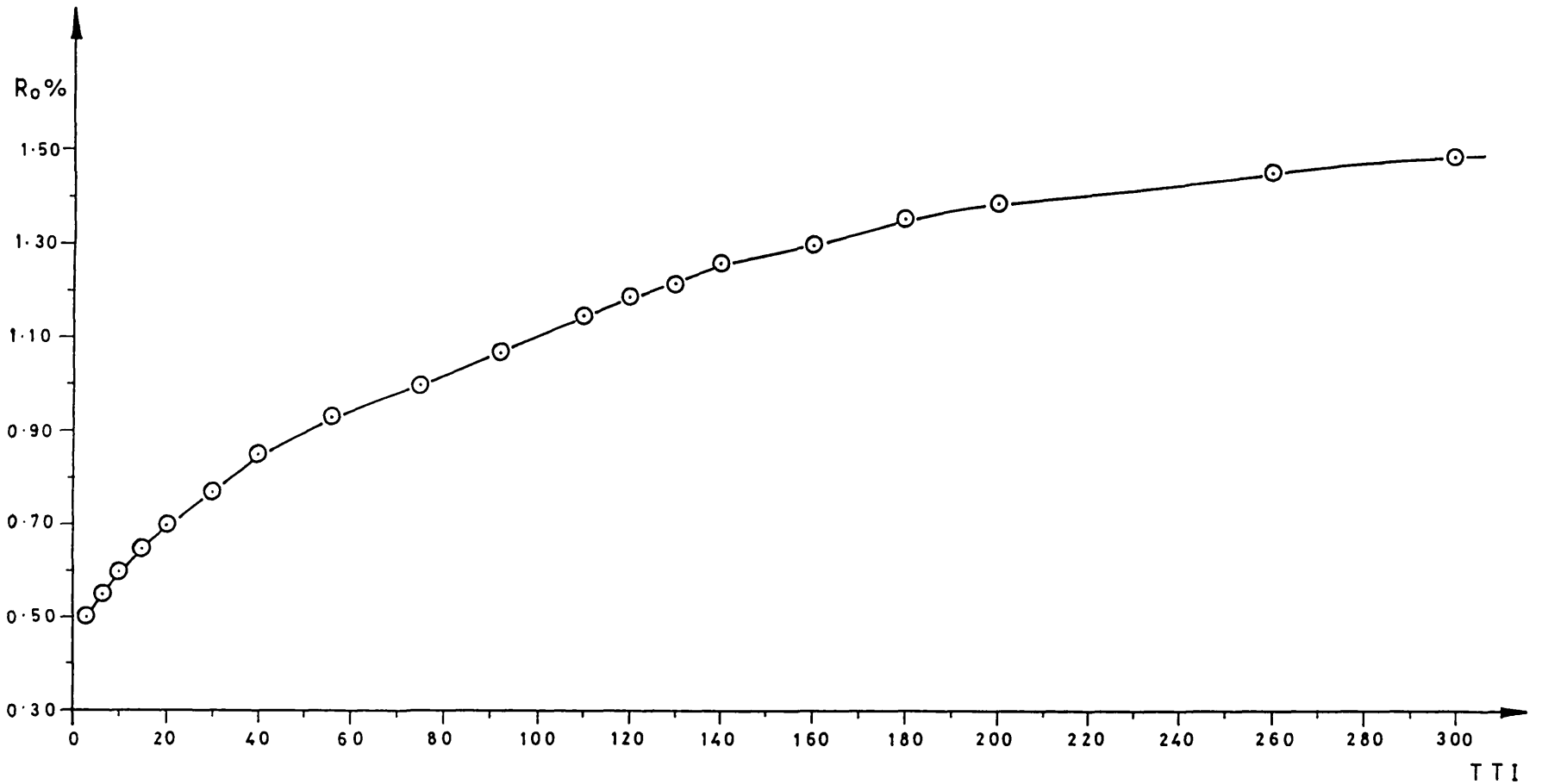


FIG. 9.1 CORRELATION OF TIME-TEMPERATURE INDEX OF MATURITY (TTI) WITH VITRINITE REFLECTANCE (Ro) (BASED ON DATA FROM WAPLES, 1980)

An attempt is being made here to apply the Lopatin method to the three potential Jurassic hydrocarbon source-rock formations (Kimmeridge Clay, Oxford Clay, and Lower Lias) in order to predict the present organic maturity levels in these formations across southern England and to compare the theoretical predictions with the results of organic geochemical analyses so far considered. Another objective of this exercise is to investigate the nature and timing of hydrocarbon generation in these rock units across the study area. As already noted, in order to use the Lopatin method to predict the present organic maturity of strata, both the burial and the thermal histories of the region must be adequately known. Thus an accurate reconstruction of the depositional and tectonic history of the geologic section of interest is necessary for a successful implementation of the method. In a situation where either the thermal or the burial history is not known but the actual organic maturity of the strata has been measured, the method can be applied to a range of possible thermal or burial histories, and the resulting predicted maturities compared to the observed maturities in the basin. The thermal-burial history that results in predicted maturities most similar to the observed maturities is then a reasonable estimate of the basin's actual thermal and burial behaviour through time.

The geologic history of southern England, including the formation and evolution of the Mesozoic basins in the Dorset - Hampshire and Wealden areas, was reviewed in Chapter 2. Apart from the rifting episode associated with the basin formation, the Jurassic strata in southern

England were affected by four main recorded earth movements:- (i) the pre-Albian earth movement which followed the deposition of the Wealden Beds, (ii) the post-Aptian Trangression earth movement, (iii) the earth movement which caused the regression of the Chalk Sea during the end of Cretaceous to Earliest Tertiary, and (iv) the Early Miocene Alpine orogenic phase. These earth movements resulted in varying degrees of deformation and erosion of the Jurassic, Cretaceous, and Tertiary strata across southern England. A detailed documentation of the extents of these deformations and erosion in various parts of southern England is, however, lacking and thus geologic reconstructions of the Jurassic sections across the study area will, in many cases, represent the best guess. The thermal history of these Mesozoic basins has not yet been established but the estimated average present-day geothermal gradient in the area is about $30^{o}C/km$ or $26.2^{o}F/1000$ ft. (J. Wheildon, personal communication).

Geologic reconstructions of some Jurassic horizons and application of the Lopatin method are attempted in two broad areas: (i) the Isle of Wight - Dorset area where the localities of the Arreton No. 2 Well, the Wytch Farm Oilfield, and the Winterborne Kingston Well are considered; and (ii) the Weald-Hampshire area where the localities in the Penshurst Well, the deepest part of the Wealden Basin, and the Winchester No. 1 Well are considered (Fig. 9.2). The Well data for Arreton No. 2, Winterborne Kingston, Penshurst, and Winchester No. 1 were supplied by the Deep Geology Unit of the British Geological Survey while the

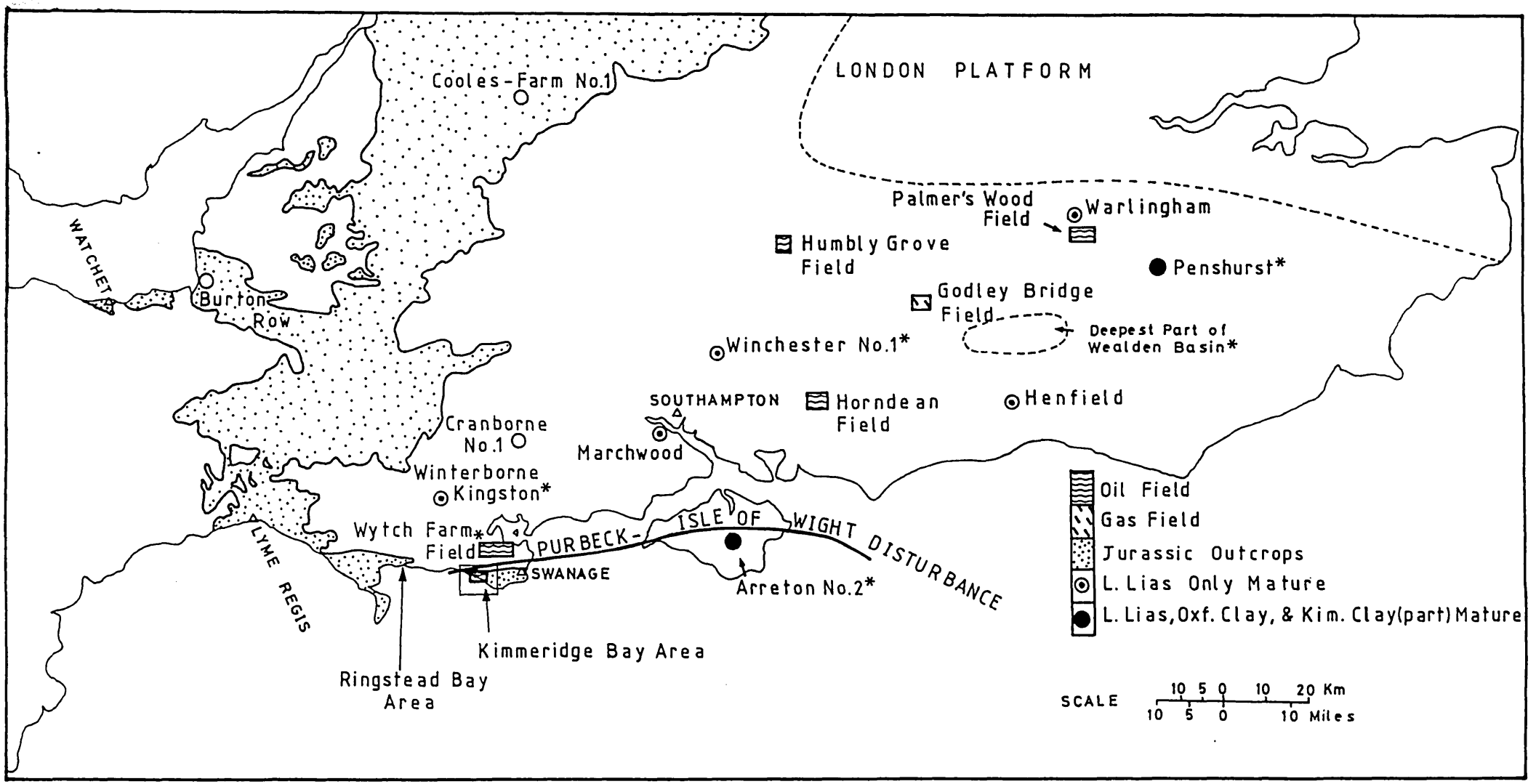


FIG. 9.2 MAP SHOWING LOCALITIES IN S. ENGLAND (MARKED *) WHERE GEOLOGIC RECONSTRUCTIONS OF THE JURASSIC ARE ATTEMPTED

subsurface information for the Wytch Farm Oilfield is based on Colter and Havard (1981).

9.2 ISLE OF WIGHT - DORSET AREA

9.2.1 Arreton No. 2 Well (Isle of Wight)

This Well was drilled in 1974 on the southern side of the Purbeck - Isle of Wight Disturbance and it was started in the Lower Greensand. The stratigraphic data used for the reconstruction of the history of the Bases of Lias and Kimmeridge Clay in this locality are shown in Table 9.3(a). The estimated thicknesses of the eroded Cretaceous and Tertiary Beds indicated in the table are based on the outcrop data in the Isle of Wight by Melville and Freshney (1982). Fig. 9.3 shows the geologic model for the two Jurassic horizons, and Table 9.3(b) shows the calculation of the present TTI values for the model.

On the basis of the calculation, it is noted that the Base Lias attained a TTI value of 3 or 0.50% Ro in the Aptian - Albian (Early Cretaceous), a TTI value of 10 or 0.60% Ro in the Late Cretaceous, and a TTI value of 15 or 0.65% Ro in the Paleocene. At maximum burial of this horizon during Oligocene - Early Miocene prior to the Miocene Alpine tectonic inversion, a TTI value of 70.75 was attained which is equivalent to vitrinite reflectance value (Ro) of about 0.98%. The present-day total TTI value of 74.65 suggests that the Base Lias in this locality has not yet attained the peak oil generation stage but that it is very close to that maturity level. The results of organic geochemical analyses in the present work

TABLE 9.3(a) STRATIGRAPHIC DATA OF ARRETON NO. 2 WELL (ISLE OF WIGHT) USED FOR BURIAL HISTORY RECONSTRUCTION OF THE LOCALITY

Age (m.y.)	Depositional Unit(s)	Unit Thickness in Feet (metres)	
		Measured in Well	(Estimated) Actual Prior to Erosion
Base Lias (196) – Base Middle Jurassic (177)	Lias	1258(383)	Same
Base Middle Jurassic (177) – Base Kimmeridgian (151)	Inferior Oolite - Corallian Beds	1446(441)	"
Base Kimmeridgian (151) – Base Early Cretaceous (141)	Kimmeridge Clay - Purbeck Beds	1522(464)	"
Base Early Cretaceous (141)	Wealden Beds	2032(619)	
(113) Aptian (106)	Lower Greensand	210 (64)	807(246)
	Gault		98(30)
Albian	Transition Beds		44(13.4)
	Upper Greensand		90(27.4)
Base Late Cretaceous (100)	Chalk – Lower		197(60)
	Chalk – Middle		197(60)
	Chalk – Upper		1325(404)
Base Paleogene (65)			
Paleocene (55)	Reading Beds		
	London Clay		
Eocene	Bagshot Beds of Isle of Wight		2296(700)
	Bracklesham Group Formation		
	Solent and Bembridge Fms.		
(38) Oligocene	Hampstead Formation		
Base Miocene (23)			

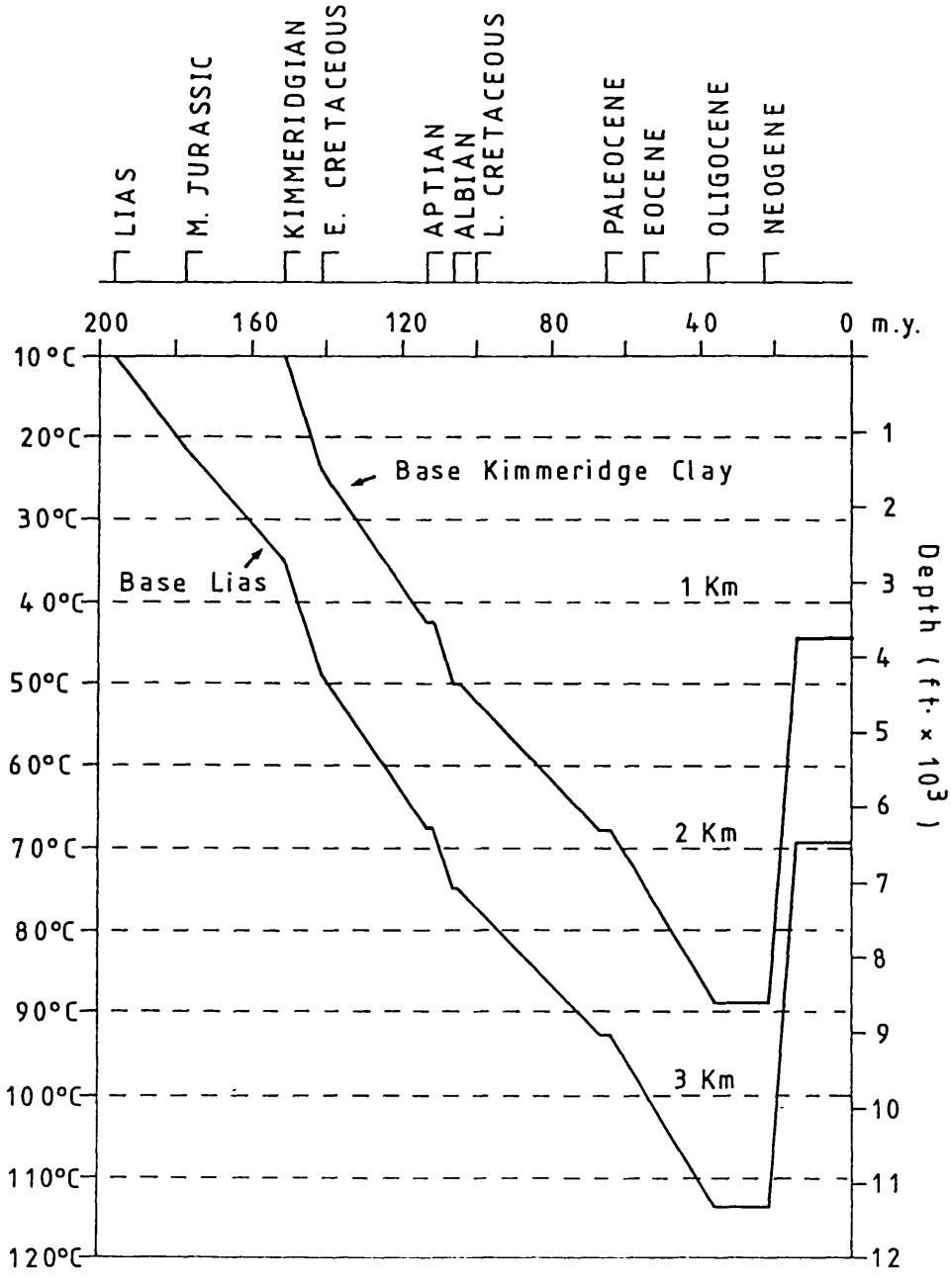


FIG. 9.3 GEOLOGIC MODEL FOR BASE LIAS AND BASE KIMMERIDGE CLAY IN THE LOCALITY OF ARRETON NO. 2 WELL (ISLE OF WIGHT)

TABLE 9.3(b) CALCULATION OF PRESENT TTI VALUES FOR THE GEOLOGIC MODEL IN FIGURE 9.2 (ARRETON NO. 2 WELL)

Temperature Interval (°C)	r^n	ΔTime (m.y.)	Interval TTI	Total TTI
Base Lias				
10-20	2^{-9}	16.0	0.03	0.03
20-30	2^{-8}	19.4	0.08	0.11
30-40	2^{-7}	13.4	0.10	0.21
40-50	2^{-6}	7.6	0.12	0.33
50-60	2^{-5}	15.2	0.48	0.81
60-70	2^{-4}	15.0	0.94	1.75
70-80	2^{-3}	16.4	2.05	3.80
80-90	2^{-2}	21.6	5.40	9.20
90-100	2^{-1}	18.1	9.05	18.25
100-110	2^{0}	12.5	12.50	30.75
110-120	2^{1}	20.0	40.00	70.75
110-100	2^{0}	1.6	1.6	72.35
100-90	2^{-1}	1.6	0.80	73.15
90-80	2^{-2}	1.6	0.40	73.55
80-70	2^{-3}	1.6	0.20	73.75
70-60	2^{-4}	14.4	0.90	74.65
Base Kimmeridge Clay				
10-20	2^{-9}	7.0	0.01	0.01
20-30	2^{-8}	11.8	0.05	0.06
30-40	2^{-7}	15.2	0.12	0.18
40-50	2^{-6}	10.8	0.17	0.35
50-60	2^{-5}	23.2	0.72	1.07
60-70	2^{-4}	22.6	1.41	2.48
70-80	2^{-3}	13.4	1.67	4.15
80-90	2^{-2}	27.2	6.80	10.95
80-70	2^{-3}	1.6	0.20	11.15
70-60	2^{-4}	1.6	0.10	11.25
60-50	2^{-5}	1.6	0.05	11.30
50-40	2^{-6}	15.0	0.23	11.53

indicate the organic maturity level of the Base Lias in Arreton No. 2 Well to be at about 0.90% Ro (e.g. see Chapter 6, Table 6.3d, Sample: AR/LL.9). For the Base Kimmeridge Clay, the calculation shows that this horizon attained a TTI value of 10.95 or about 0.60% Ro at maximum burial during the oligocene - Early Miocene. The present TTI value of 11.53 suggests that this horizon has not yet achieved an organic maturity equivalent of 0.65% Ro. Organic geochemical analyses indicate an organic maturity equivalent of about 0.52% Ro for the Base Kimmeridge Clay (e.g. see Chapter 6, Table 6.3b , Sample: AR/KC.9).

The theoretically predicted present organic maturity levels for the Base Lias and the Base Kimmeridge Clay in this locality appear comparable with the results of organic matter analyses in the present investigation. The slightly higher thermal maturities suggested by the Lopatin method for these horizons are probably suggestive of the fact that the paleogeothermal gradient in this locality was somewhat lower than the present day average value of about 30^{o}C/km for southern England or that the thicknesses of the eroded Cretaceous and Tertiary Beds have been over-estimated. However, the method does show that the Lower Lias evolved into the catagenesis stage (top $\approx$ 0.50% Ro) in the Early Cretaceous although the onset of the main phase of oil generation was not achieved until the Late Cretaceous. The prediction that the Lias did not attain thermal maturity beyond the peak oil generation stage in this area prior to the Miocene uplift probably explains the absence of dry gas deposits in the Dorset hydrocarbon province.

9.2.2 The Wytch Farm Oilfield (Dorset)

This Dorset Oilfield is about 10,000 ft (about 3 km) to the north of the Purbeck - Isle of Wight Disturbance. Drilling in this locality often starts in the Tertiary Beds. The stratigraphic data used for the reconstruction of the burial history of the Base Lias are given in Table 9.4(a). The estimated total thickness of the Tertiary Beds in this locality is assumed similar to the value at Wareham Heaths given by Melville and Freshney (1982) due to the proximity of the two localities. The thicknesses of the Upper Jurassic, Wealden and Lower Greensand Beds are considered to be similar to the value in the locality of Arreton No. 2 Well - based on the similarities noted in the thicknesses of the Lias, Inferior Oolite - Oxford Clay, and the Upper Cretaceous Chalk units. The geologic model and the calculation of the present TTI values for the Base Lias are shown in Fig. 9.4 and Table 9.4(b) respectively. As shown by the model, the deepest burial of this horizon occurred in the Early Cretaceous after the deposition of the Wealden Beds and prior to the pre-Albian earth movement which produced a major tectonic inversion of the Lias.

The present day total TTI value of 2.81 for the Base Lias in this locality suggests that this horizon has not yet attained an organic maturity of 0.50% Ro. This predicted immaturity of the Jurassic organic matter in this Oilfield based on Lopatin method is in conformity with the results of organic geochemical analyses of samples from this locality by BP Research Centre at Sunbury-on-Thames

TABLE 9.4(a) STRATIGRAPHIC DATA OF WYTCH FARM OILFIELD (DORSET) USED FOR BURIAL HISTORY RECONSTRUCTION OF THE LOCALITY

Age (m.y.)	Depositional Units	Unit(s) Thickness in Feet (Metres)	
		Measured in Well	Estimated Actual Prior to Erosion
Base Lias (196)	Lias	1040 (317)	Same
Base Middle Jurassic (177)	Inferior Oolite - Wealden Beds	1055(321.6) (Inferior Oolite to Oxford Clay only present)	5000(1524.4)
Base Aptian (113)	Lower Greensand	30(9.1)	807(246)
Base Albian(106)	Gault Upper Greensand	140(43)	Same
Base Late Cretaceous (100)	Chalk — Lower	140(43)	Same
	Chalk — Middle	190(58)	Same
	Chalk — Upper	1010 (308)	Same
Base Paleogene(65)			
Paleocene (55)	Paleogene Beds	444(135.4)	566(172.5)
Eocene (38)			
Oligocene			
Base Miocene(23)			

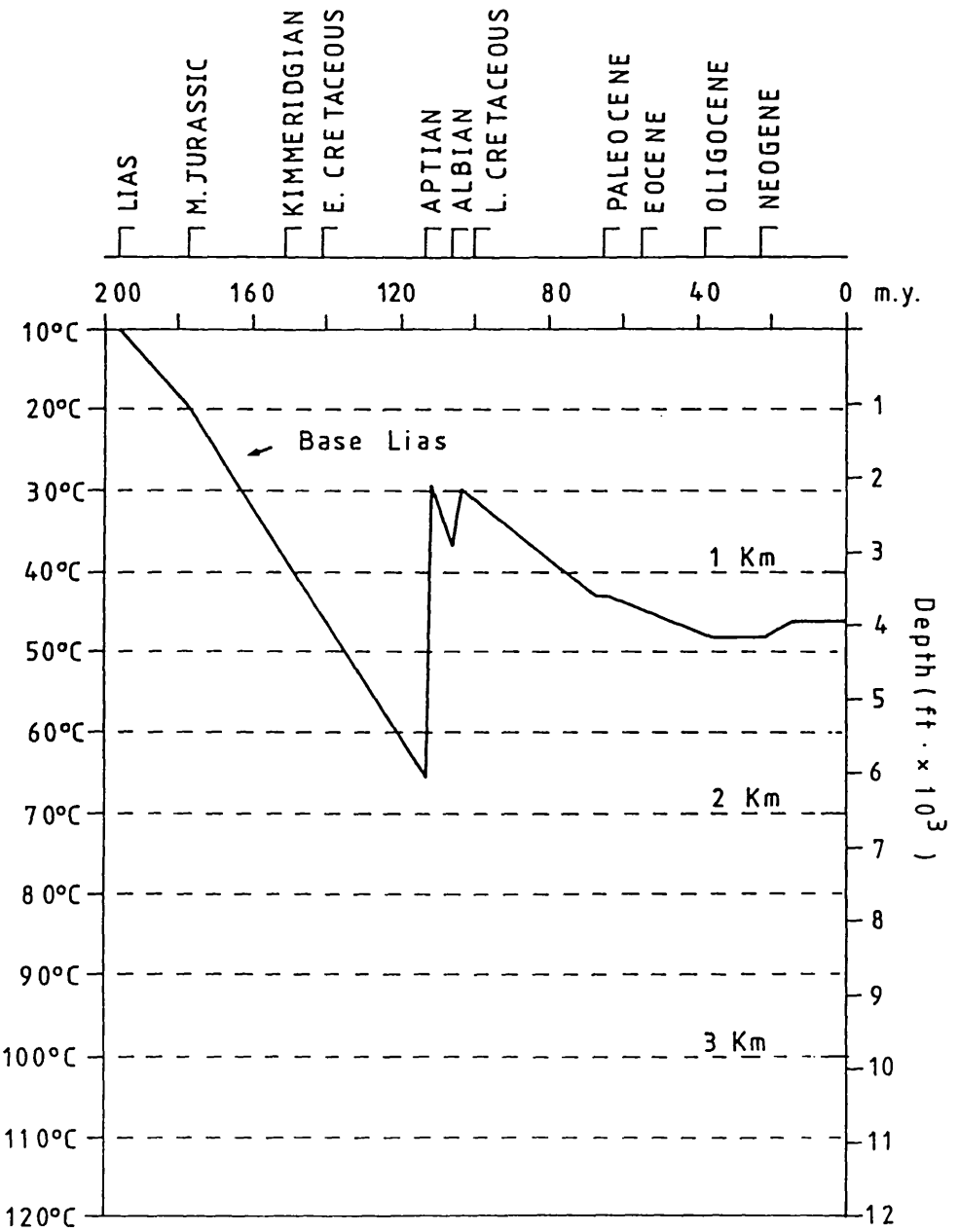


FIG. 9.4 GEOLOGIC MODEL FOR BASE LIAS IN THE WYTCH FARM OILFIELD (DORSET)

TABLE 9.4(b) CALCULATION OF PRESENT TTI VALUES FOR THE GEOLOGIC MODEL IN FIGURE 9.3 (WYTCH FARM OILFIELD)

Temperature Interval (°C)	r^n	ΔTime (m.y.)	Interval TTI	Total TTI
Base Lias				
10-20	2^{-9}	19.4	0.04	0.04
20-30	2^{-8}	14.0	0.05	0.09
30-40	2^{-7}	14.0	0.11	0.20
40-50	2^{-6}	14.0	0.22	0.42
50-60	2^{-5}	14.0	0.44	0.86
60-70	2^{-4}	7.8	0.49	1.35
60-50	2^{-5}	0.4	0.01	1.36
50-40	2^{-6}	0.4	0.01	1.37
40-30	2^{-7}	0.4	0.00	1.37
30-20	2^{-8}	0.8	0.00	1.37
30-40	2^{-7}	7.6	0.06	1.43
30-20	2^{-8}	0.8	0.00	1.43
30-40	2^{-7}	27.6	0.21	1.64
40-50	2^{-6}	74.8	1.17	2.81

and by Geochem Laboratories (UK) Ltd. reported by Colter and Havard (1981). This apparent good correlation between the results of the theoretical model and the geochemical analyses indicates that the burial-thermal history projected by the geologic model in Fig. 9.4 is a reasonable estimate of the actual burial and thermal behaviour of the Lias in the Wytch Farm through time.

The immaturity of the Jurassic in the Wytch Farm Field shows that the reservoired oils in this locality migrated from somewhere else. It was indicated in Chapter 8 (Section 8.3) that the main source for these oils is most probably the mature Lower Lias Formation to the south of the Purbeck - Isle of Wight Disturbance.

9.2.3 Winterborne Kingston Well (Dorset)

This well starts in the Upper Chalk at the surface. Table 9.5(a) shows the stratigraphic data used for the reconstruction of the burial history of the Base Lias in this locality (Fig. 9.5). The estimated actual thicknesses of the Upper Jurassic and some Cretaceous Beds prior to their erosion are believed to be similar to those in the locality of Arreton No. 2 Well based on the comparable thicknesses of many of the fully preserved Jurassic and Cretaceous rock units in the two localities. The estimated thickness of the Paleogene Beds in this locality is also considered similar to the value at Wareham Heaths on the basis of the proximity of the two localities.

The burial curve in Fig. 9.5 shows that the Base Lias in this locality attained its maximum burial depth

TABLE 9.5(a) STRATIGRAPHIC DATA OF WINTERBORNE KINGSTON WELL (DORSET) USED FOR BURIAL HISTORY RECONSTRUCTION OF THE LOCALITY

Age (m.y.)	Depositional Unit(s)	Unit(s) Thickness in Feet (metres)	
		Measured in Well	(Estimated)Actual Prior to Erosion
Base Lias(196)	Lias	2120(646)	Same
Base Middle Jurassic (177)	Inferior Oolite - Corallian Beds	1741(530.8)	"
Base Kimmeridgian (151)	Kimmeridge Clay - Purbeck Beds	156(47.6) (Lower Kimmeridge Clay only)	1522(464)
Base Early Cretaceous(141)	Wealden Beds	-	2032(619)
(113)			
Aptian	Lower Greensand	11 (3.4)	807(246)
(106)			
	Gault	151(46.1)	Same
Albian	Upper Greensand	30(9.1)	"
Base Late Cretaceous (100)	Chalk - Lower	161(49)	"
	Chalk - Middle	285(87)	"
	Chalk - Upper	508(155)	1450(442)
Base Paleogene(65)			
Paleocene (55)	Paleogene Beds	-	566(172.5)
Eocene (38)			
Oligocene			
Base Miocene(23)			

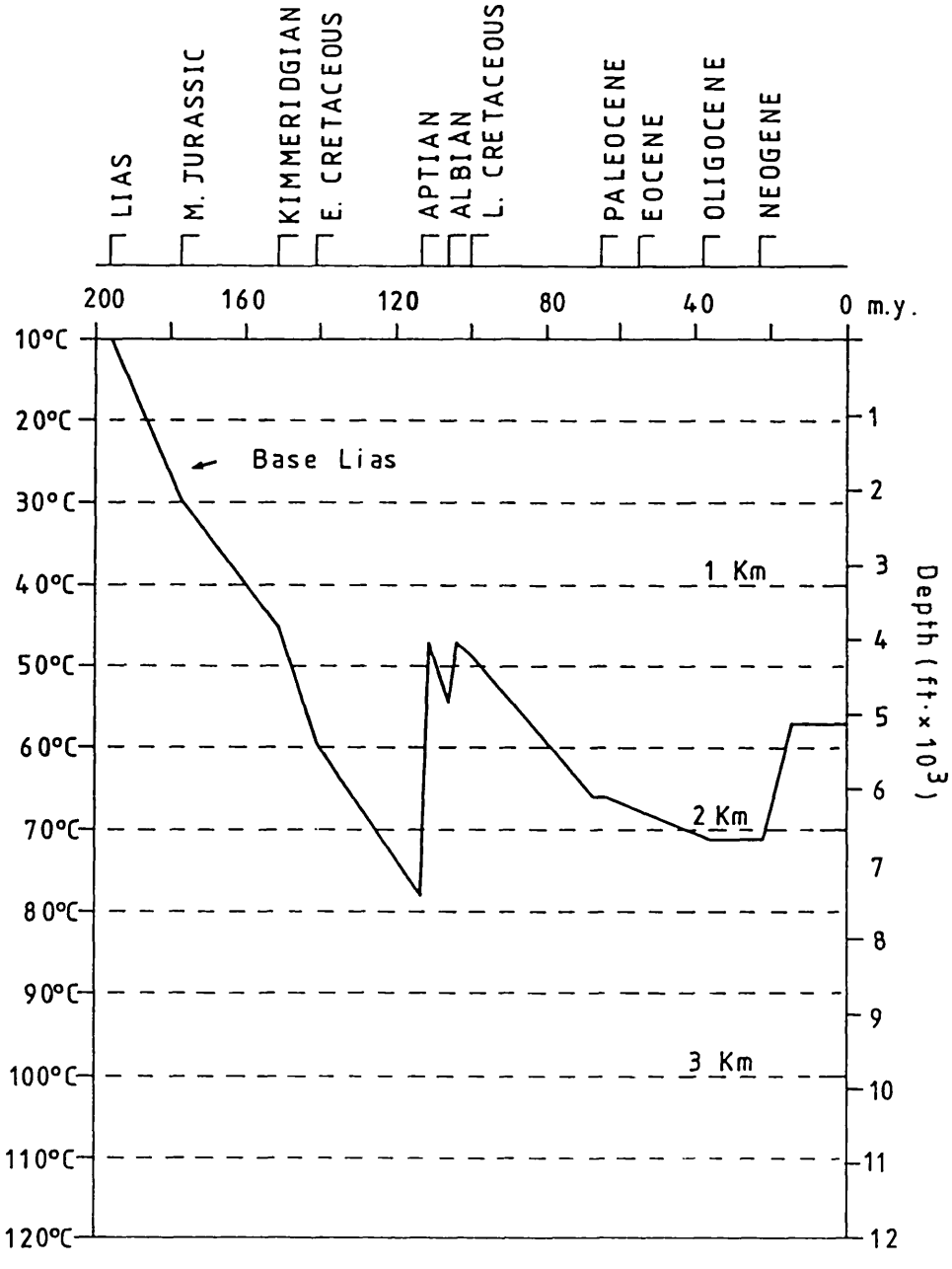


FIG. 9.5 GEOLOGIC MODEL FOR BASE LIAS IN THE LOCALITY OF WINTERBORNE KINGSTON WELL (DORSET)

TABLE 9.5(b) CALCULATION OF PRESENT TTI VALUES FOR THE GEOLOGIC MODEL IN FIGURE 9.4 (WINTERBORNE KINGSTON WELL)

Temperature Interval (°C)	r^n	ΔTime (m.y.)	Interval TTI	Total TTI
Base Lias				
10-20	2^{-9}	9.8	0.02	0.02
20-30	2^{-8}	9.8	0.04	0.06
30-40	2^{-7}	16.4	0.13	0.19
40-50	2^{-6}	12.0	0.19	0.38
50-60	2^{-5}	7.8	0.24	0.62
60-70	2^{-4}	15.2	0.95	1.57
70-80	2^{-3}	12.4	1.55	3.12
70-60	2^{-4}	0.6	0.04	3.16
60-50	2^{-5}	0.6	0.02	3.18
50-40	2^{-6}	2.4	0.04	3.22
50-60	2^{-5}	4.4	0.14	3.36
50-40	2^{-6}	6.8	0.11	3.47
50-60	2^{-5}	19.4	0.61	4.08
60-70	2^{-4}	37.2	2.33	6.41
70-80	2^{-3}	20.2	2.53	8.94
70-60	2^{-4}	5.2	0.33	9.27
60-50	2^{-5}	15.8	0.49	9.76

in the Early Cretaceous after the deposition of the Wealden Beds and prior to the pre-Albian earth movement - a situation similar to the case in the Wytch Farm Oil-field. The calculation of the present TTI values for the Base Lias shown in Table 9.5(b) suggests that this horizon attained an organic maturity of 0.50% Ro (TTI value of 3) by the Earliest Aptian, and the present total TTI value of 9.76 indicates that the present level of maturation of the Lower Lias organic matter in this locality is slightly below a vitrinite reflectance value of 0.60% (Ro). In the present work, an organic maturity level of about 0.56% Ro is estimated for the Base Lias here on the basis of organic matter analyses (e.g. see Chapter 6, Table 6.3e, Sample: WK/LL.8).

There is a good agreement between the predicted and the observed organic maturity levels of the Base Lias in this locality. This shows that the geologic model in Fig. 9.5 is reasonably close to the actual burial-thermal history of the Lias in the locality of the Winterborne Kingston Well.

9.3 THE WEALDEN DISTRICT AND ADJACENT PARTS OF HAMPSHIRE COUNTY

9.3.1 Penshurst Well (West Kent) and the Deepest Part of the Mesozoic Wealden Basin

The Penshurst Well was drilled in 1938 starting at the surface in the Wealden Beds. Table 9.6(a) shows the stratigraphic data used for the reconstruction of the burial history of the Base Lias and the Base Kimmeridge

Clay in the locality of this Well shown in Fig. 9.6. The estimated thicknesses of the eroded Cretaceous to Tertiary Beds are based on the outcrop data in the Wealden District by Gallois (1965). The burial curves show that both the Base Lias and the Base Kimmeridge Clay attained their maximum burials in the Oligocene - Early Miocene. A similar situation was noted for the two Jurassic horizons in the locality of Arreton No. 2 Well in the Isle of Wight. In general, the tectonic histories portrayed by the burial curves in these two localities bear much similarities, with a major tectonic inversion of the Jurassic associated with the Miocene Alpine orogenic episode.

The calculation of the present TTI values for the Base Lias and the Base Kimmeridge Clay in the Penshurst Well is given in Table 9.6(b). The calculation shows that the Base Lias attained a TTI value of 3.0 or 0.50% Ro in the Albian (Early Cretaceous), a TTI value of 10 or 0.60% Ro and a TTI value of 15 or 0.65% Ro both in the Late Cretaceous, and at maximum burial in Oligo-Miocene, a TTI value of 51.06 which is equivalent to a vitrinite reflectance value of about 0.90% Ro (based on Fig. 9.1). The present total TTI value of 53.03 for the Base Lias suggest that the thermal maturity of this horizon is still below 0.93% Ro. Organic geochemical analyses in the present work indicate an organic maturity of about 0.85% Ro for the Base Lias in this locality (e.g. see Chapter 6, Table 6.3j, Sample: PH/LL.5). For the Base Kimmeridge

TABLE 9.6(a) STRATIGRAPHIC DATA OF PENSHURST WELL (KENT) USED FOR BURIAL HISTORY RECONSTRUCTION OF THE LOCALITY

Age (m.y.)	Depositional Unit(s)	Unit(s) Thickness in Feet(metres)	
		Measured in Well	Estimated Actual Prior to Erosion
Base Lias (196)	Lias	845(257.6)	Same
Base Mid Jurassic (177)	Inferior Oolite - Corallian Beds	1307(398.5)	"
Base Kimmeridgian (151)	Kimmeridge Clay - Purbeck Beds	1978(603)	"
Base Early Cretaceous (141)	Wealden Beds	450(137.2)	2950(899.4)
(113)			
Aptian	Lower Greensand	-	770(245)
(106)	Gault	-	300(91.5)
Albian	Upper Greensand	-	200(61)
Base Late Cretaceous (100)	Chalk — Lower	-	230(70)
	Chalk — Middle	-	210(64)
	Chalk — Upper	-	650(198.2)
Base Paleogene(65)			
Paleocene	—		
(55)			
Eooene	Eocene - Oligocene Beds	-	642(196)
(38)			
Oligocene			
Base Miocene (23)			

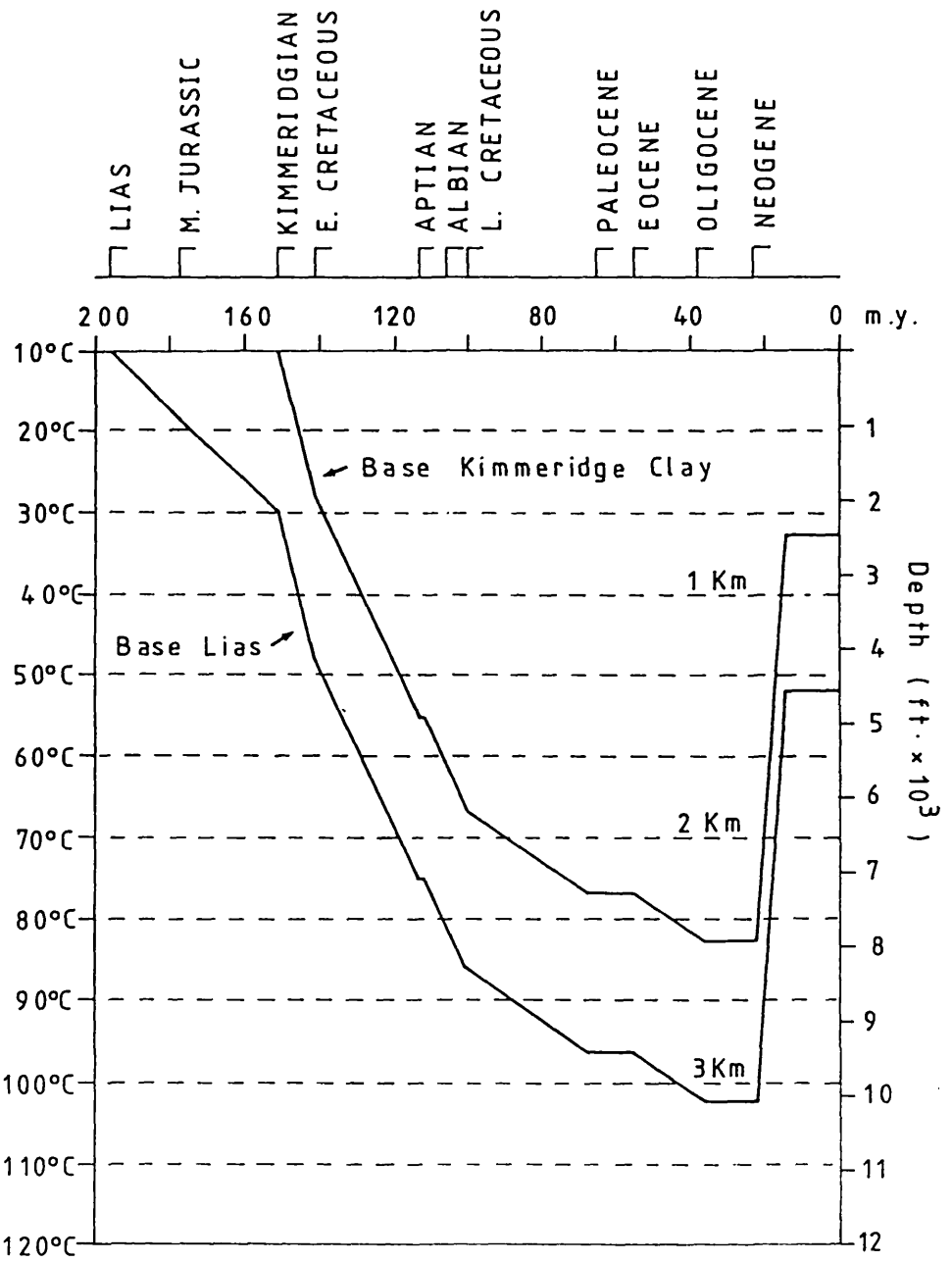


FIG. 9.6 GEOLOGIC MODEL FOR BASE LIAS, AND BASE KIMMERIDGE CLAY IN THE LOCALITY OF PENSHURST WELL (KENT)

TABLE 9.6(b) CALCULATION OF PRESENT TTI VALUES FOR THE GEOLOGIC MODEL IN FIGURE 9.5 (PENSHURST WELL)

Temperature Interval (°C)	r^n	ΔTime (m.y.)	Interval TTI	Total TTI
Base Lias				
10-20	2^{-9}	22.0	0.04	0.04
20-30	2^{-8}	23.0	0.09	0.13
30-40	2^{-7}	5.8	0.05	0.18
40-50	2^{-6}	6.0	0.09	0.27
50-60	2^{-5}	10.6	0.33	0.60
60-70	2^{-4}	10.6	0.66	1.26
70-80	2^{-3}	11.6	1.45	2.71
80-90	2^{-2}	19.4	4.85	7.56
90-100	2^{-1}	44.2	22.10	29.66
100-110	2^{0}	21.4	21.40	51.06
100-90	2^{-1}	1.6	0.80	51.86
90-80	2^{-2}	1.6	0.40	52.26
80-70	2^{-3}	1.6	0.20	52.46
70-60	2^{-4}	1.6	0.10	52.56
60-50	2^{-5}	15.0	0.47	53.03
Base Kimmeridge Clay				
10-20	2^{-9}	5.8	0.01	0.01
20-30	2^{-8}	6.0	0.02	0.03
30-40	2^{-7}	10.4	0.08	0.11
40-50	2^{-6}	10.4	0.16	0.27
50-60	2^{-5}	11.4	0.36	0.63
60-70	2^{-4}	17.4	1.09	1.72
70-80	2^{-3}	43.0	5.37	7.09
80-90	2^{-2}	25.2	6.30	13.39
80-70	2^{-3}	1.6	0.20	13.59
70-60	2^{-4}	1.6	0.10	13.69
60-50	2^{-5}	1.6	0.05	13.74
50-40	2^{-6}	1.6	0.02	13.76
40-30	2^{-7}	15.0	0.12	13.88

Clay, the Lopatin method predicts that this horizon attained a thermal maturity equivalent of 0.60% Ro at maximum burial in the Oligo - Miocene times, and the present day total TTI value of 13.88 suggests that a thermal maturity level of 0.65% Ro has not yet been attained by the Kimmeridge Clay organic matter in this locality. A vitrinite reflectance value of about 0.62% Ro is esimated in the present work as the maximum organic maturity level for the Base Kimmeridge Clay in the Penshurst Well (e.g. see Chapter 6, Table 6.3j, Sample: PH/KC.4).

It is again noted here that the predicted maturity levels for the Jurassic organic matter using the Lopatin method compare very well with the results of organic geochemical studies.

The maturity levels indicated above for the two Jurassic horizons at their maximum burials during the Oligocene - Early Miocene as well as at the present depths show that mainly liquid hydrocarbons (oil) could have been generated and sourced by the three potential Jurassic hydrocarbon source-rock formations in the locality of the Penshurst Well. To investigate the possibility of a Jurassic source for the recently discovered natural gas deposit at Godley Bridge in south-west Surrey by Conoco (UK), a geologic reconstruction of the Base Lias is attempted in the deepest part of the Mesozoic Wealden Basin where the thickest Jurassic section (over 5000 ft.) occurs in the Wealden District. This is located in the northern part of West Sussex - southern Surrey area (Gallois, 1965; and see Fig. 6.6). Assuming the total thickness of the Jurassic to be 5,400 ft. (1646.3 metres),

and using the same Cretaceous and Tertiary stratigraphic data as in the locality of the Penshurst Well, a constructed burial history curve for the Base Lias is shown in Fig. 9.7. The calculation of the present TTI values shown in Table 9.7 suggest that organic maturity levels of 0.60% Ro and close to 1.2% Ro were attained by the Base Lias in the deepest part of the Wealden Basin in the Late Albian (Early Cretaceous) and in Oligocene - Early Miocene times respectively.

According to Vassoevich et al. (1974) and Dow (1977), even though the principal zone of dry gas (thermal) generation is in the organic maturity range of about 2.0 - 4.0% Ro, its formation actually commences at about 1.20% Ro, while most of wet gas generation occurs in the maturity range of 1.0 - 2.0% Ro. The recent publication by Tissot (1984) shows that the assumption in the Lopatin method based on Arrhenius law regarding the doubling of the rate of organic maturation reactions with every 10^{o}C (18^{o}F) rise in temperature applies only to early oil generation stages where reactions with low activation energies mostly in the range from 10 to 20 kcal/mole are involved. According to Tissot, at peak oil generation and higher maturity levels where reactions with much higher activation energies - in the range from 40 to 60 or 70 Kcal/mole - are involved in gas generation, the reaction rates are multiplied by 4 to 10 instead of 2 for each 10^{o}C rise in temperature. On the basis of this recent idea by Tissot, it follows that the thermal maturity of the Base Lias in the deepest part of the Mesozoic Wealden Basin must have been much higher than the predicted level

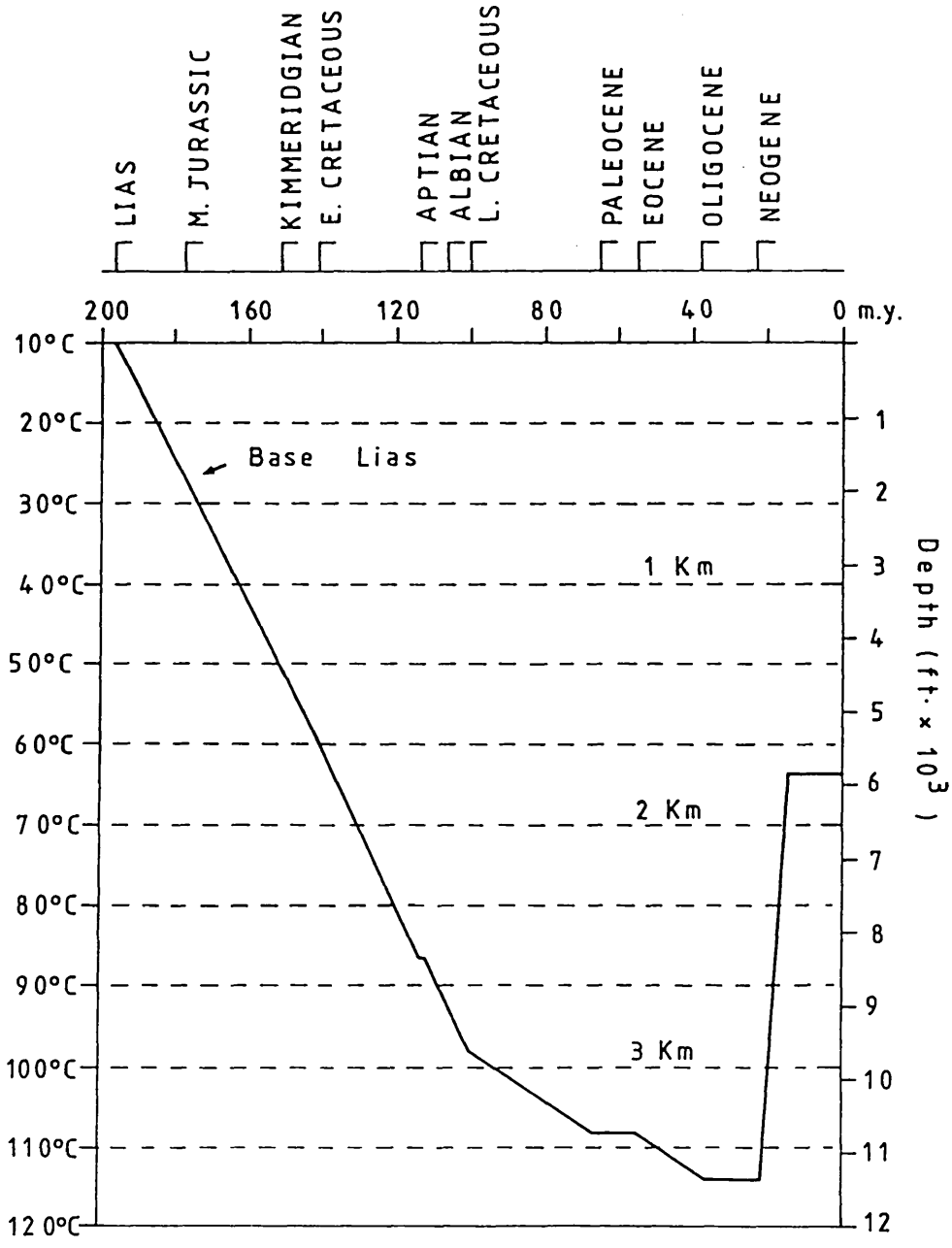


FIG. 9.7 GEOLOGIC MODEL FOR BASE LIAS IN THE DEEPEST PART OF THE WELADEN BASIN (NORTHERN W. SUSSEX - SOUTHERN SURREY)

TABLE 9.7 CALCULATION OF PRESENT TTI VALUES FOR THE GEOLOGIC MODEL IN FIGURE 9.6 (NORTHERN W. SUSSEX - SOUTHERN SURREY)

Temperature Interval (°C)	r^n	ΔTime (m.y.)	Interval TTI	Total TTI
Base Lias				
10-20	2^{-9}	11.0	0.02	0.02
20-30	2^{-8}	11.0	0.04	0.06
30-40	2^{-7}	11.0	0.09	0.15
40-50	2^{-6}	11.0	0.17	0.32
50-60	2^{-5}	11.0	0.34	0.66
60-70	2^{-4}	10.5	0.66	1.32
70-80	2^{-3}	10.5	1.31	2.63
80-90	2^{-2}	11.8	2.95	5.58
90-100	2^{-1}	15.0	7.50	13.08
100-110	2^{0}	44.8	44.80	57.88
110-120	2^{1}	27.4	54.80	112.68
110-100	2^{0}	1.5	1.50	114.18
100-90	2^{-1}	1.5	0.75	114.93
90-80	2^{-2}	1.5	0.38	115.31
80-70	2^{-3}	1.5	0.19	115.50
70-60	2^{-4}	15.0	0.94	116.44

of about 1.20% Ro at maximum burial based on the Lopatin method, and this could have been enough to result in a significant generation of natural gas in the locality. The close association of the discovered gas deposit with this region of thickest Jurassic development in the Weald appears to support the Liassic source for the gas (see Fig. 9.2). As noted in the Penshurst Well, the Lower Lias kerogens in the deep central parts of the Wealden Basin belong mainly to the oil-prone type II chemical group (see Chapter 6, Table 6.1). Thus, if the maximum thermal maturity attained by the Lias in the deepest part of the basin did not exceed the known oil preservation deadline of about 2.0% Ro (Waples, 1980), then accumulations of some of the generated oil would still be possible in this area. This would therefore imply the formation of the discovered gas field by the differential migration of the liquid and gaseous hydrocarbons (Magara, 1977; Leythaeuser et al., 1982; Tissot, 1984).

9.3.2 Winchester No. 1 Well (Hampshire)

The drilling of this Well commenced in October 1959 and was completed in March, 1960. In this locality, the rocks at the surface belong to the Lower Chalk. The Well did not penetrate through the whole Lias but was stopped in the Black Ven Marls (Lower Lias) at a total depth of 5844 ft. (1782 m). Palynologic investigation indicates the Base Pliensbachian Stage (corresponding to 185 m.y. ago) to occur at about 5837 ft (1779 m). Assuming a constant sedimentation rate for the whole Lias

(177 to 196 m.y. ago) and with the Top Lias known at the depth of 5311 ft (1619 m), the present depth of Base Lias is calculated to be at about 6560 ft (2000 m) in this locality. Table 9.7(a) shows the stratigraphic data used for the burial history reconstruction of the Base Lias (Fig. 9.8). The thicknesses of the eroded Cretaceous and Tertiary Beds in this area are assumed to be similar to those in the central Wealden District based on the comparable thicknesses of the Middle Cretaceous Gault and Upper Green-sand units in the two areas.

Using the average present day geothermal gradient of 30°C/km or 26.2°F/1000 ft, the calculated present TTI values for the Base Lias are shown in Table 9.8(b) . The calculation shows the organic matter in this Jurassic horizon attained maturity levels of 0.50% Ro in the Aptian (Early Cretaceous), 0.60% Ro in the Eocene, and about 0.67% Ro at maximum burial prior to the Early Miocene tectonic inversion. The predicted present day thermal maturity of the Base Lias in this locality is about 0.70% Ro (TTI value of 19.81). In the present work, organic geochemical analyses of samples from this locality indicate a maturity level of about 0.66% Ro for Lower Lias organic matter at about 723 ft (220 m) above the Base Lias (see Chapter 6, Tables 6.1 and 6.3c, Sample: WCH/LL.3). The observed organic maturity level of the Lower Lias in the locality of this Well is also noted to be quite comparable with the predicted thermal maturity of the Lias using the Lopatin method thus supporting the burial - thermal history illustrated in Fig. 9.8.

TABLE 9.8(a) STRATIGRAPHIC DATA OF WINCHESTER NO. 1 WELL (HAMPSHIRE) USED FOR BURIAL HISTORY RECONSTRUCTION OF THE LOCALITY

Age (m.y.)	Depositional Unit(s)	Unit(s) Thickness in ft. (metres)	
		Measured in Well	Estimated Actual Prior to Erosion
Base Lias (196)			
	Lias	1249(381)	Same
Base Mid. Jurassic (177)			
	Inferior Oolite - Corallian Beds	1899(579)	Same
Base Kimmeridgian (151)			
	Kimmeridge Clay - Purbeck Beds	1651(503.3)	Same
Base Early Cretaceous (141)			
	Wealden Beds	1119(341)	2950(899.4)
(113)			
Aptian	Lower Greensand	82(25)	770(245)
(106)			
	Gault	250(76.2)	Same
Albian	Upper Greensand	133(40.6)	Same
Base Late Cretaceous (100)			
	Chalk — Lower	177(54)	230(70)
	Chalk — Middle	-	210(64)
	Chalk — Upper	-	650(198.2)
Base Paleogene(65)			
Paleocene			
(55)			
Eocene	Eocene - Oligocene Beds	-	642(196)
(38)			
Oligocene			
Base Miocene (23)			

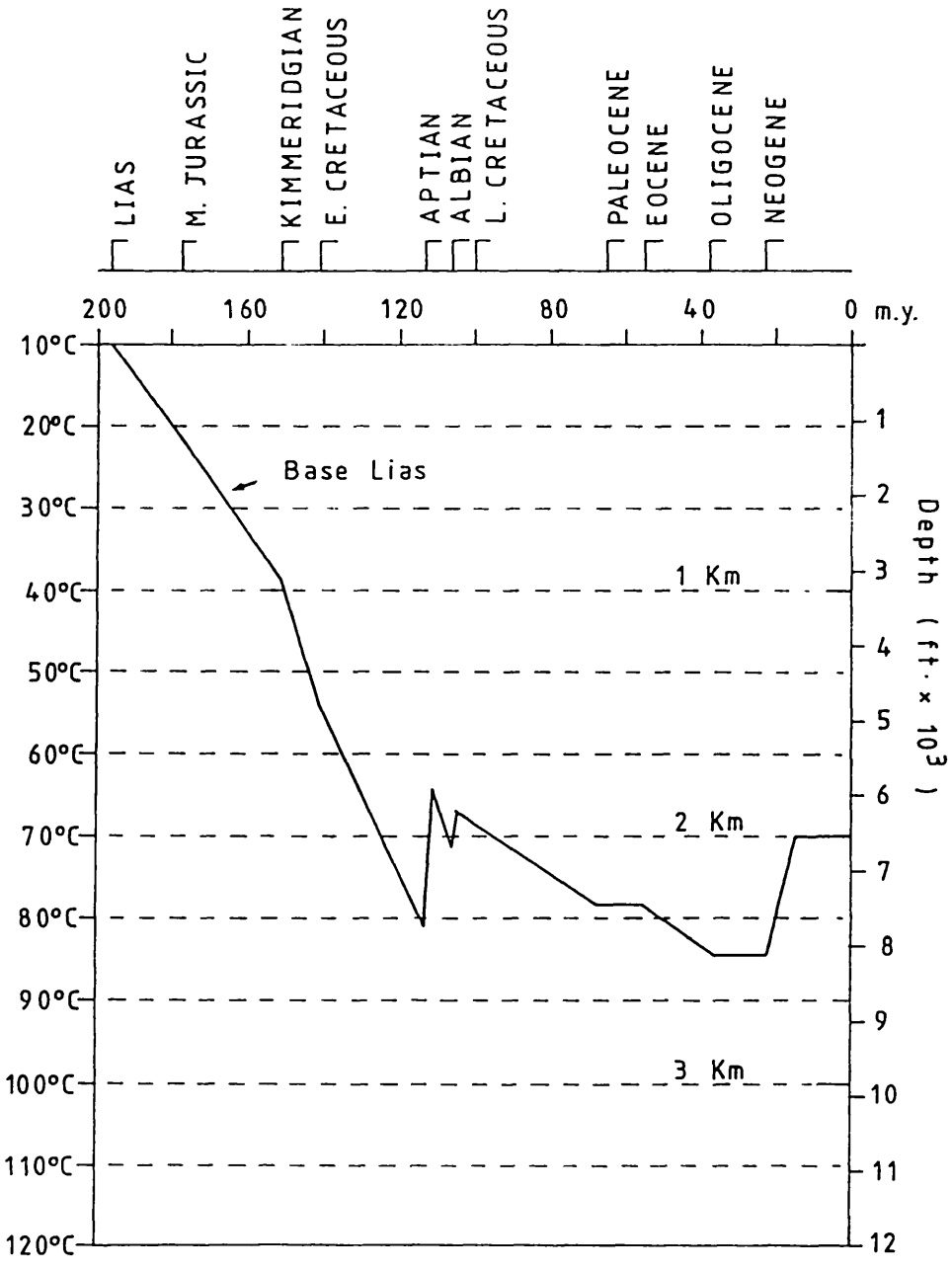


FIG. 9.8 GEOLOGIC MODEL FOR BASE LIAS IN THE LOCALITY OF WINCHESTER NO. 1 WELL (HAMPSHIRE)

TABLE 9.8(b) CALCULATION OF PRESENT TTI VALUES FOR THE GEOLOGIC MODEL IN FIGURE 9.7 (WINCHESTER NO. 1 WELL)

Temperature Interval (°C)	r^n	△Time (m.y.)	Interval TTI	Total TTI
Base Lias				
10-20	2^{-9}	16.0	0.03	0.03
20-30	2^{-8}	15.6	0.06	0.09
30-40	2^{-7}	14.4	0.11	0.20
40-50	2^{-6}	6.0	0.09	0.29
50-60	2^{-5}	9.2	0.29	0.58
60-70	2^{-4}	10.2	0.64	1.22
70-80	2^{-3}	10.2	1.27	2.49
80-90	2^{-2}	1.4	0.35	2.84
80-70	2^{-3}	1.4	0.17	3.01
70-60	2^{-4}	5.0	0.31	3.32
70-80	2^{-3}	1.2	0.15	3.47
70-60	2^{-4}	10.4	0.65	4.12
70-80	2^{-3}	45.0	5.62	9.74
80-90	2^{-2}	30.6	7.65	17.39
80-70	2^{-3}	19.4	2.42	19.81

9.4 STRUCTURAL DEVELOPMENT OF THE MESOZOIC BASINS IN SOUTHERN ENGLAND AND MATURATION OF JURASSIC ORGANIC MATTER

The geologic models shown in Figs. 9.3 - 9.8 representing various localities in southern England, and the application of the Lopatin method to these models discussed above seem to illustrate two important points: (i) that the structural evolution of the Mesozoic Basins was not uniform across southern England and (ii) that the level of maturation of Jurassic organic matter at any given locality and time in southern England was dependent on the structural development of that area. The geologic models confirm the fact that the four main earth movements which occurred in the Cretaceous to Tertiary Periods had varying degrees of deformations associated with them across southern England. In the Isle of Wight - Dorset area for example, while the two Mid-Cretaceous earth movements had very minor deformational effects in the locality of Arreton No. 2 Well to the south of the Purbeck - Isle of Wight Monocline, they were associated with serious tectonic implications in the Wytch Farm Oilfield and the locality of the Winterborne Kingston Well to the north of this line of disturbance. Thus while the Jurassic in these latter localities experienced its major tectonic inversion in the Mid-Cretaceous, such an inversion did not occur in the former locality (Arreton No. 2 Well) until the Early Miocene. The results of the application of the Lopatin method, as well as the geochemical analyses, show that high organic maturities are associated with Jurassic sections

that experienced almost continuous burial before the late tectonic inversion in the Miocene such as in the central Wealden Basin and in areas to the south of the Purbeck - Isle of Wight Disturbance. In Dorset, higher maturity of Kimmeridge Clay organic matter is noted in outcrop samples from the southern side of the Purbeck Monocline (Kimmeridge Bay - Chapman's Pool) than in samples from the northern side of that line (Ringstead Bay) (see Chapters 6 to 8).

In terms of hydrocarbon exploration in southern England today, it is seen here that the early major tectonic interruptions in the burial history of the Jurassic in the Mid-Cretaceous noticed in some parts of the study area produced a retardation in the organic maturation processes and this has limited, to some extent, the petroliferous nature of southern England.

CHAPTER X

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

The Lower Lias and the Kimmeridge Clay Formations show a wide range of lithologic types - from shales through mudstones to limestones (laminated and normal). Alternations of these various lithologies occur at various stratigraphic levels in these formations. By contrast, the Oxford Clay Formation shows a restricted lithologic range - consisting mainly of shales in the lower part and mudstones in the middle and upper parts. These variations in the lithology of the three major Jurassic mudrock formations is interpreted to indicate variations in their depositional environments.

The clay mineralogies of the three formations are similar. The clay mineral composition is made up principally of discrete illite and illite-smectite mixed layers with kaolinite, chlorite, and vermiculite forming minor components. Both random and ordered illite-smectite interstratified clay minerals occur but the ordered varieties appear more common in the Jurassic samples. The common occurrence of these ordered phases both in very shallow as well as in deeply buried samples is indicative of the fact that at least part of the muddy sediments of the Lower Lias, the Oxford Clay, and the Kimmeridge Clay were recycled from pre-Jurassic rocks which must have been heated beyond 100°C (212°F). The implication of this finding is that the expulsion of large volumes of clay interlayer water, frequently proposed to aid primary migration of generated hydro-

carbons at depth, is unlikely from these rock units.

The organic matter contents in almost all the rock samples analysed from the three formations are in excess of the minimum required for potential hydrocarbon source rocks. A relationship between lithology and organic matter content is noted. In each of the formations, the shales are the richest organically followed by the mudstones and then the limestones. The organic carbon contents of the laminated limestones are much higher than those of the normal limestones. This variation in the organic matter contents with lithology is related to the variation in the oxic-anoxic conditions of the depositional bottom waters.

There appears to be a relationship between the sedimentation rate and the organic matter content of the various lithologies in the three Jurassic formations. For any given lithologic type, the Kimmeridge Clay with the highest average sedimentation rate shows the highest TOC value while the Lower Lias with the lowest average sedimentation rate also shows the lowest TOC value. The relatively high sedimentation rate of the Kimmeridge Clay Formation probably explains the wide occurrence of oilshale units in this formation compared to the other two in South England.

Wide variations in the kerogen elemental composition occur in samples from each of the three formations. The kerogen facies range from type II through the mixed type II/III and type III to type IV in the Lower Lias and the Oxford Clay, whereas only the first three types

are identified in the Kimmeridge Clay. Amorphous organic material constitutes the most abundant fraction of all the kerogen samples. The herbaceous and the humic matter constitute, relatively, minor components. The amorphous matter in the type II kerogens is mostly sapropelic and light in nature whereas the amorphous components in the other kerogen types are the heavy, biodegraded varieties.

The type III kerogens have potential for oil and gas generation. Though the type IV kerogens show potential for liquid as well as gaseous hydrocarbon generation, it is doubtful if they can source commercial accumulations in Southern England.

No simple relationship is noted between the kerogen types and the associated lithologies. The various kerogen types occur both in the argillaceous as well as in the carbonate rocks. But there appears to be a relationship between kerogen type and the organic richness of the containing rock sample: Kerogen type II is mostly associated with the very organic-rich rock samples whereas the other kerogen types are associated with samples with moderate to low organic carbon contents. The fluctuating anoxic-oxic depositional bottom conditions during the Jurassic, probably associated with small scale eperiogenic movements, is suggested to have been the major factor controlling the organic richness of the sedimentary facies as well as the distribution of the kerogen facies.

Organic matter in the Oxford Clay and the Kimmeridge Clay Formations are mostly immature to marginally mature

(i.e. < 0.60% R_o) in most parts of Southern England. They are mature only in the deep central parts of the Mesozoic Wealden Basin. The Lower Lias organic matter is mature in the central parts of the Wealden Basin and in the adjacent central parts of Hampshire County as well as on the southern side of the Purbeck - Isle of Wight Disturbance. The maturity level estimated for the most mature sample analysed (a basal Lower Lias sample from Arreton-2 Well in Isle of Wight) is 0.90% R_o.

The stable carbon isotope ratios ($\delta^{13}C$) of the kerogens tend to vary with type in each of the three formations. The Lower Lias kerogens appear to be isotopically the lightest whereas the Kimmeridge Clay kerogens tend to be the heaviest, thus indicating an isotopic age trend in the Jurassic of Southern England. No trend in carbon isotopic data with kerogen maturity is noticed as a result of the relatively low maturity levels of all the samples analysed and also due to the very pronounced influence of the primary source variability. The stable hydrogen isotope analysis (δD) of some type II kerogen samples shows that even though the kerogens belong to the same chemical group, they are very diverse in nature.

On the bases of very similar n-paraffin distribution, CPI values, Pristane/Phytane ratios, as well as the very narrow range of topped oil $\delta^{13}C$ values, the three Dorset reservoired crude oils - the Cornbrash Oil (Kimmeridge Bay), the Bridport Oil and the Sherwood Oil (Wytch Farm Oilfield) - appear to have been derived from the same source or from very similar sources.

The deeply buried Lower Lias Formation (prior to the Miocene tectonic inversion), on the southern side of the Purbeck - Isle of Wight Disturbance, particularly in the locality of Arreton No. 2 Well, seems to be the main source of the Dorset Crude Oils on the bases of adequate organic maturity, n-alkane distribution, alkane ratios and the stable carbon and hydrogen isotope ratios.

Attempted constructions of geologic models of the Jurassic sections at various localities in Southern England, and the application of the Lopatin method (both original and modified) suggest that (i) the structural evolution of the Mesozoic Basins was not uniform across southern England, (ii) the present maturity levels of Jurassic organic matter at any given locality are dependent on the structural development of that area through time, (iii) the average paleogeothermal gradient in Southern England was quite similar to the present average value of about $30^{\circ}C/km$ or $26.2^{\circ}F/1000$ ft., and (iv) the Lias in the deepest part of the Mesozoic Wealden Basin (northern West Sussex - southern Surrey) is a possible source for the recently discovered natural gas deposit in south-west Surrey.

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