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Oil Shale Resources in Great Britain

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1. Introduction

1.1 HISTORICAL BACKGROUND

It has been estimated that the known world resources of oil shale contain a potential 3×10^{13} tons of oil (Matveyev, 1974, p. 13). Only about 1 to 2 per cent of this is thought to be recoverable by present-day technology, but even this modest amount would more than satisfy the world's needs until well into the 21st century. In practice there are formidable problems in utilising this potential resource and oil shales currently make a negligible contribution to the world energy scene.

The name "oil shale" is misleading. Some oil shales contain small amounts of organic matter (bitumen) that can be extracted with solvents, but most of their organic content is in the form of insoluble complex organic compounds (kerogens) which yield oil artificially on heating or, naturally, under the action of the geothermal gradient and overburden pressure in the Earth's crust. The term kerogen covers an enormously variable group of multi-polymers with molecular weights in the range of thousands to ten of thousands. Those in the oil shales have been formed in the sediment by chemical alteration of fats, waxes and other decay products, derived largely from algae. The atomic hydrogen-to-carbon ratio of this algal material is closer to that of petroleum than is the ratio for the higher plants (from which coals are largely derived). Consequently the kerogens in oil shales are readily broken down by heat to produce oils while those in coals more readily yield hydrocarbon gases.

There is no universally agreed definition of the term oil shale. Organic matter, in the form of kerogen, bitumen and hydrocarbons, occurs in various concentrations in most fine-grained sedimentary rocks. Where the organic concentration is sufficiently high to noticeably affect the lithology of the rock, or where it imparts an organic smell to the freshly broken rock, the name 'bituminous mudstone' has commonly been used. This is usually inappropriate since the 'bitumen' fraction of an organic-rich rock is that part which can be extracted with organic solvents, whereas in most of the rocks referred to as 'bituminous' the organic fraction is almost wholly present as insoluble kerogen. Hatch and Rastall (1965, p. 286) proposed terms such as 'kerogenite', 'shale-kerogenite', 'dolomite-kerogenite' etc., as being technically more correct, but these have been ignored and the old term 'oil shale' (i. e. yielding appreciable quantities of oil on destructive distillation by

breakdown of the kerogen) remains popular.

Yen (1976, p. 1) has suggested that the lower limit for oil shales should be rocks which yield 10 gallons of oil per ton of shale¹ when destructively distilled. This has the practical value that 10 gal/ton is probably the lowest grade of oil shale that is likely to be workable in the foreseeable future. It is less satisfactory as a lithological term since rocks yielding as little as 5 gal/ton can have the characteristic aromatic smell, low density and brown streak of oil shale.

Some authors have sought to place an upper limit on oil shales in order to exclude rocks such as tar sands and coals from the definition since they too can be made to yield oil by pyrolysis. The richest oil shales, those with yields greater than about 120 gal/ton, grade imperceptibly via torbanites and cannel coals into normal coals. They differ from the last named only in their organic composition, being composed predominantly of kerogens of algal rather than higher-plant origin.

In practice, the great majority of oil shales have potential oil yields in the range 10 to 70 gal/ton and they form a lithologically distinctive group of rocks.

Oil shales range in age from Precambrian to Recent, although in Cambrian (500 to 570 million years ago) and older rocks they are uncommon because their organic content has usually been altered by geological processes to graphite. The distribution of oil shales through time shows two marked peaks, in the Permian and early Tertiary, which correspond to periods when proportionately large areas of the Earth were covered by lakes and shallow seas. This relationship is explained by the common coincidence in such environments of the two most important requirements for the formation of oil shales - prolific organic growth and a means of preserving the organic material in the sediment. A large proportion of the world's oil shale is believed to have formed from algal blooms in lakes, marine basins or shallow shelf-seas in which the organic material has been saved from the destructive action of aerobic bacteria by sinking into an anaerobic zone.

Major deposits of oil shale occur on every continent and have, at one time or another, been worked in most industrialised countries. However, these workings have never been on a large scale for a number of reasons. First, oil shales have to be retorted to about 500° C before they yield oil in commercial quantities. The energy profit from this process is small because of the inefficiency of the retorting and the cost of winning, retorting, refining and land reinstatement; shale oil could, therefore, only be competitive with naturally occurring

¹ US gallons/US (short) ton are used in the general text of this report. Where specific analyses are quoted the terms US gallon, UK gallon, US ton, UK ton, metric tonne etc. are used following the recommendations of British Standard 350: Part 1 (1959 with later amendments).

COUNTRY	LOCALITY	YEAR							GRADE OF SHALE WORKED U. S. gal/ton	SEAM THICKNESS (m)	AGE OF DEPOSIT				
		1840	1860	1880	1900	1920	1940	1960				1980			
U. K.	Lothians, Scotland			1850	—————				1963	15 to 120 (25 av)	1 to 4	Carboniferous			
France	Autun	1838	—————				1957		10 to 18	2 to 11	Permian				
	Severac le Chateau					1943	—	1949	12	1 to 6	Jurassic				
Sweden	Kvarntorp					1921	—————		1965	15	15	Cambro-Silurian			
Spain	Puertotollano					1922	—————		1966	30 to 35	3 to 4	Carboniferous			
Switzerland	Meride (Jura)					1915	—	1930	55	10	Triassic				
Australia	Glen Davis			1865	—————				1962	20 to 100	1 to 2	Permian			
Brazil	Paraiba			1881	—————		1900		1941	—————		1957	21 to 33	2	Tertiary
	Irati*								1972	—	1978	15 to 25	7 to 9	Permian	
U. S. A.	Western Colorado**											→ 1979	27	c 30	Eocene
U. S. S. R.	Estonia					1921	—————			1979	50 to 70	1 to 2	Ordovician		
China	Fushun (Manchuria)***					1929	—————			1979	c 5 to 30	c 100 to 200	Oligocene		

*Full scale pilot plant

**Commercial plant under construction

***Details of yield and seam thickness uncertain

Table 1 History of working, yields and thicknesses of selected oil shales

oils if worked on a vast scale. Secondly, because the spent shale after retorting has a similar volume to the raw shale, has few uses and may include small quantities of carcinogens, its disposal presents formidable environmental problems.

A large number of countries, including Great Britain, have sustained small oil shale industries in the past but these have commonly begun during the economically artificial conditions of depression or wartime and have subsequently failed when subjected to competition from crude oil once free world trade has been re-established (Table 1). At the present time only China and the U. S. S. R. have active oil-shale industries. These are ageing but apparently thriving and produce the equivalent of about 22 million tons of oil per annum. A commercial plant is currently under construction in Colorado, U. S. A.

Britain holds an important place in the historical development of oil shale working. The first oil shale patent "A way to extract and make great quantities of pitch, tarr and oyle out of a sort of stone" (Crown Patent No. 330) was granted to a group of English entrepreneurs in 1694, and the first substantial shale-oil industry was begun in the Lothians of Scotland (based on Carboniferous oil shales) in 1851 by John Young and others. By 1865 some 120 shale oil works were operating in Scotland and in 1913 a maximum annual production of over 3.2 million tons of shale was achieved. The industry declined slowly but steadily from this peak, with minor expansions during the war periods, due to the increasing availability of cheap crude oil. It finally closed down in 1962.

Oil shales occur at a number of other stratigraphical levels in Great Britain (Table 2), notably in the Devonian (Caithness Flags) and the Jurassic (Lias, Middle Jurassic, Oxford Clay, Kimmeridge Clay) (Table 3). Of these, the Kimmeridge Clay has long seemed to be the most interesting prospect but repeated attempts at commercial exploitation have all ended in failure. The existence of the Kimmeridge Clay oil shales has been known since the Iron Age. At various times since then they have been used at outcrop in the Dorset cliffs as a local coal substitute and, in the 17th century, as the heat source for alum, glass and sea-salt works at Kimmeridge, Dorset. During the latter half of the 19th century no less than 8 companies were set up to exploit the Kimmeridge Clay oil shale, but none was lastingly successful. In each case the unacceptably high sulphur content of the shale oil (4 to 8 per cent), combined with the high cost of working thin seams, was blamed for the failure.

As assessment of the extent and value of the Kimmeridge Clay oil shale in Dorset and Lincolnshire was made by the Ministry of Munitions during the First World War (reported in Strahan, 1918, 1920) and a similar assessment was made in Norfolk (Forbes-Leslie, 1917a) by commercial companies during and shortly after the war. Commercial attempts to exploit the oil shale in Norfolk between 1916 and 1936 also failed and again the high sulphur content of the oil was claimed to be the major problem.

Table 2 The major oil shale occurrences in the British land area

Age (m.y.)	System	Formation	Main locality	Presumed depositional environment
65	Quaternary and Tertiary			
141	Cretaceous			
195	Jurassic	Kimmeridge Clay Oxford Clay Brora Oil Shale Dun Caan Oil Shale Jet Rock Series Kilve oil shales	See Table 2 for details	
230	Triassic			
280	Permian			
345	Carboniferous	Coal Measures	Local thin torbanites in England and Wales	freshwater marsh
		Oil Shale Group	Lothians of Scotland	freshwater marsh
395	Devonian	Caithness Flags	N. E. Scotland	freshwater lake
435	Silurian			
500	Ordovician			
	Cambrian			
570				

Table 3 The major oil shale occurrences in the Jurassic of the British land area

Sub-system	Stage	Formation	Main Locality	Presumed depositional environment
UPPER	Volgian/ Portlandian	Purbeck Beds*	Weald	freshwater lake
	Kimmeridgian	Kimmeridge Clay	Dorset to Yorkshire	shelf sea
	Oxfordian			
	Callovian	Oxford Clay (Lower)	Dorset to Lincolnshire	shelf sea
MIDDLE	Bathonian	Brora Oil Shale	Brora, Sutherland	brackish lagoon
		Dun Caan Oil Shale	Raasay and Skye, Inner Hebrides	brackish lagoon
	Bajocian			
LOWER	Toarcian	Jet Rock Series	Whitby, N. Yorks	shelf sea
	Pliensbachian			
	Sinemurian	Lower Lias	Kilve, Somerset	shelf sea
	Hettangian			

*reported in Lees and Cox (1937, p. 165) but not subsequently seen

Analyses were made of the Middle Jurassic oil shales of Brora, Sutherland and Raasay, Inner Hebrides in the early part of the century but the yields were too low to compete with Lothian oil shales. Thin seams of poor quality oil shale have been recorded from the Lias of Somerset and a retort was set up shortly after the First World War to exploit those in the cliff sections at Kilve. This too was a commercial failure.

At the present time the only organic-rich sediments (poor quality oil shales) that are used commercially in the U.K. are those in the Oxford Clay. Here, oil shales in the lower part of the formation provide the calorific value on which the 'self-firing' Fletton brickmaking process is based.

In 1973, at the time of an unprecedented rate of increase in world crude oil prices, the Department of Energy commissioned Mr A. M. Macleod Matthews to assess, on the basis of existing data, the possible prospects for exploitation of U.K. oil shales. The Macleod Matthews Report (Department of Energy Paper No. 1, HMSO, 1975) suggested that an economic case did not appear to exist for re-opening the Scottish mines and recommended that the Institute of Geological Sciences should undertake a study of the Kimmeridge Clay oil shales since they were largely unexplored.

The Institute had at that time already embarked upon a desk study of the Scottish Carboniferous oil shales (Tulloch and McAdam, 1973; Cameron and McAdam, 1978) and a

Table 4 Continuously cored boreholes drilled for the oil shale pilot project † and the present study

Borehole	National Grid Reference	One-inch geological sheet	Date of drilling	Ground level (Datum): m above OD	Final Depth (m)
North Runcton, † Norfolk	TF 6404 1624	145 (King's Lynn)	1974	16	107
Donington-on-Bain, † Lincolnshire	TF 2399 8188	103 (Louth)	1975	73	200
Swindon, Wiltshire †	SU 1413 8349	252 (Swindon)	1975	143	134
West Lavington, † Wiltshire	ST 9898 5633	282 (Devizes)	1975	81	231
Hartwell, Buckinghamshire	SP 7926 1223	237 (Thame)	1976	100	77
Tisbury, Wiltshire	ST 9359 2907	297 (Wincanton)	1977	137	230
Portesham, Dorset	SY 6214 8554	341 (Fleet)	1977	67	208
Kimmeridge Bay, Dorset	SY 9097 7899	342 (Weymouth)	1977	18	110
Encombe, Dorset	SY 9446 7785	343 (Swanage)	1977	40	133
Reighton, North Yorkshire	TA 1465 7581	55 (Flamborough)	1978	55	162
Marton, North Yorkshire	SE 7230 8285	53 (Malton)	1978	162	212
Foudry Bridge, Berkshire	SU 7033 6604	268 (Reading)	1977	58	411 to 513*

*Kimmeridge Clay interval only

pilot study (including a limited amount of drilling) of the Kimmeridge Clay oil shales in southern England in order to assess whether a full scale study of the latter would be worthwhile. This pilot study showed the Kimmeridge Clay oil shale seams to be extensive but to consist of groups of thin seams (individual seams range in thickness from a few centimetres to a maximum of about 60 cm) separated by barren clays. Some of the individual seams have high yields and the best prospects, groups of closely spaced seams which would need to be worked en bloc and separated from the intervening clays before being retorted, are potentially richer than oil shales which were once worked commercially elsewhere in Europe (Gallois, 1978).

1.2 AIMS OF THE INVESTIGATION

As a result of the pilot study, the Department of Energy commissioned the Institute in 1976 to carry out a more detailed study of the occurrence and geochemistry of the

Kimmeridge Clay oil shales and shale oils in England and Scotland to enable informed decisions to be made on their use as an energy or petrochemical source should the need ever arise. In addition to their potential use as a direct source of oil the Kimmeridge Clay oil shales are believed to be the major natural source rock in the North Sea oil province and an attempt has therefore been made to assess their source-rock potential beneath the land and continental shelf areas. The nature and occurrence of the more important of the other British shales has also been reviewed and a small amount of analytical work has been carried out to enable their potential to be assessed in relation to that of the Kimmeridge Clay.

The continuously cored boreholes drilled at Donington on Bain, Lincolnshire; North Runcton, Norfolk; Swindon, Wiltshire and West Lavington, Wiltshire in 1974 and 1975 for the pilot study suggested that the oil shales were thin, but laterally persistent, and that they were concentrated at five levels within the formation (op. cit.). Seven additional boreholes have been drilled for the present project at Reighton and Marton, North Yorkshire; Hartwell, Buckinghamshire; Tisbury, Wiltshire and at Portesham, Kimmeridge Bay and Encombe in Dorset (Table 4) to provide material for stratigraphical studies and chemical analyses in the outcrop area. In addition a continuous core of Kimmeridge Clay was obtained, in collaboration with the National Coal Board, from the subcrop area at Foudry Bridge, Berkshire and this, when compared with the cores from the IGS borehole at Warlingham, Surrey (Worssam and Ivimey-Cook, 1971), has enabled comment to be made on a large part of the subcrop. The Kimmeridge Clay outcrops in Cromarty, Sutherland and the Inner Hebrides were also examined, as were other Jurassic oil shales in the same areas.

Stratigraphical work, aimed at defining as precisely as possible the levels at which oil shales occur in the Kimmeridge Clay, has been carried out on all the boreholes drilled for the pilot and the present studies. It was found in the pilot study that the oil shales were sufficiently distinctive in lithology in the cores for the levels of likely economic interest to be determined from a visual examination. In the present work the cores at these levels were cut in half and one half was used to provide bulk samples to determine the potential oil yield. The remaining half core was used for stratigraphical work and to provide material for detailed chemical analysis. A representative set of specimens has been chosen for permanent retention in the National Rock Collection at IGS.

Geochemical studies have been carried out on the shale oils produced by pyrolysis of the Kimmeridge Clay oil shales and on the solvent-extractable (bitumen) fraction of the organic content of the oil shales. This latter material is potentially mobile and an attempt has been made to compare its chemistry with that of a number of naturally occurring crude oils from the land and continental shelf areas of the U. K.

Most methods of oil shale treatment involve the production of large volumes of shale

waste and it is clearly economically and environmentally desirable that some use should be found for this material. Tests have therefore been carried out on the shales and the associated mudstones and the burnt shale waste to determine their mineralogy and possible usefulness as materials for the manufacture of structural clay products. Many organic-rich mudstones show enrichment of trace elements, especially metals, in sufficient quantities to suggest that those elements might be a valuable, extractable by-product of oil shale working. Analyses have therefore been carried out to determine the major and minor element compositions of representative Kimmeridge Clay oil shales and oil shale/mudstone mixtures.

A selection of geophysical logs was run in each of the boreholes to assist with the stratigraphical correlations and to assess the usefulness of various geophysical techniques as an aid to identifying the presence and possible quality of oil shales in uncored boreholes.

1.3 ACKNOWLEDGEMENTS

The work was carried out by the East Anglia and South-East England Unit in collaboration with a number of other departments. Mr R. W. Gallois, with the assistance of Miss M. B. Simmons, and under the direction of Dr P. A. Sabine and later of Mr W. B. Evans, supervised the work and compiled the present report. Miss L. M. Wahl has drawn the figures. Dr R. A. B. Bazley, District Geologist, East Anglia and South-East England Unit has edited the report.

Mr J. Dangerfield and Mr R. J. Merriman of the Petrographical Department, under the direction of Mr R. K. Harrison, supervised the preparation of samples for oil yield analysis and carried out an X-ray diffraction study on selected samples respectively. Mr G. E. Strong of the same department determined the specific gravities of a number of oil shales. Trace element analyses were carried out by Miss E. Waine of the Analytical and Ceramics Unit; Mr J. Bain and Mr D. E. Morgan of the Applied Mineralogy Unit have examined the properties of a number of oil shale/clay mixtures with respect to their potential use in the manufacture of structural clay products. Dr M. E. Coleman of the Isotope Unit determined the carbon/sulphur isotope ratios of selected kerogens and oil shales.

Miss B. M. Cox of the Palaeontology Department has advised on Kimmeridgian stratigraphy and has assisted, together with Dr W. Mykura of the Highlands and Islands Unit, in the Scottish field work. Dr B. Owens of the Palaeontology Department has described the organic constituents of selected oil shales and Dr A. W. Medd and Mr I. P. Wilkinson of the same department have determined the coccoliths and ostracods respectively of stratigraphically critical samples.

Collaboration with the National Coal Board, in particular with Mr M. Allen of the Headquarters Division, enabled a continuous core of Kimmeridge Clay to be obtained from an

NCB borehole near Reading. Mr L. Salmon of the Environmental and Medical Sciences Division of the AERE, Harwell measured the total gamma-ray counts of selected core samples.

The Energy Research Center of the United States Department of Energy, at Laramie, Wyoming under the direction of Dr J. W. Smith, have assayed oil shale samples by the modified Fischer Assay method to enable the Kimmeridge Clay results to be directly compared with those from shales elsewhere in the world.

The assistance of a number of companies who supplied crude oils from the North Sea is also gratefully acknowledged. These are Esso Petroleum Company Ltd, Mobil North Sea Ltd, Occidental of Britain Inc, and Shell U. K. Exploration and Production.

A number of contractors have been involved in the work. Drilling was carried out by B. B. Drilling Ltd of Bolden, Farrods Ltd of Ripon, Drilling and Prospecting International Ltd of Rickmansworth and Thompson International Ltd of Alberta. Geophysical logs were run in the boreholes by British Plaster Board Ltd.

Assays of potential oil yield and selected organic analyses have been carried out by Robertson Research International Ltd under the supervision of Dr B. S. Cooper; detailed organic analyses have been made by Dr P. F. V. Williams of the Organic Geochemistry Unit at Newcastle University under the direction of Dr A. G. Douglas and Dr D. Grant of the British Carbonisation Research Association has analysed some of the shale oils to identify possible carcinogenic compounds.

Dr C. V. Jeans of Cambridge has determined the clay mineralogy of a representative selection of clays and oil shales. Elemental analyses of kerogens and shale oils have been made by Butterworths Ltd of Teddington under the direction of Mrs D. Butterworth and Dr D. B. Lisle of the Laboratory of the Government Chemist has determined the physical properties of a number of shale oils.

Dr B. Kelk and Mr J. R. V. Brooks have acted as liaison officers for the project at the Natural Environment Research Council and the Department of Energy respectively.

2. Kimmeridge Clay: distribution of the oil shales

2.1 INTRODUCTION

The occurrence of oil shales in the cliffs of Kimmeridge Clay at Kimmeridge Bay, Dorset, has been known since Iron Age times. The most famous seam, the Blackstone, has been used locally as a coal substitute, both domestically and industrially, and has yielded at various times products ranging from lubricating oil to fertilizer and a sanitary deodorizer. Combustible shales have also been recorded in the Kimmeridge Clay elsewhere in Dorset and in Wiltshire, Norfolk, Lincolnshire and Scotland.

The Blackstone was commercially exploited on a small scale in Dorset at various times in the 17th to 19th centuries, but without lasting success. Assessments were made of the potential value of the Kimmeridge Clay oil shales as a source of fuel in Dorset and Lincolnshire (Strahan, 1918, 1920) and Norfolk (Forbes Leslie, 1917a, 1917b) during the First World War and although substantial quantities of good quality oil shale were proved to be present no major industry was developed.

The Kimmeridge Clay has an extensive outcrop and subcrop in England (Fig. 1). The outcrop runs in an almost continuous strip from Dorset to North Yorkshire and is broken only in north Dorset, Wiltshire, between Buckinghamshire and Cambridgeshire and across the Market Weighton axis in Humberside, where the formation has been removed by erosion during the Lower Cretaceous. The English subcrop of the Kimmeridge Clay underlies the whole of the land area to the east of the outcrop with the exception of a large area of want (on the London Platform) beneath East Anglia and a smaller area on the Market Weighton Axis (Fig. 1).

Throughout most of its outcrop and subcrop the structure of the Kimmeridge Clay is simple (Fig. 2). The base of the formation dips approximately eastwards at less than 1° away from the outcrop in most areas other than the complexly faulted areas of south Dorset and North Yorkshire.

The maximum proved thickness of preserved Kimmeridge Clay is 560 m in the Weald of Sussex. Thicknesses of over 500 m have been recorded in south Dorset, but elsewhere the formation is generally less than 250 m thick, (Fig. 3). The present distribution of thickness in the formation is related to two factors, the original depositional thickness and late Jurassic and Lower Cretaceous erosion. The thick succession of the Dorset coast is complete, being conformably overlain by Portland Beds. It is separated from the north

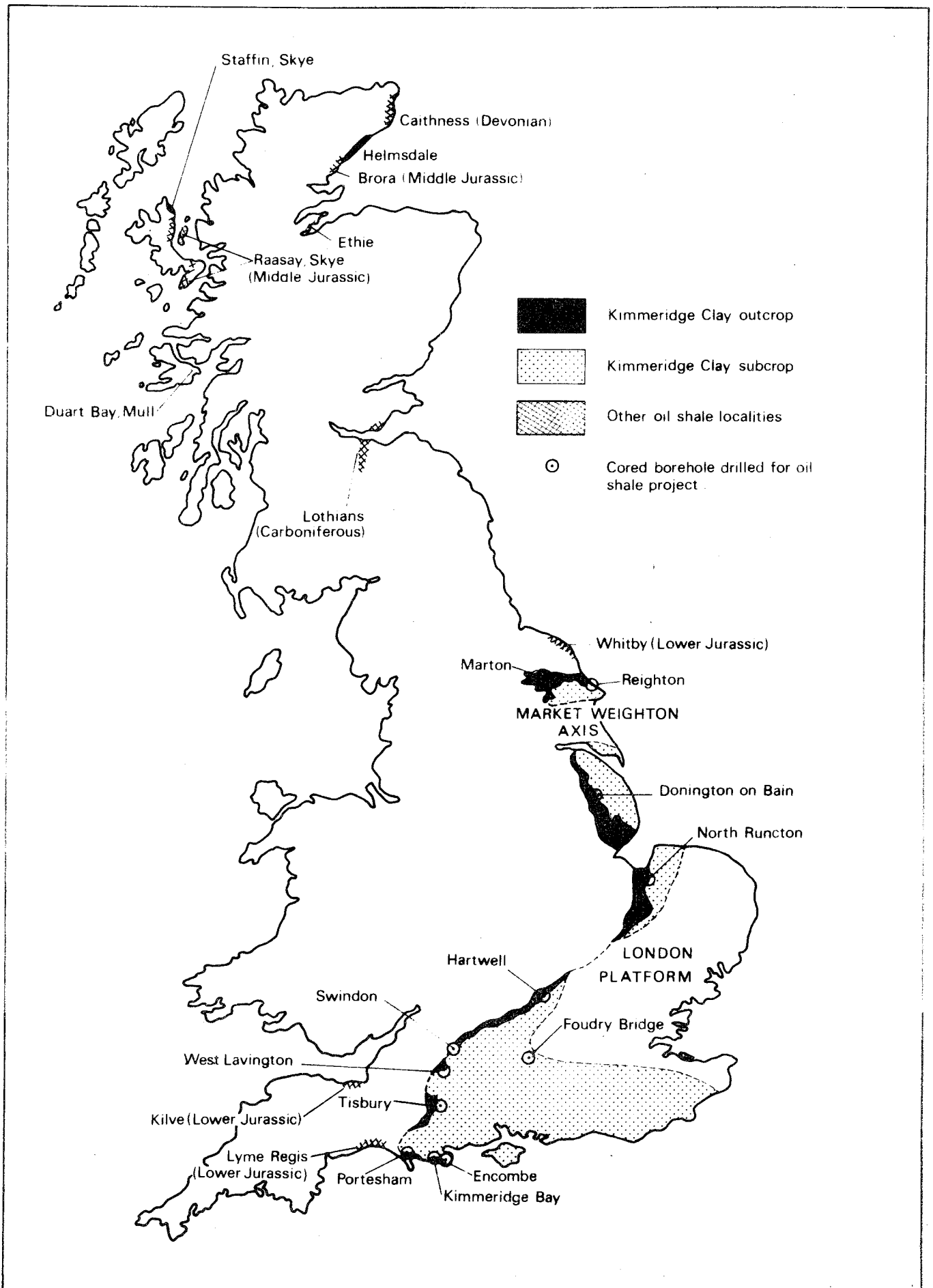


Figure 1 Geological sketch map showing the Kimmeridge Clay outcrop and subcrop and the positions of cored boreholes drilled for the study

Dorset and Wiltshire outcrop sequences, which are also complete, by the complex west-east trending fold and fault belt that includes the Isle of Purbeck and Isle of Wight structures. Within this belt the Kimmeridge Clay is thin and incomplete and has been locally removed by erosion during post-Portlandian to pre-Aptian times. Between north Dorset and Buckinghamshire the Kimmeridge Clay at outcrop thins steadily northwards, an original feature that reflects the transition from the Dorset depositional basin to the stable shelf that fringed the London Platform. Thin Kimmeridge Clay sequences also occur along the southern edge of the London Platform beneath Berkshire, Surrey, Sussex and Kent. The more easterly of these sequences thicken southwards into the Wealden depositional basin where the Kimmeridge Clay is again complete and more than 500 m thick. The Wealden and Dorset basins are separated by an area of thinner Kimmeridge Clay beneath the western Weald and Hampshire Basin where the sequence has been partially eroded.

The formation thickens steadily northwards from Aylesbury to the River Humber. Nowhere is it complete in this area but only the highest beds have been removed by erosion and this thickening is largely a true depositional thickening. Kimmeridge Clay is absent due to erosion across the Market Weighton axis but reappears as a relatively thick, and much faulted sequence, in the Vale of Pickering in North Yorkshire.

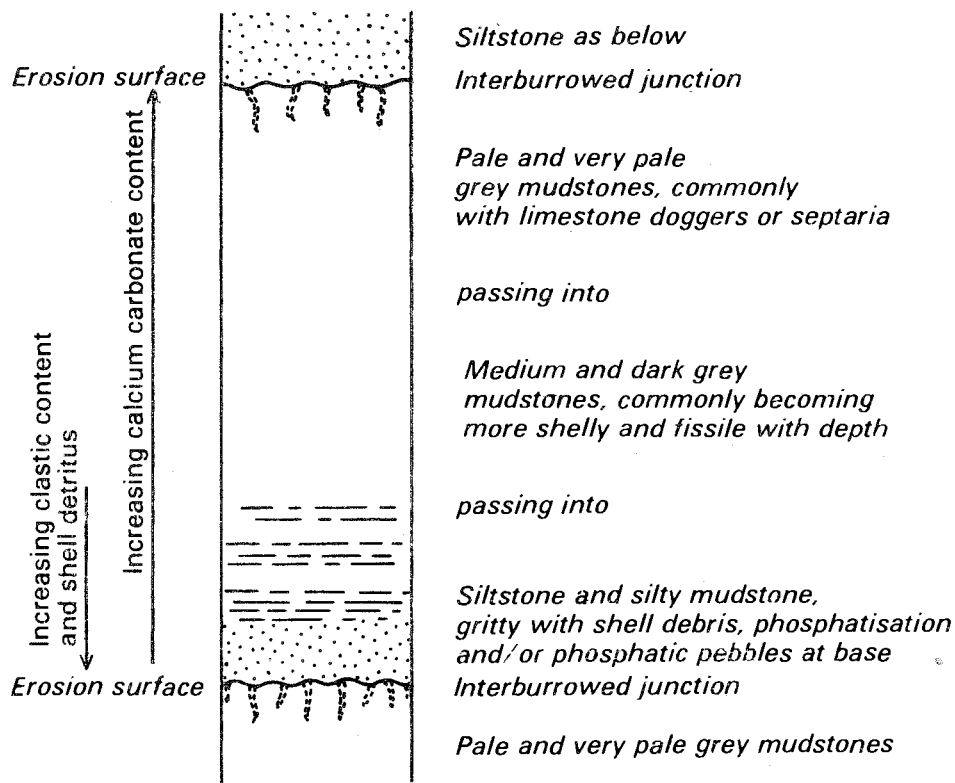
2.1.1 Stratigraphy

The Kimmeridge Clay of much of the English outcrop is made up of a complex sequence of small-scale rhythms. In the lower part of the Lower Kimmeridge Clay these rhythms consist of thin silts or silty mudstones overlain by dark grey mudstones and pale grey calcareous mudstones (Fig. 4a). In the upper part of the Lower Kimmeridge Clay and the Upper Kimmeridge Clay they consist of oil shales overlain by dark grey mudstones and pale grey calcareous mudstones (Fig. 4b). Type B rhythms, mostly 1 to 2 m thick, are well displayed in the cliffs at Kimmeridge Bay (Plate 1A). The highest part of the Kimmeridge Clay consists of sandy and calcareous mudstones (Plate 1B) and is devoid of oil shales.

Many of the individual rhythms can be correlated over distances of tens of kilometres (Gallois and Cox, 1976). Superimposed on this rhythmic sequence are broader lithological changes, from more to less calcareous and from more to less oil-shale-rich, which can be regarded as larger scale rhythms and which can be correlated throughout the English Kimmeridge Clay. Coarser sediments occur locally near the edges of the outcrop and subcrop and replace parts of the rhythmic sequence. Sandy ironstone occurs in the basal Kimmeridge Clay at Abbotsbury, Dorset, sands occur in the Upper Kimmeridge Clay between Devizes, Wiltshire and Aylesbury, Buckinghamshire, and sandstones occur in the Lower Kimmeridge Clay in east Kent and at Elsham, Lincolnshire.

Kimmeridge Clay also crops out on the east coast of Scotland at Ethie, Cromarty and

TYPE A



TYPE B

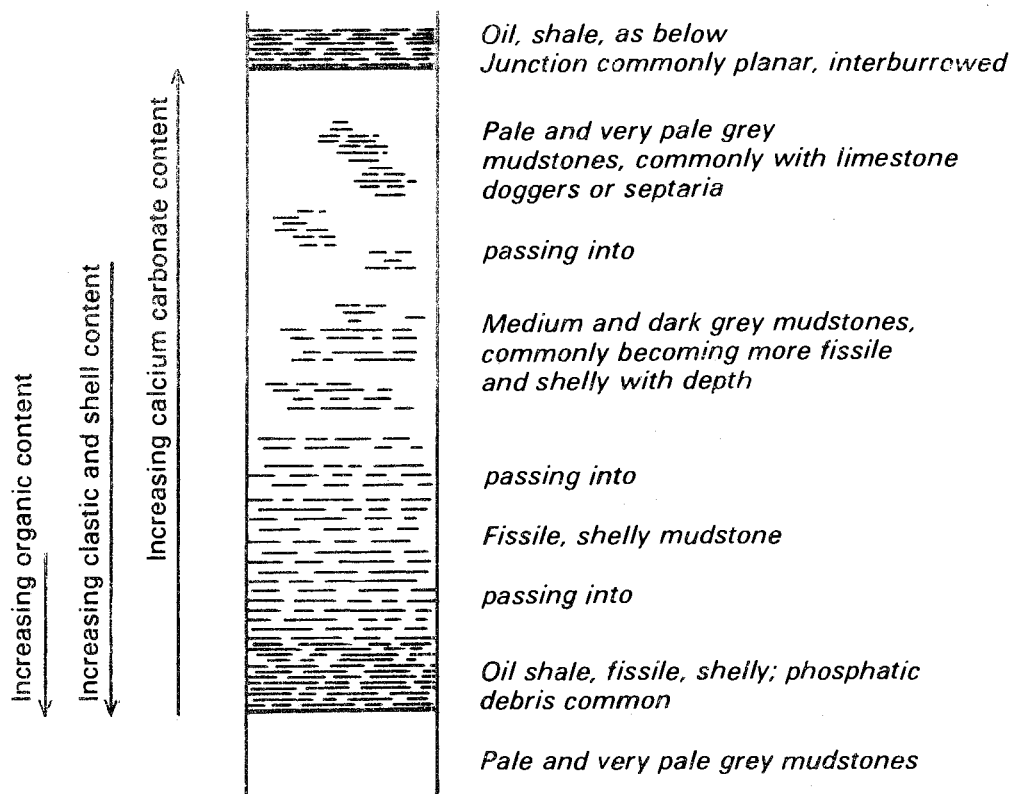


Figure 4 Generalized Kimmeridge Clay rhythms

PLATE 1

A. Type B rhythms, in which oil shales pass up into very calcareous mudstones, are well displayed within the Aulacostephanus autissiodorensis Zone (Beds 33 and 34) in the cliff sections at Kimmeridge Bay, Dorset. The oil shales (because of their inert kerogen content) are more resistant to weathering than the calcareous mudstones and form hard bands in which a rectilinear joint pattern gives rise to characteristically serrated ribs. The thickest hard rib, on which the figure is standing, is a persistent tabular dolomitic limestone, the Washing Ledge Stone Band, which forms a useful local stratigraphical marker bed.

B. The highest part of the Kimmeridge Clay, Pavlovia rotunda and Virgatopavlovia fittoni zones, consists of sandy and calcareous mudstones and is devoid of oil shales. The highest oil shales in the Kimmeridge Clay crop out as a series of hard ribs in the lowest part of the cliffs at Chapmans Pool, Dorset. The overlying mudstones degrade to a landslipped steep slope that becomes progressively steeper upward as the sandy Portland Beds (in the distant cliff) are approached.

Helmsdale, Sutherland and on the Hebridean islands of Mull and Skye. Rhythmic mudstone sequences occur at these localities but the rhythms are less obvious due to the presence of large amounts of silt and carbonaceous debris derived from nearby land areas.

Using the parameters of colour, texture, grain size and shell content a number of lithologies can be readily recognised in borehole cores and outcrop sections in the Kimmeridge Clay. The more distinctive lithologies include barren mudstones (pale, medium or dark grey), shelly mudstones (pale, medium or dark grey), silty mudstones, thin limestones (muddy, septarian, coccolith-rich etc.) and oil shales (shelly or barren) and thinly interbedded, interlaminated and interburrowed combinations of many of the above.

These distinctive lithologies are made up of a limited number of clastic, biogenic and chemogenic components which occur in varying combinations and amounts. The principal components have been determined by microscope studies and X-ray diffraction analyses and are as follows:

a. Clastic components

- i clay minerals: mostly illite and kaolinite: generally 30 to 65% of whole rock.
- ii crystalline quartz: angular silt and clay-grade particles: up to 23% rarely <15%: silt grade quartz is the major component of the thin siltstone horizons
- iii re-worked biogenic and chemogenic materials: shell and plant debris, phosphatic nodules.

b. Biogenic components

- i calcareous macro- and micro-fauna and flora: predominantly ammonites bivalves and foraminifera with brachiopods, serpulids, crinoids, ostracods and coccoliths important at some levels.
- ii phosphatic fauna: vertebrate debris, mostly fish scales, vertebrae and faecal pellets.
- iii kerogen: sporomorphs (e.g. pollen, dinoflagellates), plant debris, diagenetically formed kerogen.

c. Chemogenic components

- i calcium carbonate: possible primary precipitation of microscopic aragonite needles: diagenetically formed concretions.
- ii phosphate: early diagenetic formation.
- iii pyrite: early diagenetic formation.

The gross mineralogy of the commoner Kimmeridge Clay lithologies can be expressed in terms of the three components clay minerals/quartz, calcium carbonate and kerogen (Fig. 5). The typical composition of these common lithologies can be summarized as follows:

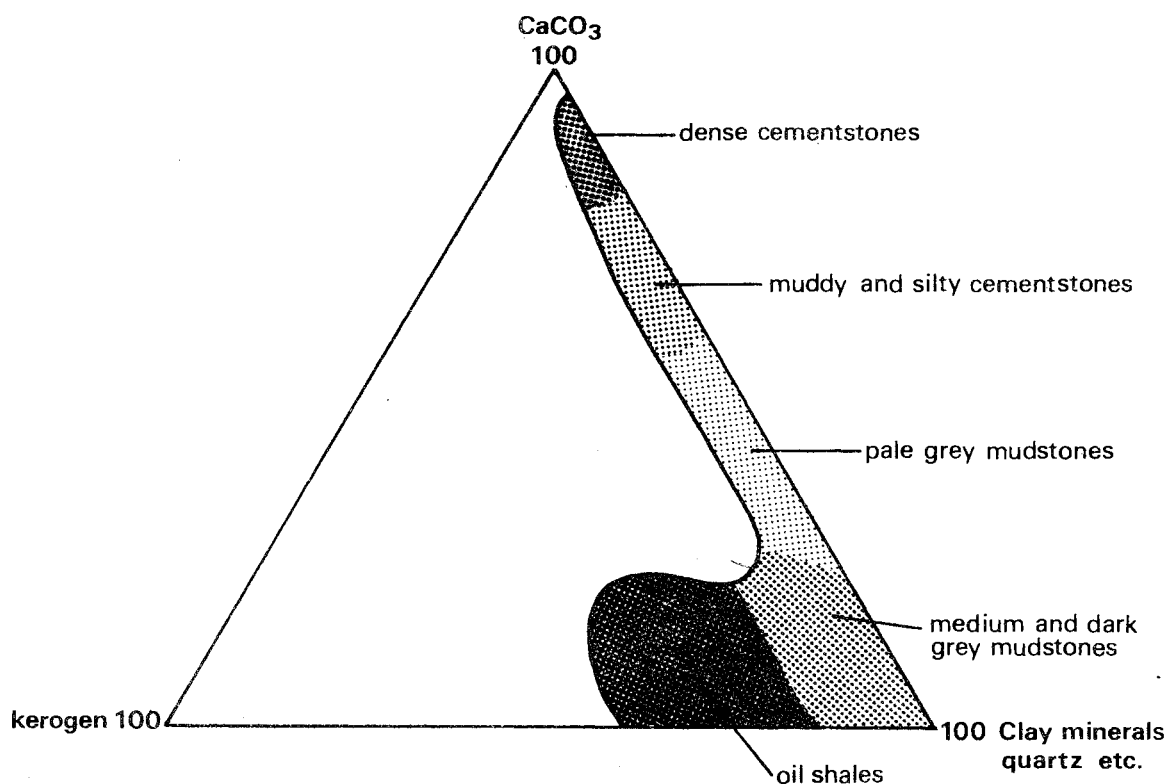


Figure 5. Diagrammatic representation of the bulk chemistry of some of the more distinctive Kimmeridge Clay lithologies

- i dark grey mudstone – clay minerals 45 to 65%, quartz 10 to 30%, calcium carbonate 5% to 20% depending upon shell content, kerogen <1%.
- ii medium grey mudstone – clay minerals 35 to 55%; quartz 10 to 15%; calcium carbonate 20 to 35%; kerogen <1%
- iii pale grey mudstone – clay minerals 25 to 45%; quartz 8 to 15%; calcium carbonate 25 to 55%; kerogen <1%
- iv cementstone – clay minerals 10 to 20%; quartz 2 to 6%; calcium carbonate 60 to 90%; kerogen <1%
- v oil shale – clay minerals 20 to 40%; quartz 10 to 15%; calcium carbonate 10 to 25%; kerogen 10 to 45%.

Detailed analyses of selected Kimmeridge Clay lithologies are given in Section 5.2 and Appendix C.

The Kimmeridge Clay is wholly marine throughout Britain and at most levels is rich in ammonites and bivalves. The formation has been zoned on the basis of ammonites (Ziegler, 1962; Cope, 1967, 1978) and has been further subdivided on the basis of a combination lithological and faunal characters (Gallois and Cox, 1976; Cox and Gallois in Gallois, 1979). This latter classification has been shown in the present work to be applicable to the argillaceous Kimmeridge Clay sequences throughout the English outcrop and subcrop and has been used to define the positions of the oil shales.

The most useful single feature for determining the stratigraphical position of any quarry, cliff or core section within the Kimmeridge Clay is the ammonite assemblage. Most sections are sufficiently fossiliferous for the zonal position to be determined and, in many cases in the Lower Kimmeridge Clay, the position within the zone (either low or high) can commonly also be determined from the ammonites alone. In addition to the zonal indices, species of Amoeboceras, Amoeboceras (Nannocardioceras), Aspidoceras and its aptychal plate Laevaptychus, Aulacostephanus, Propectinatites, Rasenia, Sutneria and Xenostephanus are exceptionally useful markers at many levels and enable subdivisions of zones to be identified with confidence. In boreholes the zonal boundaries and selected marker beds can be rapidly identified using a combination of a small number of core specimens and geophysical logs.

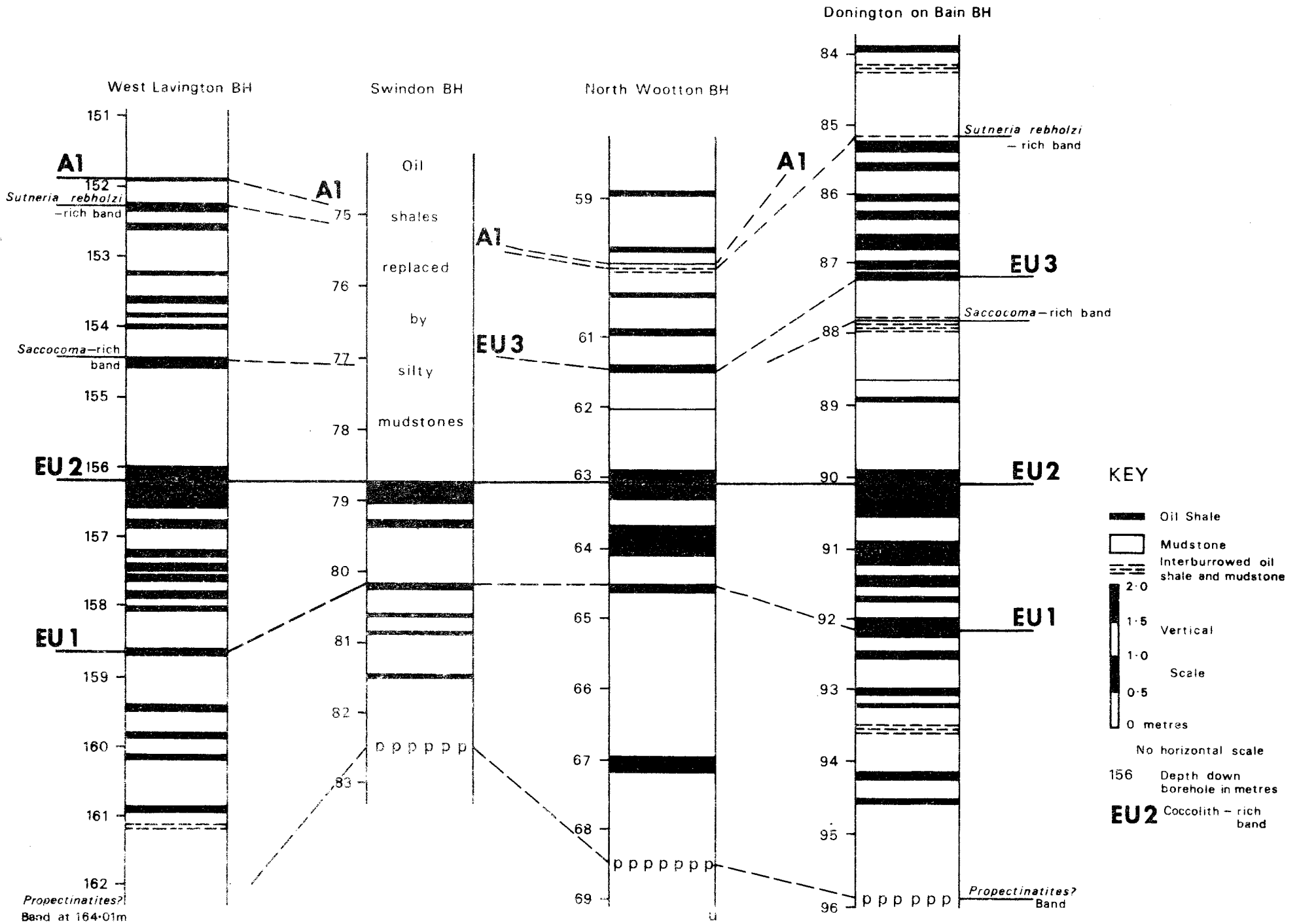
Thin marker bands containing flood occurrences of coccoliths, crinoids, certain species of bivalve, brachiopods or serpulids occur at many levels and these provide additional stratigraphical information. When combined with the rhythmic variation in lithology that occurs throughout the Kimmeridge Clay these faunal markers provide a ready means of subdividing the formation. In many cases faunal changes coincide with lithological changes that can be recognised throughout southern England. This suggests that the associated faunal and lithological features reflect widespread events affecting the Kimmeridge Clay basin of deposition. The oil-shale-rich parts of the sequence provide a good example of a distinctive lithology, with its own characteristic faunal marker bands, that can be traced throughout the English outcrop and subcrop.

Correlations between the oil-shale-rich bands in the cored boreholes drilled for the present work, based on the method described above, are shown in Fig. 6. An example of the type of detailed correlation that can be achieved at stratigraphical levels where a sufficient number of faunal marker bands is present is shown in Fig. 7 (after Gallois and Medd, 1979). It can be seen here that correlation of some individual oil shale seams only a few centimetres thick can be made over distances of more than 200 km.

2.1.2 Distribution of oil shales in the Kimmeridge Clay

The generalized vertical section of the argillaceous facies of the English Kimmeridge Clay is shown in Fig. 8. Organic-rich mudstones with potential pyrolysis yields of up to about 5 gal/ton occur throughout the formation but oil shales are confined to the interval between the upper part of the mutabilis Zone (Bed 19) and the lower part of the rotunda Zone (Bed 55). The main concentrations of the better quality seams occur in the lower part of the eudoxus Zone (Bed 29), the upper part of the eudoxus Zone and the lower part of the autissiodorensis Zone (Beds 32 and 33), the elegans Zone (Bed 36), the upper part of the wheatleyensis Zone and the basal part of the hudlestoni Zone (Bed 42) and the upper part of

Figure 7 Correlation of oil shale seams by means of faunal and floral marker bands



huddlestoni Zone and the lower part of the pectinatus Zone (Beds 45 to 47). Lesser concentrations of oil shales of generally inferior quality occur in the upper part of the mutabilis Zone (Bed 19), the middle part of the eudoxus Zone (Beds 30 and 31), the scitulus Zone (Bed 37), the pallasioides Zone (Bed 50) and the rotunda Zone (Bed 55).

The five main oil-shale-rich bands were named, for ease of reference in the pilot study, after the ammonite zones in which they occur or largely occur. This practice is continued here, the bands being referred to, in ascending stratigraphical order, as the Lower eudoxus Band, Upper eudoxus Band, elegans Band, wheatleyensis Band and pectinatus Band.

The distribution of seams, area by area, is discussed below.

2.2 DORSET

The Kimmeridge Clay crops out in two main coastal areas in Dorset. Between Brandy Bay [SY 888 795] and Chapman's Pool [SY 955 770], near Kimmeridge village, beds ranging from the middle part of the eudoxus Zone to the top of the fittoni Zone are exposed in about 8 km of continuous cliffs (Fig. 9). Further west, at Ringstead Bay [SY 760 814] and Osmington Mills [SY 730 819] a series of much smaller exposures show most of the Kimmeridge Clay. Westwards from Osmington Mills the outcrop of the formation can be traced through Upwey to Portesham as a clay vale between the Corallian Beds and Portland Beds escarpments. At Portesham the outcrop ends abruptly at the Ridgeway Fault (Fig. 10).

The structure of the Kimmeridge Clay section exposed to the east of Kimmeridge Bay is simple (regular dips of 1° to 5°) since it lies within the flat lying southern limb of the Purbeck Monocline. Between Kimmeridge Bay and Brandy Bay the cliff section approaches the steep limb of the monocline and the dip increases westwards to 25°. The Ringstead Bay and Osmington sections lie within the steep limb of the same fold. Dips of 65° to 85° are present and the structure is further complicated by faulting and extensive landslipping.

At Kimmeridge Bay the oil shales weather out as prominent ledges in the cliff sections and fallen blocks that are resistant to weathering are common on the foreshore. The richest and thickest seam, the Blackstone or "Kimmeridge Coal", is especially tough and forms large boulders. It was probably this fallen material that was used in Iron Age, Roman and Saxon times for ornamental purposes (cf Jet) and fuel for pottery making. A succession of attempts was made to exploit the oil shales at Kimmeridge (Green, 1886), almost all based on the Blackstone, during the 17th to 19th centuries (Table 5). Some were successful for short periods but all had failed by late Victorian times. Some of the shafts and adits of these workings are still visible and although the extent of the workings is not known it is likely to have been small.

In evidence given to the Royal Commission on Coal Supplies (1904, p. 270) it was

Table 5 Summary of attempts to exploit the Kimmeridge Clay oil shales at Kimmeridge Bay in Dorset

Commencement Date	User	Product or use
Iron Age, Roman and early Saxon periods	Local tribes	Ornaments: fuel for potteries
late 16th century	Baron Mountjoy	Alum: $KAl(SO_4)_2 \cdot 12 H_2O$
1613	Sir H. Clavell	Alum
c1620	Sir H. Clavell	Fuel for sea-salt and glass works
1848	Bituminous Shale Co.	Lubricants, naphtha, pitch, paraffin wax, varnish and fertilizer
1854	Ferguson and Muschamp	Fertilizer (from organic residue) and pesticide; some lubricants etc.
1858	Wanostrocht & Co.	Lubricants, naphtha, paraffin wax etc.
1865	Wareham Oil and Candle Co.	Lubricants, naphtha, paraffin wax etc.
1872	Emmens Ltd	Lubricants, naphtha, paraffin wax etc.
1876	Sanitary Carbon Co.	Absorbent coke for sanitary purposes (deodorizing, decolouring etc)
1879	De Grelle and Co.	Lubricants, naphtha, paraffin wax etc.
c1880	Kimmeridge Oil and Carbon Co.	Lubricants, naphtha, paraffin wax etc.

stated that experiments carried out in Glasgow on the Blackstone had shown that it was dearer to distill than Scottish oil shales, that it produced an unsaleable, high-sulphur-content oil, an unsaleable coke, an ammonia yield that was too small to be worth recovering and an offensive smell when distilled.

The extent and value of Kimmeridge Clay oil shale in Dorset and Lincolnshire was investigated by the Ministry of Munitions in 1917-1918. This investigation confined itself to the Blackstone and an adjacent group of seams and no attempt was made to examine the formation as a whole. Three cored boreholes were drilled near Kimmeridge and it was estimated that a 1.3 m thick seam (the Blackstone plus the overlying 0.6 m of inferior shale) could be worked beneath an area of 2,900 acres to yield 4.55×10^8 gallons of oil and about 112 tons of ammonium sulphate (Strahan, 1918, p. 31).

The sulphur content of the oil ranged from 5.1 to 6.2% and was a major factor that acted against further attempts at development. In a study of the properties of the Blackstone and its oil shale MacDougall and Cawley (1951) subsequently concluded that the

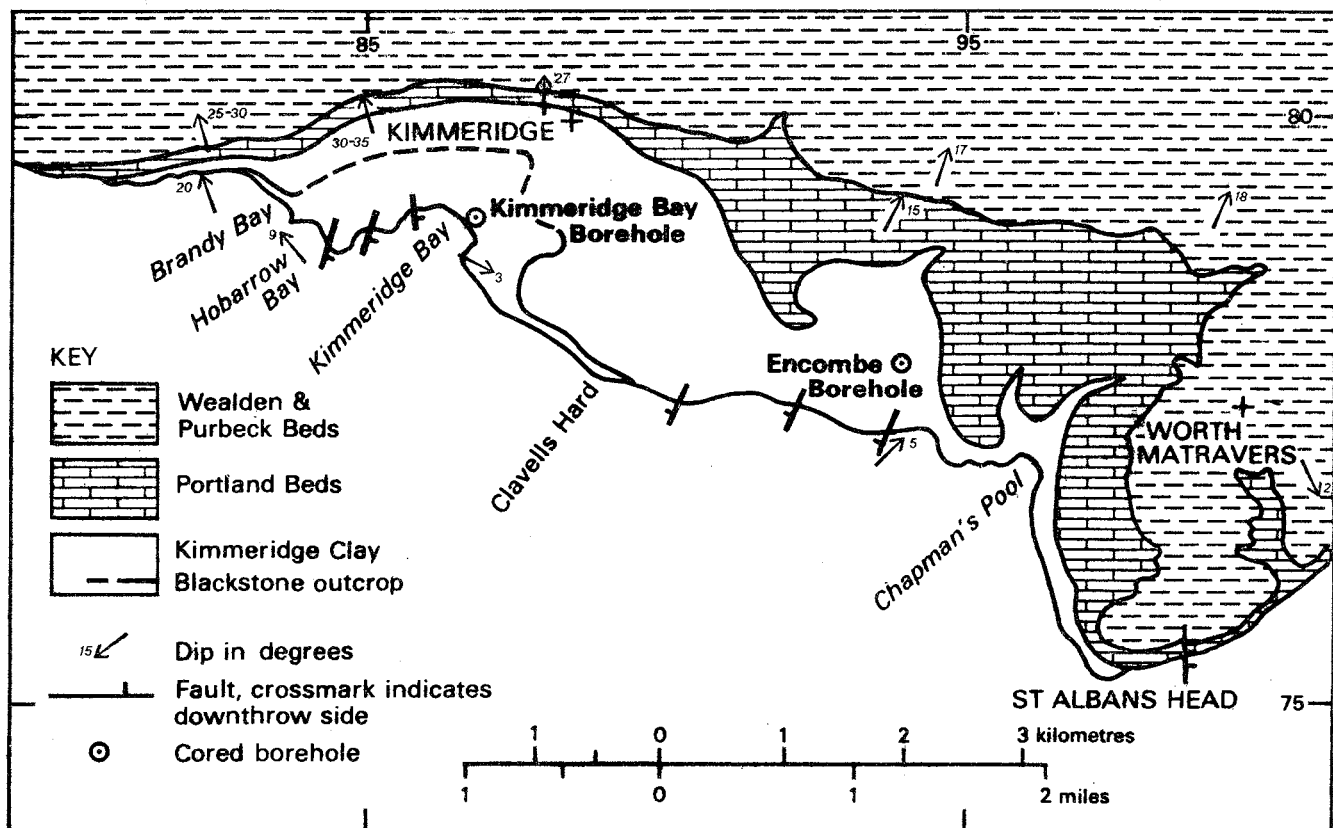


Figure 9 Geological sketch map of the Kimmeridge Bay area (after Strahan, 1918)

shale oil could be readily hydrogenated to provide a sulphur-free spirit, the sulphur being removed as hydrogen sulphide.

Elsewhere in Dorset oil shales at the approximate stratigraphical level of the Blackstone were dug for domestic purposes in the Isle of Portland (Woodward, 1895) and were to be the basis of a major industry near Portesham. A few tons of oil shale were worked at Portesham Dairy in 1856 and about 2000 tons of the shale and clay, dug from the cutting on the east side of the station, were burnt for ballast when the railway was built in 1877 (Strahan, 1898). A shaft and inclined adit were dug to intersect the thickest seam of oil shale (the Portesham 'Blackstone') in 1883, but little shale was worked. In 1917-1918 the Ministry of Munitions drilled four cored boreholes close to the outcrop of the 'Blackstone' between Portesham and Corton as a part of the survey of Dorset oil shales. It was concluded that a 3 m thick sequence of shale and inferior shale from beneath an area of 1500 acres could yield 4.42×10^8 gallons of oil and about 82 tons of ammonium sulphate (Strahan, 1918, p. 31). As at Kimmeridge the oil was rich in sulphur (3.9 to 7.2%) and no attempt at working was made.

According to Arkell (1947, p. 85) the Kimmeridge Clay thins westwards from over 500 m thick at Kimmeridge to less than 250 m in the Osmington area. The overall sequence was described as lithologically constant in both areas but Strahan (1918, p. 34) had earlier suggested that the Blackstone passed laterally into an inferior 'bituminous shale'. It was

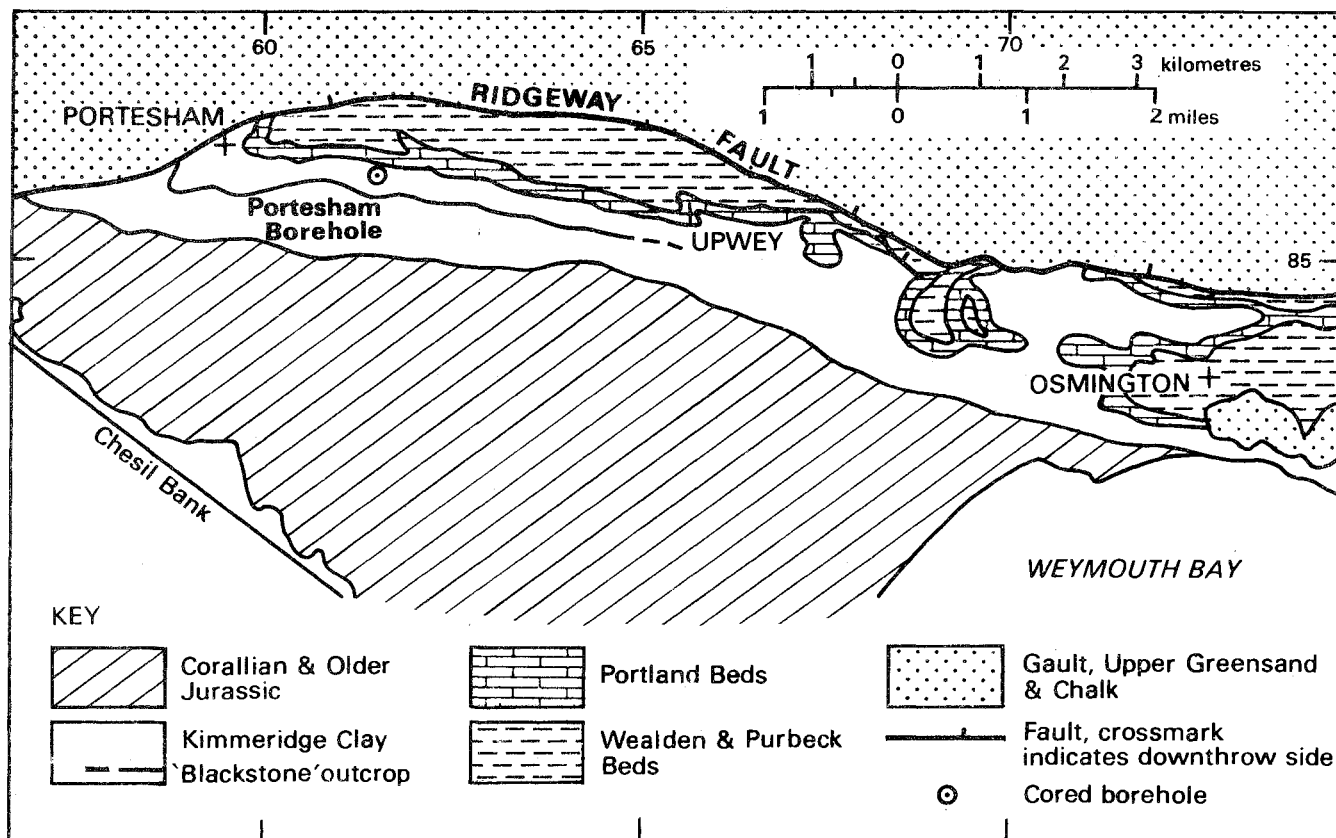


Figure 10 Geological sketch map of the Osmington-Portesham area (after Strahan, 1918)

therefore decided in the present work to sample the oil-shale-rich parts of the sequence in both the Kimmeridge and Portesham areas. At Kimmeridge the cliff sections were measured and it became clear the the greatest concentrations of oil shale seams were in the lower part of the pectinatus Zone, the basal part of the hudlestoni Zone (at the level of the Blackstone) and the eudoxus Zone. Much of the intervening section contains thin oil shales of inferior quality, but these seams could be sampled in the cliffs. Continuously cored boreholes were therefore drilled at Encombe [SY 9446 7785], at the nearest accessible point to the pectinatus Zone outcrop, to sample the pectinatus and hudlestoni zones and at Kimmeridge Bay [SY 9097 7899] to sample the eudoxus Zone. A third borehole was drilled at Waddon Farm, Portesham [SY 6214 8554] to sample the full sequence of the eudoxus to pectinatus zones.

The sequence proved in the Encombe and Kimmeridge Bay boreholes could be closely matched with cliff sections. The oil-shale-rich parts of the boreholes are summarized in Figs 11 and 12. The Portesham Borehole was sited on the pectinatus Zone at a level a little above the oil-shale-rich band in that zone. The borehole was terminated just below the base of the eudoxus Zone at a depth of 208 m, suggesting that the full thickness of the Kimmeridge Clay in that area is about 300 m. The thickness and distribution of the oil shales in the oil-shale-rich parts of the sequence are shown in Fig. 13.

PLATE 2

The greatest concentration of oil shale seams in Dorset occurs on either side of the junction of the Pectinatites wheatleyensis and P. hudlestoni zones in the cliff sections near Kimmeridge Bay. This group of seams, the wheatleyensis Band, includes the Blackstone, the thickest and richest oil shale recorded to date in the Kimmeridge Clay in Britain.

A. The Blackstone (at the level of the axe) and adjacent oil shales dip at about 20° as the steep limb of the Purbeck Monocline is approached at Brandy Bay. These oil shales, and the oil shales in the underlying scitulus, elegans and autissiodorensis zones (visible in the middle and far distance) form hard ribs that contrast with the uniformly degraded slope of the thick bed of calcareous mudstone (Bed 44) that forms the upper part of the hudlestoni Zone (upper centre).

B. The Blackstone was formerly mined at Clavells Hard, but all that remains of the workings are a levelled area of cliff (foreground) and a short length of adit. The Blackstone and adjacent seams form a prominent band of hard ribs (centre left) which dip eastward at 2° to 3°. They are separated from the oil shales of the pectinatus Band (top of cliff in middle distance) by the thick calcareous clays of the hudlestoni Zone. The Blackstone can be seen as a prominent hard band that forms an overhang at the base of the wheatleyensis oil-shale-rich band (centre left).

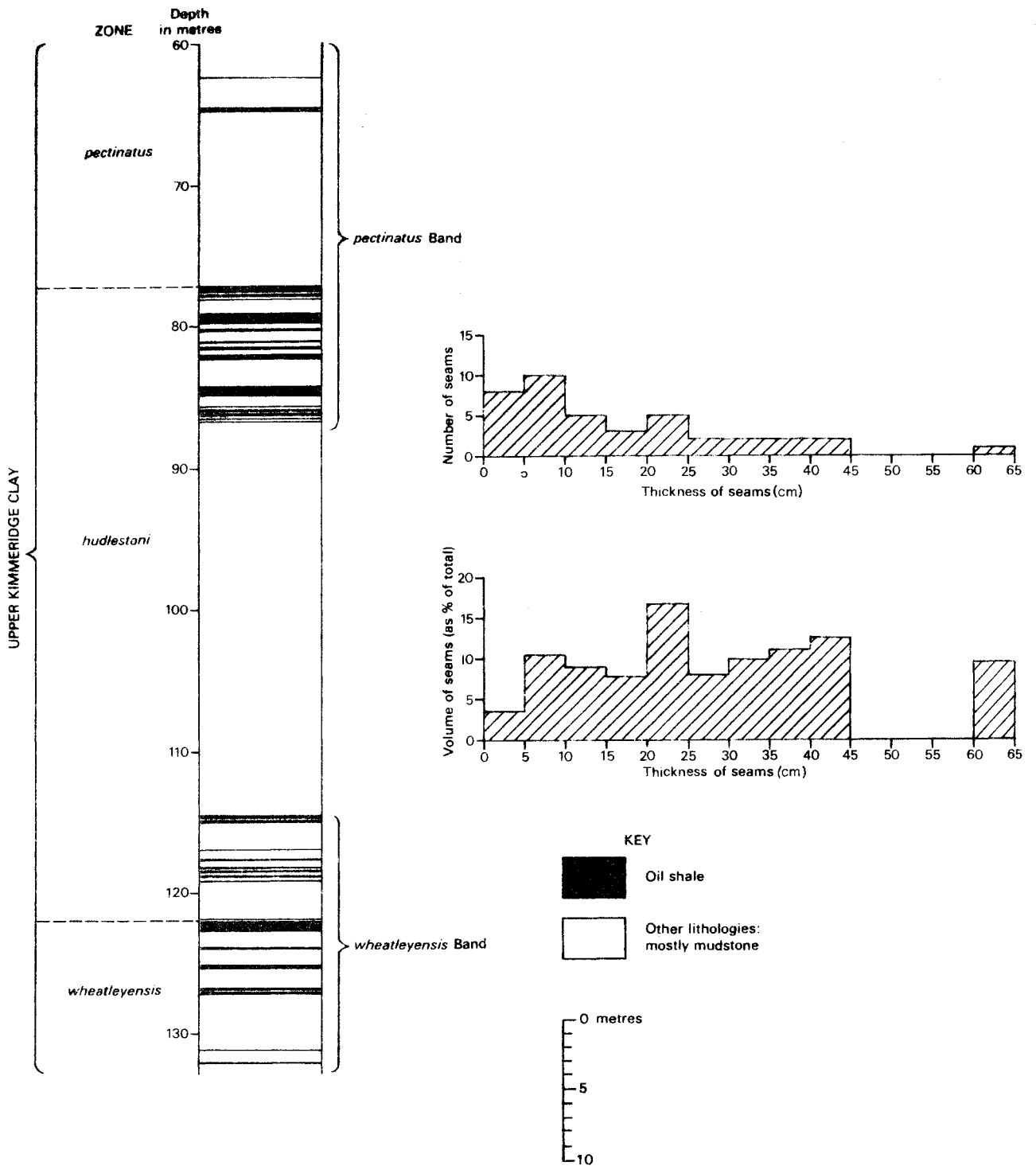


Figure 11 Encombe Borehole, distribution and thickness of seams

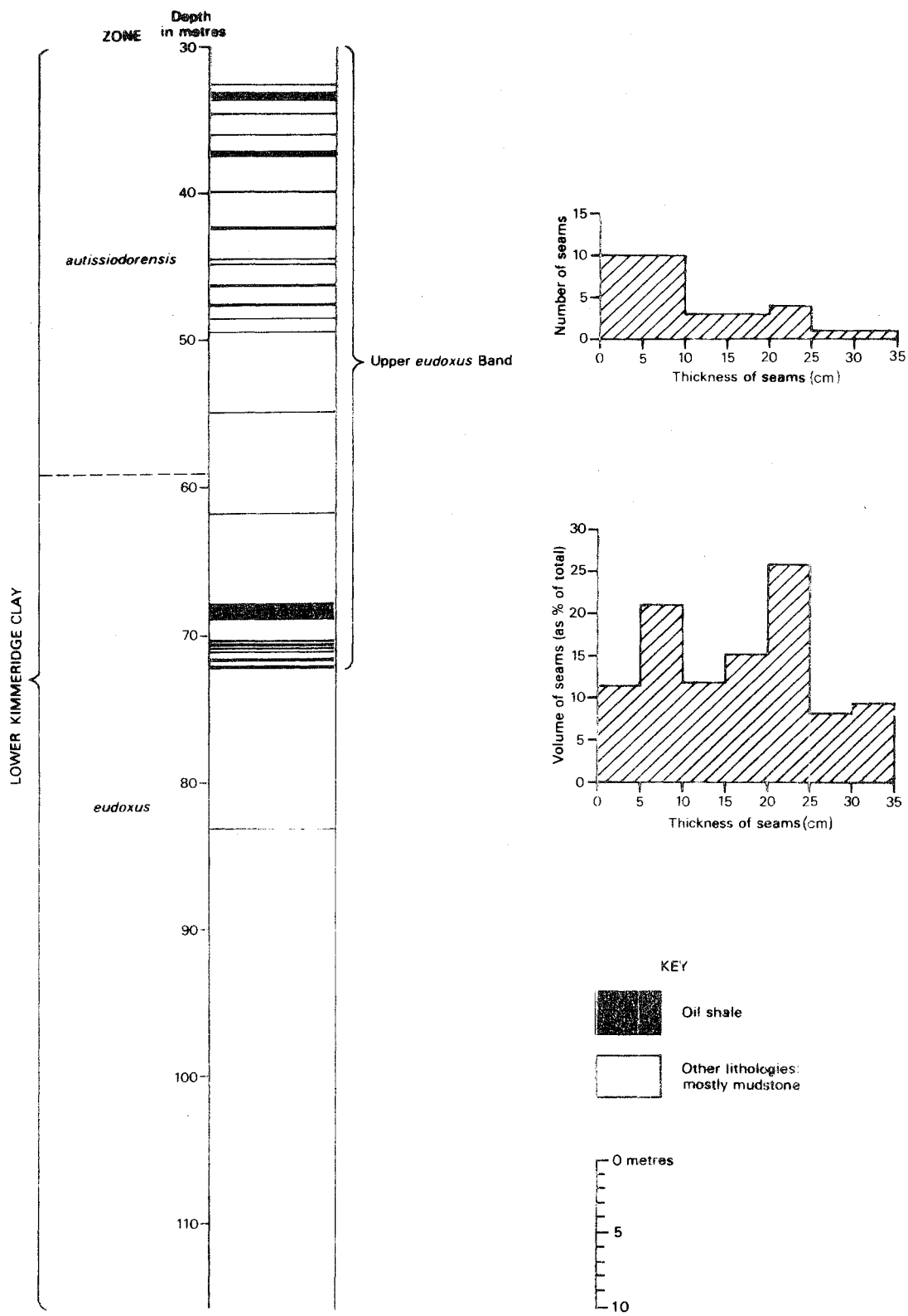


Figure 12 Kimmeridge Bay Borehole, distribution and thickness of seams

The richest part of the Encombe Borehole proved 6.59 m of oil shale in 40 seams ranging from 2 to 62 cm in thickness: 69% of the seams were more than 20 cm thick. A total 3.22 m of oil shale, in seams ranging from 2 to 30 cm in thickness, was proved in the richest part of the Kimmeridge Bay Borehole.

At Portesham a total of 8.27 m of oil shale was recorded in 53 seams ranging from 1 to 53 m thick at the levels of the main oil shale concentrations. 69% of these seams, representing 36% of the total volume of the oil shales, were less than 20 cm thick. The greatest concentrations of seams occur in the Upper eudoxus and wheatleyensis bands, the latter band containing a single thick seam that has been correlated with the Blackstone. The Kimmeridge Clay outcrop between Osmington and Portesham is largely drift free and the outcrops of the 'Blackstone' seam has been traced with little difficulty in the past (Fig. 10).

2.3 VALE OF WARDOUR

Between south Dorset, and north Dorset and the Vale of Wardour, Wiltshire the Cretaceous outcrop overlies and conceals a complex series of west-east trending horsts and graben in the Jurassic. These structures extend from the Jurassic outcrop of the Abbotsbury to Crewkerne area and run beneath south and mid Dorset and Hampshire to the Isle of Wight (Fig. 3). Within the horsts the Kimmeridge Clay is commonly absent or only partially preserved (Dingwall et al., 1977).

The full Kimmeridge Clay sequence is again present in the Tisbury area of the Vale of Wardour. Southwards from Tisbury the formation is rapidly overstepped by the Lower Greensand, to the north it is brought into contact with the Cretaceous by the Mere Fault. The Kimmeridge Clay is poorly exposed in the area. Woodward (1895) recorded the presence of a few shallow brickpits but these are all long since defunct and overgrown. There is no record of 'bituminous' shale in the area and Strahan (1918, p. 25) concluded that this lithology appeared to be absent since it had not been noted in any of the boreholes drilled on the outcrop even though at least one of these was drilled specifically to prove the 'Kimmeridge Coal'.

The Kimmeridge Clay succession is only complete at the eastern end of the Vale, around Tisbury, where it is conformably overlain by Portland Beds. Arkell (1933, p. 454) noted that little was known about the formation in the 30 km of outcrop between Buckland Newton, Dorset and Mere, Wiltshire but the normal clay facies seemed to be everywhere present.

The pilot study boreholes at Swindon and West Lavington, Wiltshire had shown that the oil shale horizons in the Upper Kimmeridge Clay in the more northerly parts of Wiltshire were replaced by fine-grained sands and sandy clays. It was also clear, however,

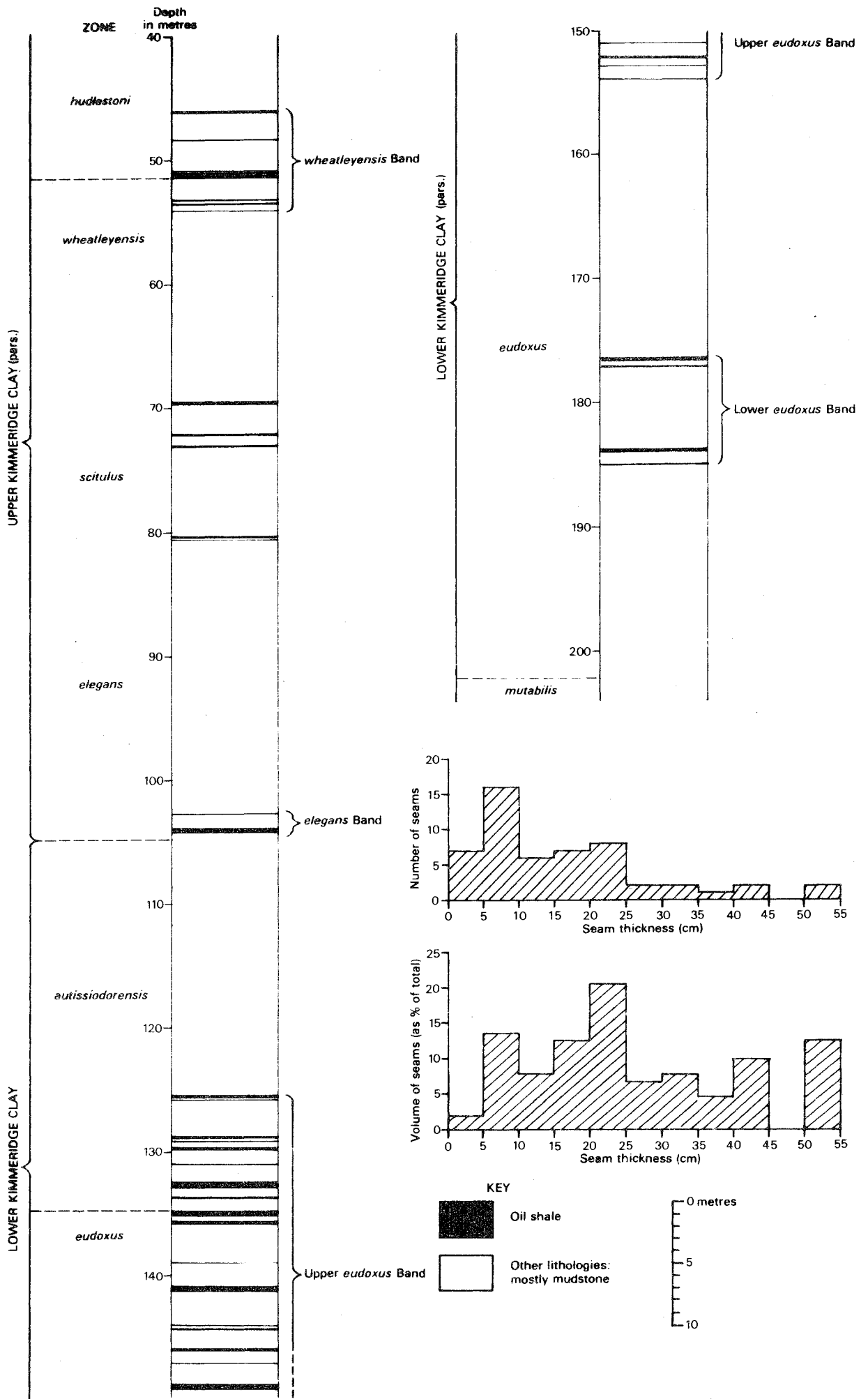


Figure 13 Portesham Borehole, distribution and thickness of seams

that these sands were stratigraphically higher in the succession at West Lavington than they were at Swindon and that, if present at all, had probably climbed to a level above the highest oil shales in the Vale of Wardour. A cored borehole was therefore drilled on the Portland Beds outcrop at Tisbury [ST 9359 2907] to determine the nature and extent of the oil shales in the vale.

The succession proved to be much thicker than would have been expected from a consideration of the thickness of the formation to the north (110 m at Swindon) and south (250 m at Osmington). The Tisbury Borehole was terminated at the base of the eudoxus Zone, a short distance below the lowest oil shales of interest, after proving 201 m of Kimmeridge Clay. A complete Upper Kimmeridge Clay succession was proved and although this was sandy in its upper part it was in the normal argillaceous facies at the level of the oil shales. The full thickness of the Kimmeridge Clay at Tisbury can only be estimated by assuming the beds the eudoxus Zone to be comparable in thickness with those elsewhere in southern England in sequences away from the edge of the London Platform. Making this assumption, the full thickness at Tisbury is probably > 250 m.

The oil-shale-rich parts of the succession proved in the Tisbury Borehole are summarized in Fig. 14 and the full stratigraphy is correlated with that of the other boreholes in Fig. 6. All five oil-shale-rich bands are present at Tisbury, the sandy upper part of the Kimmeridge Clay at this locality being restricted to the Pavlovia zones and therefore stratigraphically above the level of the oil shales.

Oil shales were present throughout the eudoxus to pectinatus zones inclusive but only the main concentrations of seams were slabbled and analysed. At these levels a total of 3.61 m of oil shale was recorded in seams ranging from 2 to 34 cm in thickness. 82% of the total of 34 seams were less than 20 cm thick representing 60% of the total volume of the oil shale. The most promising concentrations of oil shales occur in the wheatleyensis and Upper eudoxus bands. As elsewhere, the Upper eudoxus seams are commonly thicker than those at other levels, but are very shelly.

The Kimmeridge Clay outcrop of the Vale of Wardour is free from drift, other than local weathering products, and gives rise to heavy, arable land without any natural exposure. Kitchin and Pringle (in Osborne White, 1923) recorded fragments of shale with Nannocardioceras in a stream bed at Okeford Fitzpaine: this was almost certainly oil shale within the Upper eudoxus Band. The full sequence of the formation is only present in a small area and is progressively overstepped to the north and south. The positions of the main oil seams could be determined by a limited amount of field work coupled with a programme of shallow trenching.

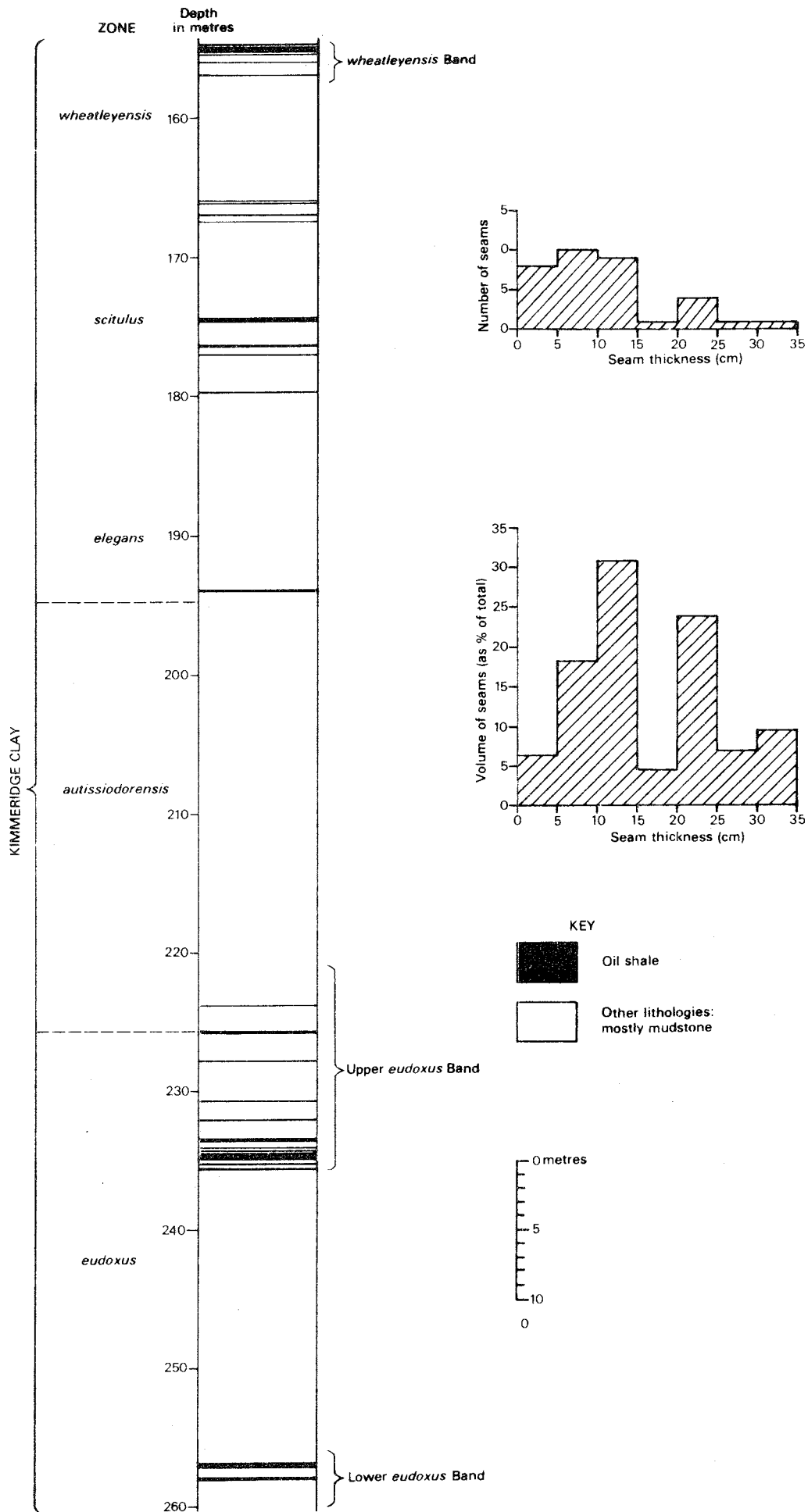


Figure 14 Tisbury Borehole, distribution and thickness of seams

2.4 VALE OF PEWSEY

Between Mere and Westbury, Wiltshire the Kimmeridge Clay outcrop is overstepped by the Cretaceous of Salisbury Plain and may, as in mid Dorset, be locally much eroded due to concealed structures within the Jurassic. The outcrop runs for some 20 km from Westbury to north of Seend and forms low ground at the western end of the Vale of Pewsey. As in the Vale of Wardour the most complete Kimmeridge Clay succession is at the eastern end of the vale, around Potterne, Marston and West Lavington, where the Kimmeridge Clay is conformably overlain by the Portland Beds. Northwards from Potterne the formation is rapidly and irregularly cut out by the markedly angular unconformity at the base of the Lower Greensand.

The stratigraphy of the Kimmeridge Clay of the Vale of Pewsey is virtually unknown. Jukes-Browne (1905, p. 5) recorded a number of small brickpits in sandy clays that had formerly been worked in the Pavlovia zones. There is no record of exposed oil shale, but Lonsdale (1835, p. 265) noted that 'bituminous strata' (presumed to be in the Kimmeridge Clay) had been struck in a shaft in a brickyard (on the Gault clay) at Devizes and that the shale had been used for fuel.

The maximum thickness of the Kimmeridge Clay in the Vale of Pewsey was estimated by Jukes-Browne (1914, p. 448), from boreholes at Marston, to be about 165 m. The West Lavington Borehole, drilled for the pilot project, proved the Kimmeridge Clay succession to be complete in the area and about 240 metres thick. Not only is the Kimmeridge Clay succession at West Lavington much thicker than had previously been anticipated but it also contains appreciable amounts of sand in its upper part (Fig. 15). The wheatleyensis and elegans Bands are replaced by clayey sands and sandy clays and the elegans Band is weakly developed within a sandy clay sequence. However, the Lower and Upper eudoxus bands are well developed and contain 36 seams ranging from 1 to 85 cm in thickness. All but two of these seams are less than 20 cm thick. Ignoring scattered thin seams the main concentration consists of 24 seams totalling 3.06 m in which the only two seams thicker than 20 cm (58 and 85 cms) represent 47% of the total oil shale volume. The outcrop situation in the Vale of Pewsey is similar to that in the Vale of Wardour with little drift cover but an almost complete absence of exposure. Shallow trenching would be sufficient to enable the oil shale outcrops to be traced.

2.5 HAMPSHIRE BASIN AND WEALDEN SUBCROP

The Kimmeridge Clay can be traced by means of boreholes beneath much of Dorset, Wiltshire, Berkshire, Hampshire, Sussex, Surrey and Kent (Figs. 16 to 19). Details of the Kimmeridge Clay interval in boreholes in the subcrop area are summarized in Appendix G and in Figures 2 (structure contours on the base of the formation) and 3 (isopachytes for

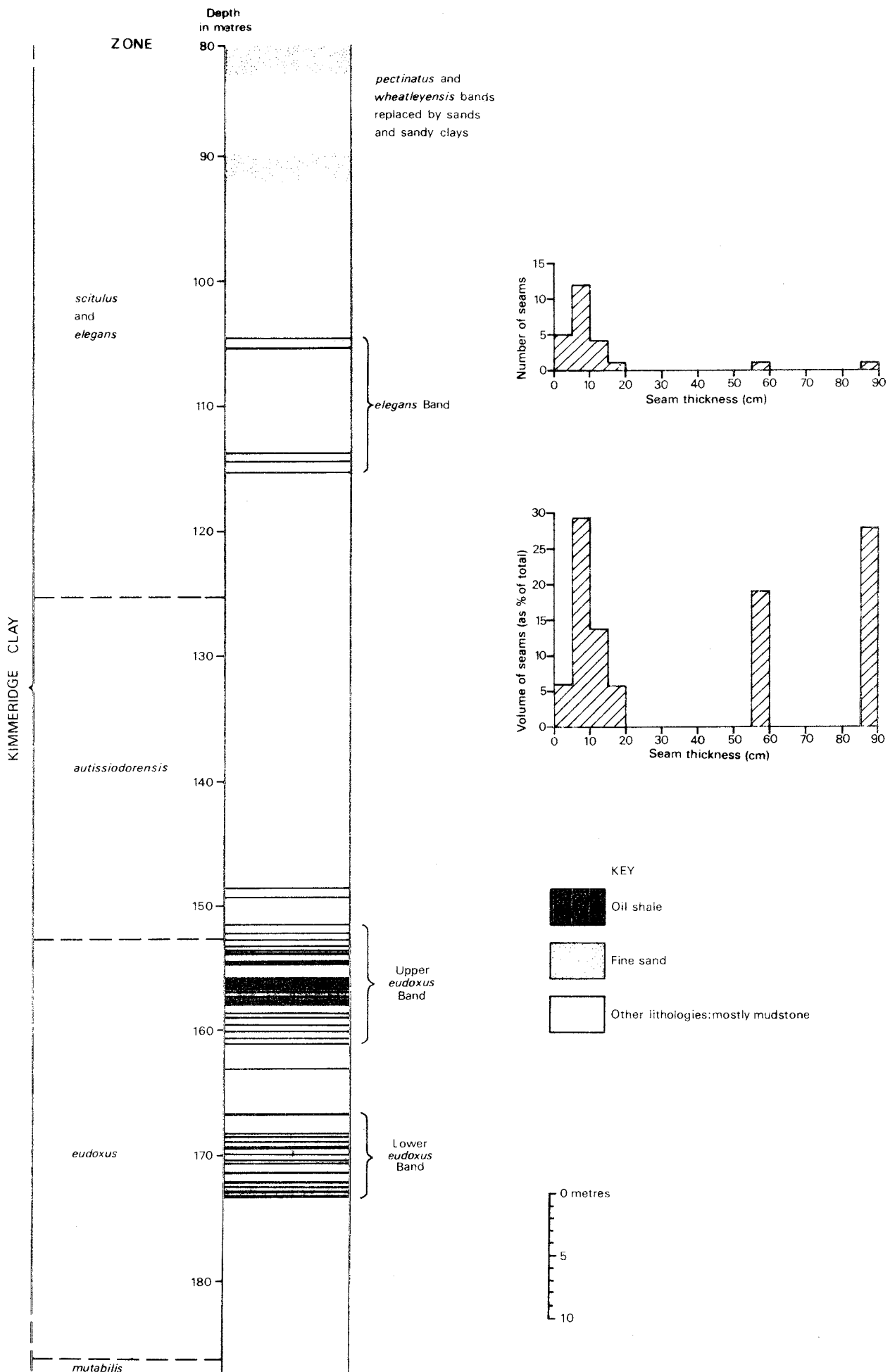
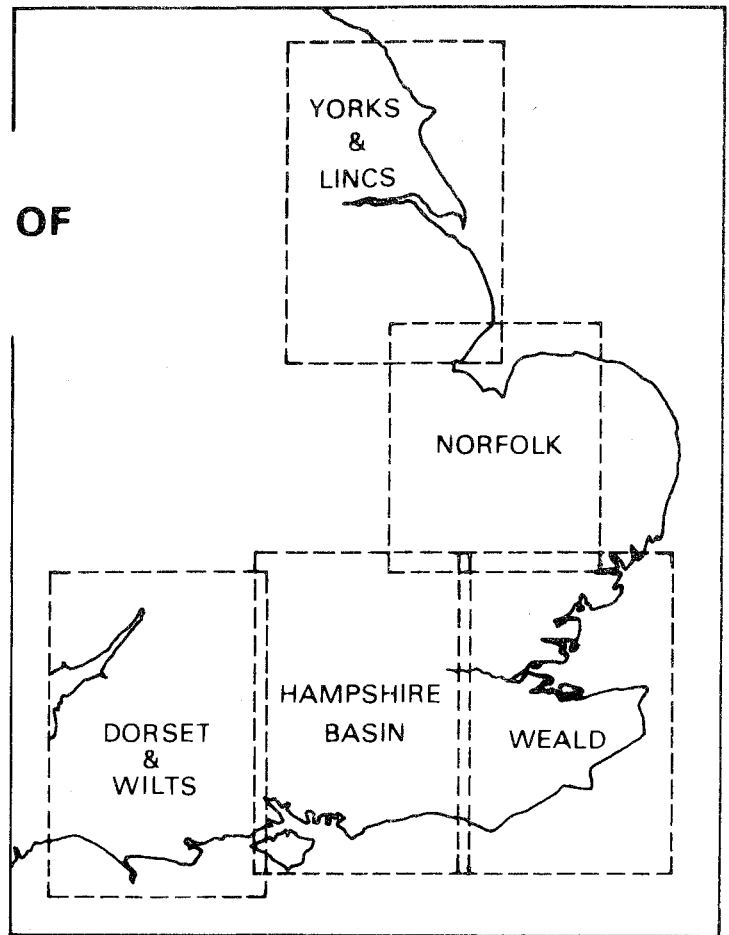
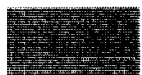


Figure 15 West Lavington Borehole, distribution and thickness of seams

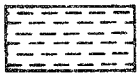
KEY TO POSITIONS OF MAP AREAS



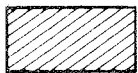
LEGEND



Kimmeridge Clay at surface



Kimmeridge Clay overlain by drift deposits



Kimmeridge Clay overlain by solid deposits



Kimmeridge Clay absent due to erosion or non-deposition



Borehole drilled for oil shale project



Selected boreholes proving Kimmeridge Clay



Selected boreholes proving Kimmeridge Clay to be absent



Town or village



Fault, crossmark indicates downthrow side



Edge of Upper Jurassic/Cretaceous escarpment

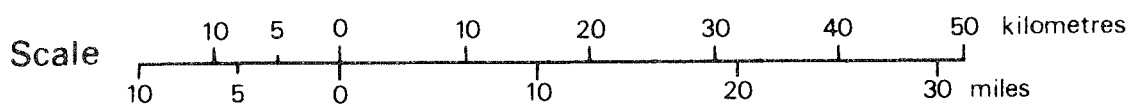


Figure 16 Key to map areas in Figures 17, 18, 19, 23 and 26

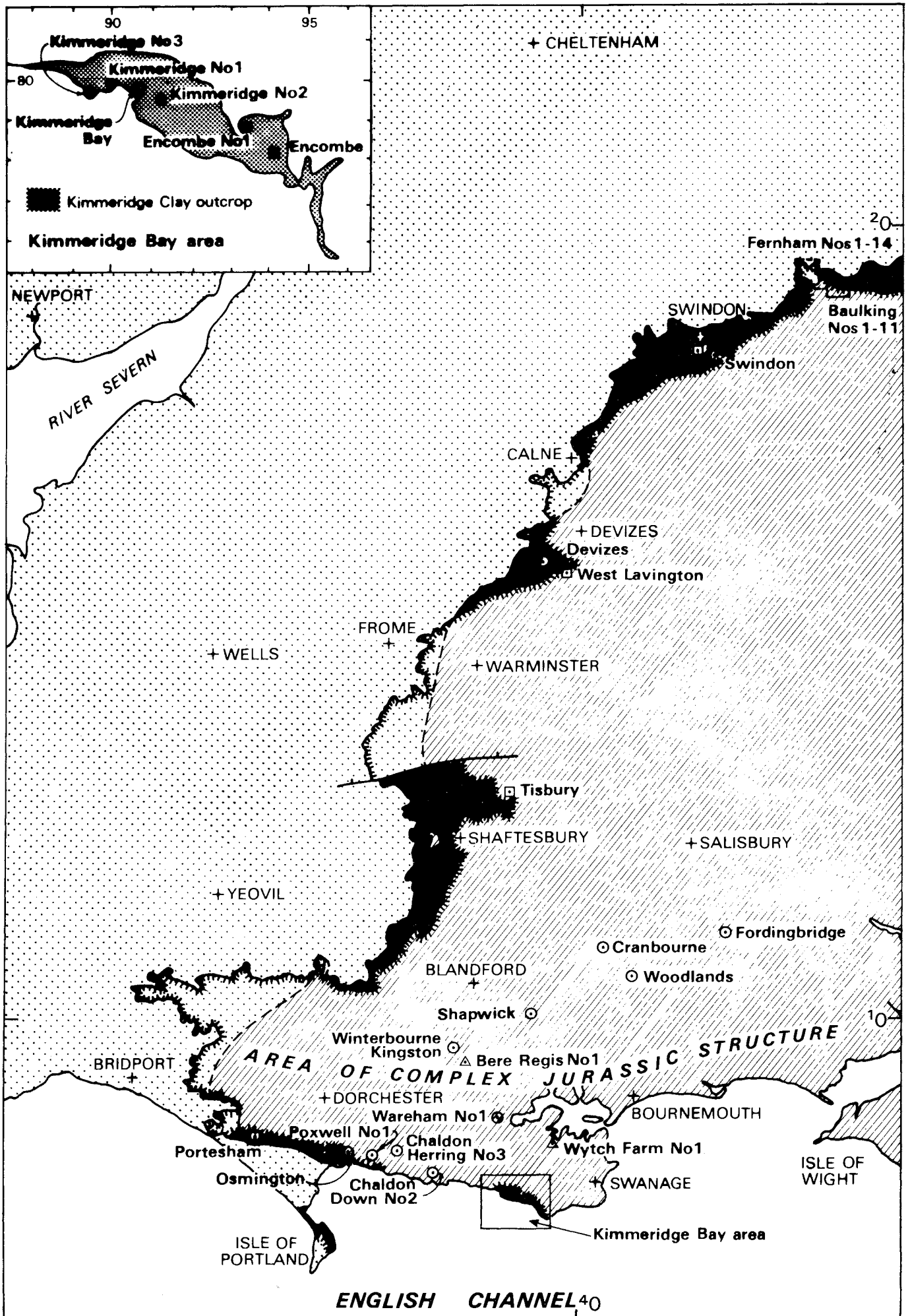


Figure 17 Kimmeridge Clay outcrop and subcrop: Dorset, Wiltshire and Hampshire

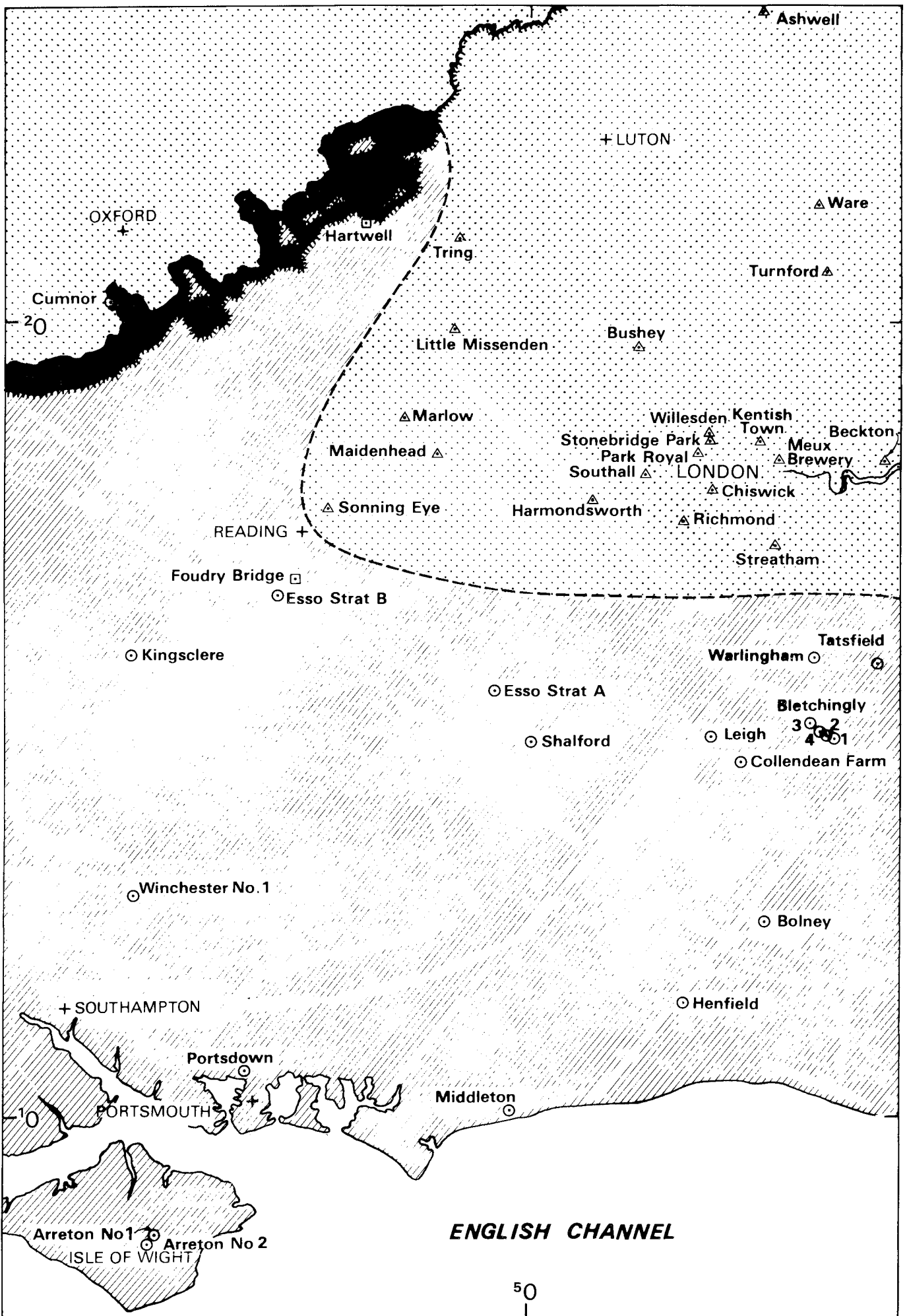


Figure 18 Kimmeridge Clay outcrop and subcrop: Bucks, Oxon, Hampshire Basin and central Weald



Figure 19 Kimmeridge Clay subcrop: eastern Weald

preserved thickness). With the exception of an area of complex structure that runs eastwards from the Dorset outcrop to the Southampton-Isle of Wight area, between the vales of Wardour and Pewsey and a broad area bounding the western and southern edges of the London Platform, the preservation of the Kimmeridge Clay is complete throughout most of its subcrop.

The best documented Kimmeridge Clay sequence in the subcrop area is that in the continuously cored IGS borehole at Warlingham, Surrey (Worssam and Ivimey-Cook, 1971). Here, the Kimmeridge Clay is conformably overlain by Portland Beds and, at its base, is faulted against Corallian Beds. The sequence is entirely argillaceous and proved all five oil-shale-rich bands to be present. It is clear from the extensive collections of core held at IGS that the succession can be matched in faunal and lithological detail with that proved elsewhere in southern England. A total of 217 m of Kimmeridge Clay was proved at Warlingham (op. cit., p. 6). When allowance is made for the absence of the lower part of the mutabilis Zone and the underlying zones through faulting, the full original thickness was probably > 250 m. A full set of geophysical logs was run in the borehole (Burley in Worssam and Ivimey-Cook, 1971) and these were subsequently used to establish detailed correlations with the Kimmeridge Clay sequences in boreholes throughout much of southern England (Dingwall et al., 1977).

The Kimmeridge Clay is thick and complete beneath the central Weald and all five oil-shale-rich bands are probably present throughout the area. The formation thins rapidly around the northern and eastern edges of the Wealden depositional basin before being overstepped by the Cretaceous on the London Platform. A continuous core of Kimmeridge Clay was obtained from an NCB borehole at Foudry Bridge, Berkshire [SU 7033 6604] within this area of attenuated sequence. Here, a total of about 83 m of Kimmeridge Clay was proved, much of it Upper Kimmeridge Clay (Fig. 20). The sequence was argillaceous throughout and at the level of the oil-shale-rich bands was condensed and the oil shales unusually thick, presumably due to the amalgamation of numerous thin seams. A total of 4.32 m of oil shale was proved in 16 seams ranging from 4 to 71 cm in thickness, 78.3% of the total volume of the oil shales being contained in seams more than 35 cm thick.

Westwards from Foudry Bridge the Kimmeridge Clay sequence remains attenuated but becomes sandy in its upper part (see Section 2.6) and oil shales are poorly developed. To the east, along the southern edge of the London Platform, the sequence is largely unexplored but may also become locally sandy at the levels of the oil shales, since sands were recorded in the basal part of the Kimmeridge Clay in the Dover area (Lamplugh and Kitchin, 1911). To the south the thick Kimmeridge Clay sequence of the Weald and its western extension into Hampshire is everywhere complete and all five oil-shale-rich bands are probably present. Only in the area of complex structure in Dorset and south Hampshire

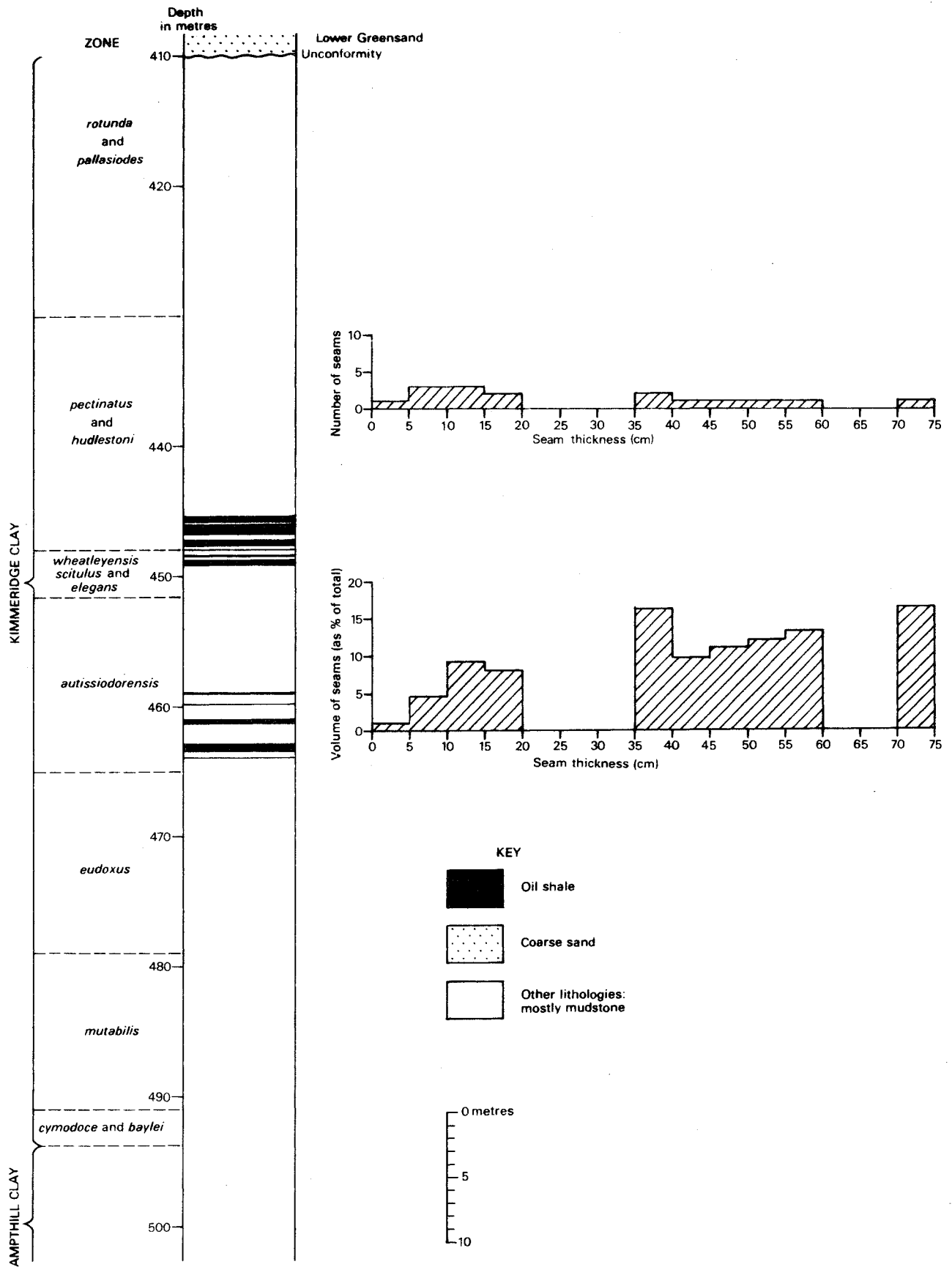


Figure 20 Foudry Bridge Borehole, distribution and thickness of seams

(Fig. 17), where the Kimmeridge Clay has been wholly (e.g. Wych Farm Borehole) or largely (e.g. Winterbourne Kingston Borehole) removed by post-Jurassic erosion, are the oil-shale-rich bands likely to be absent.

2.6 CALNE TO LEIGHTON BUZZARD

Between Seend and Calne, Wiltshire, the Lower Greensand again oversteps the Kimmeridge Clay outcrop, but from the latter locality there is an almost unbroken outcrop of Kimmeridge Clay for about 105 km to the vicinity of Leighton Buzzard, Berkshire. The formation is complete throughout this distance except for a small area near Baulking, Berkshire, where a channel infilled with Lower Greensand cuts across it.

Despite its completeness the Kimmeridge Clay is poorly exposed in this area. The sequence thins rapidly northwards from the Vale of Pewsey (c 240 m) to Swindon (110 m) and from there to Aylesbury (45 m) due to its approach to the stable margin of the London Platform. This attenuation is accompanied by lithological change and much of the upper part of the formation between Swindon and Aylesbury consists of fine-grained sands and sandy clays. Part of the attenuation is due to minor erosion surfaces within the Kimmeridge Clay, but the greater part is due to differences in the rates at which different parts of the depositional basin subsided. Between Swindon and Aylesbury, close to the London Platform, the rate of subsidence was low and sedimentation was probably further inhibited by winnowing currents.

The sand and sandy clay parts of the formation have been well exposed at times in the past in sand and brickpits and have attracted much attention from stratigraphers. Arkell (1933, 1947) has summarized the conclusions reached concerning the age relationships of the Cemetery Beds (sands at Swindon), Shotover Grit Sands, (sands at Shotover, Oxon), Thame Sands (sands at Thame, Oxon) and the Hartwell Clay (sandy clay at Hartwell, Bucks). Ballance (1962) and Oates (1970) have added more recent comment on the age and depositional environment respectively of the Hartwell Clay.

The lower, argillaceous part of the Kimmeridge Clay is commonly obscured by down-wash from the overlying loose sands over much of its outcrop between Swindon and Aylesbury. Conybeare and Phillips (1822, p. 178) noted that several abortive attempts had been made to find the 'Kimmeridge Coal' by means of boreholes in Berkshire and Oxfordshire. Pringle (in Strahan, 1918, p. 25-26) recorded shales with a trace of oil at Abingdon but, despite the fact that most of the sequence has been exposed at some time or another in brickpits around Swindon and in Oxfordshire, this remains the sole record of oil shale in the area.

The Swindon Borehole [SU 1413 8349] was drilled for the pilot study to determine to what extent the sands in the Kimmeridge Clay affected the oil shale seams. It was found that all the higher seams were replaced by sands and that the lower seams, which were present in

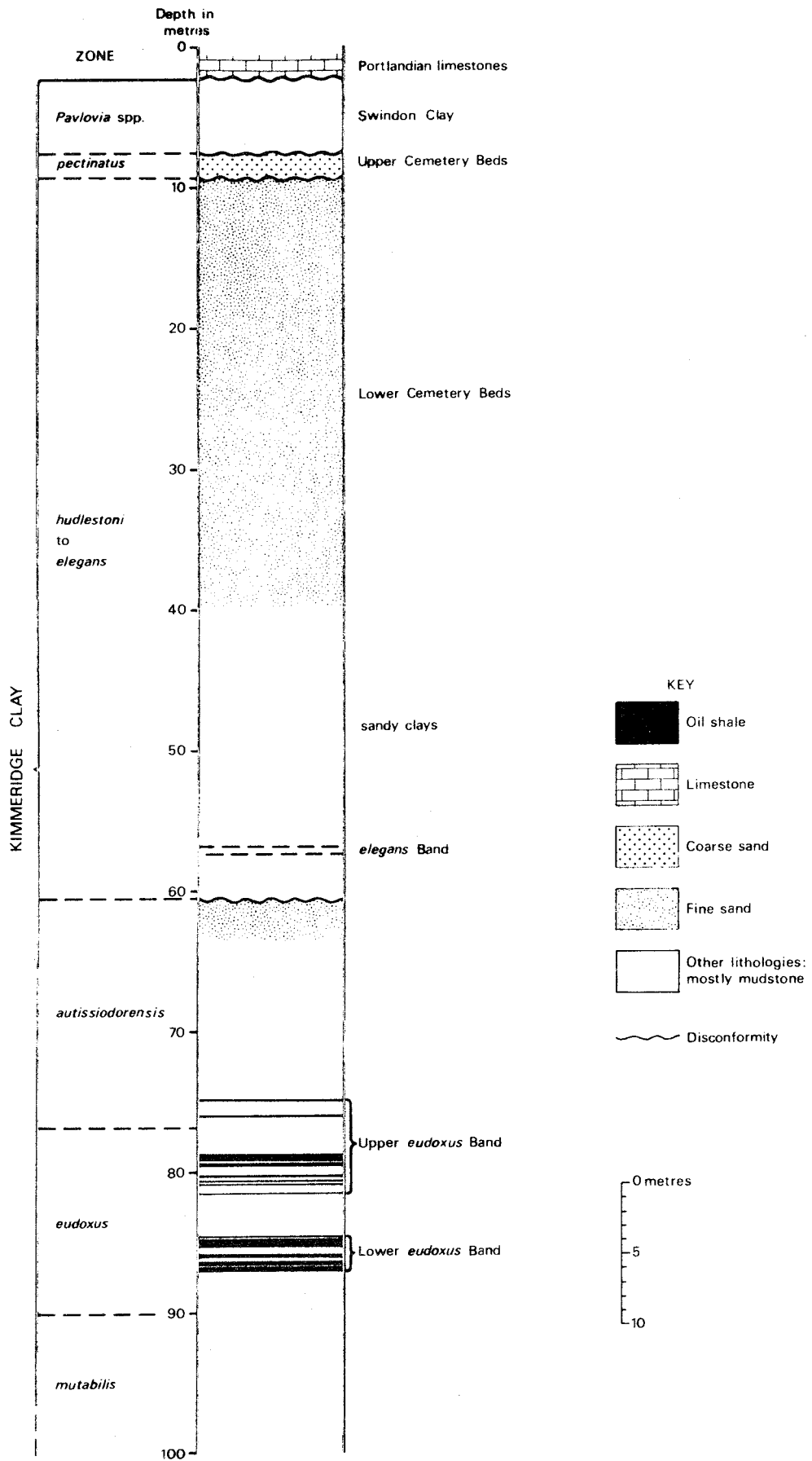


Figure 21 Swindon Borehole, distribution of seams

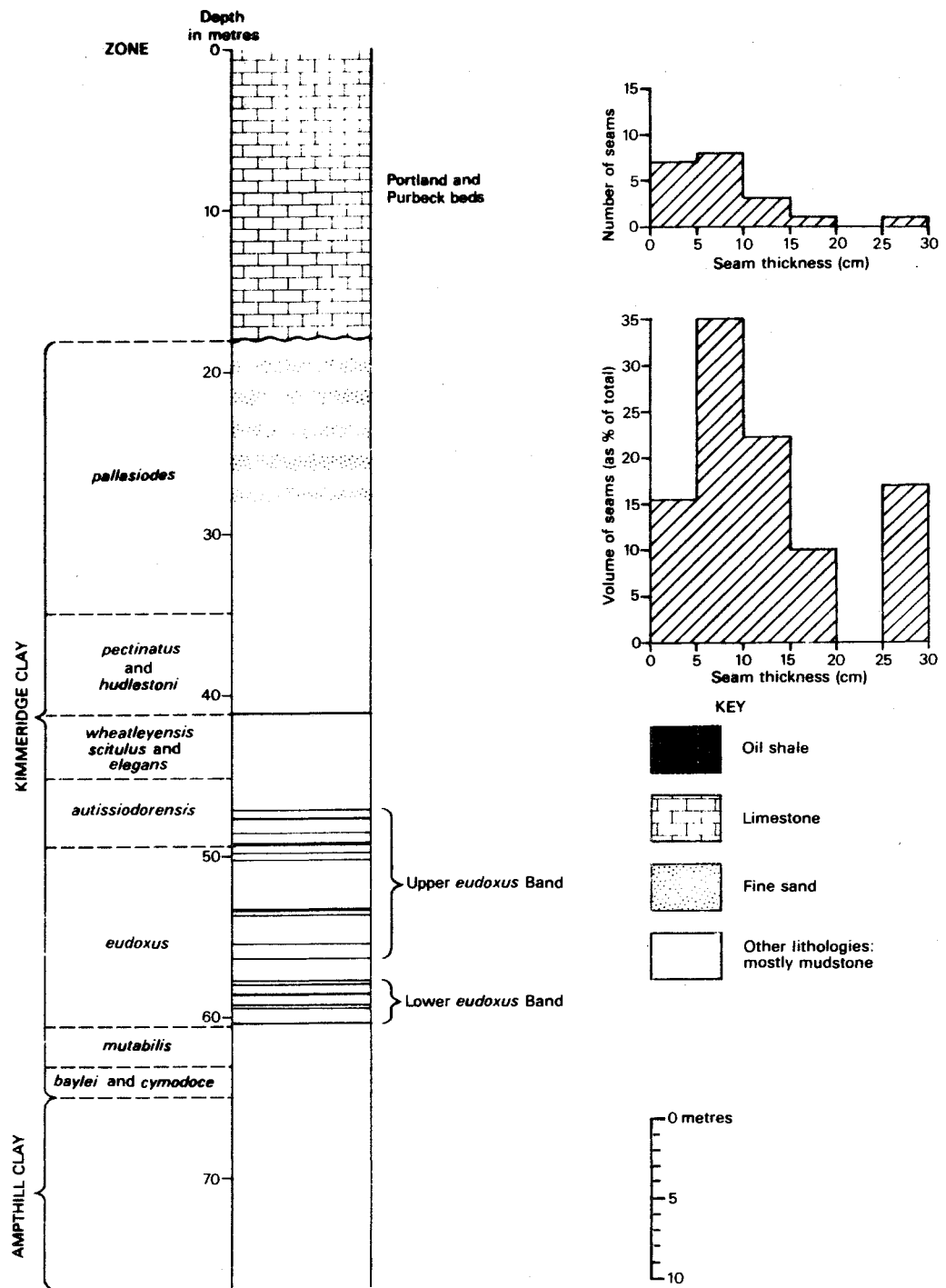


Figure 22 Hartwell Borehole, distribution and thickness of seams

a normal clayey sequence containing only a few wisps of fine-grained sand, were markedly poorer than the equivalent seams elsewhere.

A second borehole was therefore drilled, at Hartwell [SP 7926 1223], at the most northerly outcrop of the complete Kimmeridge Clay sequence in order to make comment on the occurrence of oil shales in the whole of the Calne to Leighton Buzzard outcrop.

The Swindon Borehole proved a complete Kimmeridge Clay sequence in which most of the Upper Kimmeridge Clay (elegans to pectinatus zones) was in a sandy facies (Fig. 21). Only the elegans Band oil shales were present in the Upper Kimmeridge Clay and these were represented by only a few thin seams within a sandy clay sequence. In the Lower Kimmeridge Clay the Lower and Upper eudoxus bands were present, but wisps of sand occur even at this stratigraphical level and the oil-shale seams are much thinner than the equivalent seams elsewhere.

The Hartwell Borehole also proved a complete, but condensed, Kimmeridge Clay sequence. It resembles the sequence proved in the Foudry Bridge Borehole in that both have a thick (largely pallasiodes Zone) Upper Kimmeridge Clay (Fig. 22). In other respects the Hartwell sequence is similar to that at Swindon in that the oil shales normally present in the Upper Kimmeridge Clay are replaced by sandy clays. Only the Lower and Upper eudoxus bands are present at Hartwell and although the oil shale seams are slightly better developed than at Swindon they are still very thin. A total of 1.48 m of oil shale was proved in the Hartwell Borehole in 20 seams ranging from 2 to 25 cm in thickness: 83.1% of the volume of the oil shales is in seams less than 20 cm thick.

The field evidence combined with the data from the Swindon and Hartwell boreholes suggests that the Upper Kimmeridge Clay consists largely of fine-grained sands and sandy clays throughout its outcrop between Calne and Leighton Buzzard and that oil shales are absent or weakly developed at this stratigraphical level throughout the area. In the Lower Kimmeridge Clay the Lower and Upper eudoxus bands are everywhere present, but are weakly developed.

2.7 CAMBRIDGE TO THE WASH

The Kimmeridge Clay reappears from beneath the basal Lower Greensand unconformity near Caxton, Cambridgeshire and from there can be traced northwards by means of boreholes and temporary sections to The Wash. In this area the formation crops out in low ground and is almost entirely overlain by drift deposits (Fig. 23). Between Caxton and Littleport much of the outcrop is obscured by thin glacial deposits: north of Littleport the entire outcrop, with the exception of a narrow strip on the eastern border of Fenland between Downham Market and King's Lynn, is overlain by the Recent deposits of Fenland and The Wash.

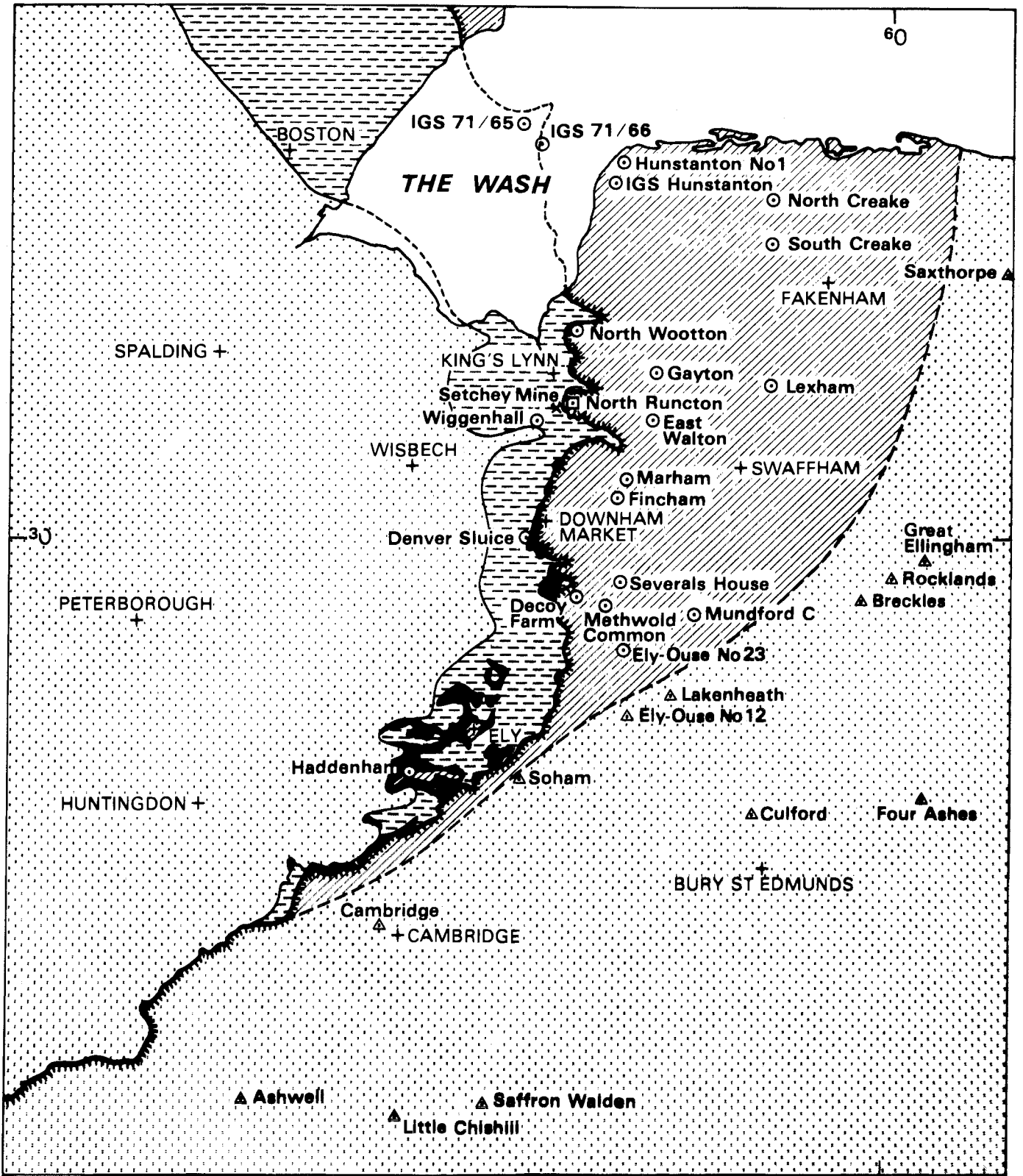


Figure 23 Kimmeridge Clay outcrop and subcrop: Cambridge to The Wash

The first published record of oil shale in this area was that of William Smith on his geological map of Norfolk (1819) where he noted that the "Oaktree Clay" [Kimmeridge Clay] was "part slaty and bituminous as at Kimmeridge in Dorset". Rose (1835, p. 175) subsequently recorded inflammable shales in the Kimmeridge Clay in a brick pit at Southery, Norfolk [TL 617 958] and oil seepages, supposedly derived from the Kimmeridge Clay, were noted in the Puny Drain at Setchey, Norfolk [TF 626 146] (Forbes Leslie, 1917a).

It was largely on the evidence of these supposed seepages and the possible prospect of finding oil shales comparable to those that had been worked at Kimmeridge, that oil shale exploration was begun in Norfolk during the First World War. A pilot operation was begun at Setchey by English and Foreign Oil Finance Ltd. in about 1916 with W. Forbes Leslie as geologist. This work received much publicity from two papers by Forbes Leslie on the occurrence of petroleum in Britain in general (1917b) and on the occurrence in Norfolk in particular (1917a). In the latter account it was stated that at least three 6 ft (1.8 m) thick oil shales seams were present (p. 16-17) and that two of these yielded more than 50 imperial gal/long ton. Up to 75% of the oil was described as free-oil filling cavities in the shale (1917b, p. 181) and yellow sandstones impregnated with bitumen were also said to be present (1917a, p. 16).

In 1918 a new company (English Oilfields Ltd.) was formed with a share capital of £300,000 in order to exploit the Norfolk oil shales. Between 1918 and 1919 the thickness and quality of the proved oil shale seams increased steadily in Forbes Leslie's statements to the English Oilfields shareholders. Yields of 20 to 40 gal/ton are quoted in the 1918 share prospectus, the oil containing 4.5 to 8% sulphur. By September 1919 yields of 50 to 80 gal/ton of "practically sulphur free" oil had been achieved. By December 1919 an 85 to 95 gal/ton seam had been discovered and it was envisaged that an exceedingly profitable industrial complex would be built which, in addition to the oil, would produce cheap Portland cement (from the shale waste and nearby Lower Chalk), high quality bricks (from the Kimmeridge Clay overburden), electricity (from the waste gas from the retorts) and metalliferous minerals (from the beds beneath the Kimmeridge Clay). In addition, it was claimed that large quantities of free oil had been discovered together with a widespread 70 ft (21.3 m) thick seam of ozokerite.

The shareholders of English Oilfields approved an increase in the share capital to £1.5 million in 1919 and in the next few years an opencast pit and a mine were dug, pilot retorts were operated, a rail link was built to the works and work was begun on four full scale retorts with a view to processing 1000 tons of shale per day (Plate 3). The company acquired a petroleum exploration licence covering about 1000 sq km of west Norfolk and between 1919 and 1923 probably drilled more than 50 cored boreholes in the area (see Fig. 24

PLATE 3

A. Oil shale was worked at Setchey by English Oilfields Ltd between about 1916 and 1923 in a mine and a small opencast pit. The pit, seen here in about 1920, worked the wheatleyensis Band beneath a thin overburden of cryoturbated gravelly head (top of pit, far left) and the calcareous mudstones of the hudlestoni Zone (upper level of pit on right). The thin oil shale seams can be seen in the lower face: angular broken pieces of cementstone from the hudlestoni Zone overburden can be seen in the spoil on the left.

B. English Oilfields Ltd embarked upon an ambitious programme aimed at processing 1000 ton shale/day. The retorts, seen here during the construction stage, were never completed, supposedly due to lack of capital. A more likely cause of failure was the diversion of capital into exploratory drilling and the difficulties of perfecting a technique, even on a laboratory scale, of producing a low-sulphur shale oil.

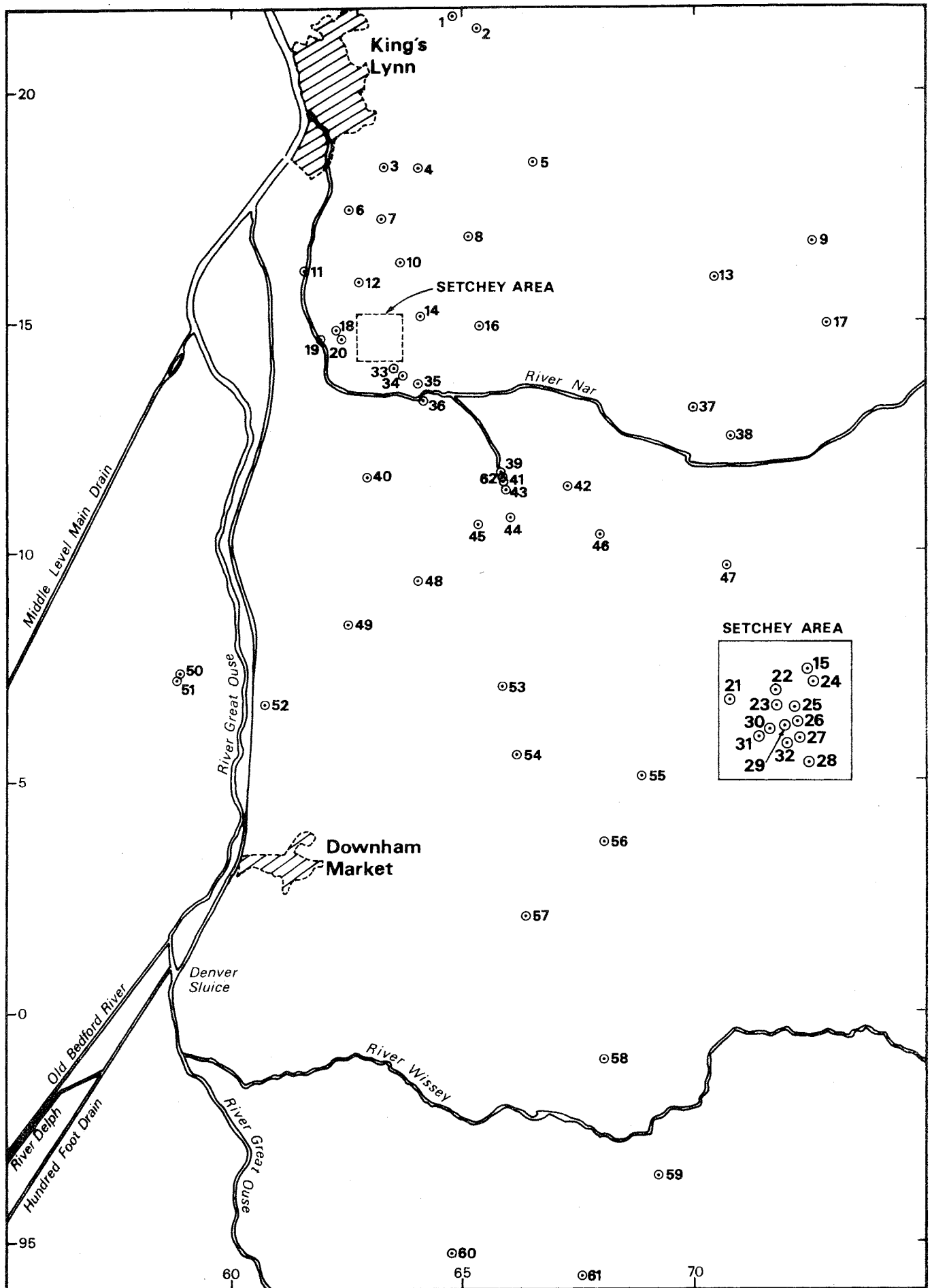


Figure 24 Boreholes drilled for oil shale exploration in west Norfolk, 1916-1923

and Appendix G for details). Few geological details have survived from these boreholes because of the secrecy maintained by the company.

The full scale retorts were never completed, the mine and opencast pit were abandoned and there was little activity after about 1923. The company operated on a small scale as a wholesale distributor of oils during the 1920s and 30s and produced oil for use in medicinal soaps under the trade name Icthyol (ichthysaur oil). However, none of this oil was derived from Norfolk. The company was wound up in 1966.

Several small syndicates of local landowners were formed to explore the oil shales in their particular parts of west Norfolk at the time when the activity at English Oilfields was at its peak. None of these found seam thicknesses or yields remotely comparable to those reported by Forbes Leslie and all the syndicates were disbanded after only a few boreholes had been drilled.

Continuously cored boreholes were drilled through parts of the Kimmeridge Clay sequence in Norfolk by IGS in 1970 to 1972 (Gallois, 1973, Gallois and Cox, 1974) and by the Central Water Planning Unit (for The Wash Water Storage Scheme feasibility study) in 1972 (Gallois, 1979). These boreholes proved a large number of oil shale seams to be present in the Kimmeridge Clay, but all were less than 0.4 m in thickness and were separated by barren mudstones.

A continuously cored borehole was therefore drilled through the full thickness of the Kimmeridge Clay at North Runcton [TF 6404 1624] in 1975, close to the Kimmeridge Clay outcrop and about 1.5 km down dip from the former workings at Setchey. The borehole proved an unbroken sequence of Beds 1 to 47 to be present with groups of thin oil shales concentrated in Beds 26 to 46. The stratigraphy of the borehole is summarized in Fig. 25; the lithological and faunal sequences can be closely matched with that proved in other boreholes in Norfolk, The Wash and Lincolnshire.

A total of 7.17 m of oil shale was proved in 80 seams ranging from 1 to 47 cm in thickness. The average seam thickness was 9.0 cm. 82 per cent of the seams were < 20 cm thick and 60 per cent of the total volume of oil shale proved occurred in seams < 20 cm thick. The distribution of the thicknesses of the seams and the relationship of seam thickness to volume of oil shale is shown in Fig. 25.

The greatest concentrations of oil shales occur in the five oil-shale-rich bands described in Section 2.1, the Lower and Upper eudoxus Bands, the elegans Band, the wheatleyensis Band and the pectinatus Band. The structure of the Kimmeridge Clay of Norfolk is simple. Much of the outcrop of the pectinatus Band has been geologically surveyed in recent years and its position at outcrop and in the subcrop (because of the large amount of borehole data available) can be accurately determined. The positions of the lower

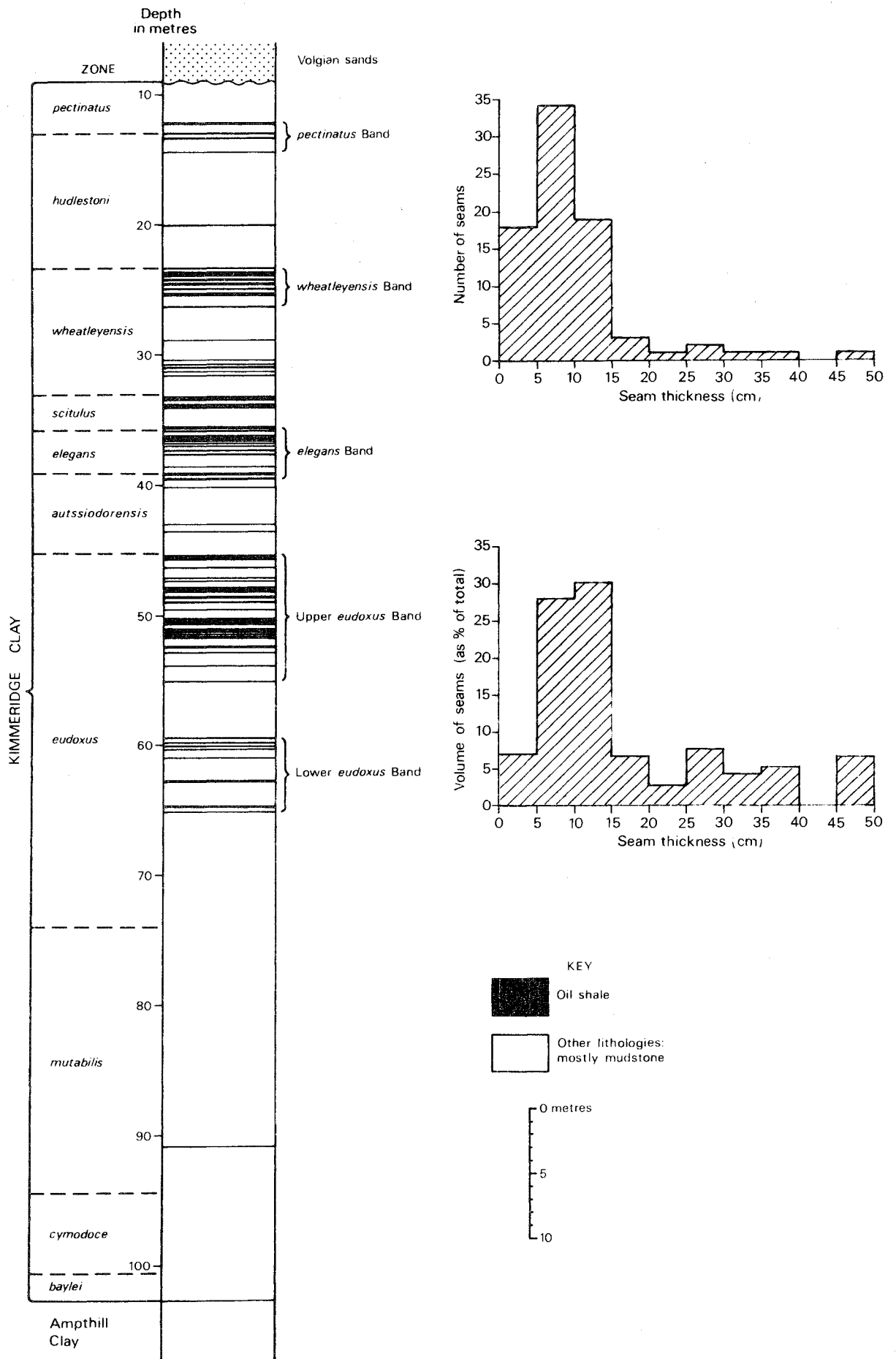


Figure 25 North Runcion Borehole, distribution and thickness of seams

oil-shale-rich bands can also be determined with some confidence from the borehole data. In south west Norfolk and Cambridgeshire the Upper Kimmeridge Clay is progressively overstepped in a southerly direction by Lower Cretaceous rocks. Northwards from Downham Market all five oil-shale-rich bands are present throughout the Norfolk outcrop and beneath The Wash.

2.8 THE WASH TO THE HUMBER

The Kimmeridge Clay outcrop is almost entirely obscured by Quaternary deposits in Lincolnshire and Humberside. The formation rises from beneath the Holocene deposits of the East and West fens of Lincolnshire near Horncastle and runs north westwards from there to the River Humber as drift-covered, low ground in front of the Cretaceous escarpment of the Lincolnshire Wolds. Exposures are rare and largely confined to the floors of the deeper valleys (Fig. 26). Records of oil shales are, however, surprisingly common.

A borehole in the Kimmeridge Clay in search of coal at Benniworth [TF 208 818] proved numerous layers of "inflammable and very inflammable schist". A second borehole at the same site confirmed the presence of oil shales and two samples were distilled to yield about 23 and 27 gal/ton (Woodward, 1904, p. 218). Oil shale has also been recorded in a brick pit at South Willingham, at East Keal, Driby and immediately beneath the Spilsby Sandstone in Acre House Mine [TF 115 963] (Judd, 1870).

In 1917 the Ministry of Munitions drilled a continuously cored borehole through part of the Kimmeridge Clay at Donington on Bain [TF 243 819] to explore the oil shale occurrences in Lincolnshire. The borehole penetrated 74.7 m of Kimmeridge Clay and was terminated in loose sand (Strahan, 1920, p. 39-40). Seven samples from the borehole were analysed and yielded 1.3 to 16.4 gal/ton (op. cit., p. 29). Neither the published stratigraphy of the borehole nor the yields of the shales seemed comparable with the results obtained from the same strata in Norfolk and one of the pilot study boreholes was therefore sited at Donington on Bain [TF 2399 8188] about 300 m west of the Ministry of Munitions borehole.

The Donington on Bain Borehole proved a complete Kimmeridge Clay sequence from the baylei to pectinatus zones (Fig. 27) that can be matched in detail with the Norfolk succession. All five oil-shale-rich bands were present and contained, together with minor seams at other stratigraphical levels, a total of 10.47 m of oil shale in over 100 seams. The seams ranged from 1 to 68 cm in thickness, 64% of the total volume of oil shale being contained in seams less than 20 cm thick. The structure of the Kimmeridge Clay in Lincolnshire and Humberside is simple but much of the outcrop of the formation is covered by drift deposits. The positions of the oil-shale-rich bands could therefore be determined by drilling and trenching in selected areas. North of Acre House Mine the Kimmeridge Clay is overstepped northwards by Cretaceous so that all five oil-shale-rich bands are cut out

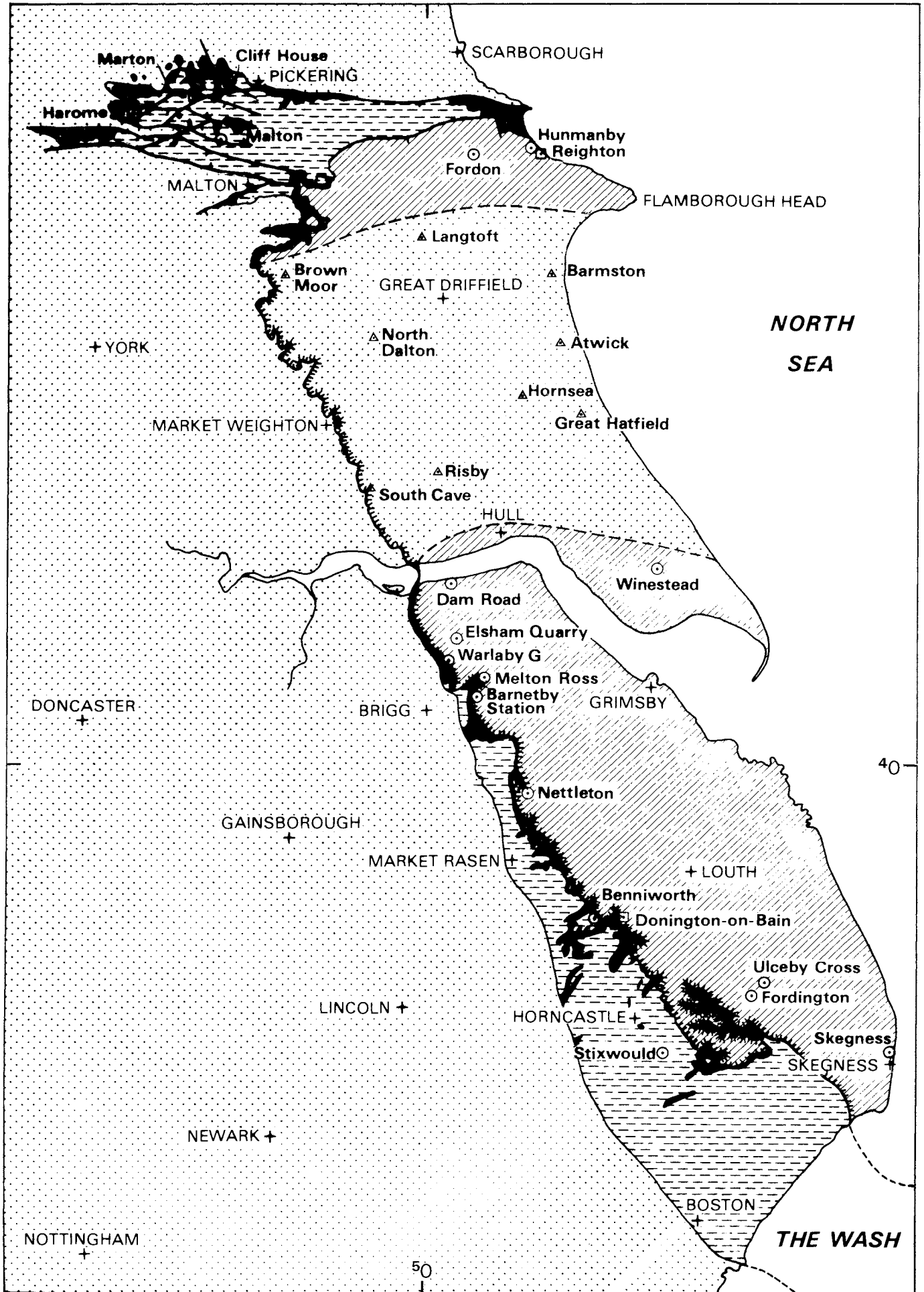


Figure 26 Kimmeridge Clay outcrop and subcrop: Lincolnshire, Humberside and North Yorkshire

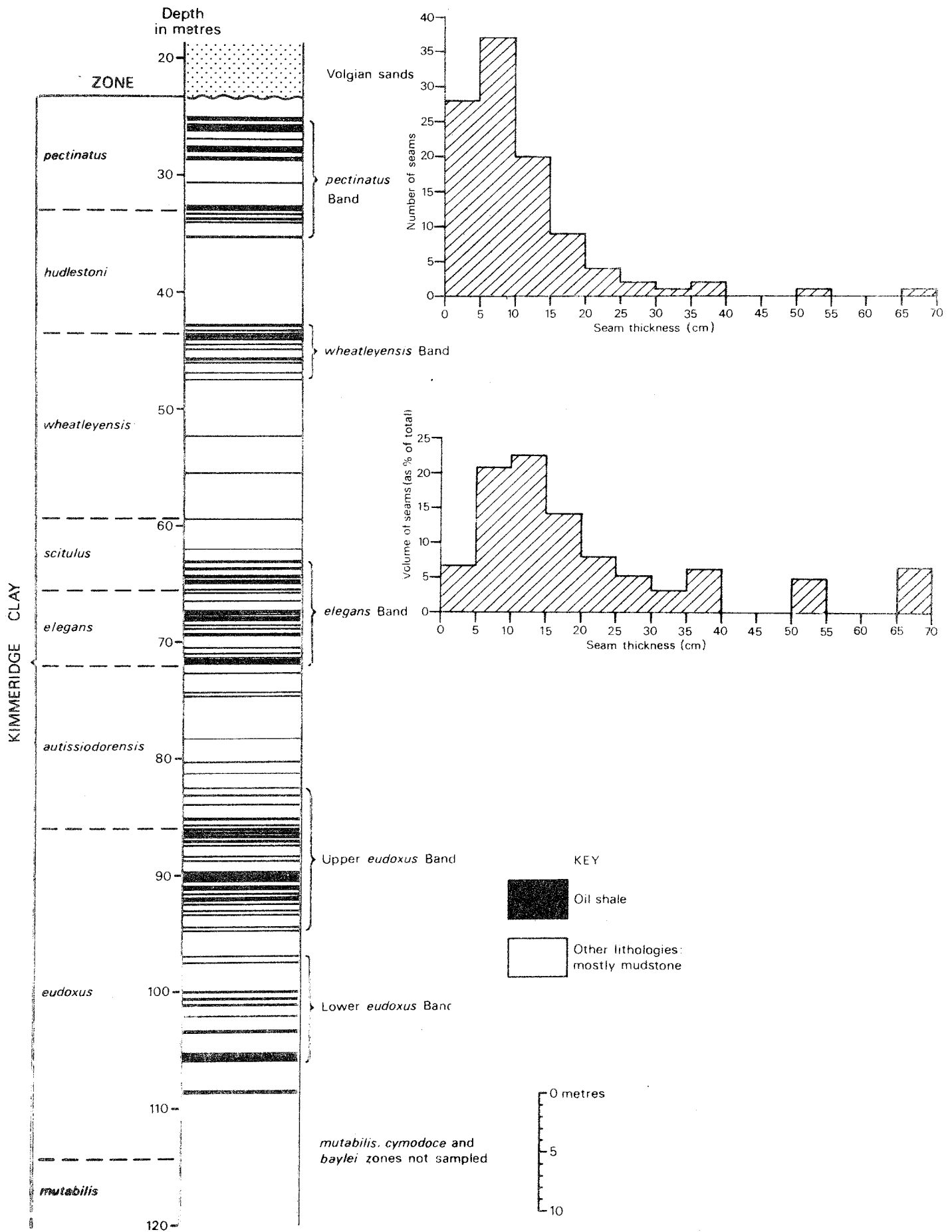


Figure 27 Donington on Bain Borehole, distribution and thickness of seams

before the River Humber is reached.

2.9 NORTH YORKSHIRE

The Kimmeridge Clay reappears, after a gap of about 30 km across the Market Weighton Axis, near Birdsall, North Yorkshire where it is faulted against the Chalk by the northern boundary fault of the axis. From Birdsall the outcrop of the formation runs north and then east to the coast at Reighton, forming low, mostly drift-covered ground to the west and north of the chalk-escarpment. The formation underlies much of the Vale of Pickering but because of the extensive cover of Quaternary deposits and the complexity of the structure the stratigraphy of the area was, until recently, poorly known. A network of faults, many of which trend west-east sub-parallel to the northern boundary of the Market Weighton structure, extends across the full width of the outcrop. Even the foreshore and cliff sections between Reighton and Filey are poorly exposed, partly because of the tectonic activity, partly because of a thick cover of glacial till in much of the section and partly because of secondary disturbances associated with the emplacement of the till and with later landslipping in the overlying Speeton Clay (Fig. 26).

Judd (1870) noted oil shales in the Kimmeridge Clay of the coastal sections and the stratigraphical positions of these were later described by Lamplugh (1889). Cope (1974) has described the stratigraphy of parts of the Kimmeridge Clay on the coast and in two inland brickpits, at Green Lane and Golden Hill, in the Vale of Pickering at Marton. Both pits expose seams of oil shale: samples of these have been analysed by Robertson Research International Ltd (Cooper and Barnard, 1978, Table 5) and have been shown to have potential yields of up to 15 gal/ton.

Because of the structural complexity of the area the thickness of the formation cannot be determined from the outcrop evidence alone. The rock-cutting and geophysical data from the deep hydrocarbon borehole at Hunmanby [TA 1301 7598], near the eastern end of the outcrop, suggested the total thickness of the formation to be less than 100 m. Evidence from cored water-boreholes at the western end of the outcrop between Helmsley and Pickering showed that the Lower Kimmeridge Clay alone was more than 340 m thick in that area (Richardson in Reeves et al., 1978). Two boreholes were therefore drilled for the project; at Reighton [TA 1465 7581] to sample the thin development of the sequence and at Golden Hill, Marton [SE 7230 8285] to sample the oil-shale-rich parts of the thick sequence.

The Reighton Borehole was sited on the cliff top at the nearest accessible point to the Kimmeridge Clay/Speeton Clay junction exposed in the cliffs. Cope (1974) recorded a pectinatus Zone fauna from the youngest Kimmeridge Clay in this cliff but concluded that the remainder of the Upper Kimmeridge Clay was attenuated due to erosion and that the wheatleyensis and hudlestoni zones were absent. It was therefore anticipated that the elgans

and pectinatus oil-shale-rich bands would be present in the borehole but that the wheatleyensis Band might be absent. In the event, the Speeton Clay was faulted against Upper Kimmeridge Clay of elegans or scitulus zone age and only a thin development of muddy oil shales in the elegans Band was present. Representatives of the oil shales in the Lower and Upper eudoxus bands were also present but were thin and muddy in comparison with other areas (Fig. 28).

The tectonic structures affecting the Kimmeridge Clay of the Reighton area are clearly even more complex than the scattered foreshore and cliff exposures suggest. The total thickness of the formation is probably about 100 m and is likely to be complete from the baylei to pectinatus zones. However, large parts of the sequence have still not been seen and it is unlikely, because of the tectonic complexity, that they could be sampled in a single borehole. The outcrop the Kimmeridge Clay inland from Reighton is largely drift-covered and it would be extremely difficult to determine the positions of the oil-shale-rich bands in the area, even with an extensive drilling programme.

The Marton Borehole was sited on the crest of a fault-bounded ridge of Kimmeridge Clay, alongside the Golden Hill brickpit. Oil shales of the pectinatus Band form the crest and western dip slope of the ridge and are well exposed in the highest part of the pit. They are however deeply weathered and unsuitable for chemical analysis. The pit section and the borehole proved a continuous sequence from high mutabilis Zone to pectinatus Zone (Fig. 6) and confirmed Richardson's (op. cit.) observation that the sequence is thick in comparison with that of the Kimmeridge Clay elsewhere in northern England.

The borehole proved representatives of the oil shales of the Lower and Upper eudoxus bands, elegans Band, wheatleyensis Band and pectinatus Band. Many of the oil-shale seams are thick but all are muddy and most consist of fine interlaminae of mudstone and kerogen-rich mudstone. Many have diffuse boundaries and pass up or down into mudstone by an increase in spacing, and eventual loss, of the kerogen-rich laminae. The same feature can be observed in the Green Lane brickpit referred to above, where the oil shales of the Upper eudoxus Band are well exposed.

The structural complexity of the western part of the Vale of Pickering makes it unlikely that any of the oil-shale-rich bands could be traced for distances of more than 1 to 2 km at outcrop.

2.10 SCOTLAND

Kimmeridge Clay crops out in small coastal areas at Ethie in Cromarty, between Brora and Helmsdale in Sutherland and on the Hebridean islands of Skye and Mull. The Cromarty, Sutherland and Mull outcrops are all faulted against much older rocks and owe their current positions to reactivation of movement along the Great Glen Fault and associated faults.

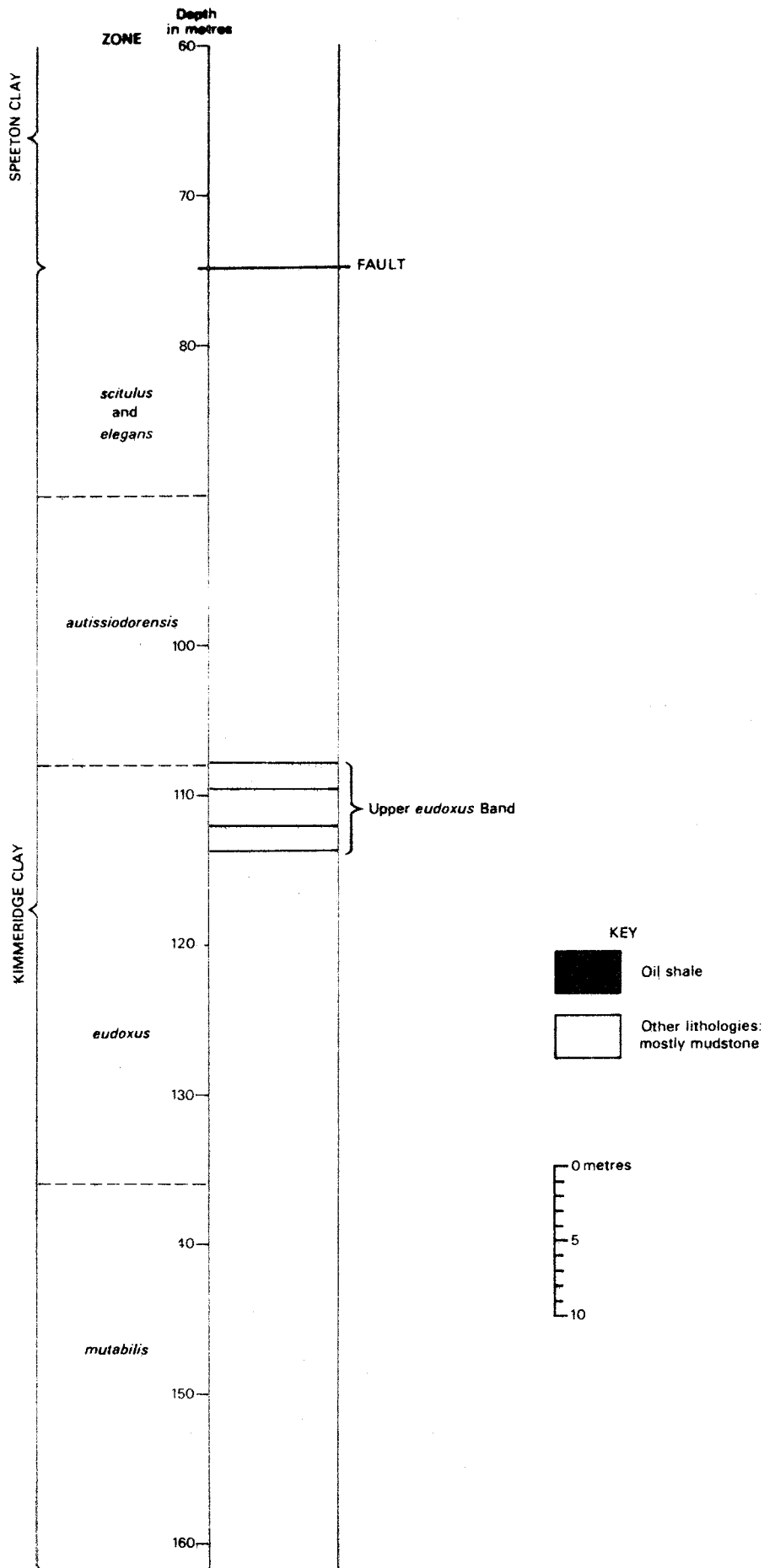


Figure 28 Reighton Borehole, distribution of seams

2.10.1 Ethie

Folded and faulted Kimmeridge Clay crops out at low-water on the foreshore at Ethie [NH 777 633] within the fault Zone of the Great Glen Fault. On its western, landward side, the Kimmeridge Clay is bounded by a branch of the fault and is in contact with Moinian and Devonian rocks. The succession has been described by Waterston (1950) who recognised about 60 m of beds within the lowest part of the Kimmeridge Clay (baylei to mutabilis zones). The succession is finely rhythmic as at this stratigraphical level in England (Type A of Fig. 4) but with sufficient organic matter present in all but the most calcareous mudstones to give the rocks a brown streak. Much of this organic matter is land-derived plant debris but some is clearly kerogen and, in the higher part of the sequence, weak silty oil shales are present. Recent work in the area immediately offshore (Fig. 29) has shown the Ethie outcrop to be at the western edge of a large submarine crop of Upper Jurassic rocks (Sheet 57°N-4°W: Moray Buchan, 1978). The Kimmeridge Clay outcrop again comes close to the coast at Port an Righ (NH 853 732) where shale debris with fossils indicative of the cymodoce and mutabilis zones have been recorded on the foreshore and a nearby reef (Three Kings Reef). None of the 'oil shales' from either Ethie or Port an Righ are comparable with those of the English outcrop, since the organic content of the former appears to be diluted with land-derived silt and plant debris.

2.10.2 Helmsdale

The Kimmeridge Clay crops out in a coastal strip some 18 km in length and up to 1.5 km wide, stretching from Kintradwell [NC 919 077] northwards to beyond Helmsdale [NC 059 172] (Fig. 30). The formation is almost continuously exposed in foreshore sections and consists of a thick (> 400 m) sequence of rapidly alternating mudstones, sandstones and boulder beds. On its western side the outcrop is bounded by the Helmsdale Fault and it is this fault, which is believed to have been active in Kimmeridgian times, that is believed to have given rise to the sandstones and boulder beds (see Bailey and Weir, 1932, for discussion). The sequence has been described by Linsley (1972) and recently reviewed by Neves and Selley (1976).

No oil shale is evident in this section which is dominated by silt and coarser clastic material that is believed to have been derived from an adjacent land area, a fringing shelf and from the submarine fault-scarp itself. The argillaceous parts of the sequence are organic-rich and have a brown streak, but this material is almost entirely comminuted plant debris derived from the nearby land area.

2.10.3 Skye and Mull

The basal beds of the Kimmeridge Clay (baylei to ?mutabilis zones) crop out on the

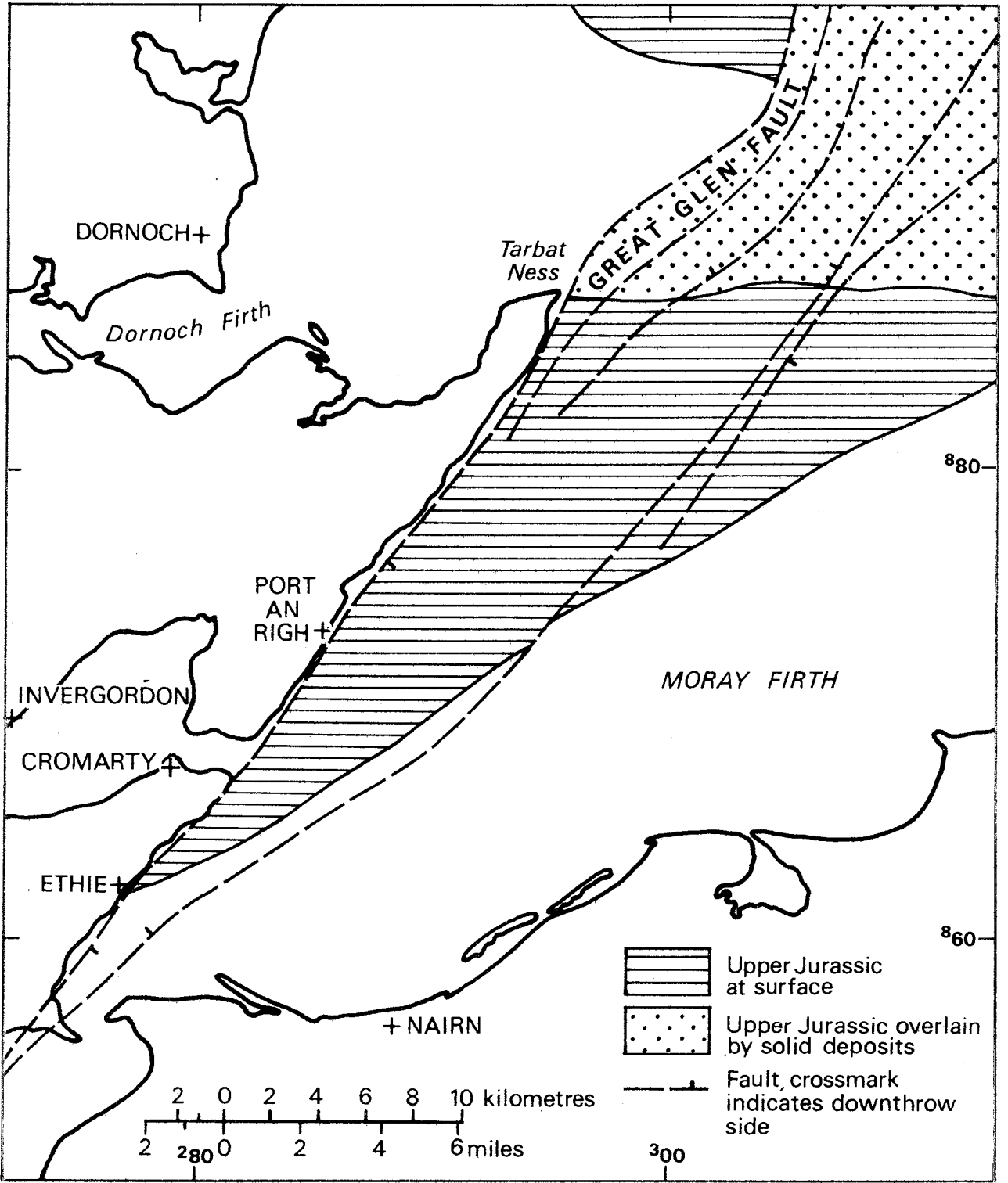


Figure 29 Geological sketch map showing the submarine outcrop of the Upper Jurassic rocks of the Moray Firth area

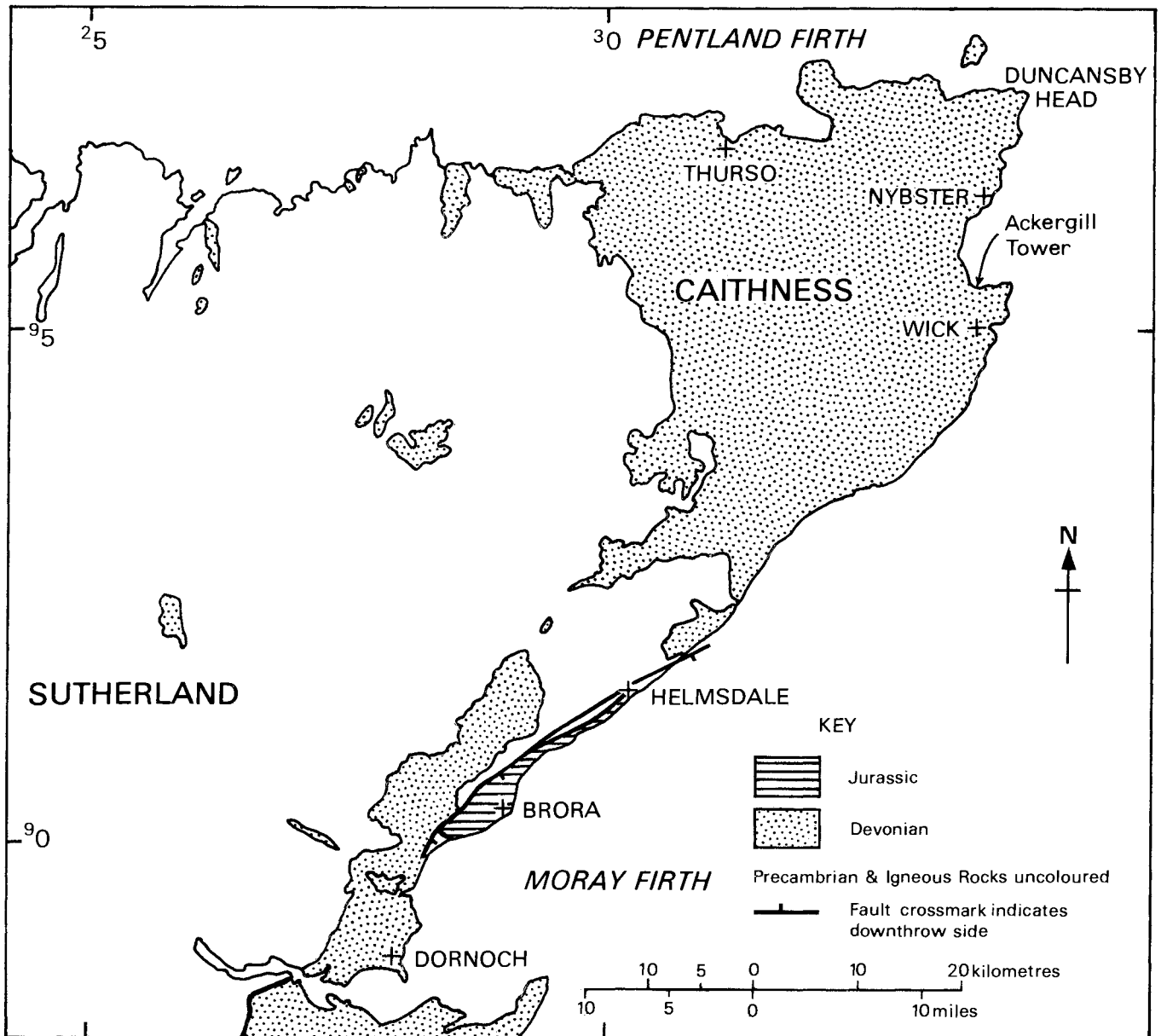


Figure 30 Geological sketch map of Sutherland and Caithness showing the positions of the Jurassic and Devonian outcrops

foreshore in Staffin Bay [NG 485 695] in the Trotternish peninsula of Skye (Anderson and Dunham, 1966). The sequence is disturbed by faulting and by very steep dips in the toe of a large landslide and appears to be overlain by a Palagonite tuff of Tertiary age. Small scale rhythms (Type A of Fig. 4) are poorly developed in a predominantly silty mudstone that contains land-derived plant debris but no oil shale.

Bailey recorded a tiny, faulted-bounded patch of Upper Jurassic mudstone near Duart Bay, Mull [NM 735 355] from which Arkell and Callomon (1963, p. 243) subsequently recorded Lower Kimmeridgian ammonites. The exposure consists of intensely sheared mudstone and baked hornfels cut by dolerite dykes and is so altered that its original lithology cannot now be determined.

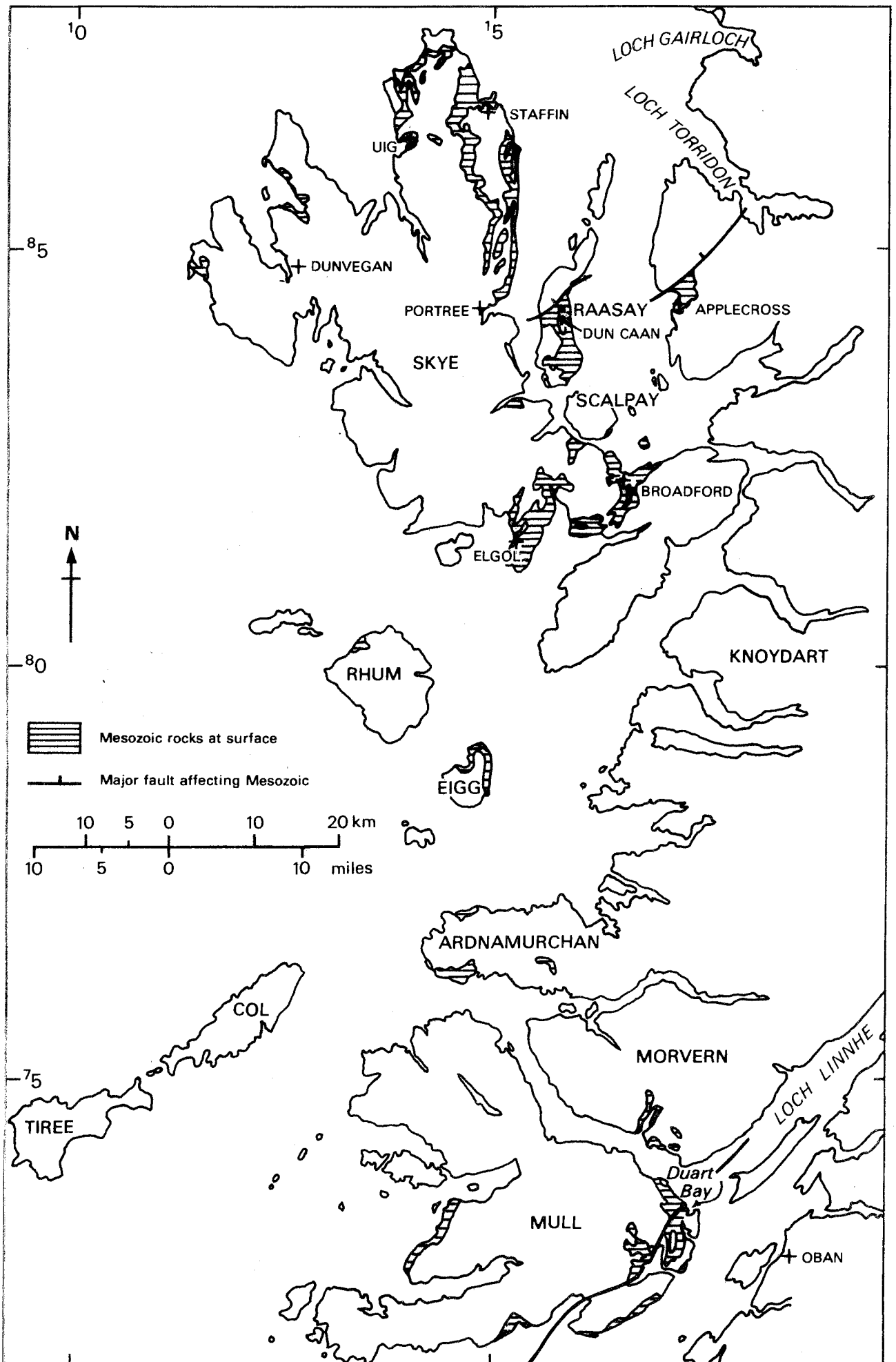


Figure 31 Geological sketch map showing the Jurassic outcrops in the Inner Hebrides

2.11 CONCLUSIONS

Seams of oil shale occur throughout much of the English outcrop and subcrop of the Kimmeridge Clay. They are confined to the stratigraphical range mutabilis Zone to rotunda Zone, the greatest concentrations of seams occurring in the eudoxus, elegans, wheatleyensis and pectinatus zones. The seams are numerous (more than 100 present in some sections), but thin (mostly < 20 cm).

The greatest concentration of oil shale seams recorded to date occurs in the sequence at Kimmeridge Bay, Dorset; the most persistent groups of closely spaced, thick seams occur in the Upper eudoxus and wheatleyensis Bands. Oil shales are only weakly developed close to the western edge of the London Platform between north Wiltshire and Buckinghamshire and in the North Yorkshire sequence. They are not developed in the Scottish land area.

3. Kimmeridge Clay: potential oil yields

3.1 INTRODUCTION

The potential oil yield of an oil shale depends on two major factors, the nature and amount of the organic component of the shale and the method by which it is retorted. Between 1694 and 1959 over 2000 oil shale retorting methods were patented (Klosky, 1949-1959) and although only a small number of these were ever used on an industrial scale the results from them have shown that there is no single retorting method capable of producing the optimum yields from all types of oil shale.

It is obviously desirable when comparing the potential yields of different oil shales to use an internationally accepted standard laboratory method of assay, even though that method may subsequently have to be correlated with the results obtained from various retorting methods on the same shale and on different shales.

The modified Fischer Assay, developed by the U. S. Bureau of Mines (Stanfield and Frost, 1949) provides just such a laboratory method. In this method a 100 gm sample of shale is heated in an inert atmosphere from ambient temperature to 500° C over a period of 20 minutes, is maintained at 500° C for one hour, and is allowed to cool. The pyrolysis products are retained in a series of cold traps and the oil yield is weighed. The specific gravity of the oil is usually determined and the yield is expressed as either weight of oil/weight of dry shale (%) or US gallons of oil/US ton of dry shale. Other methods of quoting yields are discussed below.

Prior to the advent of the modified Fischer Assay the Gray-King Assay was commonly used. This latter method uses a sample of one to several hundred grams and a pyrolysis temperature of 550° C. It gives results broadly comparable with those of the modified Fischer Assay.

In recent years there has been a rapid growth in interest in organic-rich sediments as potential natural hydrocarbon source rocks and a need has developed for an assay method that can make use of small weights of rock-cuttings from exploratory boreholes. The Institut Français de Petrole/Rock Eval method (Espitalié et al., 1977) has therefore been developed specifically to provide a rapid, inexpensive method for determining the hydrocarbon yield and other data relevant to source rock potential of large numbers of small (100 mg) samples. The method has been calibrated against potential oil yields proved by the modified Fischer Assay (op. cit. Fig. 14) and, in addition, provides two other parameters,

the Oxygen Index and the Hydrogen Index, that are claimed to be directly related to the atomic O/C and H/C ratios respectively of the kerogen in the rock (op. cit. Fig. 7).

In the IFP/Rock Eval method a 50 to 100 mg sample of powdered rock is electrically heated in a small oven at a programmed steady rate of about 25°C per minute from ambient temperature to 550°C in a helium atmosphere. As the temperature rises hydrocarbons and carbon dioxide are produced by the pyrolytic breakdown of organic materials and carbonates in the rock. The rate of evolution of these gases is continuously monitored. The hydrocarbon concentrations are measured by a flame ionisation detector: the carbon dioxide is collected at regular intervals and is subsequently determined by cathometry. When plotted against temperature the rate of evolution of the gases shows three peaks (Fig. 32) that are formed as follows:

- P₁: from ambient to about 200°C a hydrocarbon peak is formed by the vapourisation of free hydrocarbons (bitumen) within the rock
- P₂: between about 250°C and about 450°C a hydrocarbon peak is formed by the pyrolytic breakdown of kerogen in the rock
- P₃: between about 450°C and 550°C a carbon dioxide peak is formed by the breakdown of carbonates in the rock.

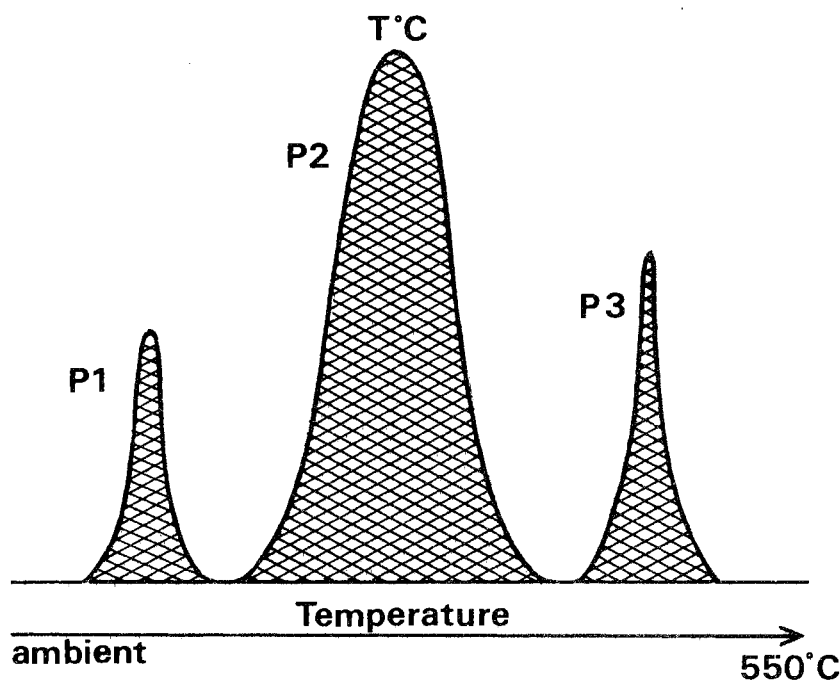


Figure 32 IFP/Rock Eval assay: diagrammatic representation of generation of volatiles (after Espitalié et al., 1977)

The combined area under peaks P_1 and P_2 is referred to as the Production Index and is a measure of the hydrocarbon production potential of the rock.

The ratio of the area under Peak P_2 to the total organic carbon in the rock and that of the area under Peak P_3 to the total organic carbon are the Hydrogen Index and the Oxygen Index respectively. These indices have been shown to have linear relationships with the atomic H/C and O/C ratios respectively (op. cit., Figs 6 and 7). When plotted against one another it is claimed that the Hydrogen and Oxygen indices give results that can be correlated with the origin of the organic matter in the rock in a manner precisely comparable to that described by Van Krevelen (1961) for the plot of atomic H/C ratios against O/C ratios. It has been found by analysis of a large variety of kerogens that those of algal origin (Type I of Tissot et al., 1974) generally have a high atomic H/C and a low to moderate atomic O/C ratio (Fig. 54). Kerogens derived mainly from land plants (Type III) have low H/C ratios and moderate to high O/C ratios. Kerogens of mixed or intermediate type are classified as Type II.

A number of other oil shale assay methods have been reported from time to time but most have been developed to satisfy some particular purpose related to either the type of sample available or the needs of the particular project in hand. All have been calibrated against the modified Fischer Assay which remains, by common consent, the accepted standard.

The apparatus necessary to carry out analyses by the modified Fischer Assay was not available in the UK at the time of the pilot project or at the beginning of the present project. The Organic Geochemistry Unit at Newcastle University purchased three Fischer retorts during the latter part of the project and these, after calibration against samples assayed by the same method at the U. S. Department of Energy Research Center at Laramie, Wyoming, were used to determine the potential yields of the oil shales that were subjected to detailed organic analysis.

The great majority of the potential oil yield analyses carried out for the present work were therefore made by the IFP/Rock Eval method. This method is very satisfactory as a technique for the rapid and relatively inexpensive assessment of large numbers of samples. It can have the additional advantages of distinguishing the bitumen yield from the shale oil yield, of indicating the temperature of the maximum rate of pyrolysis and of providing data (the Hydrogen and Oxygen indices) relevant to the composition of the kerogen in the shale. It has the severe limitation for resource assessment purposes that it can give misleading results if the very small (50 to 100 mg) sample analysed is not sufficiently well mixed and sampled to be representative of the oil shale seam or bulked core.

Most oil shales show considerable lateral and vertical variation in yield over very

short distances even though the average yield of the complete seam may be relatively constant over large areas. In the Kimmeridge Clay many of the oil shales are shelly and others contain burrowfills of largely inorganic mud. Spot samples of 100 mg-size could therefore give apparent yields of from < 1 gal/ton (shelly or inorganic mud) to > 50 gal/ton (oil shale). Even the 100 g samples used in the modified Fischer Assay can be unsatisfactory in this respect, but only assay samples of several kg would be better and no commercial equipment is available to do this.

A number of precautions were taken to try to offset these possible problems. Duplicate analyses were run to check the efficiency of the sampling procedure, samples of known Fischer Assay yield were run at regular intervals to check the calibration of the IFP/Rock Eval apparatus and the total yields of bulked runs of core were checked against results obtained in the pilot study by a different assay method (Laboratory of the Government Chemist method: see below). As an additional check on the efficiency of the sampling of the bulk cores, spot samples of the main oil shale seams within selected bulked core runs were analysed so that the general magnitude of the yield from the bulked core could be estimated and compared with the assay value for the bulked core.

Finally, when the IFP/Rock Eval analyses had been completed the 80 m of core with the highest yields were re-sampled and duplicate samples (100 g each) were analysed by the modified Fischer Assay method at the Laramie Research Center.

For the Kimmeridge Clay oil shales, peak P_1 in the IFP/Rock Eval analyses was found to be negligibly small and to indicate that only about 1% of the potential oil yield was present as bitumen. In an average quality oil shale this represents about 0.1 wt% of the rock. The integer of Peak P_2 in all the Kimmeridge Clay samples examined was therefore taken to be the Production Index. Analyses of individual oil shale seams subsequently showed that about 10% of the total potential oil yield (Fischer Assay) was solvent extractable (Fig 32; see Section 4.3 for further details). This suggests that in the present work the separation of peaks P_1 and P_2 was not satisfactorily achieved and that the yield of 'free' hydrocarbons (bitumen) is included in the total potential yield.

Peak P_2 was steep sided with little hydrocarbon generation occurring below about 280°C and the temperature of the maximum rate of pyrolysis generally in the range 410° to 425°C. In the Laboratory of the Government Chemist assay method used in the pilot study a 1 g sample was heated to 450°C and the pyrolysis products collected. At the time that these assays were made it was believed that the full yield was achieved at or below 450°C and that no kerogen remained in the rock. The pyrolysis data from the IFP/Rock Eval method confirm this to be the case.

The determination of the potential yields of hydrocarbon gases from oil shales is

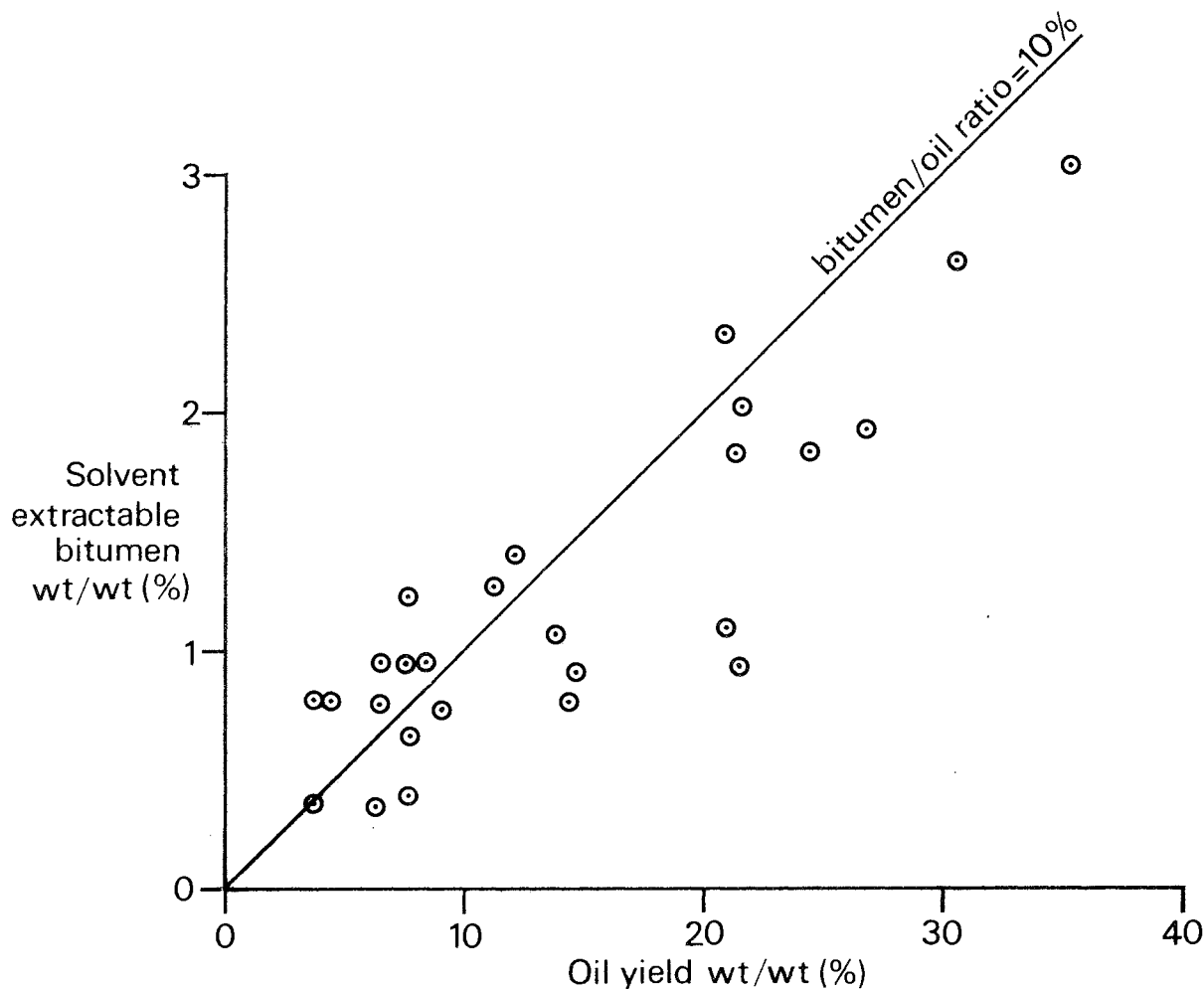


Figure 33 Relationship of potential oil yield to solvent extractable bitumen

difficult because of the presence of carbon dioxide in the pyrolysis products. In the IFP/Rock Eval method, where the hydrocarbon product is too small to conveniently condense and analyse separately, an arbitrary calibration has been developed from analyses of much larger samples in which the ratio of oil yield to total hydrocarbon yield has been shown to be 0.90 for Type I (algal) kerogens and 0.88 for Type II (mixed origin) kerogens (Tissot et al., 1974). The type of kerogen, and hence the conversion factor required to obtain the oil yield, has been determined in the present analyses from the Hydrogen and Oxygen indices. Gas chromatography of the gases and vapours that passed through the cold trap during pyrolysis of a number of the oil shales at 500°C showed the presence of the major compounds methane, ethane, ethylene, propane, n-butane, iso-pentane, 3-methyl pentane, cyclohexane, n-pentane and methyl cyclohexane, and minor components iso-butane, n-pentane cyclopentane, 2-methyl pentane, n-hexane and 2 methyl-hexane.

Over 1000 samples of Kimmeridge Clay oil shale and oil shale/mudstone mixtures were analysed by the IFP/Rock Eval method. The results are tabulated in Appendix E. Of this total, 700 samples were 0.5 m long runs of bulked core that had been sub-sampled

in the manner described by Dangerfield (in Gallois, 1978, p. 6) for the pilot study. The analytical method used to determine potential oil yield in the pilot study was developed by the Laboratory of the Government Chemist and based on a 1 g sample. There was considerable initial doubt as to whether repeatable results could be obtained from the IFP/Rock Eval method because of the small (50 to 100 mg) size of the sample and the difficulty of achieving adequate mixing and sub-sampling of the bulked core. New samples were therefore prepared from the bulked residual material from the Donington on Bain and North Runcton boreholes and these were analysed by the IFP/Rock Eval method so that comparison could be made with the Laboratory of the Government Chemist results for the same boreholes.

In the pilot study a bulked sample interval of 2 metres had been chosen: this proved to be too large an interval in relation to the thickness of the oil shale seams and led to a general smoothing of the yield histograms. In the present work an 0.5 m bulked sample was used since this gives a more accurate correlation between the oil shale seams and the potential yields. Comparison of the Donington on Bain and North Runcton yields obtained by the Laboratory of the Government Chemist and the IFP/Rock Eval methods showed good agreement (Fig. 34). For the depth interval 19.75 to 59.75 m the total yield in the North Runcton Borehole by the LGC method (area under the histogram) was 82.2 m%: that for the interval 20.00 to 60.50 m in the IFP/Rock Eval method was 78.8 m%.

Donnell (1977, p. 848) has drawn attention to the problem caused by the lack of a universal terminology for reporting oil shale assay values. At the United Nations Symposium on oil shales (held at Tallinn, Estonia in 1968) the yields of oil per ton of shale were variously reported in (i) US gallons per US (2000 lb) ton, (ii) imperial gallons per UK (2240 lb) ton, (iii) litres per metric (1000 kg) tonne (iv) litres per cubic metre, (v) weight oil/weight shale (%) and (vi) vol oil/vol shale (%).

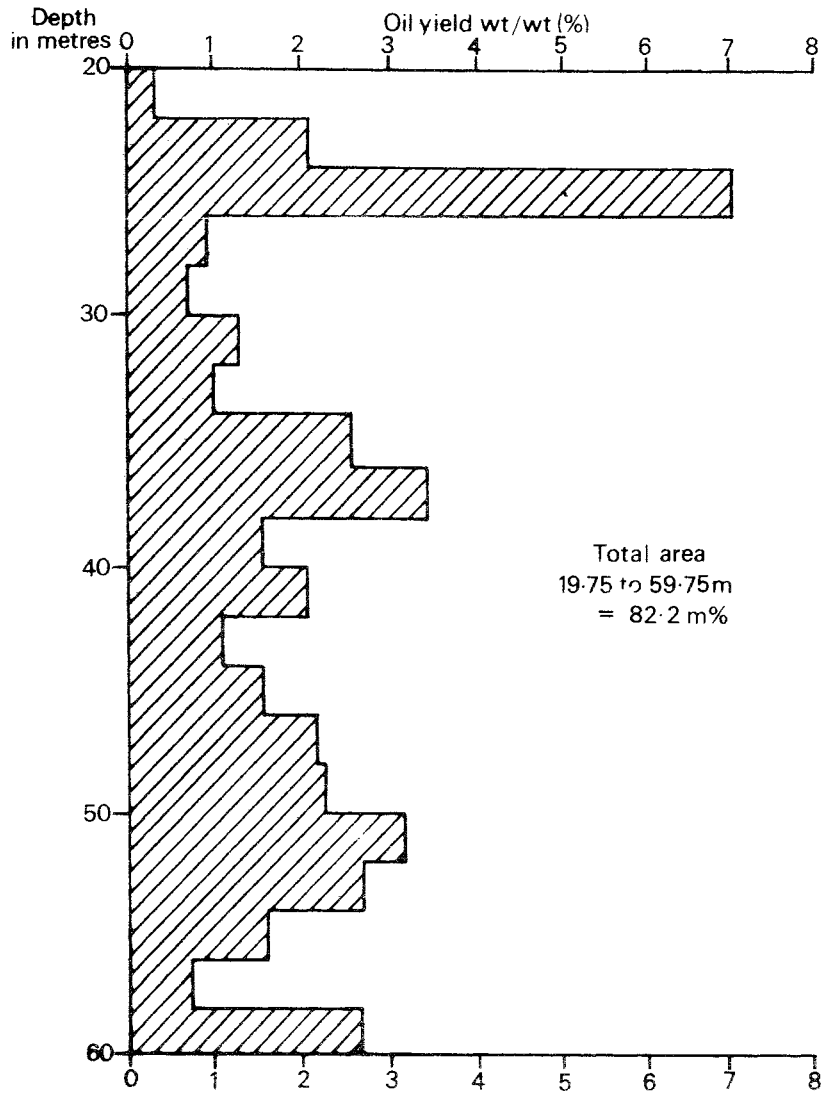
Donnell unfortunately complicated the issue further by confusing tons and tonnes and by stating that wt/wt% yields could readily be converted to US gals/US ton by multiplying the former by 2.66. This conversion is only true for an oil of specific gravity 0.90 and it may be significant that many shale oils from the United States, including that from the much-assayed Green River Formation, have specific gravities close to this figure. A selection of conversion factors for the more common assay reporting systems is given in Table 6. It should be noted here that high density shale oils, such as those from parts of the Kimmeridge Clay (see Section 4.2.1 for details), appear to have less favourable yields when quoted in gal/ton than when given as wt/wt%.

When comparing oil yields for commercial purposes the weight of oil produced from a given weight of pyrolysed shale is clearly more important than its volume. It would be advantageous therefore if wt/wt yield ratios were internationally used. Unfortunately the practise of expressing yields in US gallons/US ton has become the most commonly used since

Figure 34 Comparison of potential oil yields obtained by the LGC and IFP/Rock Eval assays

NORTH RUNCTON BOREHOLE

LABORATORY OF THE GOVERNMENT CHEMIST ASSAY



IFP/ROCK EVAL ASSAY

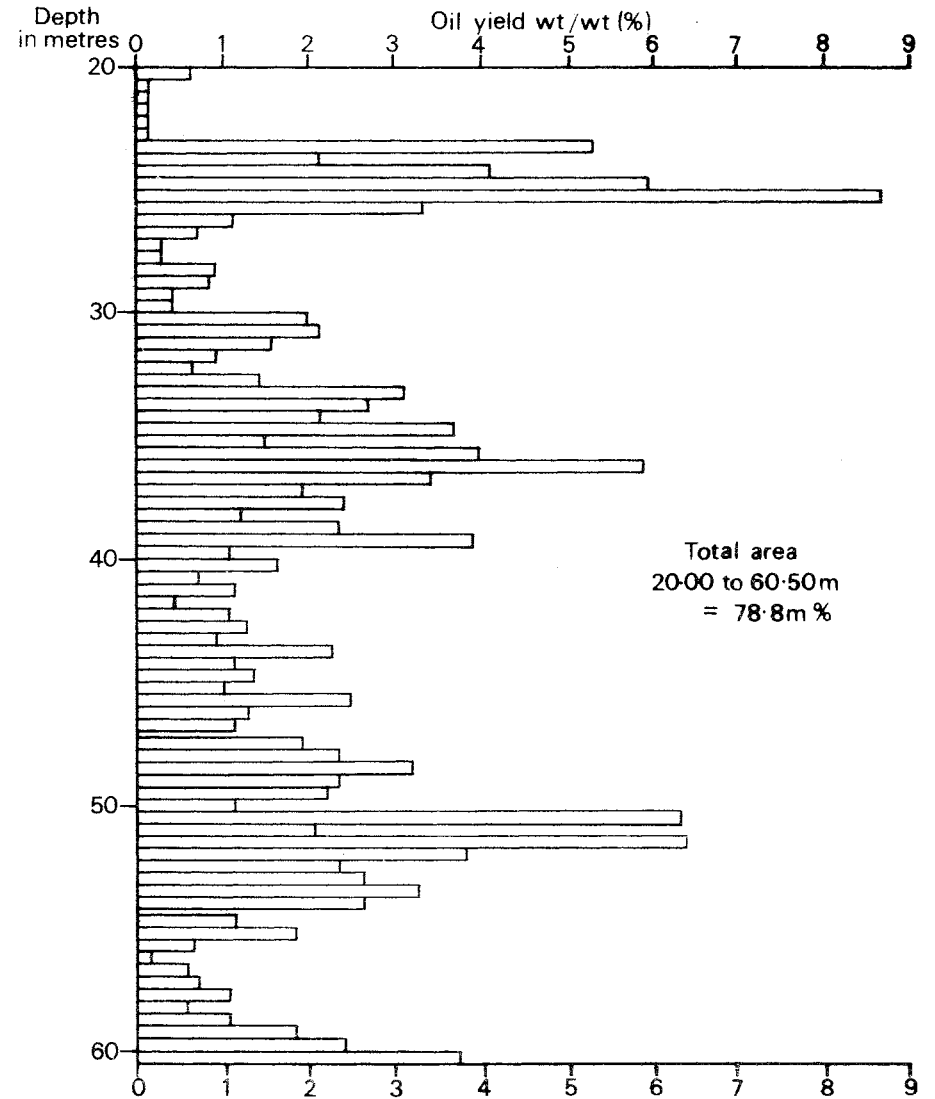


Table 6 Conversion factors

<u>Mass</u>	<u>Kg</u>	<u>lb</u>	<u>U. K. ton</u>	<u>U. S. ton</u>	<u>Metric tonne</u>
1 long (U. K.) ton	1016	2240	1	1.120	1.016
1 short (U.S.) ton	907	2000	0.893	1	0.907
1 metric tonne	1000	2205	0.984	1.102	1
<u>Volume</u>	<u>ml</u>	<u>cu in</u>	<u>U. K. gal</u>	<u>U. S. gal</u>	<u>Litre</u>
1 U. K. (imperial) gallon	4546	277.4	1	1.201	4.546
1 U. S. gallon	3785	231.0	0.833	1	3.785
1 litre	1000	61.0	0.220	0.264	1
<u>Oil Yield</u>	<u>U. K. gal/U. K. ton</u>		<u>U. S. gal/U. S. ton</u>		<u>Litre/ton</u>
1 U. K. gal/U. K. ton	1		1.072		4.474
1 U. S. gal/U. S. ton	0.933		1		4.173
1 litre/tonne	0.224		0.240		1
$Kx \frac{\text{wt/wt yield in } \%}{\text{specific gravity of oil}} = \text{yield in vol/wt}$					
where K = 2,235 for U. K. gal/U. K. ton K = 1,995 for U. K. gal/U. S. ton K = 2,684 for U. S. gal/U. K. ton K = 2,396 for U. S. gal/U. S. ton K = 10 for litres/tonne					
<u>Examples</u>					
i Kimmeridge Clay shale oil (sp. gr. 1.01; sample KOS 956): 1% wt/wt = 2.21 U. K. gal/U. K. ton or 2.37 U. S. gal/U. S. ton or 9.90 litres/tonne					
ii Green River (U. S. A.) shale oil (sp. gr. 0.91; Thorne et al. 1964): 1% wt/wt = 2.46 U. K. gal/U. K. ton or 2.63 U. S. gal/U. S. ton or 10.99 litres/tonne					

the advent of the modified Fischer Assay. In many cases quoted in the literature, the conversion to wt/wt% cannot be made because the specific gravity of the oil has not been published.

The results of the potential oil yield analyses are summarized below, area by area. Details of the IFP/Rock Eval yields and parameters and of the modified Fischer Assay yields are given in Appendix E. Potential oil yields are quoted as wt/wt% for the IFP/Rock Eval analyses and as wt/wt% and US gal/US ton for the modified Fischer Assay since the latter method produces a sufficiently large oil sample for its specific gravity to be determined.

3.2 POTENTIAL OIL YIELDS

The potential oil yields determined by the IFP/Rock Eval method are plotted against graphic sections of the oil-shale-rich parts of the cored boreholes in Figs. 34 to 44. The potential yields of the bulk samples are shown as histograms, those for spot samples from individual seams are shown in a separate column. Potential yields of more than 4 wt% (\approx 10 gal/ton) for core runs of 2 m or more could be of commercial interest and levels that attained or came close to this were therefore re-sampled using 100 g samples representative of 2-metre core runs. These were analysed by the modified Fischer Assay. The results, together with those of the IFP/Rock Eval assay, are tabulated in Appendix E.

The richest group of seams occurs in the Encombe Borehole at the level of the wheatleyensis Band. Here, 11.50 m of beds from 116.25 to 127.75 m gave an average yield of 12.1 US gal/US ton. Within this sequence the 8-metre run from 116.25 to 124.25 m gave an average yield of 13.7 US gal/US ton. These same beds crop out nearby in the cliff section at Clavells Hard (Plate 2B).

No other sequence was comparable with this although the wheatleyensis Band gave yields of more than 10 US gal/US ton for runs of more than 2 metres at two other localities. In the Portesham Borehole an average yield of 11.9 US gal/US ton was recorded between 47.74 and 51.74 m, and in the North Runcton Borehole the average yield between 23.00 and 26.00 m was 12.4 US gal/US ton. In the Tisbury Borehole an average yield of 11.5 US gal/US ton was obtained between 154.75 to 156.25 m and a similar 1.5 m run, also in the wheatleyensis Band, from 43.05 to 44.55 m in the Donington on Bain Borehole gave an average yield of 15.2 US gal/US ton. The beds between 43.05 and 46.05 m at Donington on Bain had an average yield of 9.7 US gal/US ton.

The best prospects after those in the wheatleyensis Band are in the Upper eudoxus Band in the Donington on Bain Borehole (average 9.6 US gal/US ton from 89.25 to 93.25 m), the Portesham Borehole (average 11.7 US gal/US ton from 150.74 to 152.74 m and 10.4 US gal/US ton from 176.24 to 178.24 m), the West Lavington Borehole (average 10.5 US gal/US ton from 156.00 to 158.00 m), the Kimmeridge Bay Borehole (average 9.5 US gal/US ton from 41.75 to 42.75 m) and the Tisbury Borehole (average 12.0 US gal/US ton from 228.75 to 230.75 m).

Two 2-metre runs in the pectinatus Zone, from 77.75 to 79.75 m and from 84.75 to 86.75 m in the Encombe Borehole gave yields of 11.0 US gal/US ton and 9.6 US gal/US ton respectively. The most surprising result was that the thick, closely-spaced seams of the Foudry Bridge Borehole (combined elegans to wheatleyensis bands at 445.50 to 449.50 m) gave an overall average yield of only 6.8 US gal/US ton.

Assuming a bulk density of about 2 UK tons/cu yd for the oil shales/mudstones

ENCOMBE BOREHOLE

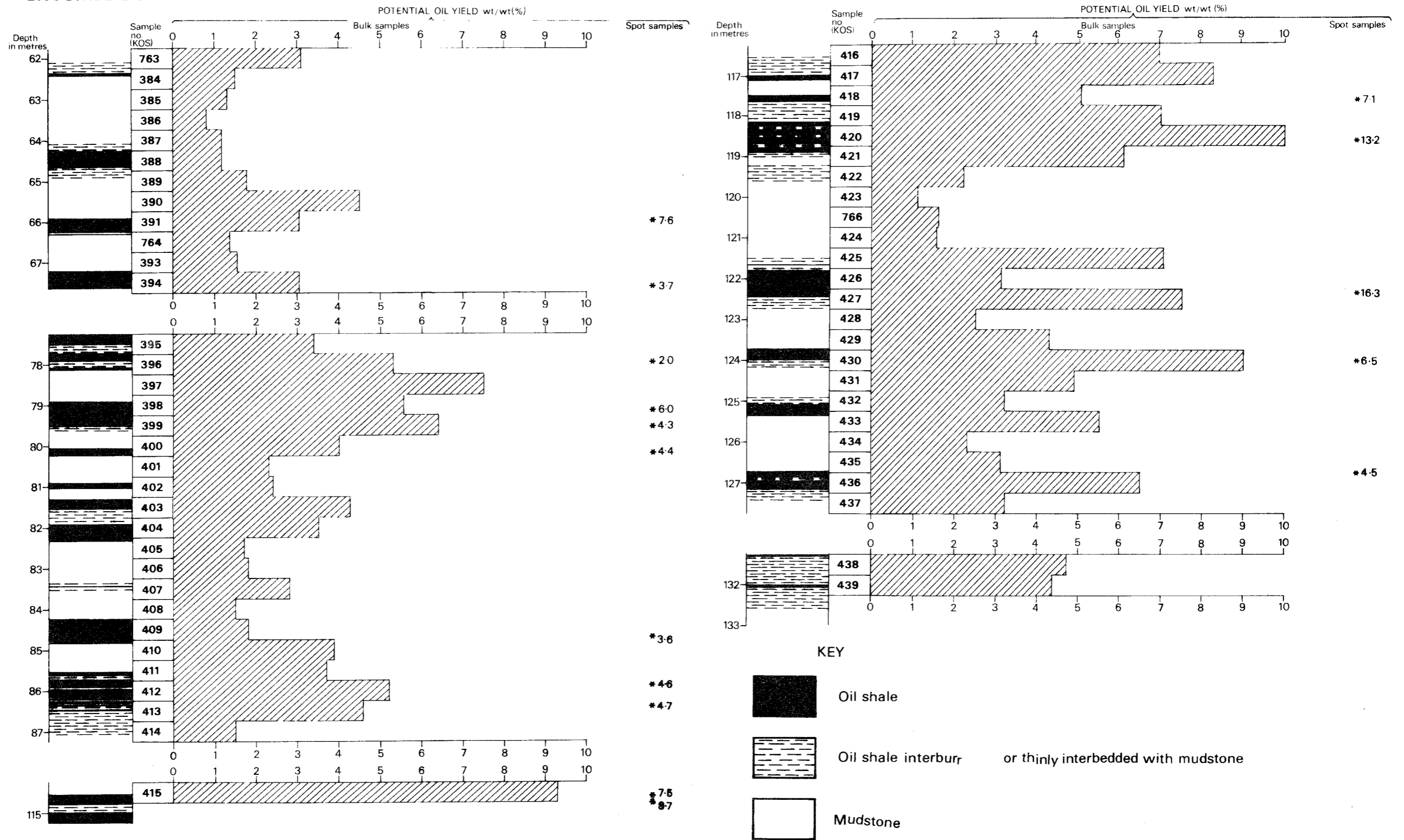


Figure 35 Encombe Borehole, potential oil yields

KIMMERIDGE BAY BOREHOLE

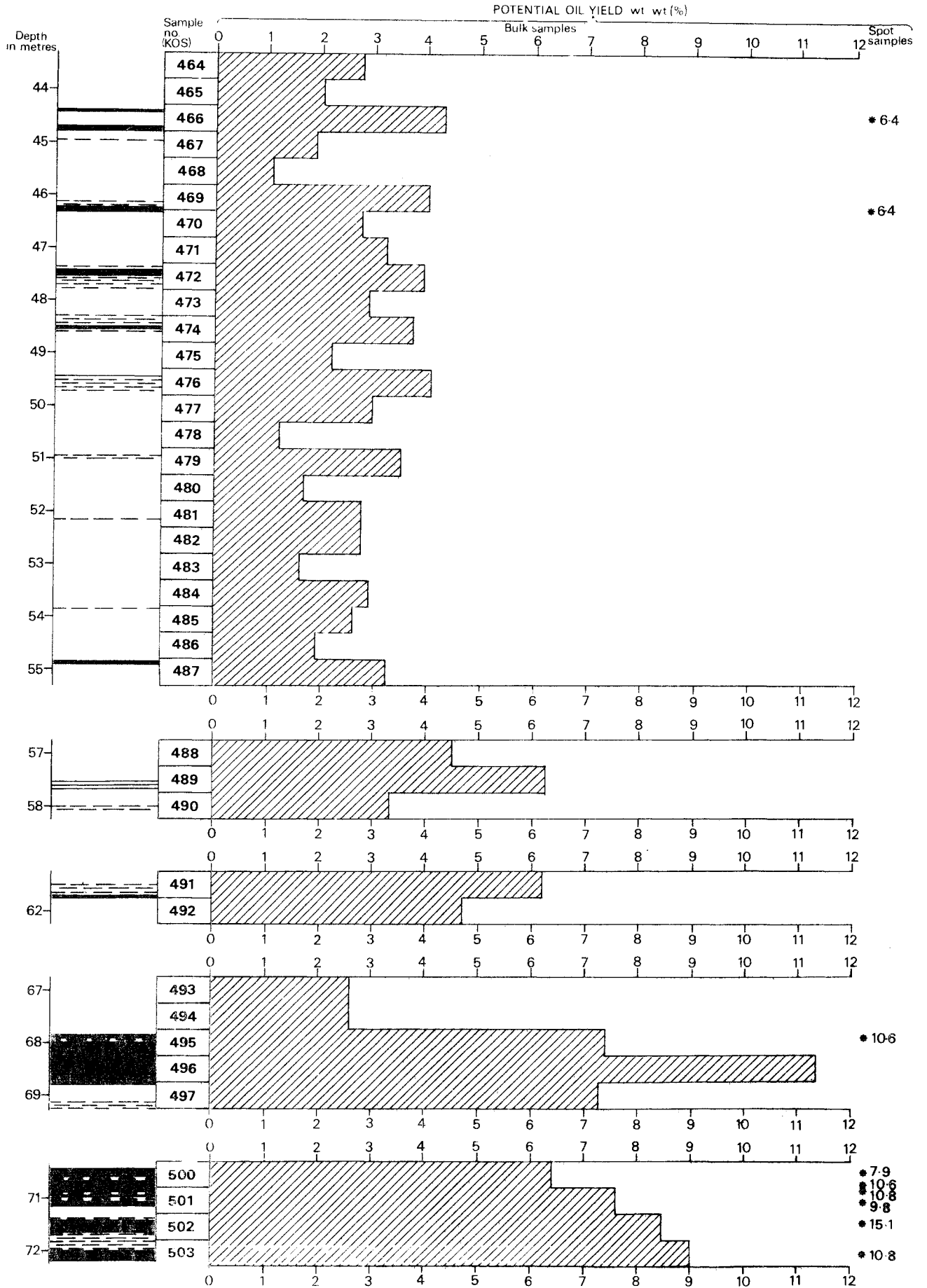


Figure 36 Kimmeridge Bay Borehole, potential oil yields (key as Fig. 35)

PORTESHAM BOREHOLE

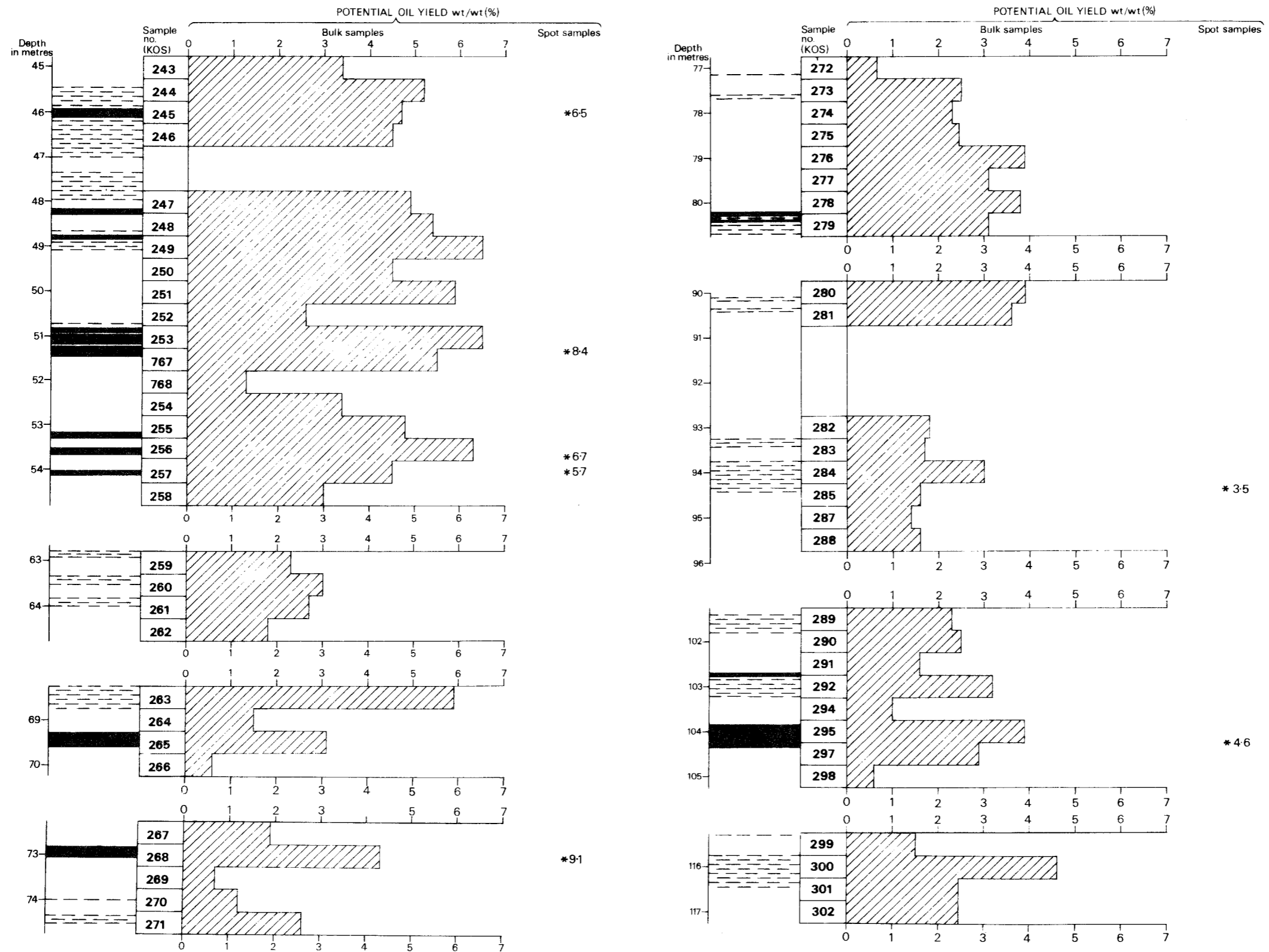


Figure 37 Portesham Borehole. potential oil yields (key as Fig. 35)

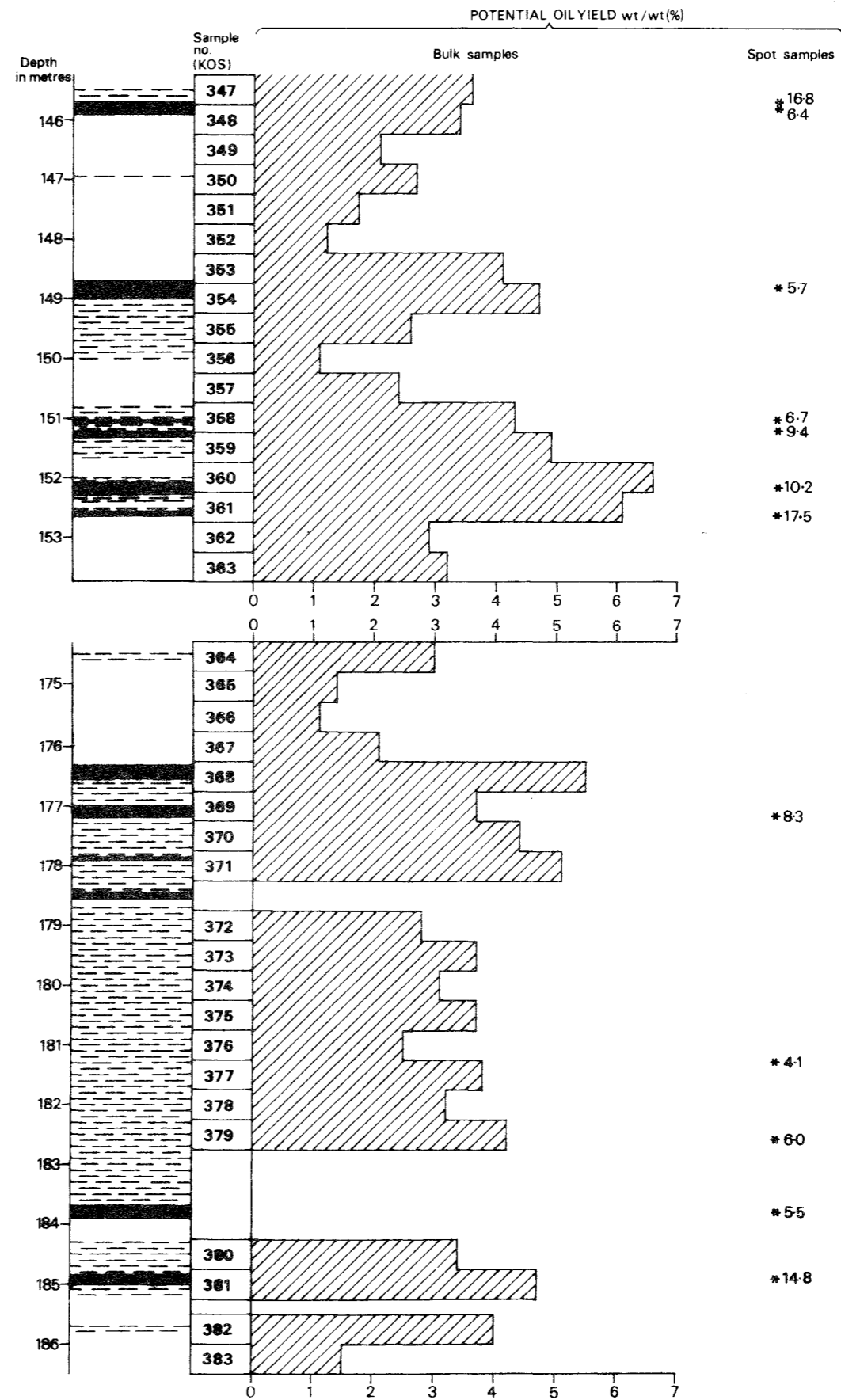
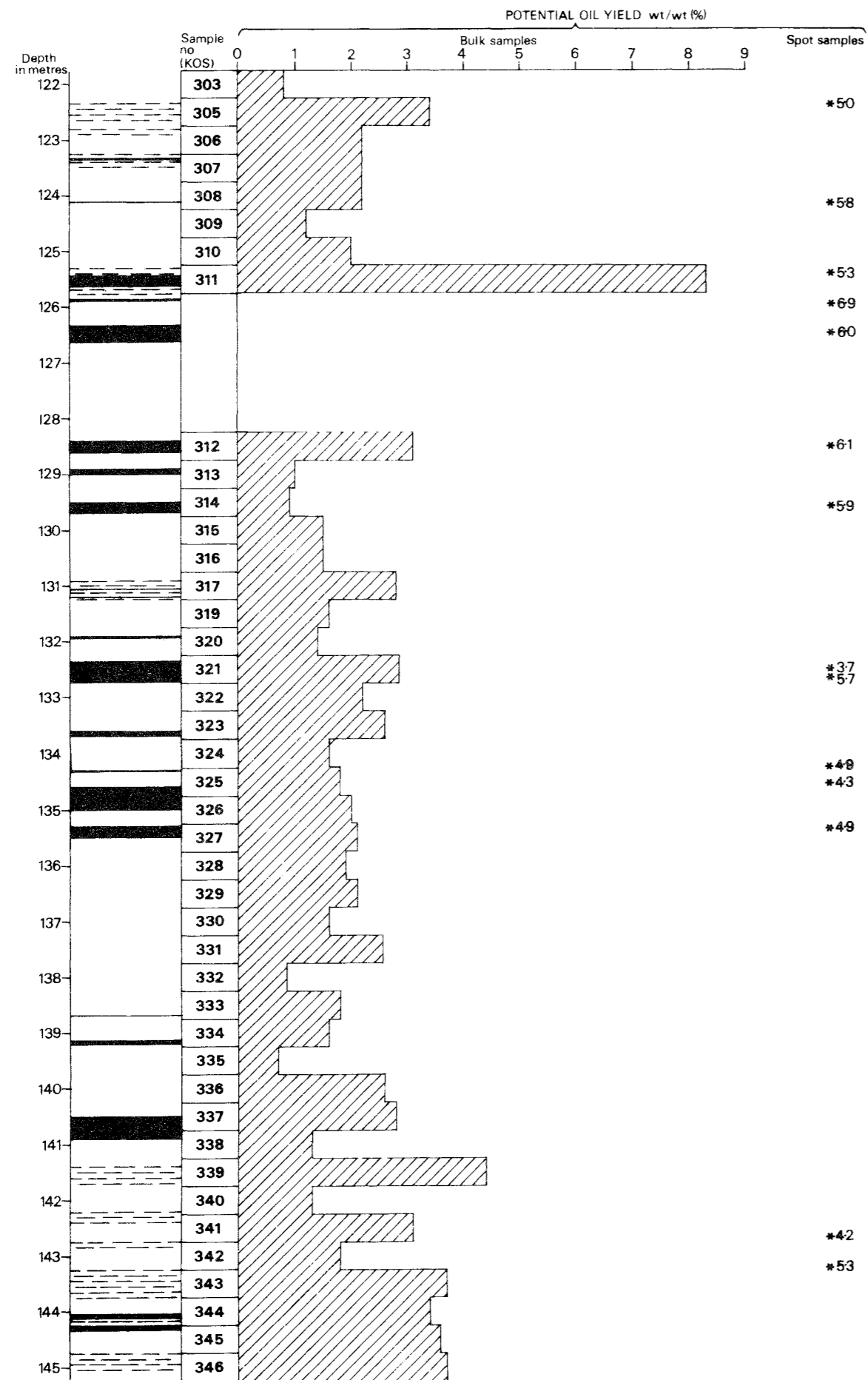


Figure 37 continued

TISBURY BOREHOLE

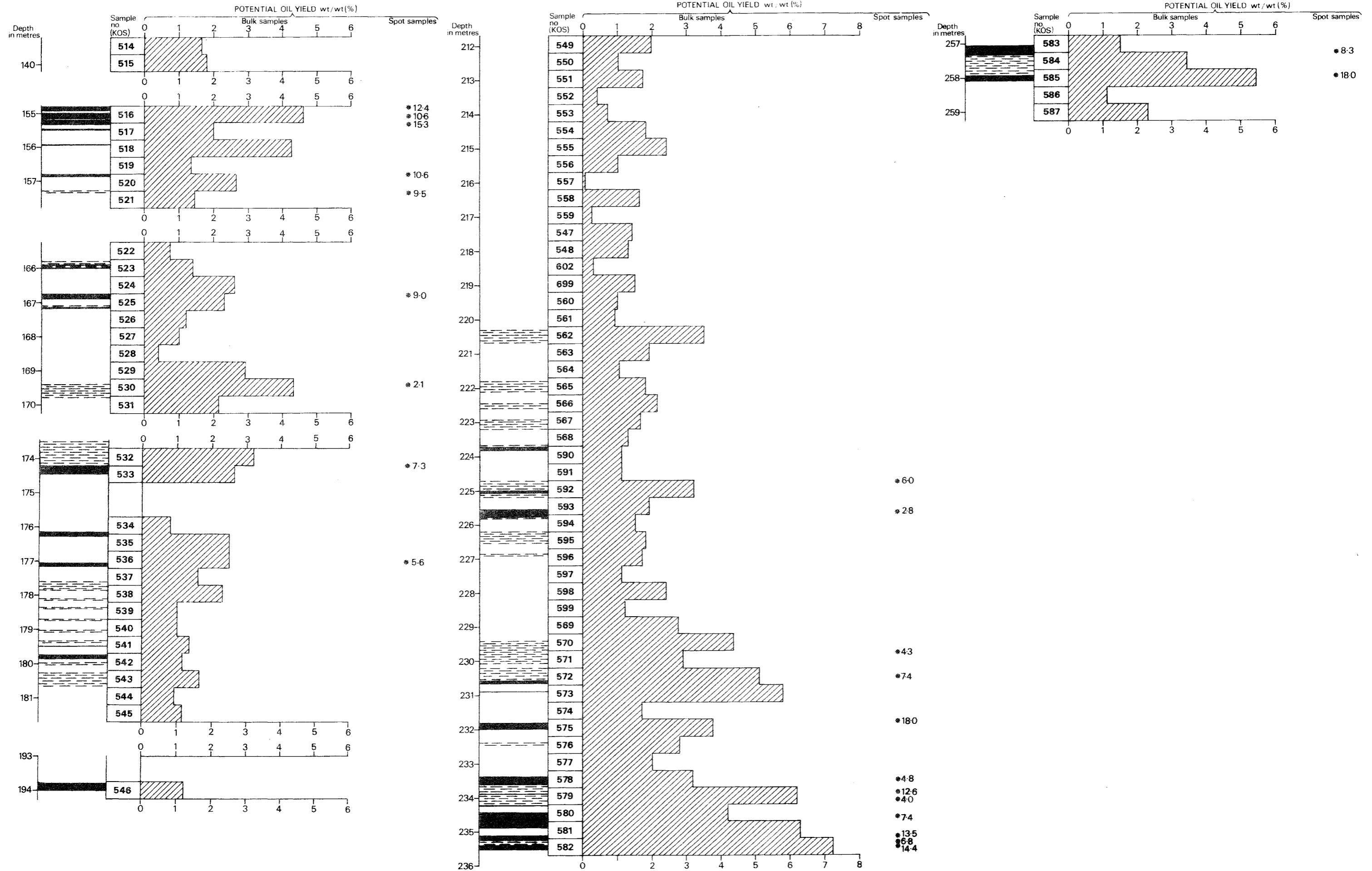


Figure 38 Tisbury Borehole, potential oil yields (key as Fig. 35)

WEST LAVINGTON BOREHOLE

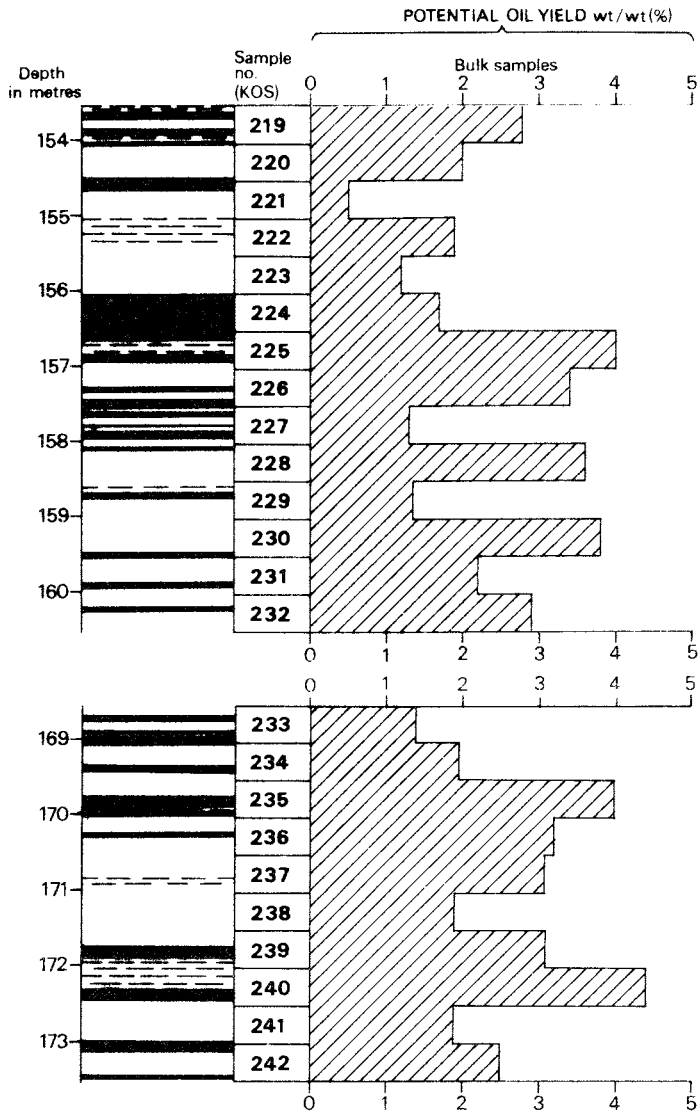


Figure 39 West Lavington Borehole, potential oil yields (key as Fig. 35)

FOUDRY BRIDGE BOREHOLE

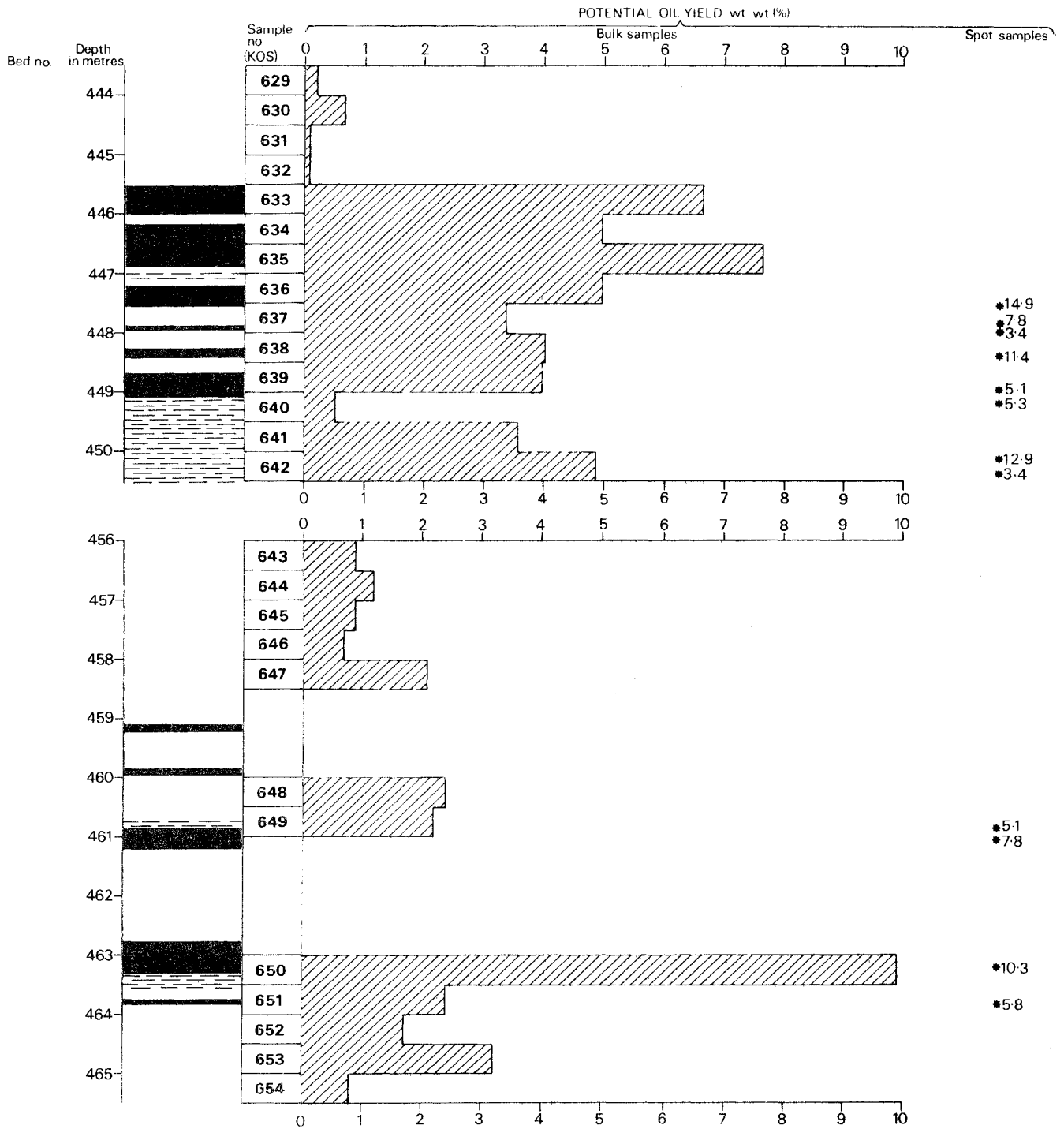


Figure 40 Foudry Bridge Borehole, potential oil yields (key as Fig. 35)

SWINDON BOREHOLE

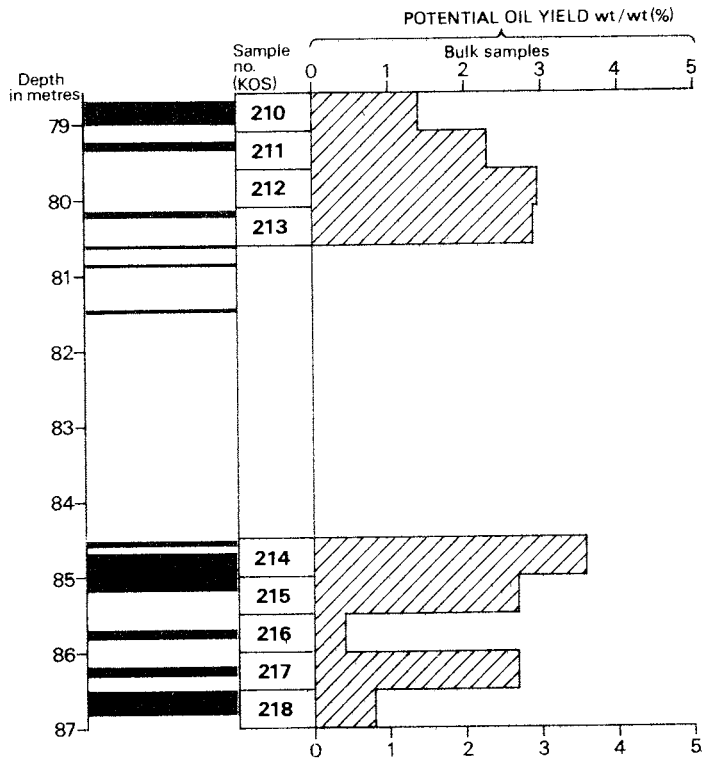


Figure 41 Swindon Borehole, potential oil yields (key as Fig. 35)

HARTWELL BOREHOLE

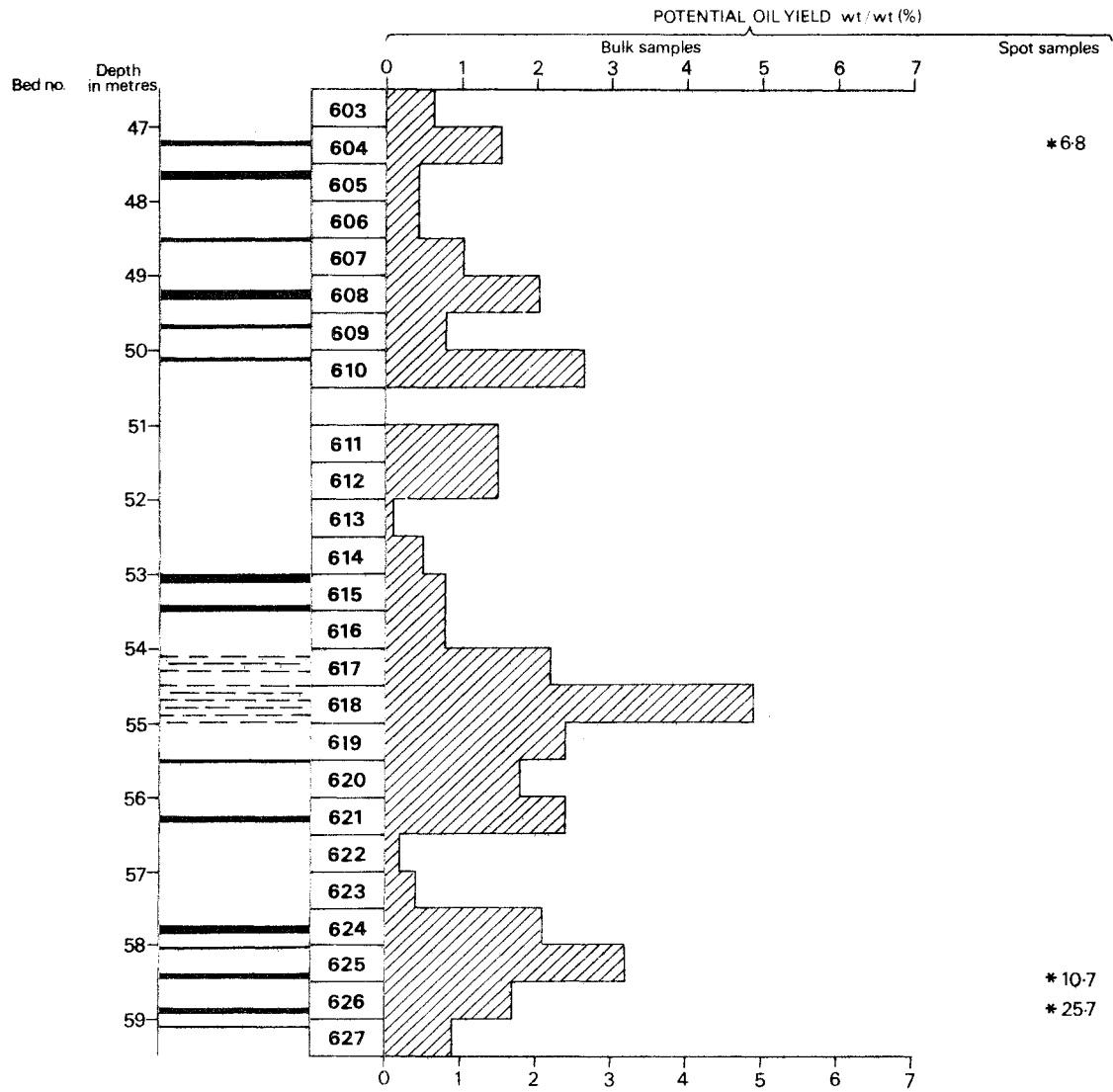


Figure 42 Hartwell Borehole, potential oil yields (key as Fig. 35)

NORTH RUNCTON BOREHOLE

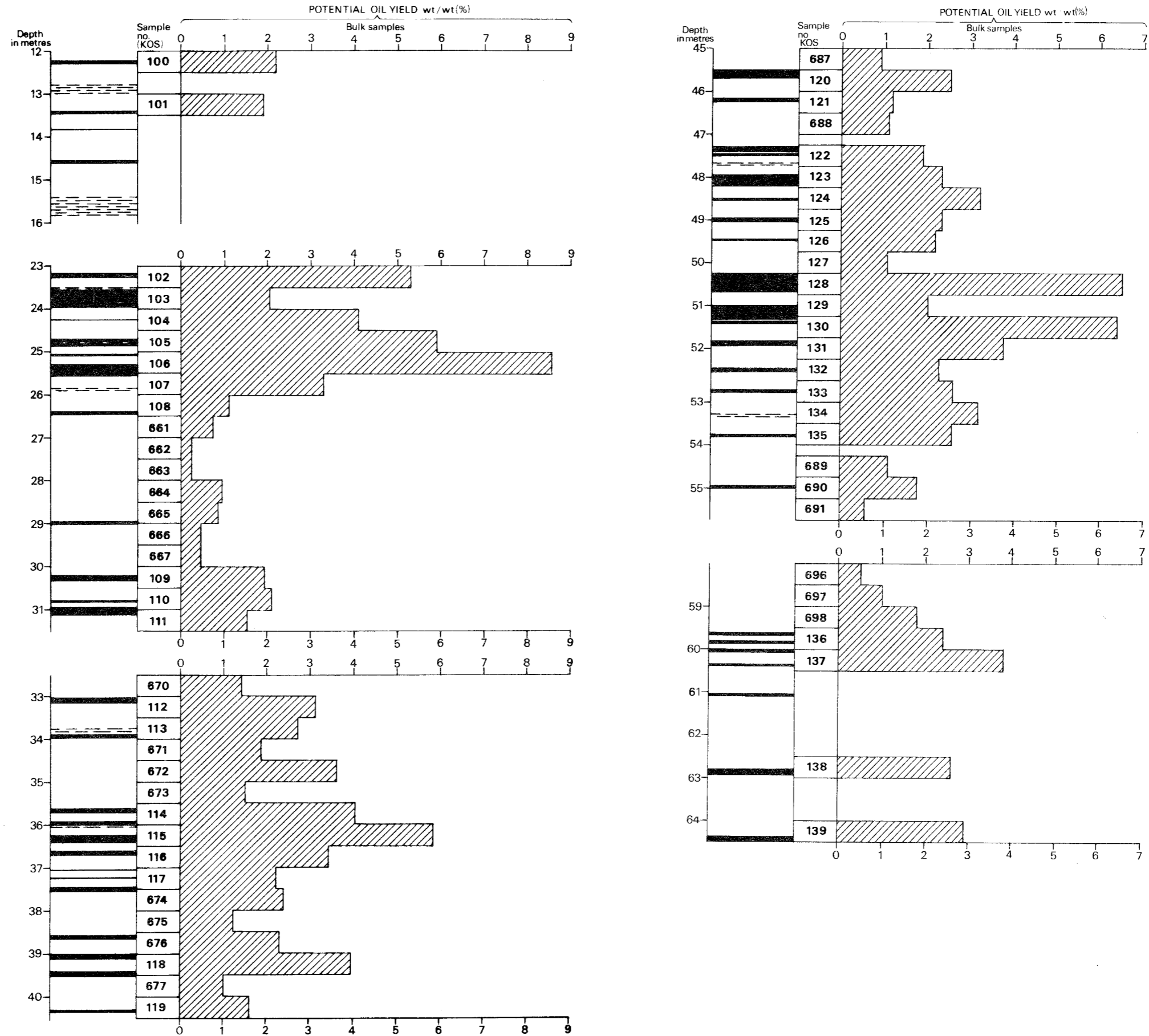


Figure 43 North Runcton Borehole, potential oil yields (key as Fig. 35)

DONINGTON ON BAIN BOREHOLE

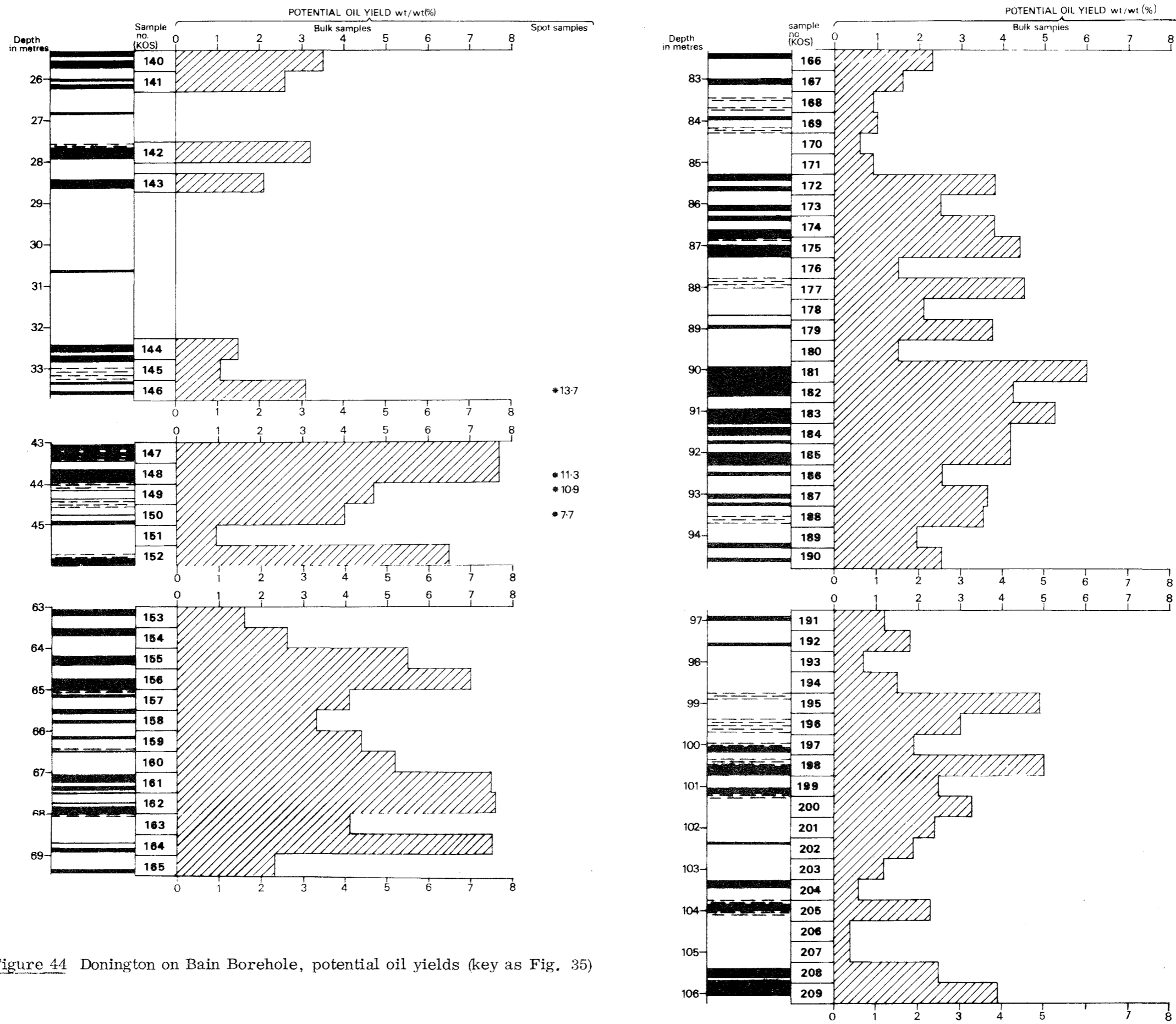


Figure 44 Donington on Bain Borehole, potential oil yields (key as Fig. 35)

REIGHTON BOREHOLE

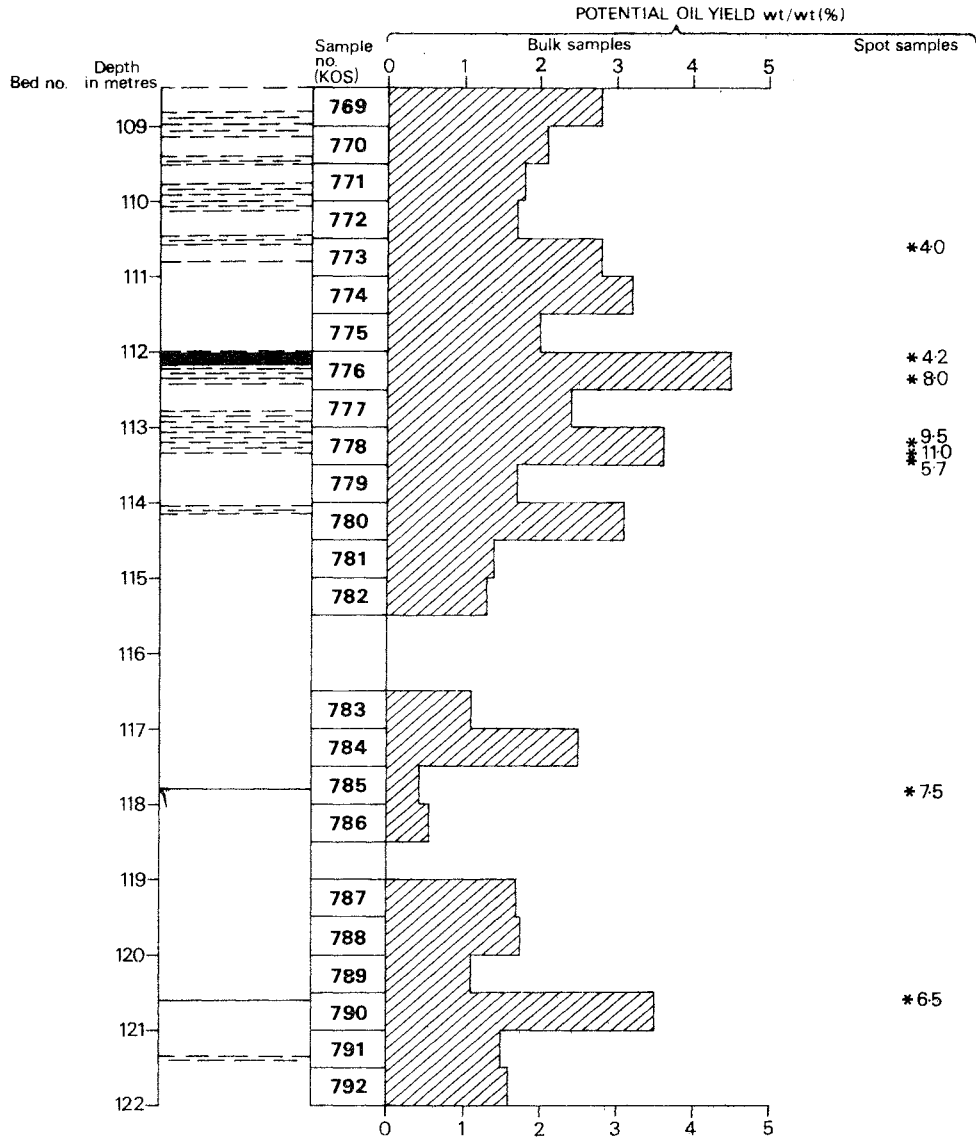


Figure 45 Reighton Borehole, potential oil yields (key as Fig. 35)

Table 8 ANALYSES OF SELECTED OIL SHALES BY MODIFIED FISCHER ASSAY

* correlated equivalent

1 US gal/US ton

Sample location	Stratigraphical horizon	SAMPLE NO. (KOS)	WEIGHT % YIELD OF				SPECIFIC GRAVITY 15° C	OIL YIELD ¹	COKING TENDANCY
			OIL	WATER	GAS AND LOSS	SPENT SHALE			
Foudry Bridge 447.42m	Blackstone*	950	21.4	9.0	3.4	66.2	1.019	50.3	none
Portesham 51.35m	Blackstone*	951	26.6	5.0	11.4	57.0	1.013	62.9	strong
Tisbury 155.20m	Blackstone*	952	20.9	3.0	9.3	66.8	1.009	49.7	poor
Tisbury 225.72m	Upper <u>eudoxus</u>	953	3.8	1.25	2.6	92.4	0.973	9.3	none
Kimmeridge Bay, cliff	<u>elegans</u>	954	6.4	2.8	4.3	86.5	0.974	15.6	none
Kimmeridge Bay, cliff	Upper <u>eudoxus</u>	955	7.6	3.3	5.0	84.1	0.960	18.9	none
Clavells Hard	Blackstone	956	35.1	2.9	14.2	47.8	1.014	83.0	strong
Clavells Hard	<u>wheatleyensis</u>	957	12.1	3.0	4.8	80.2	0.979	29.5	none
Warlingham 762.23 m	Blackstone*	958	20.7	6.0	9.3	64.0	1.013	48.9	none
Warlingham 833.33m	Upper <u>eudoxus</u>	959	6.3	2.0	3.7	88.0	0.988	15.3	none
Clavells Hard	Blackstone, middle	960	21.2	2.0	6.3	70.5	1.000	50.8	moderate
Clavells Hard	Blackstone, top	961	31.4	0.3	8.6	59.7	0.998	75.4	none
Encombe 114.54m	Blackstone*	962	21.4	1.5	7.7	69.4	0.990	51.8	none
Encombe 65.99m	<u>pectinatus</u>	963	24.3	3.5	5.2	67.0	1.003	58.1	none
Encombe 79.00m	<u>pectinatus</u>	964	8.4	1.25	2.5	87.9	0.989	20.4	none
Foudry Bridge 463.14m	Upper <u>eudoxus</u>	965	13.8	2.5	6.5	77.3	0.975	33.8	none
Portesham 181.33m	Lower <u>eudoxus</u>	966	4.3	2.0	2.3	91.4	0.963	10.7	none
Hartwell 57.78m	Lower <u>eudoxus</u>	967	7.8	2.8	3.9	85.6	0.986	18.8	none
Tisbury 174.37m	<u>elegans</u>	968	6.3	2.0	3.1	88.6	0.980	15.3	none
Tisbury 257.20m	Lower <u>eudoxus</u>	969	7.7	1.7	3.5	87.1	0.970	19.1	none
Reighton 112.04m	Upper <u>eudoxus</u>	970	3.7	0.82	4.3	91.2	0.977	9.0	none
Donington on Bain 71.60m	<u>elegans</u>	971	7.5	2.0	3.9	86.6	0.982	18.3	none
Donington on Bain 46.30m	Blackstone*	972	14.2	1.9	5.8	78.1	1.0095	33.6	none
Marton 38.68m	Blackstone*	973	11.1	1.0	4.2	83.7	0.986	26.9	none
North Runcton 23.73m	Blackstone*	974	14.7	2.6	6.9	75.8	0.983	35.8	none
Reighton 89.00m	<u>elegans</u>	975	7.6	1.5	3.1	87.8	0.980	18.5	none

The stratigraphical horizon of the Blackstone can be identified with confidence throughout the English outcrop and subcrop of the Kimmeridge Clay because of its association with a flood occurrence of the distinctive crinoid Saccocoma. It seems likely that this seam is laterally persistent throughout the area except between north Wiltshire and Buckinghamshire where it is replaced by sands. The potential oil yield of the Blackstone and its lateral equivalent is greater than 48 US gal/US ton everywhere in southern England, but the yield reduces northwards until only about 27 US gal/US ton at Marton in North Yorkshire.

With the exception of seams in the Upper eudoxus Band at Foudry Bridge and in the pectinatus Band at Encombe, that yielded 33.8 and 58.1 US gal/US ton respectively, the yields determined by the modified Fischer Assay from other oil-shale-rich bands were all less than 20 US gal/US ton. IFP/Rock Eval assays of a large number of spot samples showed a much greater spread of results, as would be expected from the small size of the samples analysed, but confirmed the general result that the wheatleyensis Band, and some thin seams in the pectinatus Band, were consistently the richest and that the Upper eudoxus Band were the poorest. The seams in the Lower eudoxus and elegans bands fall between these two extremes.

3.3 WINNING AND RETORTING THE OIL SHALE

Several thousand oil-shale winning and retorting techniques have been patented since that granted to the British entrepreneurs of 1694. Few of these have been used in practice. The thinner (1 to 3 m thick) oil shale seams that have been worked in the past (e.g. the Lothians oil shales of Scotland) have been won by conventional pillar and stall mining techniques or by opencast mining. Seams of a similar thickness continue to be worked by these methods in the USSR. The thicker (> 3 m thick) oil shales have been worked by opencast mining. Some of the worked oil shales have been burned as fuel, but most have been retorted to yield oil.

During the past 50 years the level of research activity into retorting techniques has fluctuated in response to variations in the cost of other energy sources. The stimulus provided by the 1974 energy crisis resulted in a marked increase in activity in large scale retorting experiments in the U. S. A. A number of consortia there have built pilot plants at sites on the Eocene Green River Oil Shales, in the Rocky Mountains, some of which have successfully retorted 1000 tons of shale per day for long periods. Most of the pilot operations have used pillar and stall mining in a very thick, horizontally bedded shale sequence in which the shale has been blasted and transported direct to a nearby retorting plant in dump trucks.

A number of retort designs have been used, but most are variations on one of two basic types. In the 'direct heating' methods, a retort is filled with broken shale and fired at one end. A steady temperature is then maintained in the retort by carefully balancing the supplies of air and raw shale, to give a combustion zone (at about 900°C), a retorting zone

(450° to 500°C) and a cooling zone. In the 'indirect heating' methods heated ceramic spheres (or some other heat transfer device) are mixed with the oil shales in a rotating drum to achieve retorting. The spent mixture is then sieved so that the spheres can be re-heated and re-circulated, some of the shale oil product being used for heating.

These retorting methods have given rise to a number of environmental problems - disposal of spent shale and aqueous distillate, both of which contain biologically active contaminants; the need for cooling water (a commodity in short supply in the semi-arid climate of the Rockies); air pollution and general disturbance to wildlife, recreational activities and scenic amenities caused by the mining and retorting processes.

These factors have provided a powerful incentive for the development of in situ retorting techniques. The principle behind such techniques is to produce a fractured layer or column of oil shale within the ground so that, by maintaining a steady input of air through either boreholes or adits, controlled burning and a steady output of hydrocarbon products can be achieved in a manner analogous to the 'direct heating' retorts.

The advantages of in situ retorting are that it eliminates air pollution and the spoil problem, uses little or no cooling water, produces little alteration to the surface or subsurface waters and has a smaller impact on the environment in general. The main disadvantage is gross inefficiency due to irregular and incomplete burning of the oil shale. The major practical problem seems to be that of creating a sufficiently uniformly fractured layer or column of oil shale to prevent the fire-front from moving forward along preferred pathways and leaving large areas of unburnt shale. Only conventional explosives and hydraulic fracturing have so far been used to break up the shale: the use of electric arcs, lasers and nuclear explosions has also been suggested. Other in situ methods of extraction that have been attempted, but only on a laboratory scale, have included attack with a combination of hot acids and organic solvents and bacteriological degradation.

Only one oil shale retorting method seems to be commercially viable and environmentally acceptable at the present time in the U. S. A. and that is an in situ stoping method developed by Occidental Oil Inc. Work on the first commercial plant at Logan Wash, Colorado is at an advanced stage (Oil and Gas Journal 29. 5. 78). It is anticipated that a production rate of 57,000 bbl/day of shale oil will be achieved in the early 1980s from a series of caverns partially filled with broken shale within a 30 m-thick seam in the Green River Formation and having an average potential oil yield of 27 US gal/US ton. Total oil recovery is estimated to be 1.2×10^9 bbls.

The Kimmeridge Clay oil shales have been worked on a small scale at Kimmeridge Bay and Portesham, Dorset and at Setchey, Norfolk. The Dorset workings, all 19th century, used shafts and adits and were probably designed on a pillar and stall pattern. No mine plan has survived but the amount of shale won was very small and the workings may not have been

much more than a collection of short adits. The only adit currently open is at Clavells Hard (SY 920 777) and consists of about 20 m of unsupported tunnel, with a short spur, of roughly 1.5 m width by 2+ m height. It appears to have worked a group of seams including and above the Blackstone. The Norfolk mine workings have been back-filled but appear to have consisted of two shafts about 15 m deep with a short interconnecting adit and possible short working adits. Most of the small amount of oil shale won probably came from a small opencast pit nearby (Plate 3A). Both the Dorset and Norfolk workings were in groups of thin oil shale seams that, together with the intervening waste, totalled less than 2 m in thickness.

The results of the stratigraphical and analytical work for the present project have shown that the best oil shale prospects in the Kimmeridge Clay are groups of thin seams that would need to be worked en bloc in order to obtain sufficient yields to establish a retorting and oil-upgrading plant. The engineering properties of the Kimmeridge Clay have only been described from Norfolk (Gallois, 1979) where it is a stiff fissured clay with shear strengths mostly in the range 100 to 400 kNm² and moisture contents ranging from 10 to 25%. This material would require extensive supports if mined, but could be readily opencast by means of the mechanised techniques currently in use in winning the Lower Oxford Clay for brickmaking.

Assuming a bulk yield of 10 USgal/US ton to be the minimum of economic interest, the most promising group of seams in England is contained in 11.5 m of strata at the level of the wheatleyensis Band at Kimmeridge, Dorset. Elsewhere the richest seams are grouped in beds 2 to 4 m thick. With the possible exception of those at Kimmeridge, none of these groups of seams could be worked by in situ methods. There is no published data concerning the engineering properties of the Kimmeridge Clay outside Norfolk, but a general consideration of the degree of induration of the mudstones suggests that in those areas where the former depth of burial has been greatest, the Hampshire Basin and the Weald, pillar and stall working with limited additional support might be possible. Gypsum seams over 4 m-thick in the largely argillaceous Lower Purbeck Beds of the Weald are worked unsupported by this method at Brightling and Mountfield, Sussex, but here, the top part of the gypsum seam forms a good roof and limestones form a good floor. Part of the wheatleyensis Band at Kimmeridge could be worked by using a persistent thin limestone, the Rope Lake Head Stone Band, as a roof. Elsewhere, most of the thin limestones in the Kimmeridge Clay occur as discontinuous septaria.

Extensive engineering testing would be necessary to determine the feasibility and best method of working in the Kimmeridge Clay before any mining could be contemplated. In addition to its strength characteristics the engineering behaviour of the Kimmeridge Clay en bloc will be much affected by local fracture patterns and, at outcrop, may have been

mechanically affected by periglacial weathering down to depths of 100 m. In the less indurated parts of the Kimmeridge Clay, close to the edges of the London Platform between north Wiltshire and Norfolk, it is likely that the Kimmeridge Clay oil shales could only be worked by opencast methods. Because of the low dips (mostly 2°) in these areas this would still enable relatively large areas of the oil shale subcrop to be worked.

Many of the above ground retorting methods that have already been operated on a commercial or a pilot scale would be suitable for use with oil shales from the Kimmeridge Clay providing the shale seams were separated from the intervening barren mudstones before they were pyrolysed. One method of concentrating the oil shale seams would be to immerse dried mixtures of oil shale and mudstone in water to take advantage of the greater resistance of the oil shales to slaking (Gallois, 1978). Other mechanical methods might include flotation to make use of the relatively low densities of the oil shales.

Retorting or burning methods that are currently at the research stage include electronic separation and fluidised bed combustion. The latter might be particularly applicable to oil shales since it is stated that a high ash content is advantageous in maintaining a stable fluid bed and that SO_2 produced during combustion can be harmlessly combined with a limestone bed (Piper, 1976).

3.4 CONCLUSIONS

The potential oil yields of the Kimmeridge Clay oil shales range from 10 to 85 US gal/US ton but are mostly in the range 20 to 55 US gal/US ton. Local variations occur within individual seams but the overall yield of any particular seam is likely to be relatively constant over large areas. Concentrations of seams more than 2 m thick and with potential yields of more than 10 gal/ton overall occur in Dorset, Wiltshire and Norfolk. The best prospect, at Kimmeridge, Dorset consists of 8 m of strata with an average yield of 13.7 US gal/US ton. The same section includes an 11.5 m run of strata with an average yield of 12.1 US gal/US ton. These Dorset seams could theoretically yield up to 1.78×10^6 US tons of oil per square kilometre of ground worked. Elsewhere, the maximum yields are in the range 0.2 to 0.6×10^6 US tons of oil per sq km.

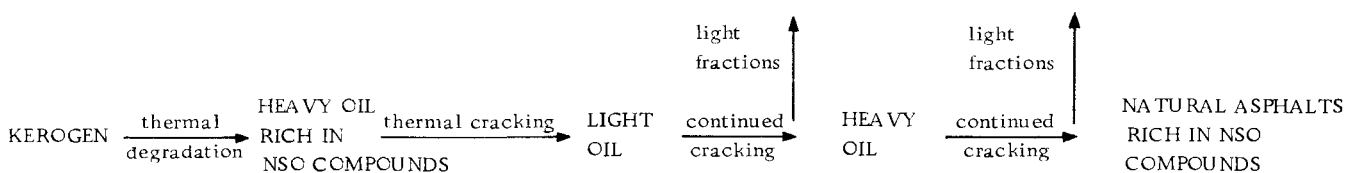
The richest individual seams occur in the wheatleyensis and pectinatus bands: by contrast, the seams in the Lower and Upper eudoxus bands are generally too shelly to have high yields. The yields of seams in the north of England are markedly lower than those from similar stratigraphical levels in the south.

The engineering properties of the Kimmeridge Clay suggest that the oil shales could probably only be worked by opencast in most of its outcrop area. The thickest group of oil shales in Dorset might, at some future date, be capable of being retorted in situ.

become denser and more viscous as their lighter fractions become mobile and are lost by migration. As a result of this process there is a gradational transition from light, low-sulphur crudes composed largely of saturated and aromatic hydrocarbons into heavy, degraded crudes and finally into natural (usually sulphur-rich) asphalts containing a high percentage of resins and asphaltenes (mostly high molecular weight N, S and O compounds) (Fig. 46).

Shale oils are chemically similar to natural asphalts but are genetically related to them only in the sense that they represent similar end members in a diagenetic progression. Whereas shale oils are rich in high molecular weight compounds because they have been formed by the very rapid (and, therefore, incomplete) breakdown of kerogens, natural asphalts are rich in similar compounds because they represent the high boiling point residue of mixtures that have undergone fractionation over a long period of time (Fig. 47).

Figure 47



Shale oils are an artefact and their properties and compositions vary with the temperature and length of time of pyrolysis. Retorting temperatures below that of the maximum rate of pyrolysis have little effect on the composition of the shale oil and, if maintained, merely extend the length of time required to obtain the full yield of shale oil. Temperatures substantially above that of the maximum rate of pyrolysis initially produce the same product but that product is then thermally cracked to a greater or lesser extent depending upon the temperature and the length of time for which it is maintained.

Experimental pyrolysis of a Kimmeridge Clay oil shale at differing temperatures from ambient to 500° C produced variations in yield but not in chemical composition. For comparative purposes it is important that shale oils should be obtained by a method of pyrolysis that can be related to the conditions likely to be used in an industrial process. The modified Fischer Assay provides a useful, widely accepted standard for this purpose and all the properties referred to in the present report have been determined on samples obtained by this method.

4.2.1 Physical Properties

Kimmeridge Clay shale oils are dense but fluid oils with a penetrating, pungent aromatic smell. Samples of shale oil from the richest (most economically interesting)

horizons have been examined and some of the physico-chemical parameters relevant to the handling characteristics of the oil have been determined. The chemical characteristics of a much larger number of samples have been determined; these showed that there was little variation in the Kimmeridge Clay shale oils other than minor differences between the properties and compositions of the oils derived from the Lower Kimmeridge Clay (L. and U. eudoxus bands) and those from the Upper Kimmeridge Clay (wheatleyensis Band: Blackstone level).

The specific gravity of the shale oils at 15° C has been determined for all the bulk and spot samples determined by the modified Fischer Assay method (Table 8 and Appendix E). Where large volumes of oil are available, as in commercial operations involving natural crudes, the density of oils is generally recorded in terms of an arbitrary (American Petroleum Institute) hydrometer scale and expressed as 'degrees API', the API number increasing as the density decreases.

The shale oils from the Kimmeridge Clay all have high densities in comparison with natural crude oils and other shale oils and range from 0.951 to 1.019 (approximately 12° to 18° API). Most shale oils have densities of between 0.88 and 0.94 and few have been recorded with densities greater than 0.98.

The densities of the Kimmeridge Clay shale oils fall into two broad groups. Oils from the Blackstone level have densities ranging from 0.983 to 1.019 and, with the exception of two samples, have densities greater than 1.000. Oils from the eudoxus Zone have lower densities (0.960 to 0.988) and those from the intervening elegans Zone have, as might be expected, densities intermediate between those of the shale oils derived from the Blackstone and the eudoxus Zone. These variations in density can be correlated with the broad chemical characteristics of the shale oils (see Section 4.2.2 for details).

Pour point is an important parameter that affects the handling characteristics of the shale oils. The pour point gives an indication of the lowest temperature at which an oil will flow or can be pumped and is defined as a temperature 3° C (5° F) above the setting point of the oil. The determination of the setting point is normally carried out to an API standard using a 40 ml oil sample. Shale oil samples as large as this were not readily available for the present work and simulated pour points were determined using 10 ml samples. Values ranging from -10 to -20°C were obtained from the five samples tested. The coking characteristics of the oil shales are summarized in Table 8 and show, with the exception of two samples, consistently low coking tendencies. The tendency of the shale oils to produce carbonaceous deposits on combustion was also low and insufficient carbon was produced for satisfactory Ramsbottom tests to be carried out. The calorific values of the shale oils ranged from 8830 to 9850 kcal/kg, values close to that generally quoted for pure kerogens (see Section 4.5 for discussion).

4.2.2 Chemical Properties

The shale oils derived from the Kimmeridge Clay, like most other shale oils and many natural asphalts, are rich in high molecular weight compounds that give rise to a high asphaltene/resene fraction. They are generally low in aliphatic and aromatic hydrocarbons (Fig. 46).

The overall composition of selected shale oils was determined by column chromatography of the residual oils after the asphaltenes had been precipitated from them. Both the aliphatic and aromatic fractions were rich in sulphur and this had to be removed by further chromatographic methods before the hydrocarbon fractions could be determined (Appendix A). The total weight of the organic-sulphur compounds in the aliphatic/aromatic fraction was determined during this second stage of separation (Table 9). Additional, probably small, amounts of sulphur compounds occur in the polar NSO fraction and large amounts are likely to be present in the residue left on the chromatographic column. This latter material consists of a complex mixture of high molecular weight compounds (pyrobitumen of some authors) derived from the partial cracking of the original kerogen.

The total elemental sulphur in the shale oils was determined by wet oxidation and back titration. Sulphur contents of 3.0 to 5.6 wt% were recorded: in the pilot study the values were in the range 4.3 to 8.5 wt%. All published analyses of shale oils derived from the Kimmeridge Clay have drawn attention to their high sulphur content, and in most cases have attributed the failure of commercial ventures to this cause (see Section 2 for details). Values of 3.9 to 7.2 wt% sulphur were recorded in the Ministry of Munitions survey of the Dorset oil shales (Strahan, 1920, pp. 25-26) and Macdougall and Cawley (1951) obtained 6.5% sulphur in shale oil produced from the Blackstone. Forbes Leslie's account of "practically sulphur free" shale oils from the Kimmeridge Clay of Norfolk (reported in The Times, 8/7/1919) has not been confirmed.

The present work has shown that the sulphur present as abundant discrete crystals of pyrite in the Kimmeridge Clay oil shales is not the major source of the sulphur in the shale oils. The chromatographic separations and elemental analyses carried out on concentrations of kerogen, made by leaching out the inorganic material from the oil shales, both indicate that a large proportion of the sulphur occurs within the kerogen (and is transmitted to the shale oils on pyrolysis) as organic sulphur compounds.

The aliphatic fraction of the shale oils examined in detail ranged from 1.1 to 13.2 wt%. As one might expect this fraction shows a number of features that reflect its pyrolytic origin and which distinguish it from the aliphatic fraction of most naturally occurring crude oils. In the shale oils a high proportion of the fraction, in many cases more than 50%, is made up of unsaturates (Table 10). In the n-alkane homologous series there are unimodal distributions with maxima generally occurring between n-C₁₅ and n-C₁₈ (Fig. 48). The

Table 9 General composition of selected shale oils

n. m. . . . not measured

* residue, yield obtained by subtraction from 100%

Sample no. (KOS)	Weight % of shale oil				Weight % of shale oil	
	Aliphatics	Aromatics	Asphaltenes	Resenes*	Polar NSO fraction	Total organic sulphur compounds
950	3.5	10.8	1.34	84.36	31.2	32.5
951	3.1	10.5	2.39	84.01	30.4	28.1
952	3.5	10.9	1.50	84.10	32.5	33.5
953	7.5	11.3	1.40	79.80	29.3	24.7
954	9.9	25.6	1.10	63.40	31.7	16.2
955	13.2	18.8	1.28	66.72	26.2	24.2
956	4.7	7.0	7.29	81.01	36.0	37.1
957	7.8	n. m.	1.26	n. m.	30.8	n. m.
958	7.6	5.8	2.23	84.37	27.5	34.2
959	1.1	10.9	1.67	86.33	31.3	31.8
960	5.0	11.1	4.30	79.60	34.8	30.6
961	1.5	n. m.	1.38	n. m.	36.6	n. m.
962	7.6	16.2	2.00	74.20	32.9	22.3
963	4.8	12.5	1.23	81.47	28.4	31.9
964	5.0	17.2	1.28	76.52	27.8	23.8
965	5.3	12.5	1.77	80.43	27.6	30.2
966	6.0	22.5	0.60	70.90	26.4	21.1
967	5.2	n. m.	1.72	n. m.	27.8	n. m.
968	5.6	15.0	1.24	78.16	32.7	24.1
969	6.4	11.2	1.27	81.13	26.9	32.5
970	5.9	24.9	2.24	66.96	26.4	15.4
971	5.9	15.7	1.98	76.42	30.0	31.7
972	2.6	28.3	0.78	68.32	31.8	16.5
973	7.3	5.4	1.87	85.43	25.6	38.6
974	4.0	7.4	0.91	87.69	27.1	37.6
975	9.1	20.1	1.10	69.70	23.7	19.2

higher number maxima, n-C₁₇ and n-C₁₈, can be correlated with the high specific gravity shale oils derived from the wheatleyensis Band whilst the lower specific gravity eudoxus Band oils have maxima at n-C₁₅. Carbon Preference Indices (CPIs) in the range n-C₂₀ to n-C₃₀ are mostly close to unity (Table 10) and in some cases have an even-carbon number preference, a feature recorded from a number of pyrolysed materials (see p. 122 for discussion of CPIs). The isoprenoids pristane and phytane are abundant in the aliphatic fraction. Their ratio ranges from 0.53 to 1.44, but is mostly close to unity, and further reflects the artificial nature of the shale oil (see p. A.10 for discussion of pristane/phytane ratio).

The aromatic fraction of the shale oils ranges from 5.4 to 28.3 wt% of the shale oil: that of the combined asphaltene/resene fraction ranges from 64.5 to 88.6 wt%. The aromatic and asphaltene/resene fractions of the shale oils are complex mixtures containing very large numbers of mostly medium and high molecular weight compounds that do not form simple homologous series and cannot readily be classified. Individual compound classes, many of them organic-sulphur compounds, can be identified by combined gas chromatography-mass spectrometry (GC-MS) techniques. Such analyses are expensive and have little bearing on the potential use of the shale oils since the first steps in any attempt at commercial working would probably need to be thermal cracking to break down the higher molecular weight compounds followed by hydrogenation to destroy the sulphur compounds.

However, one group of compounds that does require investigation is the polycondensed aromatic hydrocarbons (PAHs) of the aromatic fraction, some of which are known to be carcinogenic. A discussion of this group of compounds, and a description of the analytical work carried out to detect them, is given below.

4.2.3 Carcinogens

The occurrence of carcinogens in the imperfectly combusted products of carbonaceous materials has been known since 1775 when Pott described occupational skin cancers caused by the action of soot on the knees and elbows of children employed in climbing chimneys to clean them. Tar, pitch and mineral oil were subsequently shown to have a carcinogenic action on the skin and in some cases were believed to have caused internal cancers.

The first case of an industrial cancer in a shale oil worker was recorded by Bell in 1876 in the Lothians (Carboniferous) oil shale field of Scotland. Subsequent cases of skin cancer were reported in workers in the Scottish oil-shale industry (quoted in Henry, 1946), but the evidence was not collected that would have enabled a rigorous statistical analysis of this data to be made. Users of shale oil in the textile industry, particularly those engaged in cotton mule spinning, are also believed to have been at risk. 615 fatal cases of

Table 10 Properties of the aliphatic fraction of selected shale oils

n. m. ... not measured

Sample no. (KOS)	Pristane/Phytane ratio	Normal Alkanes		Weight % of shale oil	
		CPI nC ₂₀ -nC ₃₀	Maximum	Alkanes	Alkenes
950	0.90	1.14	C ₁₈	2.1	2.1
951	1.03	1.17	C ₁₇	2.6	1.2
952	0.91	1.06	C ₁₇	1.9	1.6
953	0.53	1.12	C ₁₅	n. m.	n. m.
954	1.02	0.94	C ₁₅	n. m.	n. m.
955	0.94	0.92	C ₁₅	n. m.	n. m.
956	0.81	1.17	C ₁₇	1.8	6.4
957	0.76	0.99	C ₁₆	n. m.	n. m.
958	1.30	0.90	C ₁₈	2.8	4.8
959	0.57	0.94	C ₁₇	n. m.	n. m.
960	1.04	1.06	C ₁₆	2.8	3.1
961	1.15	1.03	C ₁₇	1.0	1.0
962	1.11	1.04	C ₁₆	2.6	3.1
963	0.78	0.70	C ₁₈	2.1	2.6
964	0.76	1.04	C ₁₇	2.1	2.9
965	1.04	0.94	C ₁₅	2.1	3.2
966	0.93	1.16	C ₁₆	2.7	3.3
967	1.14	0.98	C ₁₅	2.4	2.8
968	0.91	0.96	C ₁₇	3.0	2.5
969	0.87	1.01	C ₁₆	2.4	4.0
970	0.97	0.95	C ₁₆	2.0	3.8
971	0.78	1.00	C ₁₆	2.8	3.2
972	1.17	0.90	C ₁₆	1.5	1.1
973	1.44	0.84	C ₁₆	3.9	3.4
974	1.06	1.10	C ₁₇	2.8	3.9
975	1.19	1.11	C ₁₆	4.0	5.1

scrotal cancer, a proportion of which were believed to have resulted from mineral oils, were recorded in the industry between 1911 and 1938 (Henry, 1946). The Mule Spinning Regulations of 1952 therefore introduced a restriction on the use of lubricating oils to those that had been drastically refined with sulphuric acid to remove the known carcinogens.

The carcinogenicity of shale oil was demonstrated experimentally by Leitch in 1922 and active carcinogens were isolated from shale oil by Berenblum and Schoental in 1943. None of these carcinogens was detected in the parent oil shale and it was concluded that they formed during pyrolysis. Subsequent work on Russian oil shales showed that the composition and concentration of the carcinogens varied with the temperature of pyrolysis.

Individual carcinogens have been identified in naturally occurring crude oil (Catchpole et al., 1971) and in cracked oil (Tye et al., 1955), but an extensive study of the carcinogenic action of mineral oils commissioned by the Medical Research Council (1968) failed to identify any single highly active carcinogen in crude oils from Kuwait, Oklahoma and Lagonillas (Venezuela). In their review of carcinogens in oil Catchpole et al. (op. cit.) concluded that refining reduced or eliminated the carcinogens in oils and this seems to be borne out by the observation that cancers of a presumed occupational origin are very rare in garage workers handling oil, diesel and petroleum spirit (Kipling, 1968).

The possible problems arising from carcinogens in shale oil would seem therefore to be confined to the handling of the material between the retorting stage and the refining stage. The problems arising from possible carcinogens in the spent shale and the aqueous distillate from the retorting process could be more complex. Studies in the U.S.A. (Ward et al., 1971; Schmidt-Collérus et al., 1976) have examined various aspects of environmental pollution that might arise from residual organic compounds (including carcinogens) in oil shale waste. Schmidt-Collérus et al. (op. cit) examined the organic residues of spent shales of various ages at a number of sites in Colorado and proved the presence of biologically active compounds in a solvent-extractable form that would be likely to become concentrated by plants and/or in groundwater. They recommended that an attempt should be made to modify the pyrolysis processes to produce a carbon-free spent shale that would avoid the potential environmental complications.

Chemical carcinogens can be classified as weakly, moderately or strongly active. Weakly active carcinogens are commonly specific to selected animal tissues whereas strongly active materials are almost universally reactive. The most important group of carcinogenic compounds found in shale oil and retorted waste are polycondensed aromatic hydrocarbons (PAHs). These compounds are not directly carcinogenic but are believed to have the ability to react with other organic molecules within the cell to produce short-lived reactive species (metabolites) which in turn interact with DNA to produce carcinogenic

events (Neidle, 1978).

Only a small percentage of PAHs are carcinogenic. Many are synthesized by higher plants, algae and micro-organisms and most of the carcinogenic forms appear to be produced as byproducts of industrial processes. Research in this field is currently concentrated in two areas, on the experimental establishment of the degree of carcinogenicity of specific compounds and on the refinement of analytical techniques designed to separate out and quantify known carcinogens from complex organic mixtures. Any search for the potentially harmful members of this large group of compounds must, for practical purposes, concentrate on the identification of specific compounds that have been shown experimentally to be carcinogenic. The most commonly reported carcinogens in mineral oils include forms and substituted derivatives of the 5 and 6 ring compounds, benzopyrene, dibenzopyrene, benzanthracene, dibenzanthracene, benzo(chrysene) and dibenzo(chrysene) (Kipling, 1976).

Because of the technical difficulties involved in identifying specific carcinogens two independent sets of analyses were carried out. The first, by Robertson Research International Ltd., was made on the aromatic fractions of two composite samples of shale oil produced by pyrolysis at 500°C (KOS 900 to 904 inclusive and 931 to 933 inclusive). The aromatic fractions were separated from the oil by column chromatography and then further separated by gas chromatography, the separated components being fed directly into a mass spectrometer.

Fourteen classes of polycondensed aromatic hydrocarbon were distinguished, ranging from naphthalene to the benzopyrenes, with the sulphur compounds, particularly dibenzothiophenes, being dominant. Benzopyrenes and benzanthracenes were proved to be present, the latter in moderate abundance (Table 11). Further tests would be required to determine whether or not the carcinogenic form benzo(a)anthracene was present; the strongly active benzo(a)pyrene was absent from four additional samples analysed subsequently (see over page). The marked differences in the concentrations of the PAHs in the two samples analysed suggests that a comprehensive study would be necessary before all the potential carcinogens had been identified in, or eliminated from, the shale oils.

The second test was made at the British Carbonisation Research Association by high pressure liquid chromatography (HPLC) on the aromatic fractions of four samples (KOS 952, 953, 956 and 958). The chromatograms of these samples did not compare with those of the potent carcinogens benzo(a)pyrene and fluoranthene, nor did their peaks fall within the regions of the spectra of other known carcinogens.

The present work suggests that carcinogenic PAHs may be present in Kimmeridge Clay shale oil. The concentration of these potentially harmful chemicals, if present, is likely to be very small. Nevertheless, it would be necessary for their distribution to be

4.3 PROPERTIES OF THE BITUMENS

The soluble organic fraction (bitumen) of the Kimmeridge Clay oil shales varies from 0.36 to 3.03 wt % of the whole rock and is generally about one tenth of the total potential oil yield (Fig. 33). Although the bitumens form only a small part of the rock they are important because they are potentially mobile and can give rise to oil accumulations. Their chemistry is therefore of considerable interest for not only does it reveal features that might be used for oil-source rock correlations but it can also enable comment to be made on the origin of the organic material in the sediment and on the depositional environment in which that material has been preserved.

The bitumens were extracted from the oil shales with a mixture of acetone, chloroform and methanol and then separated chromatographically (see Appendix A for details). The aliphatic fractions range from 1.1 to 10.0 wt % of the bitumens. They contain variable alkane/alkene distributions and in some the alkenes are dominant (Table A4). Pristane and phytane are abundant in the bitumens, their ratio varying from 0.48 to 1.6 with no obvious stratigraphical or geographical trend. Normal alkane CPI values (in the range $n\text{-C}_{20}$ to $n\text{-C}_{30}$) and peak maxima show a pattern characteristic of immature sediments with a high odd/even carbon number dominance and a bimodal distribution with maxima at $n\text{-C}_{17}$ and $n\text{-C}_{23}$ (see p. 122 for further discussion). The CPI values range from 1.5 to 3.0 (Table A5) with little stratigraphical variation although Blackstone values are generally higher than those from other levels. As with the shale oils the aromatic, asphaltene and resene fractions are complex mixtures whose detailed study was beyond the scope of the present work. Because of the immaturity of the Kimmeridge Clay oil shales these fractions are almost certainly rich in biological marker compounds and although the identification of such compounds would be difficult they would probably form the basis for a useful research topic.

4.4 USES OF THE SHALE OIL

The shale oil has little practical value in its raw state. Its high sulphur content and low hydrocarbon content would make it unsuitable as a refinery or petrochemical feedstock and direct burning of the oil would produce copious sulphurous gases.

Experiments at the Fuel Research Station immediately before and during the last war showed that it was possible to remove almost all the sulphur from Kimmeridge Clay (Blackstone level) shale oil by catalytic hydrogenation (Cawley and Kingman, 1944) and that the hydrogenation process could be controlled to produce a diesel oil of comparable properties to that obtained from the distillation of cannel coals (Cawley, 1944). Subsequent experiments with improved catalysts led to the conclusion that the Kimmeridge Clay shale oil gave a better diesel oil than that produced by the hydrogenation of low temperature coal tars but that the shale oil was a less suitable raw material than certain coal tars for the production of motor

by-product. Because of the current overproduction of sulphur in North America, largely as a by-product of sour gas refining, this material has little commercial value.

4.5 THE OIL SHALE AS A FUEL

It has been shown that most oil shales require about 250 cal/gm to heat them to 500°C. Pure kerogens have a calorific value of about 10 000 cal/gm and hence a minimum of about 2.5 wt % of kerogen is required in an oil shale before it can become a heat source (Burger, 1973). In practice about 5 wt % kerogen, which would yield approximately 6 US gal/US ton of oil on pyrolysis, is generally considered to be the lower threshold to allow for inefficient burning.

All the Kimmeridge Clay oil shales have kerogen contents well above 5 wt % and could, in theory, be used as fuels. The practical problems involved in burning any oil shale are, however, considerable since large volumes of waste shale, noxious gases and possibly contaminated water are produced by direct burning. These problems have been extensively discussed in the oil shale literature, mostly in relation to possible oil shale working in the U. S. A. , but as the U. S. S. R. is currently the only country in the world that burns oil shales (for power generation) few details of the problems encountered in plants operating on a commercial scale have been published.

The U. S. S. R. currently burns about 18 million tons of oil shale per annum in Estonia to supply electricity to north west U. S. S. R. The seams are generally thin (1 to 2 m) but have high potential oil yields (50 to 70 US gal/US ton) and consequently have high calorific values (c2200 to 3200 cal/kg) (Prien, 1976, p. 257). Granulated oil shale is burned and produces about 10 million tons of ash per annum, mostly as flyash. Some of the ash is used in construction materials, but most of it is waste. The main problems associated with the industry are believed to be fouling and corrosion of the heat exchangers and environmental problems arising from the waste products. These latter include air pollution (H_2S , SO_2 , CO , CO_2), disposal of waste, spontaneous combustion of waste and of shale stockpiles (and consequent air pollution), dust pollution and groundwater pollution (mostly by water-soluble phenols). Carcinogens (e.g. benzo(a)pyrene) have been reported to be present in the various products but, due to stringent safety precautions, no occupational cancer has ever been recorded in the U. S. S. R. oil-shale industry (Gortalum, 1968). Most of the current environmental difficulties are attributed to aging plant and neglect in the past. It is reported (Prien, 1976, p. 258) that Soviet scientists are currently considering the economics of pyrolysing the oil shales and burning the shale oil for power generation in order to eliminate corrosion in the generating plant and to reduce environmental pollution.

the richest oil shales at Kimmeridge in Dorset. This, in turn, would require over 60 sq km of ground to be worked out, at least ten times as much land-area outcrop as is present at workable depths in the area.

4.6 CONCLUSIONS

Shale oils derived by pyrolysis from the Kimmeridge Clay are markedly different in their physical and chemical properties to naturally occurring crude oils. In contrast to most crude oils, the shale oils are rich in sulphur and NSO compounds and deficient in hydrocarbons and are similar to the heavy oils and natural asphalts of tar sands and mineral veins. The shale oils would need to be upgraded to form a synthetic crude to provide a refinery or petrochemical feedstock. Methods of upgrading, by means of thermal cracking and catalytic hydrogenation, are currently being used on a commercial scale for the chemically similar heavy oils from the Athabasca Tar Sands.

The shale oils, spent shale and aqueous distillate from pyrolysis or burning may contain low concentrations of biologically active compounds including carcinogens. Pyrolysis of the oil shales to produce shale oil, and their direct burning as a fuel, produces sulphurous gases and large volumes of spent shale. The richest groups of seams produced 85 wt % of ash when burned and some form of enrichment would be necessary before they could be used as a fuel for power generation.

No locality was found at which the total volume of oil shale concentrated in the oil-shale-rich parts of the sequence was sufficient to support a medium-sized power station for a life of 25 years.

5. Kimmeridge Clay: possible by-products

5.1 INTRODUCTION

Most of the world's oil shale industries (and prospective industries) have attempted to find a commercial use for the large volumes of spent material produced when the shales are either pyrolysed or burned. Many pyrolysis processes produce a spent shale that has 70 to 90% of the weight and 90 to 100% of the volume of the unburnt shale. Direct burning of the shale for power generation produces large volumes of flyash. Both the spent shale and the flyash are low density materials that could, if their mineralogy were suitable, be used in the manufacture of certain lightweight building materials.

In addition to those of fuel and petrochemical sources, one of the possible uses of oil shales might be as a fuel substitute in the manufacture of structural clay products or pozzolanic cement. Their suitability for these purposes would depend not only on their potential calorific value but also on the properties of the intervening mudstones which would provide much of the raw material for the products.

X-ray diffraction analyses have therefore been made to determine the overall clay mineralogy of the oil-shale-rich parts of the Kimmeridge Clay and a small number of tests have been carried out on mudstone/oil shale mixtures to assess their potential use as raw material in the manufacture of structural clay products. The possibility of producing pozzolana from these mudstone/oil shale mixtures during pyrolysis has also been examined.

Many organic-rich sediments are enriched with respect to trace elements, especially metals, that could be a valuable by-product of oil shale working. Analyses have therefore been made to compare the trace element compositions of the Kimmeridge Clay oil shales with those of the adjacent mudstones and with other organic-rich sediments.

5.2 STRUCTURAL CLAY PRODUCTS

The suitability of a rock as a feed for the manufacture of structural clay products depends upon a number of factors, the principle ones being the overall mineralogy of the rock, the detailed mineralogy of the clay fraction and the degree of crystallinity and particle size ranges of the main mineral components.

The non-clay mineralogy of 20 representative oil shale/mudstone mixtures were determined by X-ray diffraction (see Appendix C for analytical details). The results confirmed earlier observations made on Kimmeridge Clay samples from Lincolnshire and Norfolk

(Merriman in Gallois, 1978; Merriman and Strong in Gallois, 1979) that there is a generally sympathetic relationship between the clastic materials, quartz and clay minerals, and the largely chemogenic and biogenic materials, calcite and kerogen. The distribution of these minerals can be broadly related to the more common lithologies in the Kimmeridge Clay (see Section 2.1 for details).

The non-clay mineral composition of the samples analysed in the present work is summarized in Table 12. The total of quartz + calcite + clay minerals is > 95% of the whole rock except where 'other mineral' concentrations are listed in Table 12 as > 5%. Quartz ranges from 4 to > 30% of the whole rock, the higher values being from silty mudstone horizons. Calcite contents vary from just detectable to 21% in the present work, but ranged as high as 55% in the earlier studies since they sampled the full range of Kimmeridge Clay lithologies whereas the present samples were concentrated on the oil shales. Pyrite is a ubiquitous accessory mineral in the Kimmeridge Clay; feldspar, dolomite and ankerite occur more sparingly. Gypsum and natrojarosite are secondary minerals formed from the oxidation products of pyrite as the cores dry out.

The clay mineral compositions of the clay fractions ($< 2\mu$ m) of 155 samples of mudstone and mudstone/oil shale mixtures from the oil-shale-rich parts of the Kimmeridge Clay were determined by X-ray diffraction to identify any possible regional or stratigraphical variations. The analytical techniques are described in Appendix C and the results are summarized in Table C1 and the diffractograms (Appendix I).

The clay fraction of that part of the Kimmeridge Clay examined in the present work is composed of clay mica, kaolinite and a complex mixture of 'expansible' minerals with minor amounts of chlorite and smectite at some levels (Table C1). The 'expansible' minerals include interlayered mixtures of smectite/vermiculite, smectite/clay mica and smectite/kaolinite. They show little regional trend (Table 13) but tend to be more abundant in the samples from localities close to the southern western edge of the London Platform (Hartwell to Tisbury). By contrast, the largely sympathetic relationship between clay mica and kaolinite shows a well developed pattern in which the clay mica/kaolinite ratio increases southwards from North Yorkshire (Marton and Reighton), via Lincolnshire (Donington on Bain) to Norfolk (North Runcton) and the boreholes located close to the edge of the London Platform (Hartwell, Swindon, Foudry Bridge and Warlingham), decreasing again into the Wiltshire-Dorset depositional basin (Table 13).

The shapes of the peaks in the diffractograms suggests that there is no marked regional variation in the degree of crystallinity of the clay minerals. The presence of resistance to 550°C heating in the kaolinite 7 Å peak in a small number of samples may indicate the presence of well ordered kaolinite.

Table 12 XRD analyses of non-clay mineral composition of selected Kimmeridge Clay mudstones

Borehole and depth (m)	Sample no. (KOS)	Quartz %	Calcite %	Other minerals detected
Setchey excavation	801	7	20	Gypsum, aragonite, pyrite
Clavells Hard, Blackstone	802	4	15	Gypsum, pyrite
North Runcton 46.48	803	23	16	Aragonite, pyrite
North Runcton 48.37	804	16	10	Aragonite, pyrite, ankerite
North Runcton 48.96	805	14	14	Gypsum, aragonite, pyrite
Portesham 153.79	806	9	17	Gypsum, pyrite, ankerite
Portesham 152.74	807	11	12	Gypsum, pyrite, aragonite; ankerite, feldspar (j. d.)
Portesham 51.30	808	6	15	Gypsum, pyrite
Portesham 50.46	809	24	4	Gypsum, pyrite, dolomite (j. d.) feldspar (j. d.)
Portesham 53.25	810	6	21	Gypsum, pyrite, dolomite (j. d.) feldspar (j. d.)
Donington on Bain 14.00	845	10	15	Pyrite, aragonite, feldspar (j. d.)
Donington on Bain 141.80	846	14	8	Pyrite, aragonite, feldspar (j. d.)
Hartwell 19.10	847	34	(j. d.)	Gypsum, pyrite, feldspar (15-2%)
Swindon 31.24	848	24	(j. d.)	Gypsum, pyrite, feldspar natrojarosite
Encombe 41.52	849	34	10	Pyrite, feldspar (j. d.) natrojarosite
Encombe 20.00	850	17	14	Pyrite, feldspar (j. d.) natrojarosite
Tisbury 41.70	851	36	(j. d.)	Gypsum, pyrite, ankerite (10 to 15%) feldspar (j. d.)
Tisbury 62.10	852	20	6	Pyrite, aragonite, feldspar (j. d.)
West Lavington 70.56	853	25	(j. d.)	Pyrite, feldspar (10 to 15%)
West Lavington 57.00	854	38	3	Pyrite, feldspar (5 to 10%)

j. d. = just detectable

Table 13 Summary of quantitative results of XRD analyses of clay minerals

Borehole	Kaolinite %		Clay mica %		Expansible minerals %		Clay mica/Kaolinite ratio	
	Range	Average	Range	Average	Range	Average	Range	Average
Marton	28 to 44	36	28 to 57	42	8 to 34	22	0.7 to 1.8	1.2
Reighton	19 to 41	28	28 to 67	45	14 to 35	27	0.7 to 3.5	1.6
Donington on Bain	17 to 33	26	38 to 58	50	11 to 39	24	1.7 to 2.6	2.0
North Runcton	15 to 25	20	43 to 71	54	9 to 41	26	1.8 to 3.6	2.7
Hartwell	6 to 25	19	27 to 76	50	7 to 67	31	1.8 to 5.2	2.6
Swindon	12 to 23	20	44 to 62	52	19 to 42	28	2.2 to 3.8	2.6
West Lavington	16 to 27	22	37 to 56	48	22 to 47	30	1.6 to 2.7	2.2
Tisbury	12 to 28	22	33 to 68	48	9 to 55	30	1.6 to 3.0	2.2
Portesham	13 to 34	23	31 to 63	53	9 to 51	24	1.7 to 3.8	2.3
Encombe and Kimmeridge Bay	15 to 27	22	44 to 70	53	10 to 39	25	1.6 to 2.2	2.4
Foudry Bridge	14 to 25	21	46 to 77	58	< 1 to 38	21	2.2 to 3.9	2.8
Warlingham	14 to 27	19	43 to 77	60	< 1 to 37	21	2.2 to 4.2	3.2

Six samples of oil shale/mudstone mixtures from the wheatleyensis Band in the Donington on Bain, North Runcton and Portesham boreholes were examined in detail to assess their potential as raw materials for the manufacture of structural clay products. The test procedures and results are described and discussed in Appendix B.

The mixed-assemblage mineralogy of the Kimmeridge Clay mixtures limits their potential use for the manufacture of structural ceramics or building materials. For these applications the most important parameters are the handling characteristics of the worked clay, its behaviour on firing, the calorific value of the organic content and the temperatures and rates at which volatiles are evolved from the organic content (H_2O and CO_2), the calcium carbonate (CO_2) and the pyrite (SO_2).

The thermal degradation behaviour of the test samples in a nitrogen/oxygen atmosphere was examined using a simultaneous differential thermal analysis (DTA) and evolved gas analysis (EGA) technique (Appendix B), in which the heat of reaction (ΔT) and gas evolution was determined for a number of heating programmes. The results for the most organic-rich sample examined (KOS 841: Blackstone level from Donington on Bain Bh.) are shown in Fig. 51. Each profile exhibits a large endothermic peak corresponding to the oxidation of the organic content. This occurred at temperatures between $200^\circ C$ and $700^\circ C$ when the sample was continuously heated (Fig. 51A) due to the time taken for the inner part of sample to become oxidised. When the temperature was held at $400^\circ C$ (Fig. 51C) most of the organic content was burned off at this temperature. The H_2O traces in the EGA analyses show three peaks that correspond respectively to the volatilisation of held water (at c $130^\circ C$), the oxidation of the organic content (at c $300^\circ C$) and the dehydroxylation of the clay minerals (at c $600^\circ C$). These latter two peaks are of profound importance in the consideration of any possible structural clay product and pozzolanic uses the oil shale/mudstone mixture might have.

The plasticity indices and strength characteristics of the samples showed them to be suitable for the plastic shaping and handling of clay ware. However, the plastic limits were high indicating that high moisture contents would be required to achieve plasticity and the samples would therefore be expected to have moderately-high to very-high shrinkages on drying from the plastic consistency. Shrinkages were observed to be higher in the more organic-rich samples due partly to the absorption of water by the loosely packed organic material.

Heating experiments to determine the firing properties of the mixtures showed that large ignition losses occur due to the destruction of the organic content and, to a lesser extent, the calcium carbonate and pyrite contents. The resulting fired test pieces were strong but had high porosities due to the volatile losses and, in consequence, any bricks, tiles etc made from these materials would have high water absorption properties. Higher firing

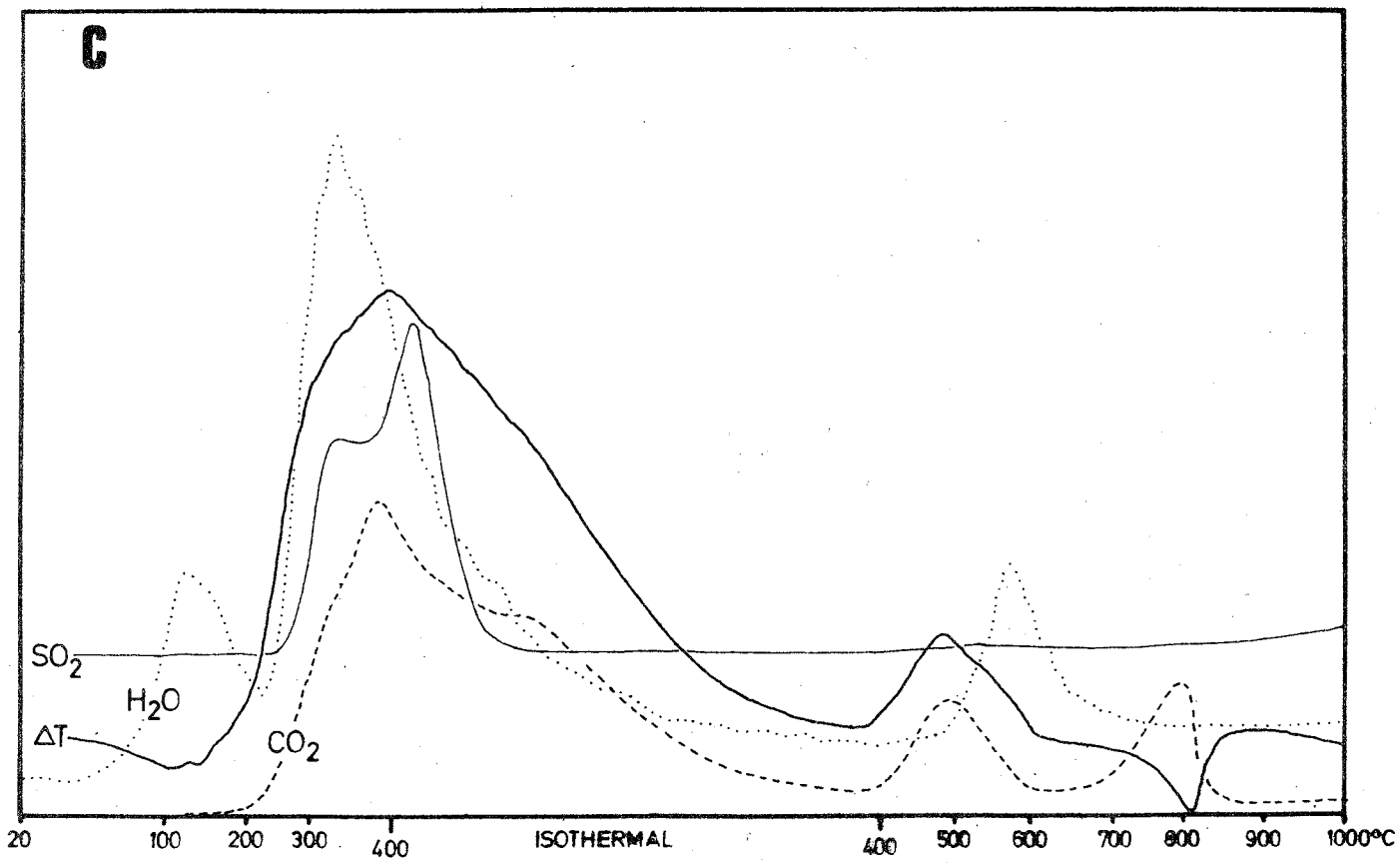
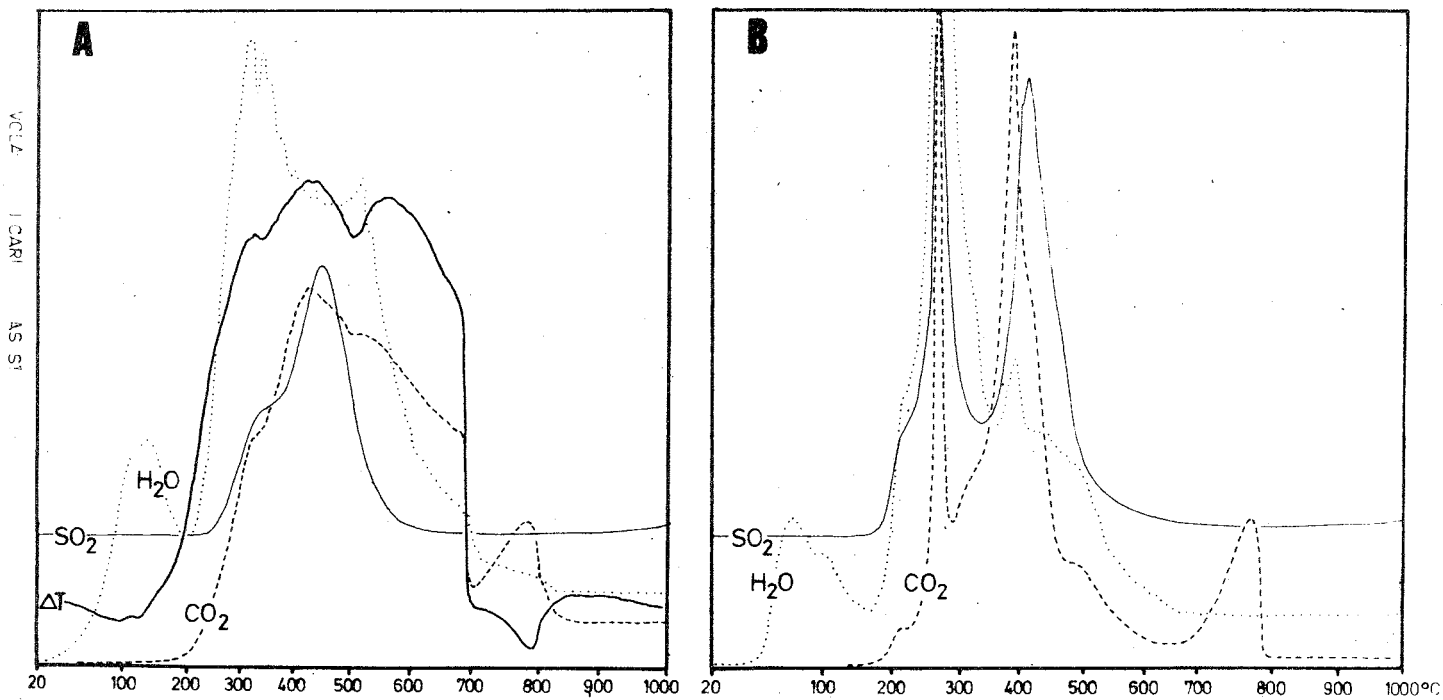


Figure 51 DTA-EGA analyses for sample KOS 841

temperatures could be used to induce vitrification and hence reduce the porosity, but this would probably also produce high shrinkage.

Test pieces were fired at various temperatures up to 1150°C to determine their vitrification behaviour. Very dense, strong fired ware was produced but the firing range was so short as to make it unlikely that a kiln could, in practice, be operated with any degree of consistency. Furthermore, the firing shrinkage was excessive, especially in the more organic-rich samples.

The presence of sufficient organic matter in the clays to act as a fuel for firing is clearly an advantage but it was noted in some of the test pieces where the organic content was high that there was a danger of igniting the kerogen and thereby destroying the sample. This phenomenon had already been observed in practice on a commercial scale. The manager of the Kirbymoorside, North Yorkshire brickworks of Crossley Building Products Ltd., in whose Golden Hill brickpit the Marton Borehole was sited, provided a graphic description of an attempt to fire bricks made from a mixture of oil shales (pectinatus Band) and Kimmeridge Clay mudstones from the Golden Hill pit. During the initial heating period the kerogen in the oil shales began to break down, the bricks overheated and small jets of burning gas, 'like miniature acetylene torches', appeared out of all sides of the bricks and as these died away the bricks collapsed into heaps of rubble. The process was accompanied by the production of acrid smoke and a pungent smell.

This last named feature was also noted when attempts were made to rapidly overfire test samples to examine the possibility of producing a lightweight aggregate by 'bloating' the clay.

In the early years of working in the Lothians oil shale industry the spent shale was entirely waste and was heaped up into large tips known locally as 'bings'. In later years some of this material was used, and continues to be used, for brickmaking: much of it has been used as fill in roadmaking schemes. Some of the Scottish spent shale is said to have pozzolanic properties, but no commercial use has been made of the feature.

The mineralogy of samples of spent shale from Kimmeridge Clay oil shales retorted at 500°C was examined by X-ray diffraction in the pilot study. It was found that little change occurred in the clay mineralogy other than an increase in the degree of crystallinity of the clay mica due to the loss of interlayered water. Grim (1962) has suggested that clay micas can develop pozzolanic (cementitious) properties when heated in the range 427°C to 981°C. This property depends upon the development of a very surface-reactive, amorphous aluminosilicate phase by the loss of hydroxyl groups. Differential thermal analyses carried out for the present work showed that dehydroxylation of the clays took place between 550°C and 650°C (H₂O peak in Fig. 51C). Further testing is in progress to determine the precise temperature at which the most active state occurs, to define the optimum calcium carbonate content of the

spent shale (since this might react with the pozzolanic fraction to form unwanted lime compounds) and to measure the cementitious strengths of test pieces of pozzolanic cement. Tests are also in hand to examine the possibility of using raw shale/spent shale mixtures as materials for structural clay product manufacture or for 'bloated' lightweight aggregate.

5.3 TRACE ELEMENTS

The association of hydrocarbons, organic-rich shales (commonly referred to as 'black shales' on account of their black, disseminated sulphide content) and the concentration of certain metals as sulphides has long been known (see Dunham, 1961, for review). High concentrations of copper, lead, molybdenum, nickel, silver, uranium, vanadium and zinc have been recorded from oil shales and black shales of various ages (Krauskopf, 1955) and in some instances the metal concentrations have been sufficiently high to suggest that they would provide a valuable by-product of shale working. Where secondary mobilisation of the metal sulphides has occurred they can give rise to bedded ore bodies of considerable economic importance (e.g. the Cu, Pb and Zn deposits in the black shales of Mount Isa, Australia).

In modern marine environments planktonic algae have been shown to be the prime agent for metal fixation. Restricted basins with anaerobic bottom conditions appear to favour the preservation of the algal concentrations of certain metals, notably uranium, in the sediment. Uranium enrichment has been reported from the present-day sediments of the Norwegian fjords (Strom, 1948), the Baltic Sea (Koczy et al., 1957) and the Black Sea (Degens et al., 1977). Enrichment of other metals such as Cu, Pb and Zn has been recorded from organic-rich sediments in open-marine environments on the continental shelf off South-West Africa (Calvert and Price, 1970) and Chester et al. (1978) have shown the same metals to be concentrated in the suspended particles of plankton-rich surface waters in the northeastern Atlantic.

Examples of trace-metal enrichment in ancient organic-rich sediments are common. Gad et al. (1969) have demonstrated a strong correlation between the organic carbon contents and the concentrations of Ag, Cu, Mo, Ni and V in the Upper Lias (Whitbian) of the Yorkshire coast. However, no element was present in sufficient concentration in the shales to be of economic interest. The average composition of the Whitbian shales is comparable to that for 'normal' shales published by Turekian and Wedepohl (1961) and the trace metal concentrations of the organic-rich part of the Whitbian sequence (the Jet Rock Series) falls within the ranges quoted by Krauskopf (1955) in his review of 'black shale' analyses.

The major and minor element concentrations of 100 samples of Kimmeridge Clay oil shale and oil shale/mudstone mixtures were determined by multi-element direct-reading emission spectrometry (see Appendix F for analytical results). A summary of the trace element data and its comparison with data from the Upper Lias, from 'normal' shales and

from 'black shales' is given in Table 1.

The Kimmeridge Clay oil shales do not contain any major concentration of trace elements. The oil shales are enriched in Cu, V and Zn and slightly enriched in Ni, Sr and Y with respect to other Kimmeridge Clay mudstones. The oil shales are deficient in B, Ga, Rb and Zr and slightly deficient in Ba, Be, Bi, Mn and Li. No discernible difference occurs in the concentrations of Ag, Bi, Co, Cr, La, Pb and Sn. Even the most enriched shales have concentrations of Cu and V that are low within the range for these elements in typical 'black shale' (Table 14).

Uranium was not determined in the present work but in the pilot study values of < 7 ppm were obtained from Kimmeridge Clay oil shales. The total gamma-ray activity of a range of Kimmeridge Clay lithologies was measured in the present work the oil shales were no more radioactive than other mudstones. Degens et al. (1977) have recently recorded uranium enrichment (55 to 114 ppm U_3O_8) in coccolith tests from the Black Sea. The limited amount of data available suggests that lithologically similar coccolith-rich bands in the Kimmeridge Clay are deficient in uranium and have a very low total gamma-ray flux.

5.4 CONCLUSIONS

Mixtures of Kimmeridge Clay oil shale and mudstone could be used as the basis for a self-firing brickmaking process such as the Fletton process providing the bricks were pressed dry or semi-dry to reduce shrinkage and porosity and providing the oil shale content and particle size were carefully controlled. Kerogen and calcium carbonate are the two most important constituents that would be required to be considered for structural clay product uses. The Kimmeridge Clay contains numerous small-scale rhythms in which the concentrations of both these constituents vary rapidly with depth but are laterally very persistent. It should therefore be possible to identify the stratigraphical horizons at which the optimum mixture was present for any particular application.

The spent shale from oil shale/mudstone mixtures retorted at 500°C does not possess pozzolanic properties. However, these properties are formed at temperatures between 550°C and 650°C and there is a possibility that self-firing oil shale/mudstone mixtures could be identified such that a pozzolanic product would be produced.

Rapid overfiring can be made to produce a 'bloated' clay that might be suitable for use as a lightweight aggregate. However, such firing produces acrid smoke (from the hydrocarbons) and sulphurous gases (from the pyrite). The same fumes are likely to be produced, but to a lesser extent, in the manufacture of structural clay products or pozzolana from a feed that includes Kimmeridge Clay oil shales.

The Kimmeridge Clay oil shales show an enrichment of a number of trace elements,

notably Cu and V, with respect to other Kimmeridge Clay lithologies but are not enriched with respect to other organic-rich shales. No trace element has been detected that would be a useful by-product of oil shale working.

6. Kimmeridge Clay: source rock potential

6.1 INTRODUCTION

Good quality oil shales and prolific petroleum source rocks are to a large extent mutually exclusive in that the main requirement for a good oil shale is that it should have suffered little thermal diagenesis, and therefore have retained its organic content, whilst that for a good source rock is that it should have undergone thermal maturation and its organic content been largely converted to petroleum products.

Observations on diagenetic changes in kerogens in various geological settings have shown that temperature and time are the two most important factors influencing maturation. In practice, for a given geothermal gradient, the degree of thermal maturation of the organic content of a sediment is directly related to the depth of burial of the sediment and the length of time for which this depth of burial (temperature) is maintained. The reaction rate for organic diagenesis is believed to vary linearly with time and exponentially with temperature, each 18°C rise in temperature doubling the reaction rate (Fuller, 1975, p. 11-8). Evans and Staplin (1971) have suggested that the threshold of perceptible reaction is at about 50°C.

6.2 SOURCE ROCK POTENTIAL

In the area of the Kimmeridge Clay outcrop and subcrop in England at the present day the minimum temperature for hydrocarbon generation (50°C) is reached at depths of between about 1200 and 1500 m (Richardson and Oxburgh, 1978, Fig. 5). The maximum present depth of burial of the Kimmeridge Clay oil shales in this area is about 1200 m (Fig. 2), beneath the central Weald. No heat flow data is available for the central Weald but results from adjacent areas suggest that 50°C is not reached until about 1500 m. When allowance is made for Cretaceous and Tertiary sediments that have been removed by erosion the maximum depth of burial of the Kimmeridge Clay in England is likely to have been about 2500 m in early Eocene times, also beneath the central Weald. Elsewhere in England the maximum depth of burial has probably exceeded 1500 m in only a few areas and, around the western edge of the London Platform, may never have exceeded 1000 m. With the exception of the structurally complex areas of south Dorset and North Yorkshire, the geothermal gradient in the Kimmeridge Clay outcrop and subcrop area may not have been markedly greater at any time since the Jurassic than it is at present. This suggests that the Kimmeridge Clay is not generating petroleum products at the present time anywhere in its English land area outcrop or subcrop

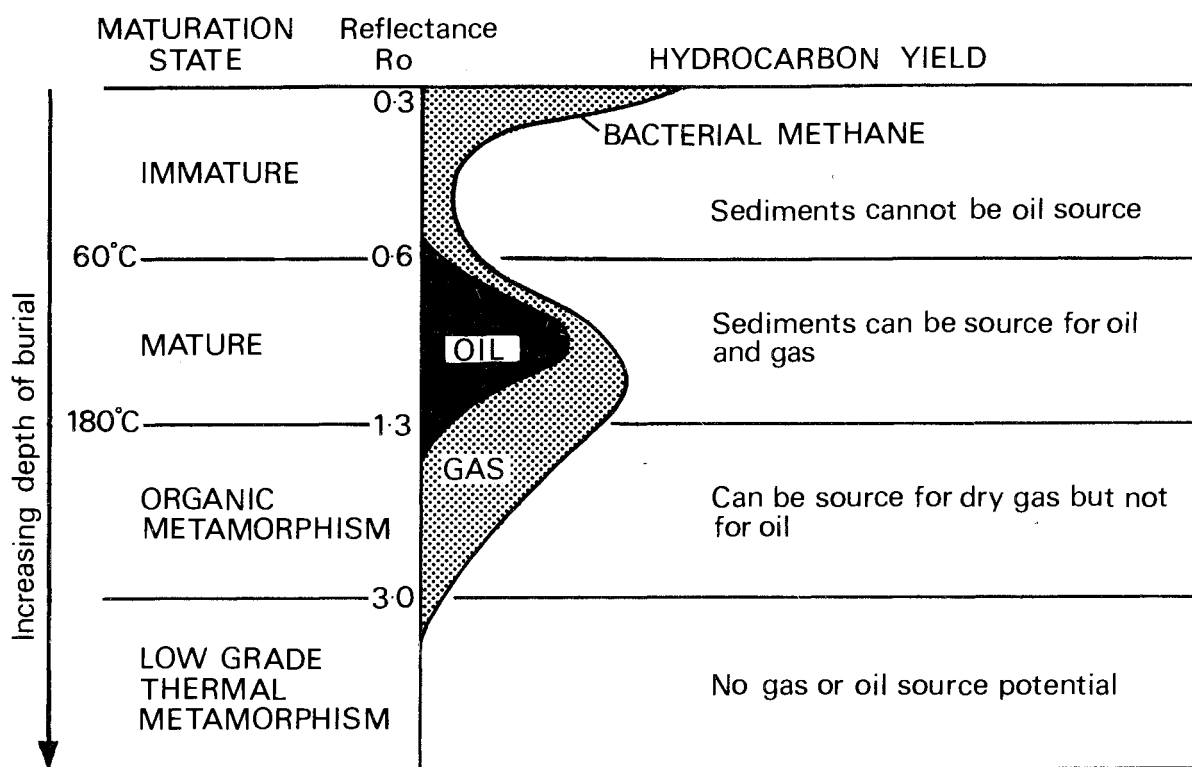


Figure 52 Relationship of thermal maturation to hydrocarbon generation

and that it has probably only generated small amounts of petroleum in the past in the central Weald. One might expect therefore that the kerogen in the Kimmeridge Clay oil shales would show little evidence of thermal maturation, especially in the outcrop areas. This has proved to be the case in the present work. The kerogen in the oil shales is pale yellow in transmitted light (Plates 4 and 5) and has reflectivity values (R_o) of 0.3 to 0.4, both features of immaturity that suggest that the oil shales lie outside the oil generation window (Fig. 52).

The chemistry of the bitumen fraction of the oil shales also indicates immaturity. The n-alkane fractions of most crude oils (and by inference the bitumen in the source rocks from which they have been derived) have a Carbon Preference Index (CPI) within the range 0.9 to 1.15 (Bray and Evans, 1965). By contrast, recent sediments have a high CPI (up to 10) a reflection of the strong odd number carbon preference in modern plants. Immature organic-rich rocks have CPIs that vary in relation to the origin of their organic content and their degree of maturation. The bitumens from the Kimmeridge Clay oil shales have CPIs in the range 1.5 to 3.2 and indicate immaturity.

The distribution of carbon numbers in the n-alkane fraction can also be an indicator of maturity. Albrecht et al (1976) have shown that increasing thermal maturation produces a progressive change in the frequency of distribution of carbon numbers within the n-alkane homologous series. In immature sediments the n-alkanes reflect their biogenic source and are dominated by carbon numbers C_{15} to C_{20} . With maturation higher carbon number alkanes

PLATE 4

Photomicrographs of kerogen concentrates in incident white light x 300

A. Donington on Bain Borehole, Blackstone level. Pale yellow-coloured coagulations of amorphous sapropel typical of kerogens from the Blackstone level. Spores, pollen and vitrinite are present in some samples at this stratigraphical level but contribute little to the hydrocarbon generating potential of the rock.

B. Kimmeridge Bay Borehole, Upper eudoxus Band. Irregular masses of amorphous sapropel (lower right) dominate the kerogen concentrate: vitrinite and spores are rare. Chitinous tests of foraminifera (seen here centre and lower left) are locally common.

form from the breakdown of kerogen and the peak of the series moves to a higher carbon number (20 to 25). With increasing diagenesis further cracking occurs and the peak carbon number falls to about C_{15} , the CPI reducing to about 1.0 at the same time.

The n-alkanes of the Kimmeridge bitumens show a bimodal distribution with peaks at about C_{17} and C_{23} (Fig. 53, top). The lower number peak is characteristic of immature, marine-derived (probably algal) organic materials. The higher peak is probably formed from land-derived, degraded high plant debris. Artificial maturation experiments (see below) showed that the n-alkane envelope changed to a unimodal trace without any odd or even carbon preference (Fig. 53, centre).

According to Tissot and Welte (1978, Fig. V.1.16) the temperature of the maximum rate of pyrolysis, as determined by the IFP/Rock Eval method, is also a measure of maturity. Most of the Kimmeridge Clay oil shales had maximum pyrolysis rates in the range 410 to 430°C, within the range ($< 435^\circ\text{C}$) of immature sediments. The Hydrogen Index can also indicate maturity, the index decreasing with thermal maturation: here again, the values for the Kimmeridge Clay oil shales indicate immaturity. Atomic H/C ratios give a similar result (Table 15). Those for the Kimmeridge Clay are all greater than 1.2 and are indicative of immature kerogens of either Type I (algal) or Type II (mixed) origin (Fig. 54). No satisfactory determination of atomic O/C ratio was possible because of the difficulty of preparing kerogen concentrates of sufficient purity for elemental oxygen analysis (see Appendix C for details). However, the Oxygen Indices from the IFP/Rock Eval analyses were mostly low and indicated a largely algal origin. By contrast, Kimmeridge Clay specimens from Sutherland, which are rich in degraded carbonaceous debris, have low atomic H/C ratios.

6.3 OIL - SOURCE ROCK CORRELATIONS

Although there has been little data published to support the correlation it has become generally accepted in recent years that much of the oil reservoired in the Mesozoic rocks of the British land area and that of many of the oilfields in the North Sea have a Kimmeridge Clay source. The oils of the Argyll, Auk, Brent, Dan, Ekofisk, Montrose and Piper fields have been suggested, or in some cases stated, as having been derived from the Kimmeridge Clay (Woodland, 1975). In one of the few accounts to discuss the geochemical evidence for the correlation, Fuller (1975) concluded that there was evidence to believe that the Kimmeridge Clay was the principal oil-generating rock in the North Sea.

A large number of techniques have been employed for oil-source rock correlation. Each method, or group of methods, has its advantages and disadvantages for particular oils and suspected source rocks. Every method attempts to identify parameters that are common to both the bitumen/kerogen fraction of the source rock and the reservoired oil and which are likely to have remained largely unaffected by fractionation, thermal or bacterial degradation

PLATE 5

Photomicrographs of kerogen concentrates in incident white light x 300

A. Kimmeridge Clay, North Kintradwell. The Kimmeridge Clay in Sutherland contains large quantities of organic matter that is probably derived from a nearby land area. This material, largely degraded fragments of higher plants, occurs in the kerogen concentrates as fusinite, vitrinite and inertinite (e.g. opaque fragment, centre) within the usual ground-mass of Kimmeridge Clay sapropel.

B. Kimmeridge Clay, Ethie. The kerogens from Ethie are similar, as one might expect, to those from Sutherland. Inertinite and spores (top left) are common and in most samples are present in almost equal proportions to the ubiquitous sapropel.

7. Other British oil shales

7.1 INTRODUCTION

Oil shales have been recorded from time to time at a number of levels in the British stratigraphical sequence. Many of these records refer to cannel coals, lignites or merely organic-rich mudstones. Cannel coal, worked in conjunction with normal coals, was used extensively for oil distillation during Victorian times: details of the production by county and by year are given in the Mining Statistics of Great Britain and Northern Ireland (H. M. Inspectorate of Mines). Other materials returned as 'oil shale' in the statistics for this period include shaley coals of Devonian age used for the manufacture of carbon pigment ('Bideford Black').

Only two true oil shales have ever been worked commercially for oil production in Britain, the Carboniferous oil shales of the Lothians of Scotland and the oil shales of the Kimmeridge Clay. Attempts have been made to work oil shales in the Lias of Somerset and analyses have been made in the past of oil shales in the Middle Jurassic of the Hebrides and Sutherland with a view to possible exploitation. The locations of the oil shales discussed below are shown in Fig. 56.

7.2 CAITHNESS FLAGS

Crampton and Carruthers (1914, p. 171) recorded bands of hard, black bituminous shale, reminiscent in lithology of the oil shales of the Lothians, in the Caithness Flags at a number of localities on the Caithness coast (Fig. 30).

The Caithness Flags are made up of a large number of rhythms of varying types, all of which are thought to reflect fluctuations in the level of a large shallow lake that covered the Orkney-Caithness area in Middle Devonian (Eifelian-Givetian) times. The characteristic rhythm (Fig. 57 after Mykura, 1976) begins with a black, finely laminated, silty mudstone rich in fish remains and passes up into siltstones and sandstones that were deposited in shallower, more turbulent water.

At a number of stratigraphical levels and localities the basal 'fish beds' member of the rhythm is sufficiently organic-rich to have been described as a 'bituminous shale'. One of the best documented of these bands crops out on the foreshore at Ackergill Tower,

4 km north of Wick. Here, up to 0.4 m of very finely laminated, almost black, calcareously cemented, organic-rich mudstone containing much plant debris occurs within a complex rhythmic sequence of sandstones, siltstones and mudstones. There are three seams

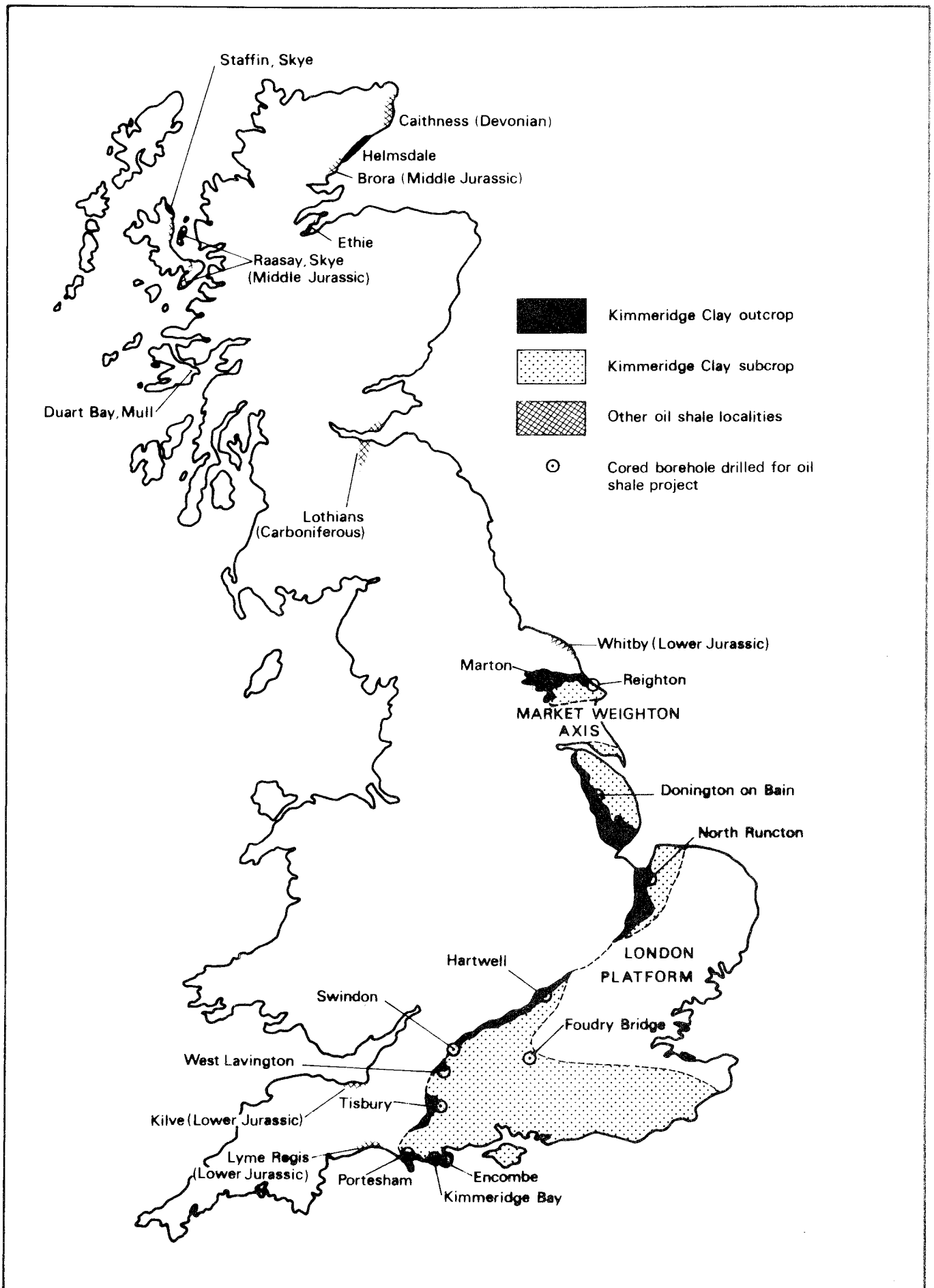


Fig. 56 Geological sketch map showing the outcrops of the more important British oil shales.

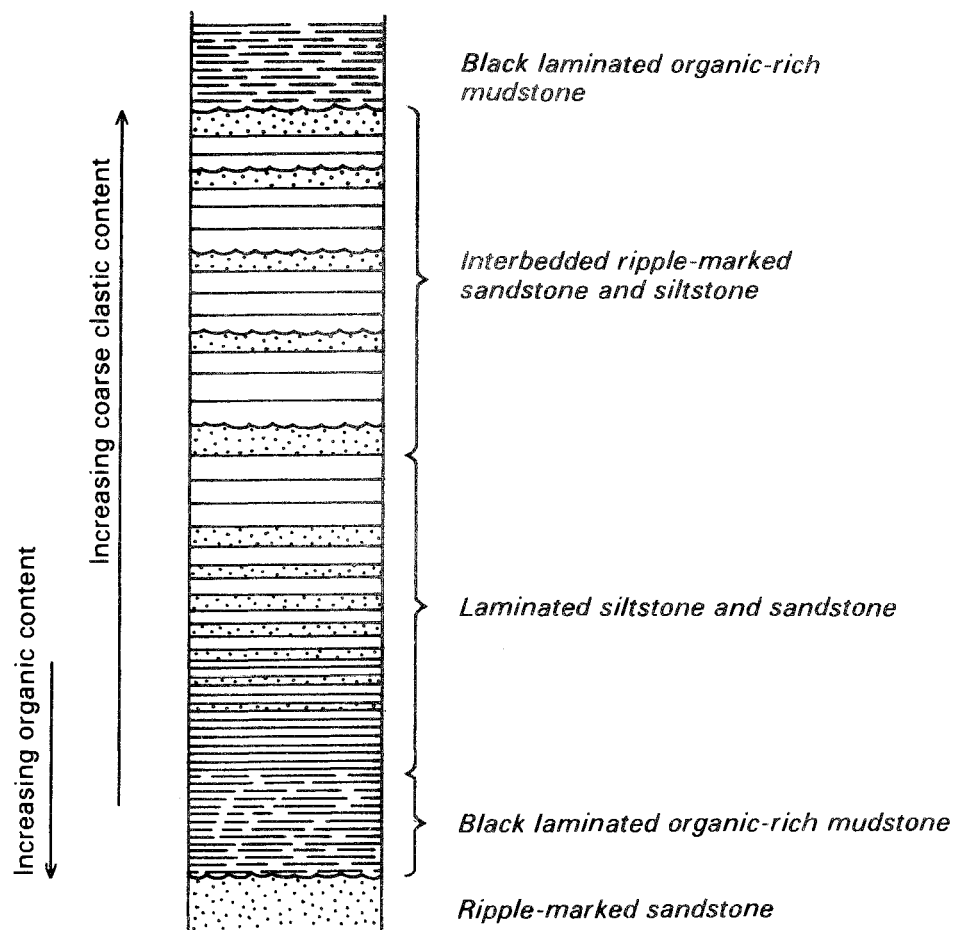


Fig. 57 Generalized Caithness Flags rhythm

of 'oil shale' at this outcrop, but the structure is complex and it is possible that these are a single band repeated by faulting. IFP/Rock Eval analyses of the middle and most easterly seams (KOS 910 and 909 respectively) gave potential oil yields of 2.8 and 0.8 wt/wt %. Organic carbon contents were moderately high at 4.0 and 5.5%.

The Caithness Flags are of no interest as a source of shale oil.

7.3 LOTHIAN OIL SHALES

The Lower Carboniferous oil shales of the Scottish Lothians crop out in an area extending southwards from the banks of the Firth of Forth between Blackness and South Queensferry via Broxburn, Pumpherston, and West Calder to Tarbrax. Small outcrops occur on the north bank of the Forth at Burntisland and on the east side of the Pentland Hills at Straiton.

The oil shales were worked continuously from 1851 to 1962 and at their maximum productivity, in the years immediately before the First World War, had an annual output of over 3 million tons of shale. The geology of the oil-shale field has been described in detail by Cadell et al. (1906), Carruthers et al. (1912), Carruthers et al. (1927), Richey (1942),

Anderson (1942) and Kennedy (1943). Details of the method of working and chemistry of the shales are given in the above and in the two Institute of Petroleum symposia on 'Oil Shale and Cannel Coal' (1938 and 1951).

The oil yield of the seams worked ranged from about 16 to 45 gal/ton, but in the later years of the industry most of the shales worked yielded 20 gal/ton or less. Yields varied considerably within the thickness of a single seam, from locality to locality in the same seam and (usually decreasing) with depth in the same seam (Bailey in Carruthers et al. 1927, pp. 175-178). Statistics provided to Macleod Matthews (1975, p. 3) by British Petroleum for a large number of years of maximum shale production showed an average yield of about 20 gal/ton. Much of the early working was by pillar and stall commencing at the outcrop, in seams mostly from 1.3 to 3.3 m in thickness. In the later years opencast working became progressively more important.

The initial purpose of the industry was to produce lubricating oils and paraffin for heating and lighting and in this it was successful and highly profitable. With changing markets and increasing competition from producers of natural crude oils, such as the USA, the emphasis later turned to the production of motor spirit which was partially (as an indigenous industry) exempted from excise duty. The industry failed in 1962 when this duty concession was removed.

Cameron and McAdam (1978) have recently reviewed the available data on past workings and have estimated the probable resources to total about 120 million tonnes of shale (op. cit. p. 18). Of this total they estimate about 65 million tonnes to be extractable and to yield about 5 million tonnes of oil. A further 240 million tonnes of possible resources and 740 million tonnes of unproven deep resources are estimated to be present. They concluded that the resources were mostly scattered, that many were on the periphery of old mines and would be difficult to work and that any attempt to revive the industry would produce a large degree of environmental disturbance for a relatively low yield.

Macleod Matthews, in his review of the financial aspects of the workings (1975), concluded that if the Lothians oil shale industry had survived until the time of the 1973 oil crisis it would have become profitable, but would have been small in size (producing about 50 to 100 000 tons of oil per annum). An economic case did not, however, exist for reopening the Scottish mines or for sinking new ones because of the heavy capital costs involved in both the mining and the retorting/refining.

7.4 LIASSIC OIL SHALES

Organic-rich sediments occur at a number of stratigraphical levels in the Lias and several of these are locally rich enough to be termed oil shales. The best documented are those in the Lower Lias of the coastal sections at Kilve, Somerset and Lyme Regis, Dorset

and in the Upper Lias (Jet Rock Series) at Whitby, North Yorkshire. Unsuccessful attempts have been made to work the Kilve oil shales. Shales of a similar age have been worked in the past elsewhere in Europe, notably in Germany (e.g. the Posidonienschiefer) and France (e.g. the Schistes Bitumineux of Severac-le Chateau).

The Liassic oil shales in Britain are similar in many respects to those in the Kimmeridge Clay but differ from them in that the former appear to have been deposited in separated, shallow basins on a broad marine shelf (Hallam, 1967). In consequence, the seams are not as persistent laterally as those of the Kimmeridge Clay. The positions of the more important Liassic oil-shale occurrences are shown in Fig. 56.

Lower Lias: Dorset and Somerset

Spontaneous combustion of thin oil shale seams occurred in the Lias of the cliff sections at Lyme Regis, Dorset in 1751 and 1908 (Woodward and Ussher, 1911). The seams are thin and probably of poor quality. Oil shales at a similar stratigraphical level occur on the Somerset coast and these are much better documented.

Between Watchet and Hinckley Point in Somerset the Lower Lias is almost completely exposed in the cliffs and foreshore. Much of the sequence is organic-rich and 'bituminous paper shales' have been recorded at a number of levels. The occurrence of true oil shales are said to have been discovered in the cliffs at Kilve, 7 km east of Watchet, by a mining engineer in 1916 but local picnic parties are reported to have used fallen slabs of the shale for bonfires prior to this date.

Test samples of the Kilve oil shales were retorted by W. Forbes Leslie of English Oilfields Limited in the early 1920s, probably at the Norfolk works, and a borehole was drilled at Kilve Priory [ST 146 440] in 1923 to a depth of 553 ft (168.6 m). No geological data has survived from the borehole but the yield from the shales was reportedly 40 gal/volumetric ton (1.5 cu yds) of shale (\approx 13 gal/ton). In 1924 Forbes Leslie toured the West Country inviting support for a scheme to exploit the shale commercially having 'proved' that the seams extended to a depth of a thousand feet over an area of 8000 acres and were capable of supporting an industry producing 5 million gallons of oil per annum.

In 1924 the Shalime Company was formed to exploit both the oil shales and the thin tabular limestones that occur with them in a combined fuel and cement-making process. Several commercial retorts were built and a few hundred barrels of oil were produced, but the oil was reportedly sulphur-rich and the company failed in less than a year due to lack of financial support.

The oil shales at Kilve are within the bucklandi Zone (Lower Sinemurian) of the Lower Lias. The seams occur within a sequence of mudstones and thin tabular limestones and are thin and of such poor quality that many of them scarcely justify being called oil shales.

Shatwell et al. (1924, Table 4) analysed a number of shales from the vicinity of the abandoned retort at Kilve by the Gray-King method. The shales yielded from 3.2 to 10.4 UKgal/UKton of oil of specific gravity 0.94 and with sulphur contents of 2.9 to 3.1%. By comparison with the Kimmeridge Clay oil shales these yields are low, but so too is the sulphur content of the oil. It seems likely, therefore, that the prospective industry at Kilve failed because of the poor quality of the shales.

Shatwell et al. (op. cit.) also examined 'oil shales' in the Lower Lias at Penarth, South Glamorgan. Here, yields of 3.6 and 5.2 UKgal/UKton were obtained.

Upper Lias: North Yorkshire

The Jet Rock Series, and to a lesser extent the Bituminous Series, of the Upper Lias of the North Yorkshire coast include organic-rich sediments capable of producing oil on pyrolysis as well as free hydrocarbons formed by natural thermal maturation. Potential oil yields of up to 19 gal/ton have been recorded from the richer bands in the Jet Rock Series (Gad et al., 1969). Organic carbon contents in the Bituminous Series and the Jet Rock Series range from 2.3 to 3.1 wt % and 4.8 to 11.7 wt % respectively and have yielded a maximum, in the Jet Rock Series, of 1.0 wt % of solvent extractable hydrocarbons (Cooper and Barnard, 1978).

In comparison with the oil shales of the Kimmeridge Clay those of the Lias are of low yield, are widely spaced and their total volume at any given locality is small.

7.5 DUN CAAN OIL SHALE

In the Hebridean islands of Raasay and Skye the base of the Great Estuarine Series (Bathonian) is marked in many areas by an oil shale up to 3.5 m thick, the Dun Caan Oil Shale. The formation takes its name from outcrops on the flanks of Dun Caan, the highest peak of Raasay. This seam is one of the thickest oil shales recorded in the United Kingdom but its low yield and high sulphur content and the geological complexities associated with its outcrop have combined to prevent its commercial exploitation.

The outcrop of the oil shale is much affected by faulting and, in many areas, the organic content of the shale has been carbonized by thermal metamorphism associated with Tertiary basaltic sills and granophyre sheets. Undisturbed shale occurs on Raasay on the eastern and southern sides of Dun Caan (Fig. 58), in the Trotternish peninsula of Skye (Fig. 58) and between Elgol and Kirkibost in southern Skye (Fig. 59). In these areas the oil shale, together with the underlying Garantiana Clay, can readily be traced as a slack between the prominent features of the underlying Bearreraig Sandstone (Bajocian) and the overlying White Sandstone (Bathonian). The oil shale is everywhere poorly exposed since it is largely covered by talus from the overlying sandstone.

A sample of weathered oil shale from Raasay was analysed at the Broxburn (Lothians)

oil works in 1913 and yield 12 gals of oil and 6.2 lbs of ammonium sulphate per ton of shale; a compounded sample from Trotternish, Skye yielded 12.8 gals of oil and 7.4 lbs of ammonium sulphate per ton of shale (Steuart, 1913, p. 53). Conacher (1917, p. 188) subsequently quoted a yield of 17 gal/ton for a sample from Raasay.

Raasay

The type section of the oil shale is a deeply weathered exposure at the top of a prominent cliff of Bearreraig Sandstone [NG 5821 3945] on the lower slopes of Dun Caan (Arkell, 1933, Plate 15A). It exposes about 3.5 m of fissile, very dark brown oil shale with sulphur-coated surfaces. The junctions with underlying and overlying beds are not currently visible. To the north of the type section the oil shale can be continuously traced as a scree-covered slack for about 4 km until it is faulted against Lewisian rocks at North Screapadal. To the south and west (Fig. 58) the outcrop is more difficult to trace due to the presence of irregular masses of intrusive granophyre: where visible (e.g. at Storab's Grave [NG 561 416]) the oil shale has commonly been burnt by the proximity of these intrusions (Gibson, 1922, p. 55).

Trotternish Peninsula, Skye

Between Portree Bay and Bearreraig Bay the oil shale and underlying Garantiana Clay form a conspicuous ledge between the prominent features of the Bearreraig Sandstone and the White Sandstone. The oil shale has been extensively metamorphosed by igneous intrusions between Portree Bay and Prince Charles' Cave [NG 516 483], but unaltered shale crops out between this last locality and Loch Leathan [NG 515 502].

Good exposures of the oil shale occur in situ and in slipped masses in the cliffs below Fiurnean at the foot of a line of crags of White Sandstone [NG 5158 4825 to 5169 4933]. The following section was measured at the northern end of these crags:

White Sandstone: massive, clean, white, fine-grained, soft sandstone	c 20 m
transition beds: very finely laminated, fine-grained soft sandstone with lamination and micro cross-bedding picked out by laminae of clean white sand, dark brown plant-rich sand and blackish brown (? kerogen-rich) sand; passing up into white sand by increase in thickness and frequency of clean sand laminae and down into bed below by increase in organic-rich layers	c 6 m
Very finely laminated plant- and kerogen-rich shales with sand partings, becoming less sandy with depth	c 1 m
Dun Caan Oil Shale: very dark brown, finely laminated oil shale weathering to pale brown paper shale with sulphur-coated	

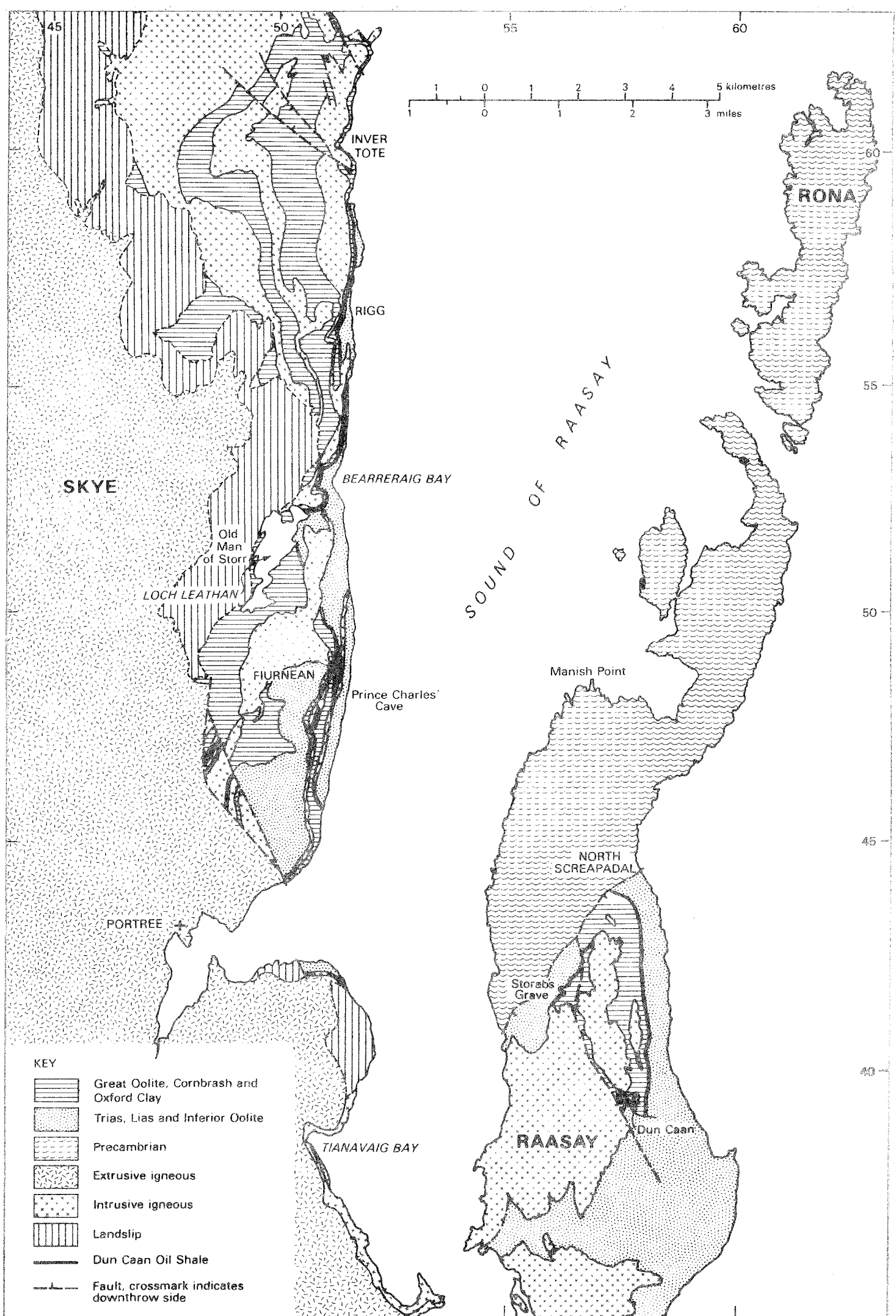


Figure 58 Geological sketch map -- Raasay and the Trotternish peninsula, Skye

surfaces; sparsely fossiliferous but with Cyrena, unionids, asteroid ossicles and fish debris common in top 0.3 m; microfauna common throughout; becoming progressively more muddy with depth in basal 0.4 m (passage to Garantiana Clay)

c 2.4 m

Northwards from here the oil shale outcrop is peat-covered for several hundred metres to a small burn [NG 5165 5035] where scrapes of rotted oil shale occur below a small waterfall in the White Sandstone. From there, the outcrop continues northwards under peat and a dolerite sill and was believed by Lee (1920, p. 56) to be represented in the shores of Loch Leathan [NG 508 517] by a black carbonaceous sandstone. This exposure was drowned when the level of the loch was raised for hydroelectric purposes.

The outcrop of the presumed sandy equivalent of the oil shale, together with a presumed sandy equivalent of the Garantiana Clay, passes northwards from the loch into a steep grassy cliff in which only the Berreraig Sandstone and a dolerite sill higher in the sequence are well exposed. Between here and Inver Tote the Berreraig Sandstone, White Sandstone and a number of sills form almost continuous cliffs 100 m to 150 m high in which the junction of the two sandstones (the presumed stratigraphical position of the oil shale or its sandy equivalent) is marked by a grassy ledge. This horizon descends to beach level at Inver Tote [NG 5218 6023] where it is marked by an 0.5 m thick band of soft, carbonaceous sandstone. Lee's (op. cit.) suggestion that the Garantiana Clay and the oil shale pass laterally into carbonaceous sandstone in the area north of Loch Leathan has yet to be demonstrated palaeontologically. In view of the lateral persistence and uniformity of lithology of the Garantiana Clay and the Dun Caan Oil Shale in Raasay, south of Loch Leathan and between Strollamus and Elgol in southern Skye, an alternative possibility is that the White Sandstone transgresses northwards across the oil shale and comes to rest directly on the Berreraig Sandstone in the area north of Loch Leathan.

Strollamus to Elgol

Between Strollamus and the head of Loch Slapin (Fig. 59) the oil shale is extensively faulted at outcrop, is difficult to follow and is poorly exposed. However, from Loch Slapin to the coast at Elgol the position of the oil shale is marked by a pronounced slack between the well developed features of the Berreraig and White sandstones. Small exposures and scrapes are common and samples were collected from a small quarry adjacent to the Torrin to Kirkibost road [NG 562 184], from the banks of the Allt Port na Cullaidh burn [NG 522 135] near Elgol and from Elgol foreshore [NG 516 137]. The oil shale at all three localities is largely carbonised due to the proximity of dolerite sills and dykes.

IFP/Rock Eval analyses of samples from the unmetamorphosed sections at Dun Caan

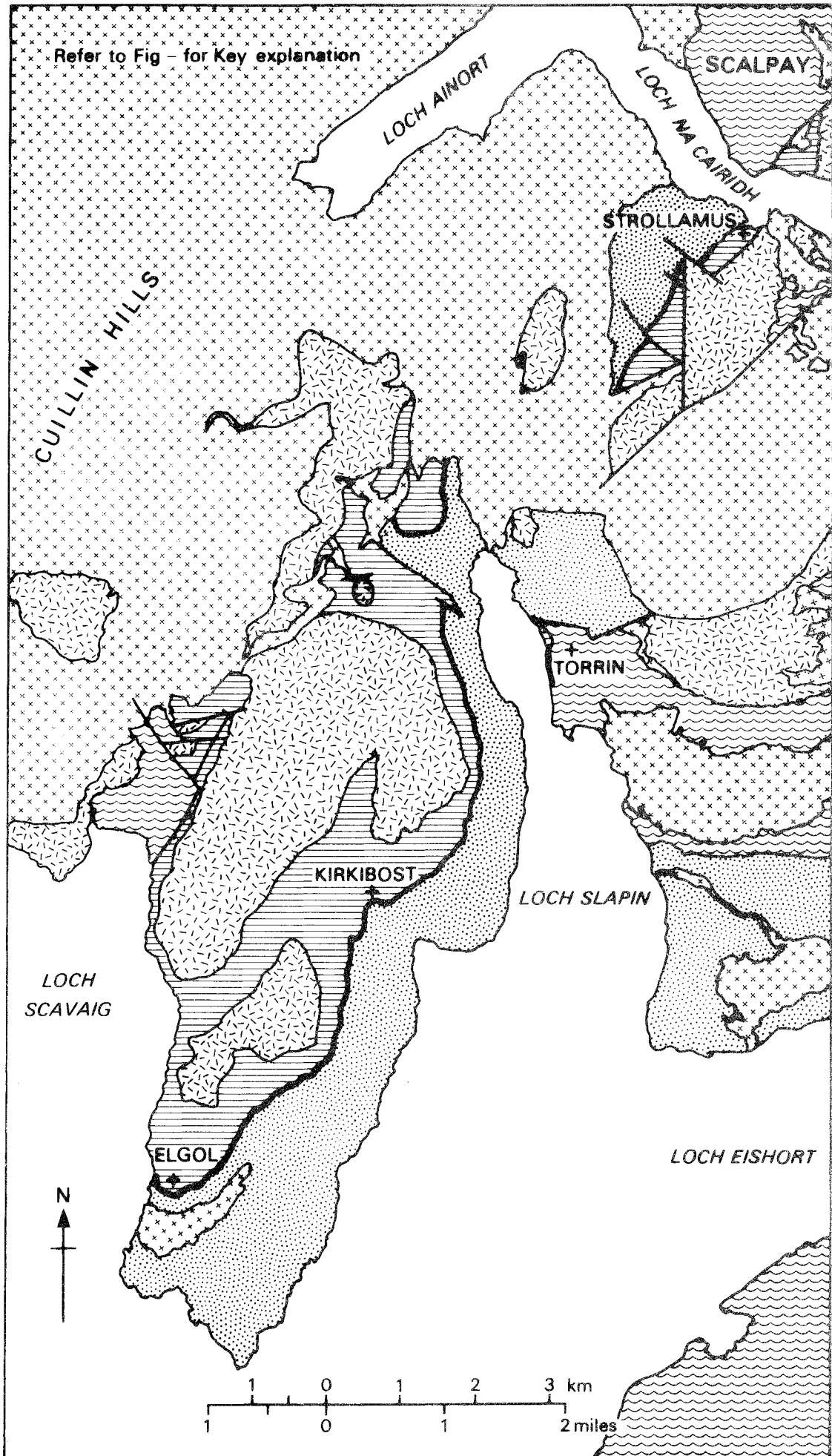


Figure 59 Geological sketch map - Strollamus to Elgol

(KOS 934 to 938) and Fiurnean (KOS 939 and 942) gave potential oil yields of 3.1 to 6.8 and 7.6 to 8.0 wt/wt% respectively. Those from the Elgol-Kirkibost area (KOS 940, 941, 943 and 944) gave no yield. Even the organic carbon contents of the last named samples are low ($< 3\%$) and it is no longer possible to state with certainty that they were ever oil shales.

The Dun Caan and Fiurnean results are broadly comparable to those obtained by Steuart (1913) and Conacher (1917) and suggest that the bulk of the Dun Caan Oil Shale has a potential oil yield of between 10 and 20 gals/ton. All the samples analysed in the present work were cleaned before analysis and there is no evidence to support the suggestion by Steuart (op. cit.) that unweathered material would give greater yields.

According to Hudson (1963, p. 338) the marine Garantiana Clay passes up into the less saline, organic-rich deposits of the Dun Caan Oil Shale. This passage is accompanied by a change from an ammonite fauna to a low diversity fauna of bivalves, ostracods, gastropods and fish scales indicative of poorly aerated bottom conditions. The presence of Isocrinus in the lower part of the oil shale in Raasay (Forsyth, 1960) testifies to marine influence at this level and the depositional environment of the shale seems to have been a variable salinity lagoon. One might, therefore, expect lateral variations to occur in the organic content of the oil shale over relatively short distances due to these lateral changes in salinity.

The Dun Caan Oil Shale is a single, medium quality seam that is much thicker than any other British oil shale except for the thickest of the Lothian seams. No attempt has been made to work it because of the moderate yield and a number of unfavourable circumstances, notably the complexity of the tectonic structure, local baking of the shale and the remoteness of the outcrops. Unmetamorphosed and unfaulted oil shale is restricted to two relatively small areas at Dun Caan, Raasay and Fiurnean, Skye. Even in these areas it is unlikely that the oil shale remains thermally unaltered for any great distance down dip since intrusive dolerites and granophyres occur close to both outcrops.

7.6 BRORA OIL SHALE

On the east coast of Scotland, in Sutherland, the Great Estuarine Series again contains organic-rich sediments laid down in near-shore lagoonal or freshwater swamp environments (Fig. 30). The most famous single bed is the Brora Coal, up to 1 metre thick, that was worked sporadically on a small scale from the 16th to 20th centuries. The coal has been described (Lee, 1920) as resting on a pyritic 'parrot' coal (oil shale), up to 13 cm thick, which in turn rests on 'bituminous shales' variously measured as 1.8 to 7.9 m thick. Heddle (1901, p. 183) quotes the 'Brora Shale' as yielding 20.3% wt/wt gas on retorting and Conacher (1917, p. 188) states that a yield of 32 gal/ton of oil of specific gravity 0.924 had been obtained but that tests at Broxburn had shown the shale to be worthless.

Brora coal mine is now closed and the Brora Coal is no longer exposed, either in the vicinity of the mine or on the foreshore at Brora where it has been worked out. However, the roof bed of the coal is well exposed on the foreshore and the former position of the seam can be clearly made out. The underlying 2 m of beds consist of very shaley detrital coal passing down into thinly interbedded oil shales, shaley coals and smooth textured grey mudstones.

IFP/Rock Eval analyses of samples of the oil shale (KOS 905 and 924) gave potential oil yields of 4.6 and 9.4 wt/wt%. A sample of organic-rich mudstone (KOS 923) gave 2.8 wt/wt%. The oil shales represent only a small part of the sequence and the beds as a whole would probably have a very low yield (< 5 gal/ton). They are of no interest as an artificial source of oil even if worked as a byproduct of any new coal mining unless, immediately adjacent to the coal seam, the oil shale is thicker and substantially richer than that which can be observed at outcrop at the present time.

7.7 OXFORD CLAY

The organic-rich mudstones of the Lower Oxford Clay have low potential oil yields and are of no interest as a source of shale oil. They are, however, of considerable commercial interest since they provide the calorific value on which the Fletton brickmaking process is based, a process that accounts for nearly 50% of U. K. brick production.

The Oxford Clay crops out as low ground stretching from the Dorset coast to North Yorkshire in a broad belt lying a few kilometres to a few tens of kilometres west of the Kimmeridge Clay outcrop. The brickworks are concentrated in the area between Oxford and Peterborough where the structure is uncomplicated and the formation dips very gently eastwards. The Lower Oxford Clay, from 14 to 23 m thick, is made up of small-scale alternations of organic-rich and calcium-carbonate-rich mudstones (Duff, 1975) that make up rhythms similar to those of the organic-rich parts of the Kimmeridge Clay (cf type B of Fig. 4). The whole of this sequence is worked and is ground and mixed to provide a uniform feed for a semi-dry brickmaking process (Horrell, 1978). The shrinkage and fired properties of the mixture depend mainly on its calcite content (Freeman, 1956) and the calorific (fuel-saving) value of the organic content. According to Duff (1972) this latter averages 5 wt% and gives rise to a calorific value of 200 to 900 cal/gm. When heated to 400 to 500° C the brickmaking mixture becomes 'self-firing' and the temperature rapidly rises to 1000° C. At this level the temperature is checked by the introduction of cold air and is then maintained at 900° C for about 35 hours to remove any residual carbon and to produce a strong, well vitrified brick (Horrell, op. cit.).

In 1978 brickworks based on the Oxford Clay and using the Fletton process were capable, at full production, of making about 75×10^6 bricks per week from about 3.6×10^5 tons of clay. The fuel saving that can be attributed in this process to the 'oil shales' is difficult to

estimate because of regional and stratigraphical variations in the organic content of the Oxford Clay and because of variation in the efficiency of brick kilns. In comparison with that using a non-organic clay feed the Fletton process probably saves more than a million tons of coal equivalent per annum.

7.8 CONCLUSIONS

With the possible exception of the Lothians oil shales none of the oil shales discussed in this section is ever likely to be used as a petrochemical or shale oil source.

The weak oil shales of the Lower Oxford Clay make an important energy contribution in the manufacture of bricks by the Fletton process.

8. Conclusions and recommendations

8.1 CONCLUSIONS

There is no single, simple definition of what constitutes a workable oil shale deposit. The relative importance of the various economic, political and environmental factors involved has varied from country to country and with time. Oil shale with yields ranging from 10 to 120 gal/ton and seam thicknesses from 1 to over 100 m have been worked in the past, the thinner (< 3 m thick) seams generally having yields of 20 or more gal/ton (Section 1.1).

Seams of oil shale occur throughout much of the English outcrop and subcrop of the Kimmeridge Clay. They are confined to the stratigraphical range mutabilis Zone to rotunda Zone, the greatest concentrations of seams occurring in the euxoxus, elegans, wheatleyensis and pectinatus zones. The seams are numerous (more than 100 present in some sections), but thin (mostly < 20 cm). The greatest concentration of oil shale seams recorded to date occurs in the sequence at Kimmeridge Bay, Dorset; the most persistent groups of closely spaced, thick seams occur in the Upper eudoxus and wheatleyensis Bands. Oil shales are only weakly developed close to the western edge of the London Platform between north Wiltshire and Buckinghamshire and in the thickest part of the North Yorkshire sequence. They are not developed in the Scottish land area. (Section 2.)

The potential oil yields of the Kimmeridge Clay oil shales range from 10 to 85 US gal/US ton but are mostly in the range 20 to 55 US gal/US ton. Local variations occur within individual seams but the overall yield of any particular seam is likely to be relatively constant over large areas. Concentrations of seams more than 2 m thick and with potential yields of more than 10 gal/ton overall occur in Dorset, Wiltshire and Norfolk. The best prospect, at Kimmeridge, Dorset consists of 8 m of strata with an average yield of 13.7 US gal/US ton. The same section includes an 11.5 m run of strata with an average yield of 12.1 US gal/US ton (Section 3).

Shale oils derived from the Kimmeridge Clay by pyrolysis at 500°C are markedly different in their physical and chemical properties from naturally occurring crude oils. The shale oils are poor in hydrocarbons and rich in resenes, asphaltenes and sulphur and are similar to the heavy oils and natural asphalts of tar sands and mineral veins. The shale oils would need to be upgraded, for example by thermal cracking and catalytic hydrogenation, to provide a refinery or petrochemical feedstock: the technology already exists to do this.

Pyrolysis of the oil shales to produce shale oil, and their direct burning as a fuel, produces sulphurous gases and large volumes of spent shale. The shale oils, spent shale and the aqueous distillate from pyrolysis or burning may contain low concentrations of biologically active compounds including carcinogens. In a densely populated and intensely utilized country such as Britain the environmental problems of opencast, underground mining or in situ retorting are greater than in most countries where an oil shale industry has been established or contemplated (Section 4).

The Kimmeridge Clay oil shales do not contain any trace element that would be a valuable by-product. Sulphur or sulphur compounds (e.g. ammonium sulphate) could be produced when the high sulphur content of the shale oil was reduced during upgrading. Mixtures of Kimmeridge Clay oil shale and mudstone could be used in a self-firing process, such as the Fletton brickmaking process, to manufacture structural clay products providing the correct mixture was selected to provide the necessary combination of calorific value and optimum clay handling and firing properties (Section 5).

The kerogens and bitumens extracted from Kimmeridge Clay oil shales show them to be thermally immature. Their present depth of burial is such that they are probably not currently producing petroleum anywhere in the British land area. They may have been oil-source rocks in the past when their depth of burial was greater (e.g. early Tertiary times) in the Weald, south Dorset and North Yorkshire, but only on a small scale. Comparison of the chemical composition of bitumens from the Kimmeridge Clay shows them to be markedly dissimilar from those of several North Sea oils of supposed Kimmeridgian origin. With artificial thermal maturation the bitumens can be transformed into oils which more closely resemble the North Sea crudes and thereby support the North Sea oil/source rock correlations and also reaffirm the immaturity of the land area Kimmeridge Clay (Section 6).

The only oil shales in Britain that are ever likely to be of interest as a source of shale oil or as a fuel are those in the Kimmeridge Clay and the Scottish Carboniferous (Lothians) (Section 7).

Oil shales could never, even under the most favourable economic circumstances, make a major contribution to the energy supply of the United Kingdom. The Lothian oil shales could probably yield about 7 million tons of shale oil and the Kimmeridge Clay oil shales several times that amount, but only over a long period of time and in workings carried out on a large scale. At the level of the richest seams in the Kimmeridge Clay, if allowance is made for overburden thickness and the inefficiency of retorting, over 50 tons of oil shale/mudstone mixture would probably have to be won for every ton of oil yield.

Oil shale could however form the energy-saving basis for local structural clay product or cement industries and might, under certain circumstances produce oil for

refinery or petrochemical feedstock. Whether or not these circumstances ever come about will depend largely upon the cost and availability of other fuels and the degree to which oil-shale winning and retorting techniques are improved.

8.2 RECOMMENDATIONS

Research into methods of oil shale utilisation is expensive and would not be justified in Britain in view of the small potential of the oil shale resources. Research has reached an advanced stage in several other countries, notably the U. S. A. , where large-scale pilot plants have been run successfully. The first commercial-scale in situ oil shale retorting plant is currently under construction in Colorado where it is proposed to work a seam that is about three times as thick, and twice as rich in potential oil yield, as the best group of seams in Dorset. If this venture is successful, thinner and poorer seams are likely to be worked in the future.

Research is also in hand, notably in the fields of fluidised combustion and electronic separation, in Britain and abroad to try to make use of low grade fuels.

Research into various aspects of oil shale chemistry, including diagenesis, oil/source rock correlations, detection of biological marker compounds, origin of shales etc. is being carried out at Bristol, Leeds and Newcastle universities on samples of Kimmeridge Clay oil shales provided by IGS: the U. S. Department of Energy, Laramie Research Center has expressed an interest in examining aspects of general interest in the same oil shales.

In view of these commercial and academic activities it would be advisable for the Department of Energy to maintain a watching brief on oil shale research in order to be able to make informed decisions as to the possible use of oil shales in the future.

A large amount of unpublished research has also been carried out by commercial companies into geochemical aspects of the Kimmeridge Clay of the U. K. continental shelf area with particular respect to its source-rock potential. Much of this data could probably be made available to the Department of Energy and IGS on a confidential basis, but it would have little value in its uninterpreted form. The Department and IGS should therefore consider the possibility of establishing an organic geochemistry unit designed specifically to collate and interpret this data, and to carry out such related research as would be necessary to enhance the data and its interpretation, in order to provide the Department with impartial expert advice on the geochemical aspects of oil exploration in the U. K.

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