A Petroleum Source Rock Study of a Kimmeridgian Section in Dorsetshire, England.

by

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....."Truth is the source of peace and power. It should be the aim of all men....." P. Bessell. MP 1977.

Especially when a student follows an interdisciplinary subject he circulates amongst a particularly large number of people of diverse backgrounds and positions.

Over the course of three years, innumerable small favours and acts of kindness inevitably and wrongly become blurred by the failings of memory and usually only people instrumental in a large or more time consuming piece of work remain very obvious; often in the capacity of everyday companions. Nevertheless it is emphasised here that all people from academic and professional circles who dispensed with seemingly trivial problems at moments in the past do rank equal in having enhanced my progress through college life.

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In retrospect, provocative argument is sometimes beneficial as a source of new inspiration; often stimulating increased determination. Defiance to accord with convention is by no means unique and not surprisingly fiery associations result; no doubt strangely inexplicable to many ill-informed observers.

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TO MY WIFE

LUDGUARDE CHRISTINE
(nee ZAMMIT-SIZELAND)

and

"W.D. Junior"

ABSTRACT

Organic geochemical data embracing 124 outcrop samples is presented for the type Kimmeridgian (upper Lower and Upper Kimmeridgian Clay Formation) at Horbarrow Bay - Chapman's Pool, Dorsetshire. Such data is also given for 9 Kimmeridge Clay samples and 32 Wealden samples from elsewhere along the southern England coastline. Reference too is made for the results of 14 Oxford Clay samples which were collected during the fieldwork of this study.

The experimental work which covers all, or nearly all, of the Kimmeridgian samples includes optical microscopy (rock thin sections); whole-rock X-ray diffractometry (XRD); gamma-ray radiation counting, solvent extraction (SE); thin layer chromatographic (TLC) extract fractionation; whole-rock and extract quantitative elemental analysis (QEA); qualitative extract (X-ray fluorescence) analysis; total organic carbon assessment and post-pyrolysis 'residual' organic carbon determination together with infra-red (IR) spectroscopic examination of the extracts and their fractions.

On a selective level, capillary gas-liquid chromatographic (CGLC) analysis of the saturate extract fractions; ultra-violet (UV) and fluorescence emission (FES) spectroscopic studies of the aromatic extract fractions; maceration with microscopic kerogen description and detailed clay-mineral (XRD) studies are offered.

For all of the 'Neocomian' specimens whole-rock XRD; SE; TLC extract fractionation; extract QEA; IR extract examination and CGLC analysis of the saturate extract fractions are given. Whole-rock QEA and pre- and post-pyrolysis organic carbon analyses are restricted to the Wealden shale facies whilst UV/FES studies are confined to a reduced number of aromatic extract fractions. Reference is also made to petrological studies upon the Wealden oil sands which were collected during the fieldwork of this study.

The experimental techniques, results and interpretations are discussed in the light of modern geochemical advances to allow the conclusion that at outcrop the Dorestshire Kimmeridge Clay is an immature source rock facies. The organic matter is dominantly 'algal' but has been diluted throughout to varying degrees by terrestrial ('humic') matter.

A previously suggested genetic link between the Wealden oil sands and the Kimmeridge Clay is discounted. The oil sands are believed to hold biodegraded (once mature) oil and to have been derived from an exposed tar sand.

Overall, the Wealden Formation contains some parameters atypical of its immature condition which warrant continued study.

Finally, the Oxford Clay along its coastal outcrop is seen to exhibit an immature source rock status but compared to the oil-rich Kimmeridge Clay, any possible offshore potential is restricted in both quality and quantity.

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SECTION ONE

ORGANIC GEOCHEMISTRY

PART ONE

INTRODUCTION

1 ORGANIC GEOCHEMISTRY: SENSUO LATO

The first oil wells were located on direct (organic) geochemical methods merely via their proximity to seepages. (Dow 1977). However, the 'anticlinal theory' shifted the style of exploration to structural studies (Dow 1977) and 'the evaluation of the oil potential of an area normally focused upon the finding of (suitable reservoirs and) traps'(Pusey 1973b). For a long time, therefore, 'organic geochemistry remained as an ancillary subject more of debate than a practical tool' (Dow 1977).

In this respect, Boyle and Garrett (1970) blamed the suppression of organic geochemistry upon the sceptical and ultra-conservative attitude of petroleum geologists and emphasised that it was "high time they took a closer look at what geochemistry has to offer in the way of prospecting for hydrocarbons". They observed that organic geochemistry is fast emerging as a major tool in its own right; imperative for the continued exploration and discovery of petroleum. The ever increasing role that such a tool will play is accentuated when costs reach new heights; particularly offshore and in the polar regions (Bailey et al 1974) and as petroleum in general becomes more difficult to find (Boyle and Garrett 1970; Dow 1977).

During an acclaimed review Cordell (1974) commented that "communication and understanding are difficult between petroleum geologists and organic geochemists". Earlier, Feugere and Gerrard (1970) had insisted that a geochemical inventory of cores and cuttings can provide evidence which favours the abandonment or upgrading of a lease whilst, atabout the same time, Boyle and Garrett (1970) had mentioned a better direction for drilling in many places is consequent from organic geochemical methods. Dow (1974) further specified that activity could be restricted in areas or strata which are isolated from source beds and concentrated in areas most likely to contain petroleum.

More recently, Milner et al (1977) stated that when the oil and gas potential of a new basin is being assessed the petroleum geochemist is an important member of the exploration team. If the proper types of geochemical surveys are conducted with geological and geophysical work (Boyle and Garrett, 1970) the

establishment of "a firm relationship between such parameters makes it possible for the geochemist to ..... predict the type, amount and quality of petroleum that may be pooled" (Milner et al 1977) and give its distribution at an early stage in the exploration (Bailey et al 1974).

Thus, Pusey (1973a) remarked that the "ignorance of the nature of potential source rocks in an area is no longer necessary or excusable". 'Without a critical source rock' he emphasised the absence of commercial production for which Hunt (1976) stated geochemical techniques define the first requirement.
As 'organic geochemistry has provided the key to understanding hydrocarbon occurrences' (Pusey 1973a) "the methods no longer need to be sold since it has now been generally recognised that they are the only direct approach to the problems of ....., oil and natural gas exploration" (Boyle and Garrett 1970).
Therefore, "it is to be hoped that petroleum geologists will take a greater interest in (organic) geochemistry in the future" (Boyle and Garrett 1970) to sustain "the close friendly co-operation between geologists and organic chemists; two groups of scientists whose jargon, methods and thought processes differ considerably" (Albrecht and Ourisson 1971).

2 ORGANIC CHEMISTRY: SENSUO STRICTO

"The past years have seen an unexpected upsurge in the investigation of organic substances in a wide range of sedimentary rocks, fossils and meteorites arising from the original studies by Treibs. This has only become possible through modern analytical methods which allow determinations in the microgram-nanogram range" (Albrecht and Ourisson 1971).

Yet, "although major oil companies have developed techniques of evaluating source rocks and used them for many years, specific methods and results have generally been kept confidential" (Pusey 1973a). Basic research on hydrocarbon geology is therefore needed outside industry even if some duplication occurs since freedom of publication can be exercised (NERC 1973).

However, 'the complexity and comparative instability of organic matter in sediments can lead to problems in their study' (Hobson 1966) and Degens in 1964 apparently reported as many as 500 different compounds were recognised from organic matter (Feugere and Gerrard 1970).

More recently Schmidt-Collerus et al (1976) confirmed that ..... "an extensive literature survey showed that frequently what appears to work well for simple synthetic mixtures of pure standard compounds was difficult to translate to complex extracts ....". Infact, "the inherent difficulties in applying analytical methods of organic chemistry to natural carbonaceous materials often demand a major research of their own" (Baker 1965) and consquently "organic geochemical procedures are diverse, sophisticated, tedious and generally costly in terms of equipment and manpower" (Baker 1972).

Not surprisingly therefore many workers have endeavoured to search for "criteria unquestionably characterising either the nature of organic matter or its evolutionary state" (Vandenbroucke et al 1976). In the extreme and particularly with regard to efficiency and economy, the least number of variables capable of best characterising a source rock have been sought (Feugere and Gerrard 1970).

However, it is obviously more safe and scientific to document as many parameters as possible and assess the results in conjunction with one another. No one single parameter can offer the answers

required in oil exploration geochemistry and where a large number are considered, any abnormality (which must occasionally arise for every specific technique) will manifest itself and can be avoided (Spears priv.comm. 1977).

Specifically for analytical techniques, contamination can be checked by control experiments. For example, Eglinton et al (1964) used rose quartz chips to test an ultrasonic extraction technique and attributed alkanes of the order of 10 microgrammes per kilogramme of rock (i.e.1 ppb) to contamination introduced during milling whilst later Eglinton (1968) observed that the possibility of contamination is increased as the weight of extract is decreased.

Unfortunately, though, as no suitable standards are available with which to referee procedures and since the preparation of a synthetic standard representative of natural sediments is out of the question, it is not possible to determine the accuracy of results of any procedure for sediment hydrocarbon determination (Ferguson 1962). Yet, Degens and Reuter (1964) commented that "in view of the magnitude and nature of internal variation that usually exists within a rock specimen, an analytical precision of $\pm$ 10-20% can be considered satisfactory for most problems encountered in organic geochemistry" and "when a sensitivity of 1-2% is desirable it can easily be achieved by a modification of the procedure" ..... but ....."unfortunately increased sensitivity means greater effort and time and the output of analyses appreciably declines". Earlier, Baker (1962) had expressed his analytical error according to Fig. 4.

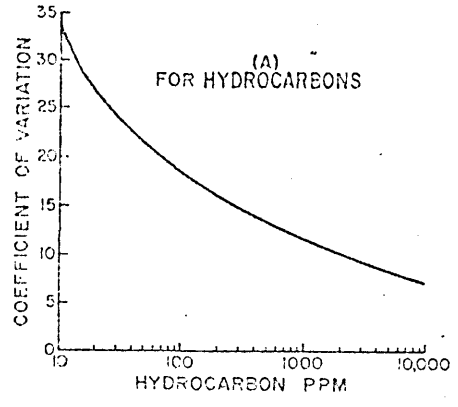


FIG 4 ANALYTICAL ERROR IN SOLVENT EXTRACTION; the standard deviation is expressed as a percentage of the mean of the parameter measured. (Baker,1962)

3 THIS STUDY

Although the precise identification of complex carbon compounds is best achieved with expensive combined GLC-MS-Computer studies (NERC 1973; Albrecht et al 1976), necessary and valuable groundwork can be completed on a limited educational budget. In this latter respect, a programme can be devised to allow direct comparison of a large number of samples over a realistic period of time where the limits and disadvantages can be found qualitatively. A degree of quantification can also be achieved by minimising analytical errors and reproducing such errors consistently (Gill et al Unpub.).

Since "broad surveys of the nature and distribution of organic constituents in ..... ancient sediments ..... are important in applied geochemistry" (NERC 1973) and in view of the foregoing, this study furnishes organic geochemical parameters necessary for the characterisation of a Kimmeridgian interval; hitherto maintained as an example of a 'classic' petroleum source rock (Sellwood verb. comm. 1971). Data is also included, with interpretation, for approximately thirty Wealden samples amongst which documentation of the 'novel' oil seepages is featured for the first time since their discovery during the late 1930's (Lees and Cox 1937; Lees and Taitt 1945).

Often in the case of research the aim of study can change with the course of time. Here fieldwork was initially executed with the original purpose of sampling the entire Rhaetic-Upper Greensand section of the Wessex Basin coastal succession, and actually terminated with coverage between Sidmouth and St. Alban's Head. Only in the field did it become blatantly apparent that in moving in an easterly (~~up~~~~dip~~) direction, the first significantly thick and uninterrupted shale section affording relatively easy access and accurate fresh sampling was the (upper Lower and Upper) Kimmeridge Clay at its type locality between Horbarrow Bay and Chapman's Pool.

Interest in this section of the overall Mesozoic succession is specifically warranted as it provides a readily examinable lateral equivalent of the postulated source of many northern North Sea Mid-Jurassic plays (see Fuller 1975 ; Hallam 1975, Selley 1977).

Also, since the Wealden oil sands follow earlier Portlandian Kimmeridgian and older strata and as all are cut by the classic Cretaceous angular unconformity, it has been hinted that the source of their oil could be the Kimmeridge Clay. The Sussex natural gas discoveries too have been attributed to possible sources which included the Kimmeridge Clay (Lees and Cox 1937; pp. 175 and 167 respectively). Finally, the Kimmeridge Clay Formation contains renown oil shales, which, with those from the Upper Calciferous Sandstones of the Carboniferous in south-east Scotland form the two principal oil shale groups of the United Kingdom (Macleod-Mathews 1975).

Now, Philippi in 1969 is usually credited with the first documentation of an oil source rock (from the Los Angeles Basin) (Collins 1975). As Degens and Reuter gave a "survey on analytical techniques for the extraction and identification of the principal constituents incorporated in sediments and natural waters" in 1964 this presentation does allow an opportunity to provide a more 'up to date' (hopefully equally self-critical as well as critical) review of organic geochemical techniques and interpretations.

In fact, both technique and interpretation are discussed as concisely as possible in their relevant context to petroleum exploration where data tabulation and schematic summaries are favoured to minimise the volume of the thesis confronting the reader.

4 ORGANIC MATTER, SEDIMENTS AND PETROLEUM

Organic matter within sediments can now be sensibly regarded as the source of commercial quantities of petroleum. The broad derivation, incorporation and ultimate fate of organic matter in sediments is outlined schematically in Fig. I (loose) and an elaboration of a chemical classification of organic matter relevant to petroleum geology is given in Fig. 2. (Loose).

Although abiogenic syntheses from meteoric, volcanic and chemical processes undoubtedly exist, despite the occasional advocate (e.g. Porife'v 1974), they admittedly make no real significant impression upon the genesis and distribution of petroleum. It is now appreciated that at least 99% of all petroleum is found in sedimentary rocks (Knebel and Rodriguez-Eraso 1956) and Hunt (1976) has generalised the estimated distribution of organic carbon within the lithosphere (Table IA). The figures are in accordance with the earlier views of Degens and Reuter (1964) who observed that sediments appear to be the "principal collectors of posthumous organic debris".

In fact, Levorsen (1954) has noted that it was Lesquereaux in 1866 who first stated petroleum was organic in origin. More recently evidence to support the organic origin of petroleum has embraced optical activity, carbon isotope ratios, porphyrins, biological markers (Hunt 1976) and optical microscopy (Sanders 1937). Now although oil globules have been found in the primary vesicles of a dolerite dyke; pristane phytane and porphyrins have been found in carbonaceous meteorites; porphyrins have been produced abiogenically and optically active compounds have been synthesised from inactive ones, such atypical exceptions can be discounted with regard to the generation of commercial quantities of crudes.

TABLE 1A. DISTRIBUTION OF ORGANIC CARBON IN THE LITHOSPHERE.

	$\times 10^{18}$ grams.	Approx. Relative Percentage.	
IGNEOUS ROCKS:	3,500	18.4%	
METAMORPHIC ROCKS:	3,500	18.4%	
SEDIMENTARY ROCKS:	12,000	63.2%	(Hunt, 1976)

TABLE 1B. DISTRIBUTION OF ORGANIC CARBON IN SEDIMENTARY ROCKS.

	$\times 10^{18}$ grams.	Approx. Relative Percentage.	Ratio.
CLAYSTONES & SHALES:	8,900	74.2%	6.9
CARBONATES:	1,800	15.0%	1.4
SANDSTONES:	1,300	10.8%	1.0

(Hunt, 1976)

5 SOURCE ROCK CONCEPT

The generalised study of pooled petroleum now invites the well accepted explanation via such basic requirements as a source, reservoir, trap and seal (cap rock) and involves the theory of (primary and secondary) migration.

The first criterion, a source rock, was apparently introduced by Winchell in 1865 (Allen. verb. comm. 1972) and arose from the belief that petroleum was not indigenous to the rock in which it was found but migrated into it. (Incidentally, through organic geochemcial studies it is now possible in some cases to actually prove migration. Barker, 1974). In fact, Bray and Evans (1961) defined a source rock as "a rock in which oil and gas have been generated" by quoting from the API (1957) Glossary.

Typically, reservoir lithologies are generally devoid of large concentrations of original organic matter and incapable of generating their own petroleum (see later). Gill (1962) observed that "there are many examples of relatively small reservoirs of sand and limestone in which the pore spaces are almost completely oil saturated" and "it is inconceivable that such rocks should have produced the oil themselves". In this respect, Palacas et al (1972) appear to have documented an exceptionally rich recent sandstone and coarse clastics contrary to their view, seem inappropriate as source rock candidates. Thus, shales are the prime choice for petroleum sources and there are many good reasons to support such a view.

Unquestionably shales harbour the vast majority of organic matter which is assigned to the sedimentary environment. Degens and Reuter (1964) noted that an overwhelming part of the organic matter trapped in sediments (3.8×10^{15} metric tons) occurs in shales (3.6×10^{15} metric tons) and suggests 95% of organic matter is preferentially held in fine grain clastics. Klemme (1972) insisted that as shales were amongst the richest sedimentary material in organic matter, they act as the source rock for hydrocarbons. The distribution of organic carbon within sedimentary rocks has been given by Hunt (1976) and in fact a more general distribution of organic carbon amongst various lithologies was expressed as well (Tables IB and 2 respectively).

A general ratio for the relative amounts of organic matter within such lithologic types as sandstones, siltstones and shales has been given as 1:2:4 by Hobson (verb. comm. 1972) whilst more recently Hunt (1976) similarly specified 1.79:2.08:6.50 for siltstones, clays (2-4μ) and clays (<2μ). Such variations have been explained by Hobson (verb. comm. 1972) who emphasised that organic particles are light, sink slowly and therefore tend to concentrate with fine grain sediments; particularly those deposited in quiet waters. Likewise, Bordovsky's (1965) opinion that, given sufficient time, organic matter will concentrate, coagulate and precipitate has been noted by Dunn (1972). Although clay minerals themselves may be able to absorb and extract organic matter from suspension (Grim 1947 in Johns and Shimoyama 1972) Dunn (1972) advocated that owing to variation in grain size and shape, clays may not show a significant correlation between their elements and organic matter.

Madani (pers comm. 1977) has cited Moore from 1969 in observing that the oxidation-reduction conditions are very important and Milner et al (1977) recalled Erdman, from 1975, in stressing that the redox potential of the depositional environment largely controls the preservation of organic matter. Generally it is accepted that shallow neritic high energy environments provoke strongly oxidising conditions in contrast to quiet intermediate-deep marine low energy depositional environments; the latter of which encourage poorly aerated waters and thus enhance the possibility of reducing conditions from within a short distance of the sediment-water interface.

Also, although carbonates, from time to time, win support for the view that they can function as a source (Knebeland Rodriguez-Eraso 1956; Gehman 1962; Halbouty et al 1970; Cordell 1972; Allen 1973) Cordell (1972) himself noted that they can lose up to 75% of their original organic matter due to recrystallisation-hydrolysis processes whilst clays, through compaction and hydrolysis, lose only 5-10%.

Hence, shales are advantageous with regard to both the accumulation and preservation of organic matter. Specifically, shallow marine shales have been found to show consistently lower organic carbon values than deeper water bathyal and abyssal shales regardless of

age (Dow and Pearson in Dow 1977). In consequence, Long et al (1962) concluded that "the analysis of clay sediments also seems promising for locating the oil source beds because the organic matter is concentrated mainly in the fine sediments" and Collins (1975) has mentioned that commercial accumulations are generally associated with (marine) shales (or organic rich fine grain limestones).

Further, "one reason for believing that shales and marls are a substantial source of petroleum is that they constitute in the geological succession the only element which has suffered volume shrinkage and has given up fluids" (Gill, 1962) thus providing a possible medium of transport for any generated hydrocarbons (Powell et al 1975 and Ishiwatari et al 1977; both after Burst, 1969). In this context, Weaver (1960 in Long et al 1962) noted some relationship existed between hydrocarbon production and expanded clay minerals (montmorillonite, mixed layer illite-montmorillonite and chlorite-montmorillonite); mentioning that the latter contain up to 10 times as much water as non-expanded clays (kaolinite, chlorite and illite). However, Palacas et al (1972) have qualified Erdman (1963) by concluding that the actual mechanism for hydrocarbon expulsion from shales is still conjectural.

Finally, the attributes of different source rock types under different conditions of burial are reproduced in Table 3 and it can now be held that shales are the agreed source for (commercial quantities of) petroleum. Although the physical and chemical properties of such shales are not very well defined, Fuller (1975) has been more exact in one aspect for a functioning source rock. Effective beds have been reported to generate an average 35 barrels of oil per acre foot for every 1% of organic carbon which they contain.

TABLE 2. DISTRIBUTION OF ORGANIC CARBON IN DIFFERENT LITHOLOGIES.

	% Organic Matter.		% Organic Matter.
SANDSTONE:	0.04	LIMESTONE:	0.56
RED SHALE:	0.05	GREY SHALE:	1.50
GREEN SHALE:	0.13	BLACK SHALE:	5.40
DOLOMITE:	0.25	CALCAREOUS SHALE:	7.90

(Hunt, 1976)

TABLE 3 SUMMARY ATTRIBUTES OF DIFFERENT SOURCE ROCK TYPES UNDER DIFFERENT BURIAL CONDITIONS (Cordell, 1972)

Summary Attributes of Carbonate Source-Type Sediments under Shallow Burial

ORGANIC FRACTION		MINERAL FRACTION		SEDIMENT FLUIDS	
CHARACTERISTIC	CONSEQUENCE	CHARACTERISTIC	CONSEQUENCE	CHARACTERISTIC	CONSEQUENCE
1. LOW TEMPERATURE, LOW OVERBURDEN PRESSURE.	a. THERMOCATALYTIC ACTIVITY FOR BREAKDOWN OF KEROGEN WEAK OR ABSENT	1. LOW TEMPERATURE, LOW OVERBURDEN PRESSURE	a. LITTLE OR NO MINERAL CATALYTIC ACTIVITY b. COMPACTION WEAK	1. LOW TEMPERATURE, LOW OVERBURDEN PRESSURE	a. PRESSURE SOLUTION ACTIVITY SLIGHT b. ORGANIC SOLUTION ACTIVITY SLIGHT
2. SPARSE BITUMEN	a. VERY LIMITED AND DILUTE SOURCE OF HYDROCARBONS b. SUSCEPTIBILITY TO ADSORPTION	2. LARGELY CARBONATES	a. WEAK ADSORPTION OF ORGANIC MATTER b. MOST INTERSTITIAL WATER LOST VERY EARLY c. SOME VERY EARLY CEMENTATION AND CRYSTALLIZATION d. CATALYTIC ACTIVITY WEAK OR ABSENT	2. LIMITED ORIGINAL AND SECONDARY PORE WATER	a. LIMITED WATER VOLUME FOR TRANSPORT OF BITUMEN AND HYDROCARBONS
3. VERY SPARSE LIQUID HYDROCARBONS	a. VERY DILUTE DISSEMINATION OF LIQUID HYDROCARBONS b. SUSCEPTIBILITY TO ADSORPTION c. LIMITED CONTACTS WITH INTERSTITIAL FLUIDS	3. WEAK ADSORPTION OF ORGANIC MATTER	a. WEAK ADSORPTION OF BITUMEN AND HYDROCARBONS	3. HIGH ALKALINE EARTH CONTENT	a. COLLOIDAL MIGRATION UNLIKELY
4. FAIRLY ABUNDANT KEROGEN	a. OLEOPHILIC TENCENCY b. IMMOBILIZATION OF BITUMEN AND HYDROCARBONS	4. MOST INTERSTITIAL WATER LOST VERY EARLY	a. WATER FOR PRIMARY MIGRATION RATHER LIMITED	4. LOW ORGANIC CONTENT	a. LITTLE CONCENTRATION OF HYDROCARBONS
		5. SOME VERY EARLY CEMENTATION AND CRYSTALLIZATION	a. COMPACTION RELATIVELY INEFFECTIVE b. ADDITIONAL LOSS OF WATER		
		6. CATALYTIC ACTIVITY WEAK OR ABSENT	a. LITTLE OR NO FORMATION OF BITUMEN AND HYDROCARBONS		

Summary Attributes of Carbonate Source-Type Sediments under Intermediate-Depth or Deeper Burial

ORGANIC FRACTION		MINERAL FRACTION		SEDIMENT FLUIDS	
CHARACTERISTIC	CONSEQUENCE	CHARACTERISTIC	CONSEQUENCE	CHARACTERISTIC	CONSEQUENCE
1. DOWNWARDLY INCREASING TEMPERATURE AND PRESSURE	a. RELATIVELY LARGE AMOUNTS OF BITUMEN, LIQUID HYDROCARBONS, AND GASES FORMED FROM KEROGEN b. KINETIC ENERGY INCREASED	1. DOWNWARDLY INCREASING TEMPERATURE AND PRESSURE	a. EXTENSIVE CEMENTATION AND CRYSTALLIZATION OF CARBONATE b. PRESSURE-SOLUTION ACTIVITY, STYLOLITE FORMATION c. FRACTURE FORMATION	1. DOWNWARDLY INCREASING TEMPERATURE AND PRESSURE	a. SOME INCREASE IN SOLUBILITY OF LIQUID HYDROCARBONS IN WATER b. MUCH INCREASED SOLUBILITY OF LIQUID HYDROCARBONS IN GAS AND GAS IN WATER c. INCREASED PRESSURE ON FLUIDS d. PRESSURE-SOLUTION ACTIVITY
2. ADEQUATE AMOUNTS OF BITUMEN	a. ADEQUATE AMOUNTS OF HYDROCARBON PRECURSORS b. ADEQUATELY CONCENTRATED SOURCE OF HYDROCARBONS c. LESS SUSCEPTIBILITY TO ADSORPTION	2. EXTENSIVE CEMENTATION AND CRYSTALLIZATION OF CARBONATE	a. INCREASED PRESSURE ON FLUIDS b. FLUIDS FORCED TOWARD LARGER PORE SYSTEMS	2. MODERATELY HIGH ORGANIC CONTENT ESPECIALLY RELATED TO GASES	a. BASIS FOR HYDROCARBON TRANSFER TO RESERVOIRS
3. ADEQUATE AMOUNTS OF LIQUID HYDROCARBONS	a. ADEQUATE AMOUNTS OF DISSEMINATED "MICRO-OIL" b. LESS SUSCEPTIBILITY TO ADSORPTION	3. STYLOLITE FORMATION	a. FLUIDS FORCED TOWARD CARBONATE RESERVOIRS	3. INCREASED PRESSURE ON FLUIDS	a. OIL-IN-GAS SOLUTION ENHANCED
4. LARGE AMOUNTS OF GAS	a. AVAILABILITY FOR OIL-IN-GAS MIGRATION	4. FRACTURE FORMATION	a. FLUIDS CHANNELED TOWARD CARBONATE RESERVOIRS	4. PRESSURE SOLUTION ACTIVITY	a. FLUIDS FORCED TOWARD CARBONATE RESERVOIRS
5. INCREASED KINETIC ENERGY	a. LESS SUSCEPTIBILITY TO ADSORPTION b. AVAILABILITY TO MIGRATING FLUIDS				

Summary Attributes of Terrigenous Source-Type Sediments under Shallow Burial

ORGANIC FRACTION		MINERAL FRACTION		SEDIMENT FLUIDS	
CHARACTERISTIC	CONSEQUENCE	CHARACTERISTIC	CONSEQUENCE	CHARACTERISTIC	CONSEQUENCE
1. LOW TEMPERATURE, LOW OVERBURDEN PRESSURE	a. THERMOCATALYTIC ACTIVITY FOR BREAKDOWN OF KEROGEN WEAK OR ABSENT	1. LOW TEMPERATURE, LOW OVERBURDEN PRESSURE	a. MINERAL CATALYTIC ACTIVITY FOR REDUCTION OF ORGANIC MATTER WEAK OR ABSENT b. COMPACTION WEAK	1. LOW TEMPERATURE, LOW OVERBURDEN PRESSURE	a. ORGANIC SOLUTION ACTIVITY SLIGHT
2. SPARSE BITUMEN	c. VERY LIMITED AND DILUTE SOURCE OF HYDROCARBONS b. SUSCEPTIBILITY TO ADSORPTION	2. ABUNDANT CLAYS	a. MUCH ADSORPTION OF ORGANIC MATTER b. TENDENCY TO RETAIN CONSIDERABLE PORE WATER c. PRESENCE OF THICK VISCOUS WATER LAYERS AROUND SEDIMENT PARTICLES AND BETWEEN CLAY MINERAL LAYERS	2. ABUNDANT PORE WATER	a. ABUNDANT HIGHLY MOBILE WATER b. DELAY OF CATALYTIC ACTIVITY FOR BREAKDOWN OF KEROGEN
3. VERY SPARSE LIQUID HYDROCARBONS	a. VERY DILUTE DISSEMINATION OF LIQUID HYDROCARBONS b. SUSCEPTIBILITY TO ADSORPTION c. LIMITED CONTACTS WITH INTERSTITIAL FLUIDS	3. MUCH ADSORPTION OF ORGANIC MATTER	a. IMMOBILIZATION OF BITUMENS AND HYDROCARBONS	3. ABUNDANT HIGHLY MOBILE WATER	a. RELATIVELY RAPID EXPRESSION OF WATER FROM MUDS DURING EARLY COMPACTION b. MUCH LOSS OF WATER BY ESCAPE TO THE SURFACE
4. VERY ABUNDANT KEROGEN	a. OLEOPHILIC TENDENCY b. IMMOBILIZATION OF BITUMEN AND HYDROCARBONS	4. TENDENCY TO RETAIN CONSIDERABLE PORE WATER	a. DELAY OF CATALYTIC ACTION FOR BREAKDOWN OF KEROGEN	4. DELAY OF CATALYTIC ACTIVITY FOR BREAKDOWN OF KEROGEN	a. LITTLE FORMATION OF BITUMEN AND HYDROCARBONS
		5. PRESENCE OF THICK VISCOUS WATER LAYERS AROUND SEDIMENT PARTICLES AND BETWEEN CLAY MINERAL LAYERS	a. DELAY OF CATALYTIC ACTION b. BARRIER TO MOBILITY OF BITUMEN AND HYDROCARBONS c. COMPACTION INSUFFICIENT TO OVERCOME SURFACE TENSION OF OIL	5. LOW ORGANIC CONTENT	a. LITTLE CONCENTRATION OF HYDROCARBONS

Summary Attributes of Terrigenous Source-Type Sediments under Intermediate-Depth or Deeper Burial

ORGANIC FRACTION		MINERAL FRACTION		SEDIMENT FLUIDS	
CHARACTERISTIC	CONSEQUENCE	CHARACTERISTIC	CONSEQUENCE	CHARACTERISTIC	CONSEQUENCE
1. DOWNWARDLY INCREASING TEMPERATURE AND PRESSURE	a. RELATIVELY LARGE AMOUNTS OF BITUMEN, LIQUID HYDROCARBONS AND GASES FORMED FROM KEROGEN b. KINETIC ENERGY INCREASED	1. DOWNWARDLY INCREASING TEMPERATURE AND PRESSURE	a. DECREASE OF VISCOUS WATER ASSOCIATED WITH CLAYS b. CHEMICAL ACTIVITY GREATLY INCREASED c. COMPACTION WITH GRAINS CONSIDERABLY DEFORMED	1. DOWNWARDLY INCREASING TEMPERATURE AND PRESSURE	a. INCREASED SOLUBILITY OF BITUMEN, LIQUID HYDROCARBONS, AND GASES IN WATER b. INCREASED SOLUBILITY OF LIQUID HYDROCARBONS IN GAS c. OVERBURDEN PRESSURE IMPARTED TO FLUIDS
2. ADEQUATE AMOUNTS OF BITUMEN	a. ADEQUATE AMOUNTS OF HYDROCARBON PRECURSORS b. ADEQUATELY CONCENTRATED SOURCE OF HYDROCARBONS c. LESS SUSCEPTIBILITY TO ADSORPTION d. COLLOID SOURCE FOR MIGRATION	2. DECREASE OF VISCOUS WATER ASSOCIATED WITH CLAYS	a. INCREASED CATALYTIC ACTIVITY b. ADDED SOURCE OF PORE WATER c. MAINTENANCE OF POROSITY d. IMPROVEMENT OF SOURCE BED DRAINAGE e. INCREASED FLUID PRESSURE	2. LOW ALKALINE EARTH CONTENT	a. COLLOIDAL SOLUTION ENHANCED
3. ADEQUATE AMOUNTS OF LIQUID HYDROCARBONS	a. ADEQUATE AMOUNTS OF DISSEMINATED "MICRO-OIL" b. ADEQUATE CONTACT WITH INTERSTITIAL FLUIDS c. LESS SUSCEPTIBILITY TO ADSORPTION	3. CHEMICAL ACTIVITY GREATLY INCREASED	a. THERMOCATALYTIC TRANSFORMATION OF KEROGEN TO BITUMEN AND HYDROCARBONS	3. MODERATELY HIGH ORGANIC CONTENT	a. ADEQUATE AMOUNTS OF BITUMEN-HYDROCARBON MATERIAL TRANSPORTED BY WATER
4. LARGE AMOUNTS OF GAS	a. AVAILABILITY FOR OIL-IN-GAS MIGRATION	4. COMPACTION WITH GRAINS CONSIDERABLY DEFORMED	a. OVERBURDEN PRESSURE IMPARTED TO FLUIDS b. FLUIDS FORCED TOWARD RESERVOIRS	4. OVERBURDEN PRESSURE IMPARTED TO FLUIDS	a. OIL-IN-GAS MIGRATION ENHANCED b. FLUIDS FORCED TOWARD RESERVOIRS
5. INCREASED KINETIC ENERGY	a. LESS SUSCEPTIBILITY TO ADSORPTION b. AVAILABILITY TO MIGRATING FLUIDS				

6 HYDROCARBON GENERATION

Since Engler between 1888-1912 (Philippi 1968) first suggested that petroleum originates from the 'thermal decomposition' of organic matter, several facts have arisen and indicate the need to advocate that hydrocarbon evolution within a sediment mainly results from the thermal alteration of organic matter; for example:

1 Smith in 1953 noted that para-naphthenics and aromatics increase with depth at the expense of asphaltics.

2 Many hydrocarbons that are present in petroleum do not occur in living matter or recent sediments. For example low molecular weight (LMW) hydrocarbons of the range C_2-C_8 (Dunton & Hunt 1962); Knevolden 1962) which constitute a substantial percentage of a crude are missing from recent sediments.

3 Recent sediments contain HMW normal carboxylic (fatty) acids which show an even dominance but ancient sediments yield extracts which hold normal fatty acids of a more odd dominance (Cooper and Bray 1963). In fact, for about fifty naturally occurring fatty acids, Fieser and Fieser (1956) observed that almost all have even numbered straight chains of carbon atoms within their molecules.

4 HMW normal alkanes from recent sediments have a pronounced odd dominance but those from ancient sediments or petroleum show little or no dominance (Martin et al 1963).

5 Hydrocarbon/organic carbon ratios increase with increasing depth and those for ancient sediments are higher than those for recent sediments (Smith 1953, Hunt 1961, Philippi 1968).

6 Thermally cracked naphtha is similar to virgin naptha compositionally but disimilar to catalytically/hydro-catalytically cracked naptha (Martin et al 1963).

7 A preference for normal hydrocarbons as opposed to branched isomers exists whilst olefins and easily reducible compounds are absent from crudes.

8 Polyaromatic hydrocarbons exist in crudes (see later; Blumer 1976).

In fact, three fundamental parameters, namely temperature, pressure and time are often assigned varying degrees of importance

with respect to the subsurface evolution of hydrocarbons.
As early as 1946, Cox (Hobson verb. comm. 1972) postulated that a minimum temperature of 65°C was required to initiate hydrocarbon evolution from organic matter and more recently Louis and Tissot (1967 in Milner et al 1977) gave the threshold value as 60°C with a phase-out value of 150°-180°C; the latter figures corresponding to the "eometamorphic threshold" or "commercial floor" of Landes (1967). Similarly, agreement was expressed by Klemme (1972) who paralleled petroleum evolution with the 'catagenesis' phase of Russian authors and gave the temperature boundaries of 60°C and 130°C. Pusey (1973a) declared figures of 120°F and 320°F with a maximum generation occurring within his 'liquid window' of 150°F-300°F (66°-150°C approx). Finally, Fuller (1975) has emphasised the importance of the role of temperature in noting that an 18°F/10°C increment in temperature generally doubles a reaction rate.
Klemme (1972) quoted a world average geothermal gradient of 1.0°-1.6°F/100 feet after Landes, but noted extremes of 0.3°F/100 feet and 42°F/100 feet exist (approx. 0.56°-0.90°C, 0.19°C and 23.5°C respectively) whilst Fuller (1975) agreed by specifying 1°-2°F/100 feet of burial. However, Pusey (1973a) put depth equivalents of confining temperatures into perspective by introducing the "liquid window" concept. In areas of high geothermal gradient the productive thickness of a source rock will be narrow and conversely in areas of low geothermal gradient the productive zone will be greater in thickness.
As pressure is usually referred to in terms of depth of burial the world average depths for major hydrocarbon deposits must indicate to some degree the influence of pressure. Klemme (1972) recorded that 48% are above 6000 feet and 43% are between 6000-9000 feet whilst only 9% are at greater than 9000 feet. In absolute terms though, pressure appears to be of minor importance (see Albrecht & Ourisson 1971).
Time too is often dismissed since in practical terms it can be regarded as interchangeable with temperature and depth of burial (pressure) (see Albrecht & Ourisson 1971). The effects of a low temperature for a long time (often the geological case) are usually accepted as the equivalent to those from a high temperature

for a short time (Bailey 1975) (and thus provide the basis for laboratory pyrolysis experiments). Also generally speaking more deeply buried rocks have to be necessarily older than shallow young rocks and therefore as depth/pressure increases time too is seen to become significant. In contrast to an exponential relation with temperature, the rate of reaction appears to vary linearly with time. Blumer (1976), for example, has emphasised the importance of time versus temperature in the formation of polyaromatic hydrocarbons.

Thus, Philippi (1968) concluded the fact that "petroleum is formed from sediment organic matter, essentially by thermal non-biological processes, is inescapable" and has been subsequently supported by Connan (1974), La Plante (1974) and Vassovich et al (1970). However, the actual mechanisms of conversion of organic matter into petroleum are still awaiting detailed elucidation. As the majority of organic matter in sediments is largely kerogen proposed routeways to date are summarised in Fig. 3. (The vagueness results from the difficulties in experimenting with kerogen especially because of its insolubility and an insight into basic kerogen types follows under General Results and Conclusions Section One; Part Three). In particular, although catalysis has advocates (e.g.Johns and Shimoyama 1972) its role in hydrocarbon generation (see especially points 6 and 7 here) remains in dispute. (See also Barker (1974), under 'Pyrolysis'; Section One; Part Two).

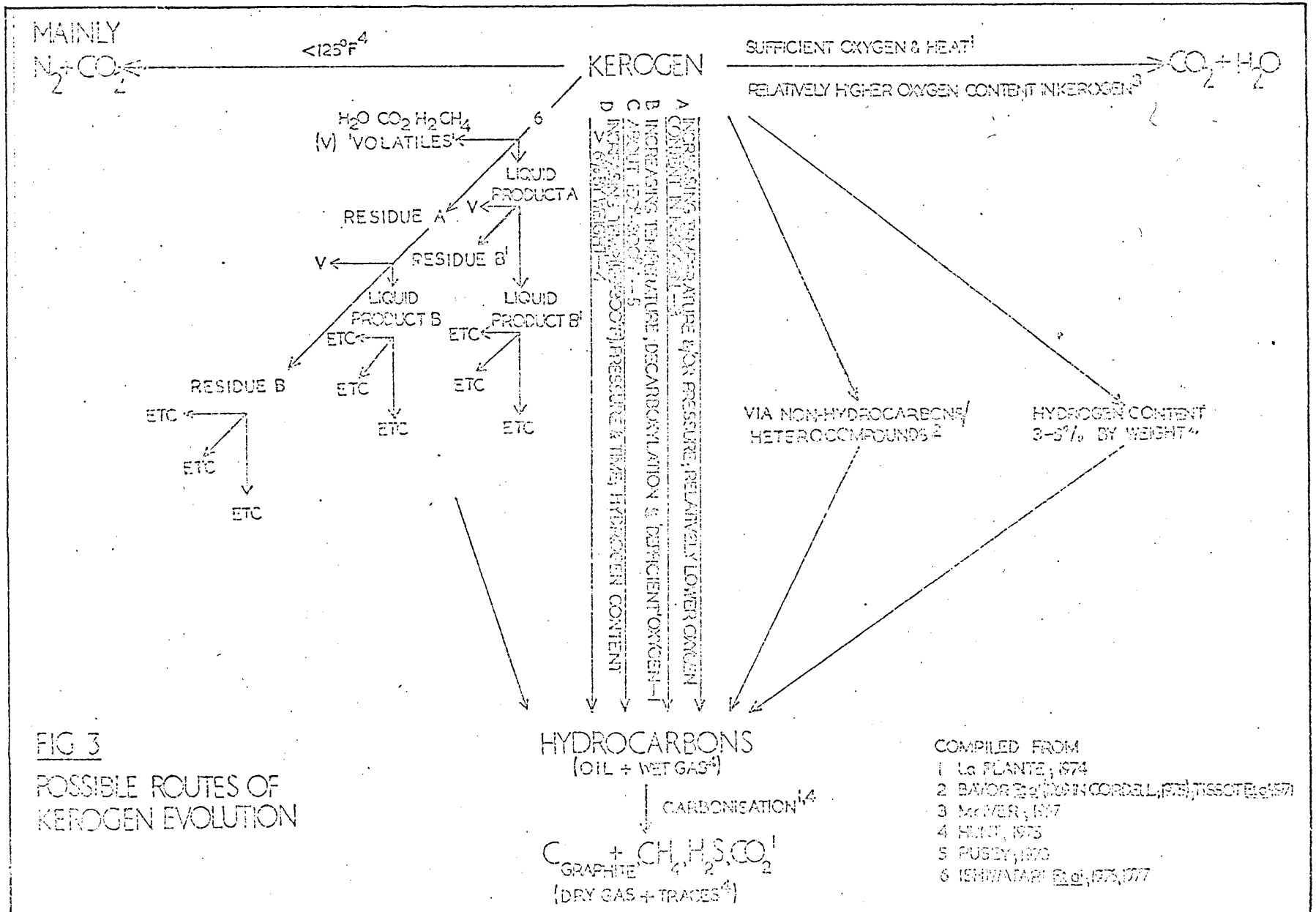


FIG 3

POSSIBLE ROUTES OF KEROGEN EVOLUTION

COMPILED FROM

1 La PLANTE, 1974
2 BAYOR [illegible] IN CORDELL, [illegible] TISSOT [illegible] 1971
3 McIVER, 1967
4 HUNT, 1975
5 RUSSEY, 1970
6 ISHIWATARI [illegible] 1975, 1977

SECTION ONE

ORGANIC GEOCHEMISTRY

PART TWO

EXPERIMENTAL WORK

1 SAMPLE TYPE

a Baker (1962) observed similar organic carbon values and saturated hydrocarbon/aromatic hydrocarbon ratios for surface and subsurface (shale) equivalents although the former samples have about 50% less actual hydrocarbons than their buried counterparts. Agreement with regard to such organic carbon values and hydrocarbon loss has been more recently expressed by Baker and Claypool (1970) although Leythaensen (in Gill et al unpub.) has apparently specified that weathering reduces organic carbon by up to 25%. Generally, though Baker (1962) and Gill et al (unpub.) have found consistent differences for organic carbon values of outcrop samples and cored counterparts.

Lately, Reed (1977b) assigned a "marked decrease" in soluble organic extracts to subaerial weathering whilst Schmidt-Collerus et al (1976) had disclosed a carbonaceous spent shale mined seven years earlier than an equivalent showed an 80% relative decrease in the amount of extractables !

With regard to hydrocarbon composition, Reed (1977b) has shown that the $n\text{-}C_{17}$ and $n\text{-}C_{18}$ alkanes decrease whilst the $n\text{-}C_{22}$ alkane increases. Also, as weathering effects increase, new compounds, notably components eluting before the $n\text{-}C_{20}$, $n\text{-}C_{21}$ and $n\text{-}C_{22}$ alkanes appear.

Evans and Staplin (1971) have said that N, S and O containing compounds mainly compose extracts from surface and shallow subsurface samples. They related the instances of these compounds to biochemical decay processes whereas Baker (1962) had more explicitly blamed the deleterous effects upon hydrocarbon content to oxidation (from oxygen-bearing waters), micro-organism attack and volatilisation/inspissation. Schmidt-Collerus et al (1976) attributed their observed loss to oxidation and volatilisation whilst Reed (1977b) deduced that "although microbial activity on surface exposures is responsible for compositional modification it does not impose a uniform organic composition on the weathered sediments".

b So, to avoid complications by chemical changes induced by weathering McIver (1967) used samples taken from below the 'obviously weathered zone of outcrop'. More recently, Baker and Claypool (1970) have stated that omission of samples showing

any signs of visible staining or alteration can minimise and perhaps even eliminate weathering effects. Similarly, Gill et al (unpub.) from a comparative study of outcrop, shallow subsurface and deep subsurface samples have concluded that "careful selection of unweathered material by experienced geologists can yield as much information as an expensive coring programme". For this study, outcrop samples were used, as in Bray and Evans (1961), Burlingame et al (1968), Baker and Claypool (1970) and Connan (1974); especially in the absence of readily available core samples which have been employed by Bray and Evans (1961), Robinson and Cummins (1965), Baker and Claypool (1970), Mathews et al (1970), Albrecht et al (1976), etc.

In passing it can be noted that drill cuttings are not devoid of problems. Obviously cavings and contamination by drilling fluids can upset a study (Mathews et al 1970; Shibaoka et al 1973) whereas artifical oxidation due to high temperatures generated through friction can also occur (Feugere and Gerrard 1970; Shibaoka et al 1973). Powell (1975), for example, used cuttings but mainly to supplement core data.

c With specific regard to reservoir type lithologies Milner et al (1977) have remarked that for aerobic bacteria to act upon an oil, the surface recharging waters must have a temperature of between about 20^{o}-50^{o}C and have about 8 mg per litre of dissolved molecular oxygen whilst the petroleum itself must be free from hydrogen sulphide.

Reed (1977a) has cited several advocates for the aerobic bacterial catabolism of crudes leading to a degradation of normal alkanes and preferentially those with short chain lengths. However, he noted that Bailey et al (1975) believed both cyclo-alkanes and aromatics are attacked simultaneously with LMW alkanes and in fact Perry and Cerniglia (1973, in Milner et al 1977) gave the biogradability of hydrocarbons in order of increasing ease as: C_{10}-C_{19} n-alkanes, C_{12}-C_{18} n-alkanes, C_2-C_4 gases, C_5-C_9 alkanes, branched alkanes of C_{12} and lower, C_3-C_{11} alkanes, branched alkanes, aromatics and cyclo-alkanes.

Yet, Reed and Kaplan (1977) referred to Brown and Huffman from 1976 in noting the relative persistence of hydrocarbons in open

ocean waters as: cycloalkanes > branched alkanes , aromatics, n alkanes and they themselves regarded aromatic and cyclic hydrocarbons as "relatively conservative components" with respect to weathering. Powell (1975) has mentioned that n-alkanes up to n-C_{18} are first removed under biodegradation.

Finally, Milner et al (1977) recorded that it is the residuum fraction of a crude which is scarcely affected by inspissation and abiogenic oxidation enriches a crude in heavier and tarrier products.

2 SAMPLE LOCALITY AND FREQUENCY

Bray and Evans (1965) commented that the variability of organic matter complicates the search for source rocks and in particular presents problems in the selection of sites as well as the frequency of sampling. It has been emphasised that a stratigraphic complex should not be condemned on the basis of sparse sampling as the amount and character of organic matter may vary geographically and stratigraphically (Shibaoka et al 1973). In fact, Bitterli (1963) observed that the environmental conditions and genesis of bitumenous rocks have been touched upon in many publications without the subjects being covered either from a sufficiently broad basis or from a sequential point of view and that an insufficient amount of representative sample (or inadequate analytical data) was to blame. Of course "the greater degree of objectivity offered by the statistical method can only improve the standard of work" (Boyle and Garrett 1970).

Now, vertical variations in organic matter have been recorded as abrupt and frequent (Bray & Evans, 1965) although Baker (1962) had earlier mentioned that such changes coincide with lithologic boundaries. Baker (1962) further specified that rock units appeared to have internally uniform organic compositions and that each unit seemed to have a fairly characteristic organic composition. On a larger scale, Eglinton et al (1964) have noted that "variations are conceivably to be expected in view of the possible fractionation effects inherent in a large rock formation".

With regard to the present day geochemistry being truly representative of the original geochemistry, Dunn (1972) noted that, although the upward expulsion of water upon compaction probably assists the chromatographic flow of particular organic compounds, certain authors implied remobilisation occurred only over a very short distance and not greater than a few decimetres. For practical purposes, hydrocarbons in impervious rocks can now be regarded as immobile (Shibaoka et al 1973).

Here in this study, the main Kimmeridgian section was sampled at intervals of approximately 10 feet except where the appearance of a different lithology warranted additional collection. In contrast, only a restricted number of lithologies were sampled for the Neocomian

(Wealden) sediments from each of the various strike outcrops and for the Kimmeridge Clay from elsewhere along the coastline (See Section Three; Part Two); this also being the case for the Oxford Clay samples.

3 SAMPLE HANDLING AND PREPARATION

a Consideration for the removal of any weathered rock together with weathered (organic) products and/or organic contaminants has received attention in the literature.

Reed and Kaplan (1977) washed samples with distilled water to remove adhering salts whilst earlier Mathews et al (1970) used distilled water and methanol for presumably the same purpose. Removal of secondary organic matter on the surfaces of samples has been attempted with cold concentrated nitric acid (12-24 hours) where 6N hydrochloric acid was used for a few minutes upon carbonates (Degens and Reuter, 1964) and hydrofluoric acid has even been employed (Eglinton et al 1964; Albrecht & Ourisson 1971).

Alternatively, another simple treatment is to cut away outer surfaces of rock samples. Eglinton (1968) and Powell et al (1975) have done this whilst Schenck and Henderson (1969) removed the exteriors with a portable drill and cleaned the samples with ultrasonic vibration. Albrecht & Ourisson (1971) actually scraped their samples prior to crushing.

Solvent extraction itself has also been employed for the purpose. Burlingame et al (1968) extracted batches of a fragmented (3-20 mesh) sample ultrasonically with 4:1 benzene-methanol and the same solvent has been applied to uncrushed rocks for half-an-hour by Mathews et al (1970). Haug and Sever (1971) used it as well to wash samples whilst Albrecht & Ourisson (1971) advocated 3:1 benzene-methanol. Similarly, Eglinton et al (1964) reported that small chips were sometimes washed with organic solvents (with or without sonication) and Eglinton (1968) used an unspecified solution of benzene-methanol to ultrasonically wash one-inch rock chips. Henderson et al (1968) favoured benzene to clean half-an-inch fragments ultrasonically for 5 mins. whereas Rubinstein et al (1975) preferred chloroform in washing rock samples. In conclusion, and for highly permeable rocks, Degens and Reuter (1964) decided that there is no way of removing organic contaminants without altering the original organic pattern.

b The question of destroying the mineral matter of a rock before extracting the sample has also arisen.

Eglinton (1968) often omitted demineralisation "since in most cases it does not greatly increase the yield of geolipids" although Downie (1955) had claimed that an increase in the solubility of organic matter after dissolution of the clay minerals indicated a close bond between the two components (actually for the Kimmeridge Clay itself). Possible reaction between acids and organic matter as well as the chance of contamination by additional organic matter from hydrofluoric acid (as the latter is stored in polythene containers) have been mentioned by Gill et al (unpub.) although no data has been offered.

However, here it can be noted that Haug and Sever (1971) extracted samples of the same rock and found that the hydrocarbons isolated from the extract of a washed sample were quite different from those of a demineralised sample. (A high percentage of probable branched & cyclic C_{15} and lower hydrocarbons for a washed sample in fact contrasted with normal hydrocarbons (showing some odd over even predominance for the C_{17}-C_{28} range and a maximum at C_{27}) for a demineralised sample).

c The drying of a rock prior to crushing is another issue sometimes taken up by authors. (Bray & Evans 1961; Mathews et al 1970).

Henderson et al (1971) dried samples in a dessicator under a flow of nitrogen whilst Schmidt-Collerus et al (1976) used air dried samples. Freeze-drying appears to have become fashionable once again (Ishiwatari et al 1977; Reed and Kaplan 1977) as Degens and Reuter (1964) did mention its immediate use stopped microbial infections in cores. Simoneit and Burlingame (1971) dried samples at 105°C.

It has been cautioned that drying may change mineral-organic matter associations and perhaps allow some oxidation (Hobson, 1966) but with respect to the latter no figures for the quantitative uptake of oxygen were offered. Yet, Schmidt-Collerus et al (1976) did observe that a wet (carbonaceous pentshale) sample will give more benzene soluble matter than a dried sample and they suggested water soluble inorganic material or complexed material explains the higher yield.

Drill cuttings incidentally, can present quite acute problems as contaminating mud cake has to be washed off and cavings and/or particulate contaminants (such as lost circulation packing and paint) have to be removed by hand picking.

d Ferguson (1962) and more recently Baker (1972) have noted that 'different kinds and amounts of products can be extracted from a sediment depending upon the degree of particle size reduction' of the sample. The variation of amount of extract with particle size can be expressed:

Particle size:	30µ	10µ	5µ
Ratio of extract:	1	2	2.75

The actual type of extractable organic matter was found to be a function of particle size down to at least 16µ since 5µ and 10µ particles of a sediment gave identical extracts but contained additional hydrocarbons with respect to a 30µ particle sized sample of the same sediment.
"Ideally, the smallest particle size attainment is desirable for a rapid and complete extraction but the labour of reducing particles has to be considered". For example a size reduction from 10µ to 5µ was found to take 100 hours of ball milling. Also the removal of sediment particles from an extract solution becomes more difficult as the size decreases (Ferguson, 1962).

Table 4 in fact summaries some of the particle sizes employed and the efforts to achieve them
With specific regard to ball milling Bennet (priv.comm. 1977) has related the fact that an increase in the weight of a sample can sometimes occur because additional material is derived from the breakdown of the mill components. For example, reduction of an iron powder in an agate mill showed an increase in weight in the order of 10% after only 3 hours of milling !
The specific documentation of the effects of increased temperature during sample reduction appears to be missing in the literature reviewed here.

TABLE 4. SEDIMENT PARTICLE REDUCTION.

AUTHOR(S) & DATE.	SEDIMENT PARTICLE REDUCTION METHOD.	MAX.SIZE OR RANGE.
FERGUSON, 1962	Braun WD Jaw Crusher & Hammer Mill.	1mm - 0.24
McIVER, 1962	Unspecified.	c.36 mesh.
EGLINTON et al, 1964	Pestle & Mortar; Braun Ore Crusher & Hammer Mill.	200 mesh.
BURLINGAME et al, 1968	Unspecified.	200 mesh.
HENDERSON et al, 1968	Disc Mill.	100 mesh.
MATHEWS et al, 1970	Unspecified.	150 mesh.
DJURICIC et al, 1971	Tyler Mill.	100 mesh.
HAUG & SEVER, 1971	Unspecified.	5μ
HENDERSON et al, 1971	Disc Mill.	'Fine powder'
MAXWELL et al, 1971	Unspecified.	200 mesh. (c.70%)
VUCHEV et al, 1971	Unspecified.	100-200 mesh.
WSZOLEK et al, 1971	Ball Mill for 10 days.	?
BAKER, 1972	As Ferguson,1962	As Ferguson,1962.
SHIBOAKA et al, 1973	Unspecified.	200 mesh.
COMMERCIAL CONCERN, 1974	Unspecified.	60 mesh.
ALLAN et al, 1975	Unspecified.	72 mesh.
KARKANIS, 1975	Unspecified.	200 mesh.
POWELL et al, 1975	Unspecified.	200 mesh,(0.074mm)
FOSCOLOS et al, 1976	Pestle & Mortar; Swing Mill.	200 mesh.
SCHMIDT-COLLERUS & PRIEN, 1976	Crushed,riffled & ground.	100 mesh.

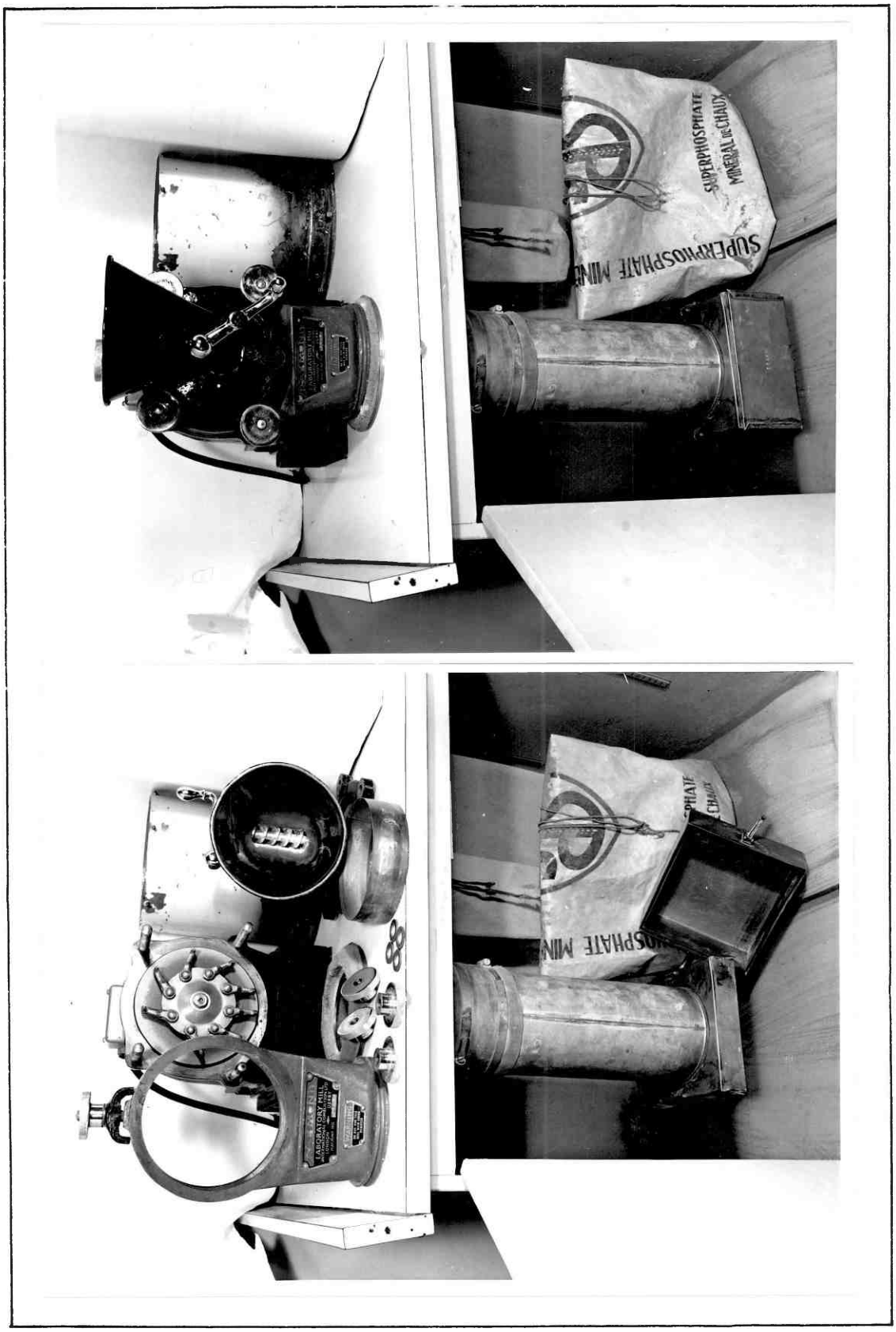
e Obviously the foregoing discussion relates to a more routine source rock evaluation programme and it should be appreciated that certain specific objectives, such as study of LMW hydrocarbons (Dunton & Hunt 1962; Knevolden 1962), require specialised handling (and analytical) techniques (Dow 1977). For this study and whenever possible only the most 'unweathered' fragments were returned from the field to constitute a sample for a particular horizon. Any weathered outermost jacket is then of initially negligible proportion with regard to the total rock mass and crushing will help to average the weathered products to a negligible distribution throughout a homogenised rock powder.

Thus, to be in accordance with previous work within the section and for the coherent fine grained clastics (claystones and shales) a pestle and mortar of cast iron were used to provide chips of approximately $\frac{1}{4}$ inch diameter. Such chips were then fed into a Raymond Rotary Mill (Plate I) containing a sieve to provide particles of a maximum diameter of 0.024 inch. (In fact a great bulk of the powdered rock was actually composed of particles of finer than 200 mesh).

After crushing each sample, the pestle and mortar and dismantled mill were cleaned as thoroughly as possible. Contamination by any residual powders was therefore kept to a minimum and with respect to the quantity of sample prepared such contamination was accepted as negligible(Gill et al unpub.)

For the friable coarse clastics (soft sandstones and conglomerates) the rocks were disseminated over a 0.0275 inch sieve. Very rich oil sands defied any attempts to disaggregate them and were extracted without any treatment. No attempts to dry any samples prior to extraction were made and washings were omitted (in continuity of other departmental work for comparative purposes).

PLATE 1 RAYMOND ROTARY MILL : ASSEMBLED AND DISMANTLED.



4 SOLVENT EXTRACTION

a Introduction

Since organic matter in a sediment can be broadly defined as solvent extractable (bitumens/lipids - Palacas et al 1972, Pusey 1973b, Roger et al 1974, Dow 1977/Eglinton 1968, Ishiwatari et al 1976,1977) and solvent intractable (kerogen - Collins 1975, Dow 1977, Ishiwatari et al 1977) matter, the first subdivision by virtue of its solubility affords a relatively more approachable and immediate subject for chemical investigation. In fact, until recently, solvent extractables have been the chief topic of study in most geochemical researches (NERC 1973). (A third type, the hydrocarbon gases and vapours lost in sampling, crushing and drying can be defined from practical considerations).

In this Chapter, the various parameters and stages of solvent extraction are discussed in a stepwise order together with the specifications of this study. For comparison and/or contrast the background information has been carefully drawn from work where sample materials include recent and ancient sediments, coals, kerogen concentrates, hand-picked macerals and spent shale. Quite often seemingly different objectives result with methods which at certain stages mirror one another in their actual functions and/or purposes.

'As different amounts and kinds of products may be extracted depending upon the extraction procedure adopted' (Baker 1972; Palacas et al 1972) detailed accounts of experimental procedure should be the rule. However many published articles are imprecise or lacking but sometimes disparity between journals indicates the fault is not perhaps entirely with the author(s). The method adopted here follows a compromise between maximum extraction, reproducibility and convenience on the one hand and minimum loss, alteration and cost on the other hand. The main theme was established in the Petroleum Geology Section, formerly Oil Technology, using an Oxford Clay sample as a 'standard' material (Gill et al, unpub.). The aim is specific in that the 'total' soluble organic extract is desirable as a basic parameter for source rock evaluation.

b Sample presentation

The actual presentation of a prepared sample for solvent

extraction is obviously dictated by the adopted method of extraction. Since the methods can include stirring, shaking, refluxing and/or soxhlet extraction either singularly or in various combination a sample can either be put in direct contact with an agitated solvent or (as in the case of soxhlet extraction) be retained in a permeable thimble.

For soxhlet extraction the use of conventionally packed thimbles was found to be "lacking" (Ferguson 1962) since condensing solvent tends to localise, channel through the sample and fails to saturate the sample completely. To overcome such a problem, Gill et al (unpub.) have used compressed filter paper thimbles containing a filter paper spiral and a plug of glass wool. The plug in fact serves a double purpose since it minimises escape of sediment particles during siphoning operations and helps to spread solvent across the top of the sample prior to downward percolation.

In this study, the method of Gill et al (unpub.) was adhered to especially since they can show modified thimbles give a marked improvement in extraction efficiency:

Solvent	% Extract	
	Conventional Thimble	Modified Thimble
Benzene	0.062	0.085
Azeotropic Benzene Methanol	0.25	0.44

c Solvents

Although the choice of solvent is essentially governed by the specific aim of an extraction the list of possible candidates and their various combinations is probably endless. Table 5 summarises some of the more commonly applied solvents which have arisen from efforts to (initially) isolate (total) soluble organic matter from particular materials. The relative extraction efficiencies of certain solvents have been found and are given in Table 6.

In general, it seems that more polar solvents such as benzene-methanol, benzene-methanol-acetone and carbon disulphide-methanol-acetone (Brenneman and Smith 1958; McIver 1962; Palacas et al 1972) tend to extract greater quantities of non-hydrocarbons. Ferguson (1962) argued against mixed solvents on the grounds that they:

1 retain excessive non-hydrocarbon material which can interfere

TABLE 5. EXTRACTION SOLVENTS.

ACETONE:	Simoneit & Burlingame,1971.
BENZENE:	Forsman,1962; Robinson et al,1965; Baker & Claypool,1970; Sackett & Menendez, 1971; Palacas et al,1972; Gill et al,unpub.
CHLOROFORM:	Mair & Zimmerly*(?) and Hawley*1930 (*Hobson, verb.comm.1972); Long et al, 1962; Louis & Tissot,1967 (in Connan,1974); Schenck,1968; Giraud,1970 (in Barker,1974); Haug & Sever,1971; Shiboaka et al,1973; Connan,1974; Albrecht et al,1976; Durant & Espitalie,1976; Saxby,1976 (in Saxby,1977).
METHOXYETHANOL:	Gunn & Cooper,1962.
PYRIDINE:	Robertson,1911.
CARBON DISULPHIDE:	Forbes-Leslie,1916; Greene,1916 (?).
CARBON TETRACHLORIDE:	Le Tran,1975; Carlson,(?in Downs & Himus,1941).
DIETHYL ETHER:	Forbes-Leslie,1916; Bitterli,1963; Welte,1967 (in Barker,1974); Schenck, 1968; Simoneit & Burlingame,1971; Bergmann & Lester*1940 (*Hobson,verb. comm.1972)
METHYLENE OXIDE:	Sulaiman*1972 (*Kilgallin,pers.comm.1976)
BENZENE-METHANOL, Unspecified:	Knevelden,1962; Eglinton,1968.
Azeotropic:	Allan et al,1975; Karkanis,1975; Gill et al,unpub.
1:1	Djuricic et al,1971; Powell,1975; Powell et al,1975.
3:2 (Not specified as exact azeotropic ratio.):	Schenck & Havenaar,1969; Dungworth & Schwartz,1971; Foscolos et al,1976; Ishiwatari et al,1977; Reed,1977.
2:1	Wszolek et al,1971; Commercial Concern,1974.
7:3	Ishiwatari et al,1977.
3:1	Eglinton et al,1964; Burlingame et al,1968; Henderson et al,1968; Albrecht,1969 (in Connan,1974); Mathews et al,1970; Henderson et al, 1971; Simoneit & Burlingame,1971; Vuchev et al,1971; Albrecht et al, 1976.
4:1	Burlingame et al,1968; Haug & Sever,1971.
10:1	Bray & Evans,1961.
BENZENE-ETHANOL,9:1	Smith et al,1958 (in Cate,1960.)
BENZENE-CARBON DISULPHIDE, Unspecified:	Karkanis,1975.
BENZENE-METHANOL-ACETONE,70:15:15 :	Smith*1954; Stevens et al*1956; Hunt & Jameison* 1956; (*in Degens & Reuter,1962) Bonnet,1958; Hunt,1961; Meinschein,1961; Degens et al,1962; McIver,1962; Degens & Reuter,1962; Bloxam,1971.
CHLOROFORM-METHANOL,1:1 :	Harrison,1976.
CHLOROFORM-ACETONE-METHANOL,47:30:23 (Azeotropic):	Allan et al,1975; Allan & Douglas, 1977.
TETRALIN-METHANOL,2:1 :	Dunton & Hunt,1962.
TOLUENE-METHANOL, 2:1	Maxwell et al,1971.
3:1	Didyk et al,1975.
3:7	Reed & Kaplan,1977.

	SOLVENT.	% Extract.	Ratio of Extract.
A.	Cyclohexane.	0.032	1
	Benzene.	0.062	1.9
	1:1 Benzene-methanol	0.103	3.2
	Chloroform	0.117	3.7
	1:1:1 Benzene-methanol-chloroform	0.136	4.25
	Methanol	0.149	4.7
	Azeotropic Benzene-methanol	0.250	7.8
B.	Benzene	———	1
	3:1 Benzene-methanol	———	c.4

A: Gill et al,unpub. Soxhlet extraction.
B: Love & Palacas,unpub.1971 (in Palacas et al,1972). Vigorous shaking.

TABLE 6. EXTRACTION EFFICIENCY OF DIFFERENT SOLVENTS.

with chromatographic fractionation of the extract

2 retain, in some cases gross amounts of inorganic material such as sodium chloride when mixed solvents containing methanol are used.

3 produce uncontrolled variations during the course of an extraction by changing their composition.

Similarly, Forsman (1962) favoured benzene alone since he advocated the number of variables (as encountered with mixed solvents) were reduced to allow better reproducibility. Arpino et al (1971) did comment that "some limiting factors in the use of methanol and ethanol, which are used for increasing the polarity of the extraction solvent", exist but they did not elaborate. Also, Simoneit and Burlingame (1971) have agreed with Ferguson's second objection since in their work they found methanol solubles to be mainly inorganic salts (mostly chlorides) and water (with some LMW hydrocarbons (C15 and lower) and carboxylic acids (C12 and lower).

Whatever the choice of solvent it now appears universal to redistill all solvents prior to use to eliminate contamination by any heavy non-volatile residues (Ferguson 1962) and this practice applies to solvents for either extraction or chromatographic fractionation.

In fact, Eglinton et al (1964) reported using analytical grade reagents after having distilled them through an 18" column packed half full with glass helices. Burlingame et al (1968) redistilled their solvents whilst Vuchev et al (1971) purchased solvents of pesticide or nanograde quality to begin with. However, Schmidt-Collerus et al (1976) tested for the absence of polycyclic aromatic hydrocarbons by analytical TLC even though they had purchased high purity ('distilled in glass') solvent and double-distilled it themselves. The use of a 'Podbielnak' fractionating column specifically for the purification of solvent has been recorded by Powell et al (1975) and Mathews et al (1970) tested the quality of their redistilled solvents via GLC.

Benzene-methanol was used in this study in an attempt to obtain as much extractables as practical. Its use in soxhlets in azeotropic ratio dismisses Ferguson's third objection and also

allows simultaneous preparation and purification by distillation from rough volumes (measuring cylinder) of its components (3:2 benzene-methanol) through a column (130 cm x 2.5 cm ID) which was packed full of Fenske helices and surrounded by an air jacket (c.5 cm OD). Approximately two litres of azeotrope were won per day from analar reagent quality components by collection at 57.5° - 58.3°C using apparatus depicted in Plate 2.

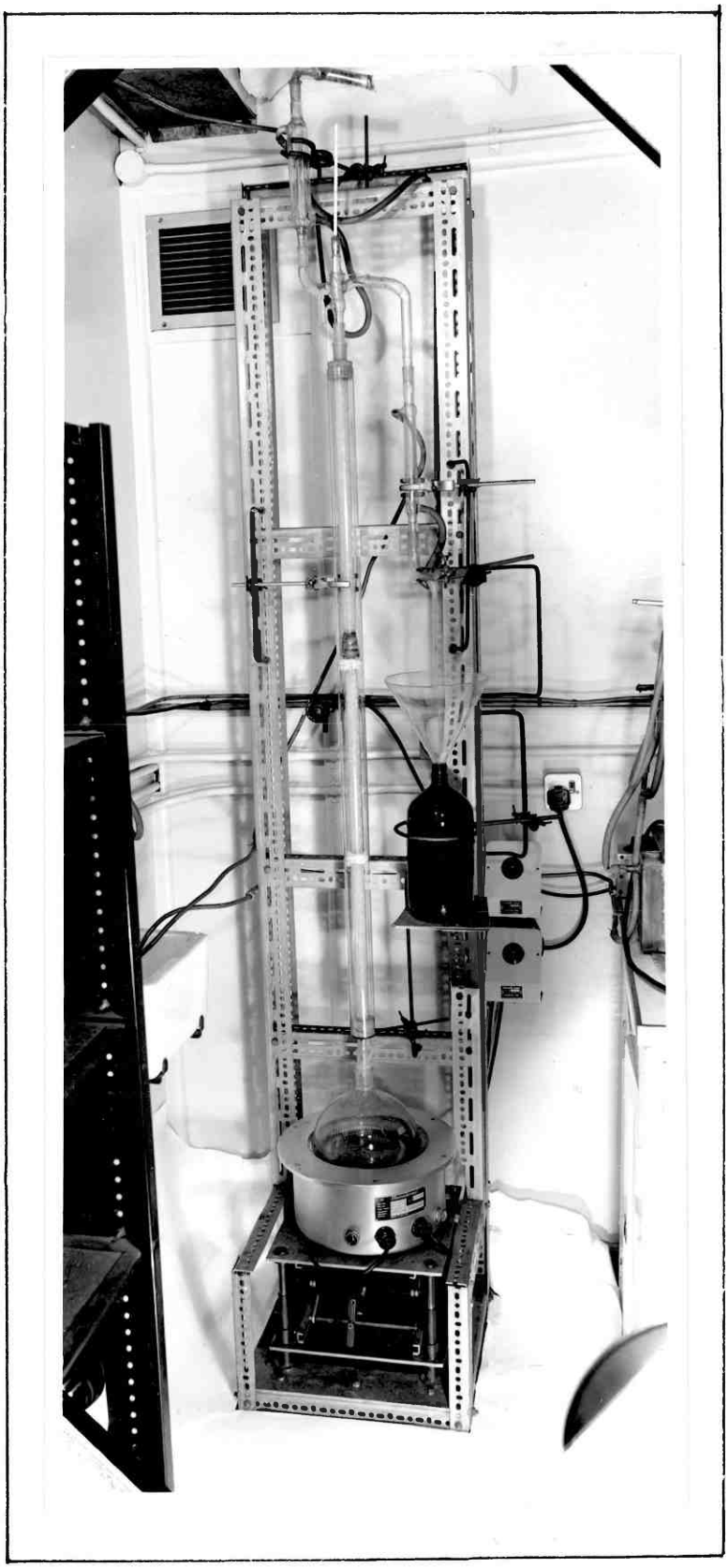
Ideally, the inner side of the air jacket should be silvered and the outer side lagged to allow the column residence under as near isothermal conditions as possible. Also, a reflux-ratio head will allow even better fractionation (Bennet and Solli verb. comms. 1977).

Here it is appropriate to mention that the components of an extracting solvent mixture are determined by the vapour phase equilibrium at reflux and not by the arbitrary ratios in the still. From an interplay of the type and dimensions of apparatus and the type and quantity of solvent it could transpire that two seemingly different applications are in fact identical.

For example, using figures for the apparatus and solvent employed in this study a solvent volume of 3.5 litres necessitates 2.625 litres of benzene and 0.875 litres of methanol if a 3:1 benzene-methanol solution was used. When heated, the first vapours of any binary mixture to condense will be those azeotropic in composition and such a solvent will continue to condense providing the initial and residual solution compositions permit. Therefore for a soxhlet siphoning capacity of 1.5 litres to be filled with benzene-methanol azeotrope, the respective amounts of components required from solution are 0.9075 litre of benzene and 0.5925 litre methanol (60.5:39.5). In this case such amounts can be provided by the initial solution and sustained during the soxhlet filling. Hence applications of azeotropic benzene-methanol and 3:1 benzene-methanol in a soxhlet are really identical as far as the sample is concerned; all other parameters being equal.

One possible difference, enhanced in the 3:1 solution with respect to the azeotrope, is that extractables soluble in methanol (0.5925 litre) may precipitate out (and char) from the residual solution after the first cycle because of repeated depletion in

PLATE 2
SOLVENT PREPARATIVE DISTILLATION EQUIPMENT.



the relevant 'active' volume of methanol. An effective volume decrease from 0.5925 litre of dissolving solvent to (0.875 - 0.5925) litre of retaining solvent occurs during each cycling operation; momentarily interrupted by replenishment to the original maximum (0.875 litre) by siphoning.
Therefore, it remains intriguing to see that the efficiencies of benzene-methanol in azeotropic and 3:1 ratio appear possibly very similar irrespective of extraction technique (?). Replicate analyses by Love and Palacas (unpub. 1971 in Palacas et al 1972) have shown 3:1 benzene-methanol is 'at least 4 times more efficient than benzene alone' (for shaking) whilst Gill et al (unpub.) record that azeotropic benzene-methanol extracted 4.11 times the quantity as benzene (in soxhlets).

d Extraction apparatus

When a source rock appraisal is being considered, shaking, stirring, shaking-stirring (vibration) and refluxing methods all appear to have greater disadvantages than soxhlet extraction. A summarised usage indicating the respective popularity for the different methods is given in Table 7 and combination methods are annotated in Table 8.
Bonnet (1958) concluded that refluxing alone was merely qualitative since the bulk of a sediment remains as an impervious pasty mass. More recently an attempt to extract a (carbonaceous spent shale) sample in a vapour-proof, sealed ball mill left a sticky material which was impossible to separate from the solvent (Schmidt-Collerus et al 1976).
Although ultrasonic vibration (as suggested by Smith in 1954 - according to Degens and Reuter 1964) can speed up an extraction and offer a greater yield and precision, as claimed by McIver (1962) and supported by Albrecht & Ourisson (1971), separation of solvent and sample upon cessation of extraction is still required. Also, high energy levels as McIver reminded can alter or degrade complex chemical molecules; particularly non-hydrocarbons (40,000 cycles/second).
Gill et al (unpub.) have observed that soxhlets with conventionally packed thimbles (A) are approximately equal in efficiency with stirred refluxing (B) although they claim reproducibility with

TABLE 7. USAGE OF INDIVIDUAL EXTRACTION TECHNIQUES.

SHAKING: Palacas et al,1972. STIRRING: Meinschein,1961. VIBRATION: Gunn & Cooper,1962. McIver,1962. Eglinton et.al,1964. Eglinton,1968. Henderson et al,1968. Haug & Sever,1971. Maxwell et al,1971. Wszolek et al,1971. Albrecht et al,1976. Ishiwatari et al,1977. REFLUXING: Degens & Reuter,1964. Eglinton et al,1964. Bonnet,1958.	SOXHLETS: Robertson,1911. Eglinton et al,1964. Tourtelot & Frost,1965* Schenck & Havenaar,1969. Baker & Claypool,1970. Durand et al,1970. Bloxam,1971. Simoneit & Burlingame,1971. Vuchev et al,1971. Haji-Vassiliou & Kerr,1973. Connan,1974. Allan et al,1975. Powell et al,1975. Rubinstein et al,1975. Schmidt-Collerus et al,1976. Reed,1977. Gill et al,unpub.
* In Gill et al,unpub.	

TABLE 8 USAGE OF COMBINED EXTRACTION TECHNIQUES.

1961. Bray & Evans:	Ball milling technique based upon Stevens et al,1956 & Meinschein & Kenny,1967.
1962. Baker: 1962. Ferguson:	Refluxing with mechanical stirring. (Solution filtered back & concentrated in boiler prior to solvent redistillation into extractor where sample held as suspension.)
1968. Burlingame et al:	Sample split into two parts & each extracted twice by mechanical stirring & sonication; followed by one week of Soxhlet extraction prior to final ultra-sonic treatment. ("Exhaustive")
1970. Mathews et al:	Magnetic stirring with refluxing. (Supernatant decanted after 24 hours settling period & combined with that from a second extraction)
1975. Karkanis:	Soxhlet extraction followed by shaking in a seperating funnel.
1976. Albrecht et al:	Stirred refluxing in Soxhlet.
1977. Ishiwatari et al:	Multiple mechanical extractions followed by Soxhlet extraction.

the latter technique is especially difficult.

Solvent	% Extract A	% Extract B
1:1 Benzene-methanol	0.103	0.099

Finally for methods where sample and solvent are in 'direct' contact, Meinschein (1962) pointed out that cooling to permit convenient handling after the extraction has finished, allows resorption of extractables upon the clay-grade size particles.

Soxhlet extraction obviates many such disadvantages as above and a diagram of a simple member of the four-fold semi-automatic assembly used in this study is given with annotated details (Figure 5). The complete assembly is illustrated in Plate 3. Danger of extract precipitation is greater when the flask contents are at a minimum (and the soxhlet is about to siphon) but measures can be taken to avoid this situation (see solvent: sample ratio).

For comparison of data of different authors achieved via soxhlet extraction using the same solvent, attention must be paid to the capacity of the soxhlet and the number of cycles constituting the extraction.

e Sample:solvent

Such a parameter is again seen to be restricted by the type of extracting procedure being followed and consequently a wide range of values can be computed (Table 9).

In the case of very rich samples Gill et al (unpub.) have applied two solvent extractions with summation of the extracts to achieve the 'total' extract. To avoid precipitation and charring of extractables benzene alone was used first and then followed by azeotropic benzene-methanol.

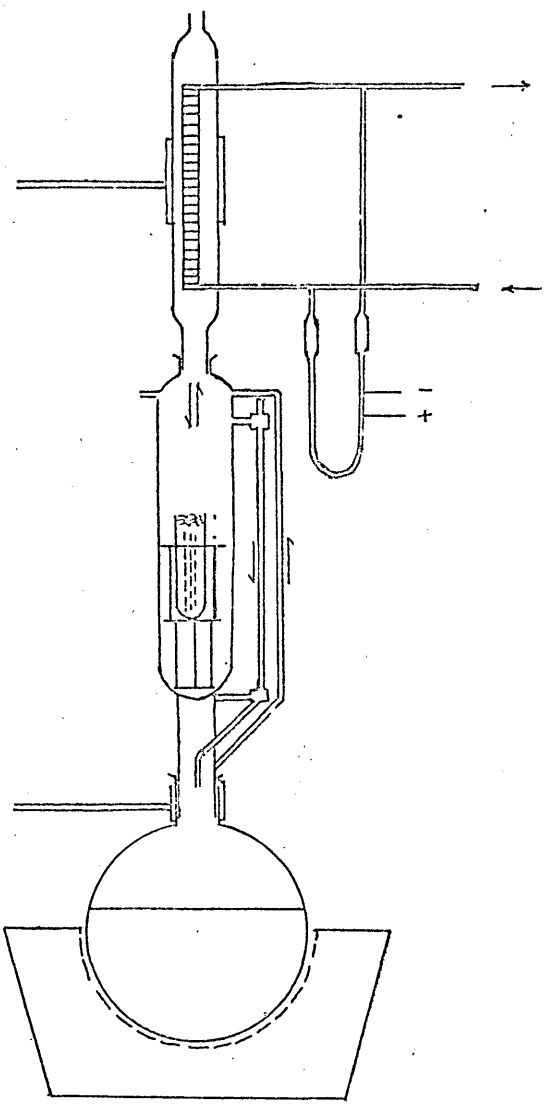
For this study a single treatment with 3.5 litres of azeotropic benzene-methanol was applied to sample weights varying between 65.0 - 551.3 grams. The lower values represent very rich samples (e.g. Wealden oil sands) and the necessary application of two solvents was avoided accordingly. The sample:solvent ratio therefore varied in the range of about 1-8.5:54.

f Extraction time

Not surprisingly there appears to be little agreement on the

FIG.5.

AN ANNOTATED DIAGRAM OF A SINGLE MEMBER OF THE FOUR-FOLD SEMI-AUTOMATIC SOXHLET EXTRACTION ASSEMBLY (Built by Coomber,c.1965)



WATER CONDENSER; water pumped from independent tank system and ideally cooled by refrigeration.

MERCURY MANOMETER cuts power supply to mantle if water su-pply is inhibited or too excessive.

SOXHLET (1½l. siphoning capa-city) with centrally placed thimble,to catch condensing solvent.

THIMBLE packed with spiral & plugged with glass wool to aid solvent diffusion through the sample.

DISTILLATION FLASK (5l.) with solvent (3½l.)

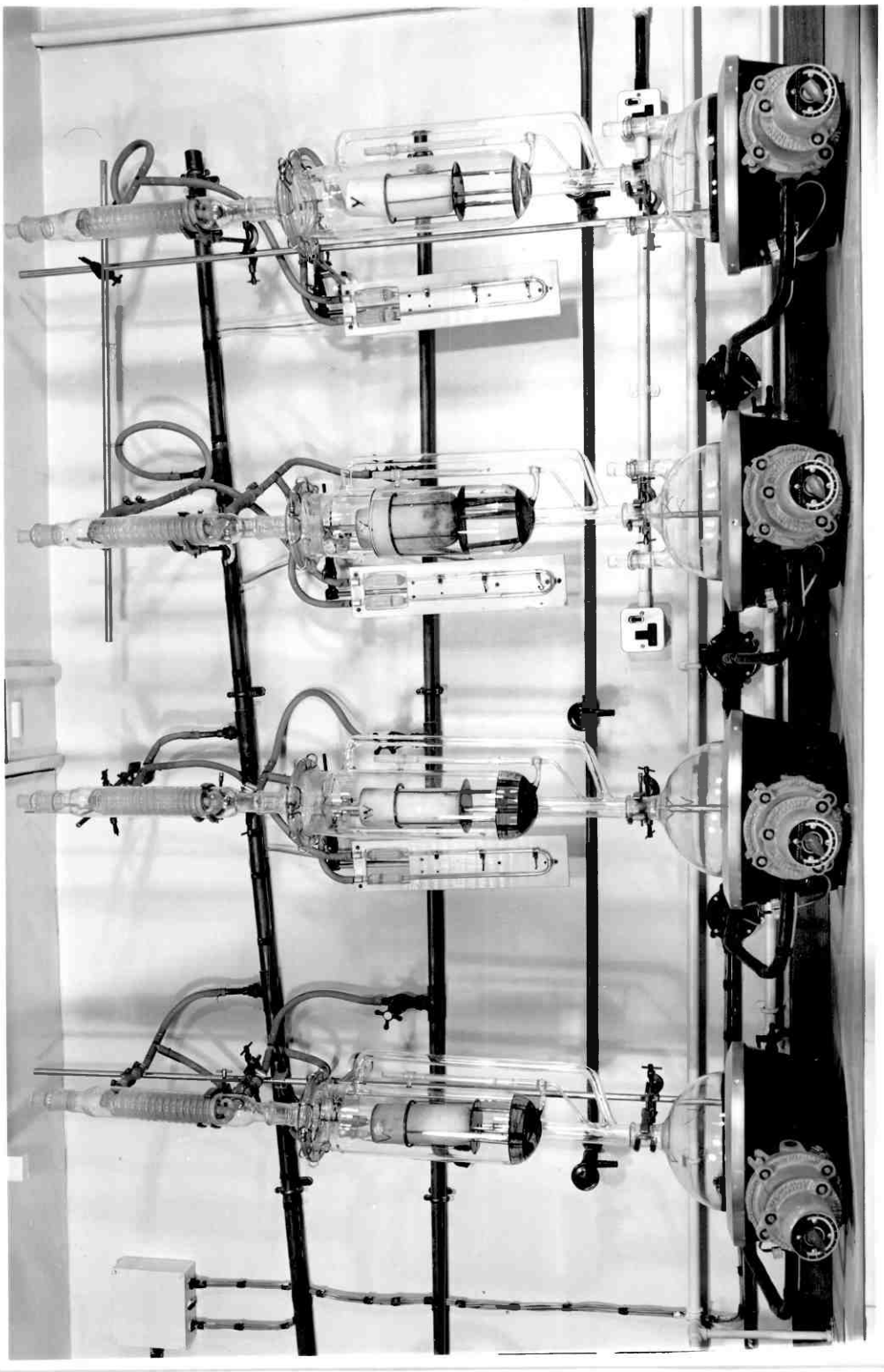
ELECTRIC MANTLE; 'flame proof'

(A difference with conventional extraction occurs with the thimble size since this usually matches the internal diameter of the soxhlet to keep the distillate hold-up to a minimum and thus maximise the number of cycles in a given time.) Not to scale.

TABLE 9 SAMPLE:SOLVENT RATIOS.

DATE & AUTHOR(S).	SAMPLE WEIGHT(gms).	SOLVENT VOLUME (mls)	SAMPLE:SOLVENT RATIO
Bonnet,1958.	c.300	c.600	1:2
Meinschein,1961.	———	———	1:2
Ferguson,1962.	100-500	2,000	1-5:20
McIver,1962.	c.250	1,000-2,000	1:4/8
Eglinton et al,1964.	100	330	1:3.3
Burlingame et al,1968.	500	4,000	1:8
Baker & Claypool,1970.	100-2,500	3,000	1-25:30
Mathews et al,1970.	400	? / 2x?	?
Bloxam,1971.	c.20	?	?
Henderson et al,1971.	10-20	?	?
Maxwell et al,1971.	2,000	800	2.5:1
Vuchev et al,1971.	154	300 x?	?
Baker,1972.	100-500	2,000	1-5:20
Palacas et al,1972.	———	———	1:3-5
Allan et al,1975.	17.3	400	1:23
Karkanis,1975.	20	?	?
Gill et al,unpub.	c.300-350.	3,500/7,000	1/1.2:11.7/23.3

PLATE 3 SEMI-AUTOMATIC FOUR-FOLD SOXHLET EXTRACTION ASSEMBLY.



necessary duration of exposure of a sediment to a solvent type for the isolation of a representative spectrum of extractables and, in particular, hydrocarbons.

With regard to absolute quantities of extract, Gill et al (unpub.) insist that it is impossible to state accurately when all solvent soluble material has been extracted. Even when coloured extractables cease to be found at the close of an extraction (the criterion used by Robertson, 1911) there is no guarantee that colourless extractables are no longer present. Allen et al (1975) did incidentally remark that after 200 hours of soxhlet extraction, when deriving 'total organic extract', "the solvent in the syphon arm appeared colourless".
In theory, Gill et al (unpub.) have postulated that elemental analysis on thoroughly dried samples after each repeated extraction would be required to approximate the ultimate duration. Consequently, several "exhaustive" extraction techniques have arisen in attempts to secure greater yields. Vuchev et al (1971) considered their method complete after 124 hours by the absence of fluorescence in the extract (under 365 mμ UV radiation) whereas Burlingame et al (1968) had followed an initial sonication with one week of soxhlet extraction and then continued with ultrasonic treatment "until no more organics could be solubilised". More recently, Allan and Douglas (1977) defined soxhlet extractions (upon macerals) after 102-1025 hours as 'exhaustive' when residues upon ultrasonic aggitation with the solvent mixture for one hour gave less than 1% by weight of the extract obtained with the soxhlets. With regard to pursuits for total soluble extracts it is relevant to mention work by Schmidt-Collerus and Prien (1976) performed upon a kerogen isolate. The material was subjected to attack by solvents of increasing polarity over a period of several weeks before leaching with acid. The acid leached material was then solvent extracted as before and finally stored for two years, Extraction after storage with n-hexane then gave 5-6% extractable hydrocarbons which were assumed to have diffused from within the matrix to the surface of the matrix (!).
It is interesting therefore to note that Ferguson (1962) claimed 90% of soluble organic matter is extracted after 10 hours of

refluxing and 99% is isolated after 20 hours before adopting a 24 hour standard evaluation time. Palacas et al (1972) have insisted three additional ½-1 hour periods of shaking are necessary after 20-24 hours of shaking to remove 90% or more of extractable material.

From this study it has been realised that often fairly strongly coloured solutions remain at the close of successive soxhlet extractions. Although the weight of each individual extract may be small, their summation continually raises the value for the total extract and thus lowers the relative individual percentage yield accordingly (Table 10).

Now also not only 'different amounts but different kinds of products may be extracted depending upon the actual length of extraction' (Baker, 1972). From this study, the available data for the elemental compositions of such multiple extracts supports the proposition and in fact the (early) trend observed by N, C and C/H warrants further investigation (Table 11).

Of course, the question of time is dependent upon the actual extraction technique itself and with respect to assessing ("total") soluble organic matter the times of other authors are summarised in Table 12.

McIver (1962), incidentally, has claimed two five minute exposures to ultrasonic treatment with cold solvent are equivalent to six hours of 'conventional' treatment with hot solvent. More recently, for soxhlet extraction, it is becoming common for time to be expressed in actual numbers of cycles (e.g.Schmidt-Collerus et al (1976) - 2000 cycles; Reed and Kaplan (1972) - 300 cycles).

For this study and as a compromise between extracting the maximum soluble organic matter, evaluating the relative organic condition of a suite of samples, permitting conformity of data with other work of the section and exercising convenience with available equipment, a standard 22 hours extraction time was adopted. With the apparatus concerned such time approximates to about 50 cycles.

g Solvent recovery

At the close of most extraction procedures the required extractables are usually held in an overwhelmingly large volume of

TABLE 10 QUANTITY OF EXTRACT VERSUS MULTIPLE EXTRACTIONS.

SAMPLE.	EXTRACTION HOURS.	%EXTRACT	RELATIVE EXTRACT %.	CUMULATIVE EXTRACT %.
W8	22	0.56	87.5	87.5
	44	0.04	6.25	93.75
	66	0.04	6.25	'100.0'
W13	22	1.50	68.81	68.81
	44	0.12	5.51	74.32
	66	0.08	3.67	77.99
	88	0.06	2.75	80.74
	110	0.06	2.75	83.49
	132	0.09	4.13	87.62
	154	0.04	1.84	89.46
	176	0.06	2.75	92.21
	198	0.06	2.75	94.96
	220	0.06	2.75	97.71
	242	0.02	0.92	98.63
	264	0.03	1.40	'100.03'
W17	22	0.43	32.82	32.82
	44	0.12	9.16	41.98
	66	0.13	9.92	51.90
	88	0.13	9.92	61.82
	110	0.13	9.92	71.74
	132	0.05	3.82	75.56
	154	0.08	6.11	81.67
	176	0.05	3.82	85.49
	198	0.09	6.87	92.36
	220	0.04	3.05	95.41
	242	0.06	4.58	'99.99'
W18	22	0.17	29.82	29.82
	44	0.06	10.53	40.35
	66	0.06	10.53	50.88
	88	0.06	10.53	61.41
	110	0.05	8.77	70.18
	132	0.05	8.77	78.95
	154	0.05	8.77	87.72
	176	0.04	7.02	94.74
	198	0.03	5.26	'100.00'
W20	22	0.82	85.42	85.42
	44	0.08	8.33	93.75
	66	0.06	6.25	'100.00'
W21	22	6.66	97.37	97.37
	44	0.07	1.02	98.39
	66	0.09	1.32	99.71
	88	0.02	0.29	'100.00'

W17 & 18: Carbonaceous sandstones
W20: Lignitic silty claystone
W8,13 & 21: Oil sands. (All from Wealden Fm.)

SAMPLE.	%NITROGEN	%CARBON	%HYDROGEN.
W8i	0.13	77.91	10.29.
ii	0.66	28.02	5.46.
iii	0.43	58.43	6.08.
W20i	0.05	35.85	5.15.
ii	0.28	26.52	5.34.
iii	0.15	44.36	6.88.
W21i	0.36	84.52	11.65.
ii	1.11*	29.69*	10.52.
iii	0.27	46.85	5.56.
iv	0.78	92.47	4.01.

*Average of two values.
W8 : Oil sand.
W20: Lignitic silty claystone.
W21: Oil sand. (All from Wealden Fm.)

TABLE 11. COMPOSITION OF EXTRACT VERSUS MULTIPLE EXTRACTION.

TABLE 12. EXTRACTION TIMES.

STIRRING:	16 hours - Meinschein,1961.
REFLUXING:	15 hours x3 - Smith,1954; Stevens et al,1956 & Hunt and Jameison,1956 (All in Degens & Reuter, 1964) c.5 hours or twice for total of 19 hours - Eglinton et.al, 1964 1 hour x2 - Mathews et al, 1970
ULTRASONIC VIBRATION:	30 mins. - Eglinton et al, 1964. 20 mins. x2 - Burlingame et al, 1968. 30 mins. x3 - Henderson et al, 1968. 15-30 mins. x2 - Wszolek et al, 1971.
SOXHLET EXTRACTION:	'several hours' - Eglinton et al, 1964. 12 hours - Commercial concern, 1974. 200 hours - Allan et al, 1975. 72 hours - Powell et al, 1975. 24 hours - Reed et al,1977. 22 hours - Gill et al,unpub.
COMBINATION EXTRACTION:	Unspecified shaking with 10-12 hours Soxhlet extraction - Karkanis, 1975.
UNSPECIFIED EXTRACTION:	720 hours - Giraud, 1970 (in Barker,1974) 36 hours - Djuricic et al, 1971.

solvent. Methods to isolate the former in a much reduced volume of the latter, prior to final separation of the extract, are variable and depend to some extent upon the extraction technique itself.

For example, where the solvent and sample are in direct contact, centrifuging (Gunn and Cooper 1962, Eglinton et al 1964, Eglinton 1968, Henderson et al 1968) and filtering have been used to assist subsequent decantation of the solvent and the extractables (Bonnet 1958, McIver 1962, Palacas et al 1972). In some cases the supernatant has been withdrawn in disposal pipettes (Eglinton et al 1964, Henderson et al 1968) prior to evaporation.

After such a stage for shaking, stirring, vibration and refluxing methods and directly after soxhlet extraction, large scale distillation affords one popular way of reducing the extract and solvent to a smaller ratio (Ferguson 1962, Bonnet 1958, Gill et al unpub.).

Bulk reductions have also been achieved under reduced pressure (Robertson 1911, Eglinton et al 1964, Burlingame et al 1968, Simoneit and Burlingame 1971, Vuchev et al 1971, Reed and Kaplan 1977). Palacas et al (1972) concentrated their extract solutions by 'flash' evaporation whilst Baker and Claypool (1970) followed a rough distillation and preceded a final evaporation with a rotary vacuum distillation.

Gill et al (unpub.) have recorded appreciable loss of LMW compounds from solutions of known compositions when these are concentrated via rotary film evaporation (RFE) over a waterpan at about 40-50°C in contrast to atmospheric distillation through columns containing Fenske helices (FLDH) (Table 13). In support of this finding, Schmidt-Collerus et al (1976) changed from a rota-vacuum method to fractional distillation for solvent stripping stating their reason was to prevent the loss of volatiles and, in particular, polycondensed aromatic hydrocarbons (!).

However, in all fairness, complete reduction by rotary vacuum pump should be compared with conventional distillation AND the final evaporation technique. Then the differences only seem to warrant serious consideration when detailed analytical studies are being undertaken (Solli pers. comm. 1977) and accordingly most source rock evaluation studies are based upon the C_{15}^{+}

TABLE 13. LOW HYDROCARBON LOSS. (From Gill et al, unpub.)

ALKANE.	BP/MP* °C.	%RETAINED RFE.	%RETAINED ADH
n-$C_{10}H_{22}$	56° 8mm Hg	0.7	0.0
n-$C_{12}H_{26}$	91° 9mm Hg	0.7	66.0
n-$C_{15}H_{32}$	144° 15mm Hg	44.0	92.0
n-$C_{18}H_{34}$	26°- 28° *	78.0	91.0
n-$C_{20}H_{42}$	36°- 38° *	83.0	92.0

TABLE 14. EXTRACTION TEMPERATURES.

SOLVENT	B.P. °C
Acetone:	56.2
Benzene:	80.1
Chloroform:	61.7
Diethyl Ether:	34.5
Pyridine:	115.5
Benzene-methanol, Azeotropic:	58.3
Various ratios:	58.3 - 80.1

Temperatures from Weaver, 1970.
Applicable for Soxhlet extraction.

hydrocarbon faction irrespective of the solvent recovery processes.

For this work, a four-fold water bath bulk distillation unit was employed and each c.3.5 l. of solvent with extractables was reduced to about 250 ml. within one working day (Plate 4). Decantation with washings then allowed further solvent recovery on a smaller individual scale using an electric mantle (Plate 5).

Both distillations employed columns packed with Fenske helices (and attached sidewall condensers). During the stage care was exercised to avoid removing too much solvent as precipitation of extractables and charring follows. The small flasks could always be suspended within the mantle jacket (to avoid direct contact) or the mantle itself could be replaced by a waterbath to reduce the likelihood of alteration precipitation and charring (Solli pers. comm. 1977).

h Extraction and recovery: temperatures, pressures and atmospheres.

Baker (1972) has impressed that 'different amounts and kinds of products may be extracted depending upon the temperature of extraction'. As seen such a rule can be extended to the solvent recovery process especially when an interplay with pressure is considered.

At atmospheric pressure the temperature range has extended from room temperature for simple extraction processes like stirring and shaking to possibly that of the highest value for the boiling point of the least volatile solvent or solvent component in the case of refluxing or soxhlet extraction (Table 14).

In particular, Eglinton et al (1964) observed that during an exploratory extraction with an ultrasonic probe of a magnetically stirred suspension of sediment cooling was sometimes needed.

Under reduced pressure Robertson (1911) retrieved the bulk of the (pyridine) solvent at 60°C whilst Palacas et al (1972) won back benzene at 40°C at low pressure. Vuchev et al (1971) stripped their extract solutions at 50°C under 2 cm Hg pressure.

An infrequent measure was taken by Degens and Reuter (1964) when they extracted samples under nitrogen and more recently such a method was used by Bloxam (1971) and Simoneit and Burlingame (1971); the latter authors in fact stressed that all subsequent operations

PLATE 4 FOUR-FOLD WATER BATH BULK SOLVENT RECOVERY APPARATUS.

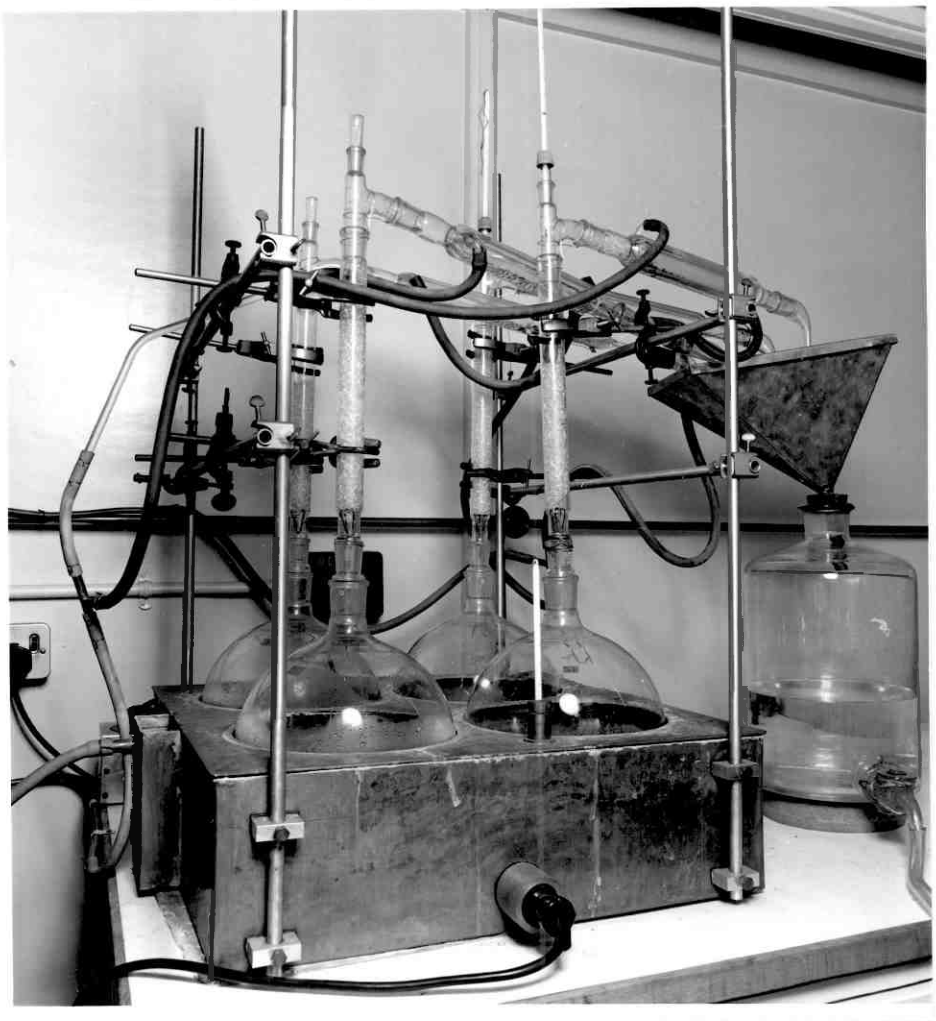
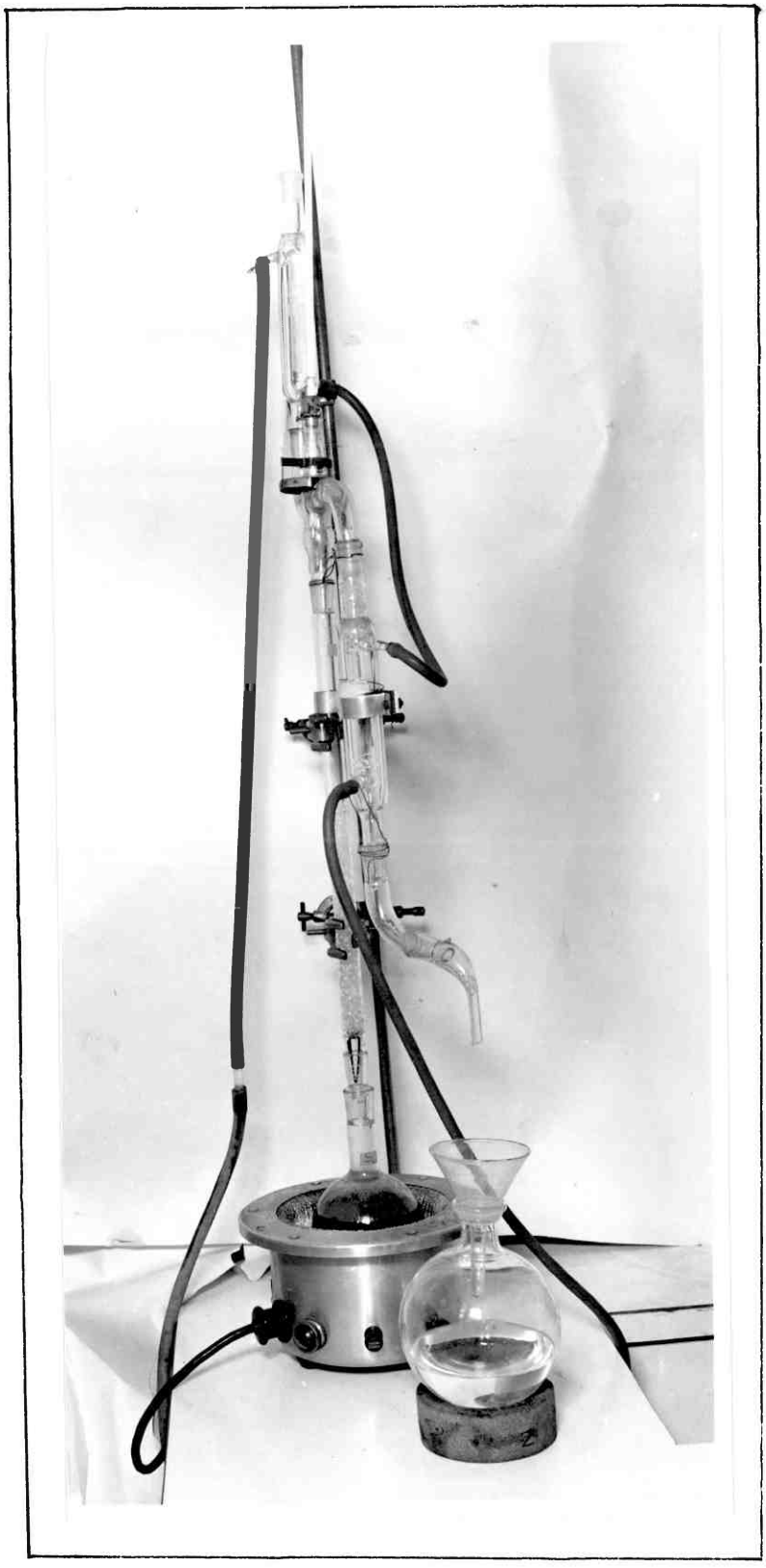


PLATE 5 SMALL SCALE INDIVIDUAL SOLVENT RECOVERY DISTILLATION UNIT.



where possible were also carried out under nitrogen. Schmidt-Collerus et al (1976) appear unique in having performed all extractions in the dark to stop changes being induced under fluorescent light. Incandescent light only when needed was used and the extracts were wrapped in aluminium foil and stored in a refrigerator prior to subsequent analysis.

For this presentation, a water bath temperature and a mantle setting of 80°C was adequate to ensure a steady retrieval of azeotrope at its boiling point under atmospheric pressure (58.3°C) for the two stage recovery process. Over a period of time, the saturate fractions of the extracts were found to darken and colour.

i Extract isolation

Many different ways for the final removal of solvent from the extractables have been used and they can be summarised chronologically as in Table 15.

For this work, the reduced solution was filtered into a pre-weighed glass tube (10 cm x 2.5 cm ID) through a No.I Whatman filter paper in order to seperate any stray sediment particles and glass wool fibres. Any paper chromatographic effects (easily noticeable for coloured extracts) were countered by repeated washings until the initial or subsequent filter paper(s) remained unstained.

The acquired solution was then evaporated at 50°C under a draught of air "continuously" until the extract appeared dry (Plate 6). Drying was then interrupted momentarily every 24 hours until a penultimate weight differed with respect to a final weight by not more than 0.0005 grams. The extract was then considered 'dry'; in particular 'dry' enough not for the estimation of a percentage yield but for subsequent elemental analysis.

In the course of drying, a skin can sometimes develop across the surface of the extract and hinder further solvent evaporation. The need to burst such a skin then arises and such a feature was especially highlighted by some Oxford Clay samples (Solli pers. comm. 1977).

Thus, the whole phase of solvent recovery and extract isolation

TABLE 15. FINAL SOLVENT REMOVAL.

Robertson,1911:	Residue dried on watch glass in vacuum dessicator over sulphuric acid.
Bonnet,1958:	Extract evaporated under nitrogen or in an oven at 110°C
Bray & Evans,1961:	Final evaporation forced at 40°C
Knevolden,1962:	Final evaporation forced at 40°C
Ferguson,1962:	10-150µg portions of residue evaporated at 70°C under nitrogen for successive 10 minute intervals followed by weighing
Degens & Reuter,1964:	Evaporation under nitrogen at 50°C & 1 Torr.
Eglinton et al,1964:	Concentration of solution on aluminium heating block under stream of alumina-filtered nitrogen
Bloxam,1971:	Extract filtered and dried under reduced pressure.
Palacas et al,1972:	Extract evaporated to dryness under stream of nitrogen at 40°C.
Schmidt-Collerus et al,1976:	Final evaporation at room temperature under gentle stream of nitrogen.
Gill et al,unpub:	Extract oven dried for c.30 hours at 50°C under draught of air.

PLATE 6 EXRACT DRYING OVEN.
(Open to show extract solutions in pre-weighed tubes under final evaporation to dryness)

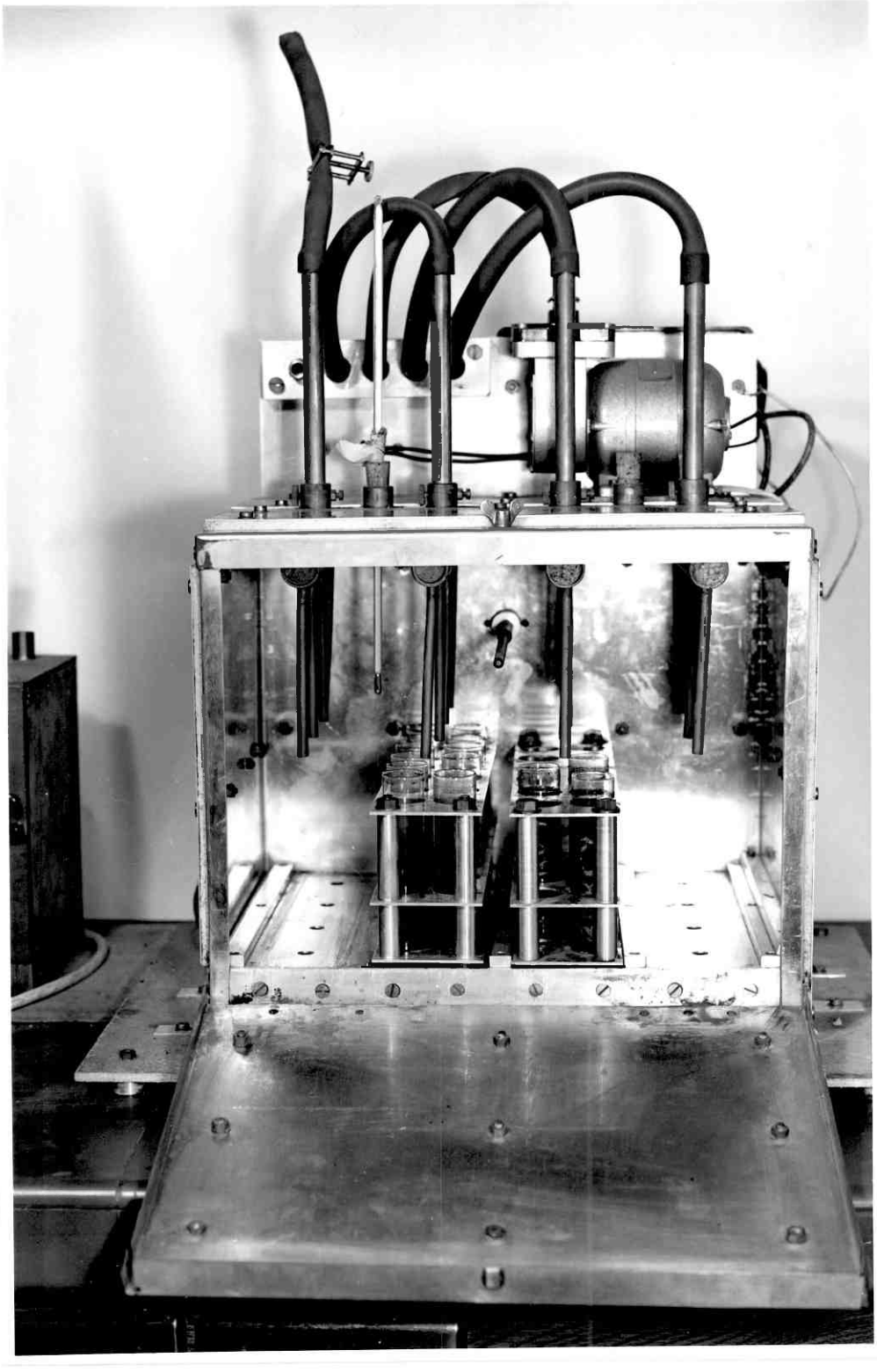


PLATE 7 ICI (METAL) DEGREASING PLANT.



is an apparently unresolvable competition between the volatiles of the solvent and the extractables. As Ferguson (1962) realised the magnitude of loss in these stages is proportional to the initial composition of an extract, the actual amount of the extract being isolated and the arbitrary definition of "constant weight".

When ultimately dry the extracts of this study were stored in the glass tubes;being tightly stoppered with cork. Eglinton et al (1964) used screw caps either of teflon or lined with aluminium foil.

Before passing on, it can be mentioned here that much less drastic conditions of recovery and final isolation of the desirable extract through water bath distillation/rotary evaporation and final solvent evaporation under nitrogen can allow retention of hydrocarbons down to C_6 (Solli pers. comm. 1977).

j Additional Measures and Comments

Quite a few workers have taken the effort to precipitate out 'asphaltenes' from the extracts. In all cases the 'insolubles' are precipitated out, filtered off, dried and weighed with the supernatant being evaporated to provide a 'deasphalted' extract. A summary of the usage and variations for the procedure is given in Table 16 but for this study the non-hydrocarbons were reported as one gross value.

Several authors have also taken steps to remove free/elemental sulphur from the extracts and such work is related in Table 17. although it was not attempted here.

Bonnet (1958) noted that the solvent (70:15:15 Benzene-methanol-acetone) attacked grease at the joints of the refluxing apparatus and consequently clean ground-glass joints were used. To avoid this problem Eglinton et al (1964) employed 'teflon socks' and 'clearfit' apparatus offers another alternative (Solli pers. comm. 1977). In fact Eglinton et al (1964) have tested for contamination by finger grease through the brief immersion of a finger in n-heptane GLC analyses revealed a few peaks below the nC_{20} position and several large peaks above the nC_{25} position.

TABLE 16. PRECIPITATION OF ASPHALTENES.

Burlingame et al,1968:	Hexane insolubles precipitated.
Mathews et al,1970:	2mls. heptane added to extract twice with heating.
Bloxam,1971:	Warm n-heptane used after Kleinschmidt,1955.
Simoneit & Burlingame,1971:	Heptane insolubles precipitated.
Commercial concern,1974:	N-pentane employed.
Connan,1974:	Minute quantity of chloroform added to extract & warm petroleum ether ($50-60^{\circ}C$) then applied.
Powell et al,1975:	Minimum quantity of chloroform followed by petroleum ether.
Foscolos et al,1976:	Small amount of chloroform added to dissolve extract & 100 mls. pentane applied.

TABLE 17. REMOVAL OF SULPHUR.

Bloxam,1971:	Polished copper strips used to couple free sulphur from extract solution; after Tourtelot & Frost,1965.
Palacas et al,1972:	Copper amalgam used to remove sulphur chromatographic -ally; after McIver,pers.comm.
Connan,1974:	Desulphurisation achieved with active copper powder.
Rubinstein et al,1975:	'Decanted' sulphur from extract.
Albrecht et al,1976:	Removed sulphur with active copper powder (but only for a few detailed studies)
Foscolos et al,1976:	Unspecified removal.
Schmidt-Collerus et al,1976:	Sulphur seperated from extract by repeated shaking with mercury.

For this work, the smallest quantity of high vacuum silicone grease was used sparingly to lubricate the joints and to enable the apparatus to be disconnected after use. Joints at the necks of flasks were wiped as clean as possible prior to decantation. In this way the quantity of contamination is negligible and as seen later the type of contamination does not manifest itself in any way which seriously interferes with subsequent analyses (particularly analyses of the saturate fractions).

Bonnet (1958) also "flushed" his residual powder with distilled water after extraction to try to retrieve more solvent and extractables. However, it should be observed that McAuliffe and Price (1964 and 1976 respectively in Milner et al 1977) have investigated the solubility of various classes and fractions of hydrocarbons and the following points have come to light.

1 For each homologous series of hydrocarbons, solubility decreases for increasing carbon number.
2 For a given number, ring formation increases solubility.
3 Branching decreases solubility for paraffins but not for naphthalenes and aromatics.
4 Unsaturation increases solubility.

In extreme cases the solubility of some organic compounds in water can be very significant (Solli pers. comm. 1977) and it should be remembered that the (hydrophilic) functionality of a compound is a very important characteristic to be considered.

k Recycling

Many workers favour (chromic) acid treatment to clean glassware with rinsing in distilled water and the appropriate organic solvent prior to use (Burlingame et al 1968, Schenck and Havenaar 1969, Vuchev et al 1971). Eglinton et al (1964) used detergent often ultrasonically before rinsing in distilled water and solvent. They kept glassware in dust-free containers when not in use and between operations flasks were either stoppered or covered with aluminium foil. In fact, ultrasonic extraction of dandruff in n-heptane allowed squalene to be isolated and cause a peak in the nC_{28} -nC_{29} range during GLC analysis.
For this study and between each complete extraction-recovery cycle, all the hardware was cleaned prior to re-use . The thimbles

after being left to dry in a fume cupboard were emptied of their residue and cleaned manually by scraping any adhering sediment particles from their walls. They were then blown clean with a jet of compressed air and degreased for at least ½ hour before subsequent use. The soxhlets, caps and filter funnels were degreased for ½ hour within the plant but the round-bottom large extraction flasks (5 litre capacity) and small recovery flasks (½ litre capacity) were partially filled with hot trichloroethylene, stoppered and left for ½ hour. Such washing was repeated three times for each flask and the equipment employed for all cleaning was an ICI metal degreasing plant (Plate 7).

Recovered solvent was reapplied in subsequent extractions on the understanding that any low boiling extractables will forever remain in a closed system, or be evaporated with the solvent during any subsequent extract isolation stage. Ideally, of course, the solvent should be redistilled prior to re-use (Schmidt-Collerus et al 1976) but in the absence of extra facilities to do this, the first aliquot of recovered solvent was discharged (especially to remove any water).

1 Conclusions

Hobson (1966) mentioned that drying, milling, prolonged extraction with heated solvents and extraction with ultrasonics "all may afford opportunities for some change".

Earlier Erdman (1961) had suggested that in some cases, certain compounds could be formed during the preparation of extracts and Degens and Reuter (1964) stated that the "chemical nature of compounds extracted by organic solvents or water is generally not altered".

Mathews et al (1970) commented that "on general chemical grounds there is little reason to expect differential retention among n-alkanes during ..... laboratory extraction" but they did emphasise that extraction procedures are more severe than natural geochemical processes within a shale. With regard to an oil, it was maintained that an extract would contain compounds which are not mobilised into a crude and similarly, those which are usually only partially mobilised would be fully extracted. Also, extracts would contain all of the residual compounds which can be

separated from the organic matter, including further diagenetic products, after compaction had caused fluid expulsion and ejected the crude.

Thus, all stages and parameters for solvent extraction, as Baker (1965) observed, are worthy of continued research in their own right to bear out any truth in the foregoing and to optimise the procedure for soluble extract determination.

(One avenue of future study arising out of this work is an investigation of the change of extract composition with respect to the duration of extraction).

It may also be concluded here that disconformity between experimental procedures in different laboratories is currently highlighted by solvent extraction; chiefly because of its hitherto ill-documented complexity. It should now be very evident that such disagreement does not allow the truthful, direct comparison of results (Bloxam 1971) and this situation in fact discourages investment from industry (Fuller pers. comm. 1976).

Finally, work presented in this study was executed with equipment approximately 10 years old and most present-day systems now function on a relatively vastly reduced scale. With improved technology it can be realised that solvent extraction in a general application for source rock evaluation may one day be omitted.

A pyrolysis technique where stepwise thermal extraction (see Martin, 1975) and collection of (where appropriate) the gas (C_1-C_4), gasoline (C_5-C_7) and solvent soluble (C_{15+}) hydrocarbon fractions (c.50°-275°C) with subsequent high temperature kerogen decomposition products (c.500°C) to allow ('on-line') GLC-MS analyses perhaps offers a rapid and feasible alternative.

m Summary of this study

It is felt that any reader should be able to reproduce the experimental work of any author immediately with confidence and without the need to search for or decipher experimental technique. Consequently, the analytical procedures used in this study are annotated in a stepwise fashion for the convenience of the reader.

1 Hand sized 'fresh' (shale) outcrop samples reduced to fragments (max. $\frac{1}{4}$ inch) in a cast iron pestle and mortar.

2 Fragments reduced to particles in a Raymond Rotary Mill

(Plate 1) through a sieve of an average maximum diameter of 0.024 inch.

3 Rock flour weighed by difference into a compressed filter paper thimble (170 cm x 65 cm ID) with a central filter paper spiral (trimmed and twisted Whatman No.1 24 cm) and plugged with glass wool.

4 Packed thimbles with iron framework support centrally placed in soxhlets (of approximate 1.5 litre capacity).

5 Soxhlets joined to 5l "boiler" flasks, each containing 3.5l of freshly prepared (Plate 2) azeotropic benzene-methanol.

6 Reflux condensers attached via caps with spring clips to soxhlets and electric (Isopad) mantles set at 80°C for 22 hours to allow gentle refluxing of the solvent at its boiling point. (The first cycle takes about two hours to be completed) (Plate 3).

7 Reflux condensers and caps disconnected upon cessation of extraction and thimbles balanced on support above the level of the solution (if any) in the soxhlet to drain.

8 Thimbles removed whilst wet but not dripping (and placed in fume cupboard to dry).

9 Frameworks removed and any contents of the soxhlets with washings decanted into respective "boiler" flasks with remainder of extract solution.

10 Boiler flasks and contents transferred to waterbath and connected to the fractionating columns (25 cm x 2.5 cm ID) which contain Fenske helices (Plate 4).

11 Waterbath maintained at 80°C to enable recovery of the bulk of solvent into reservoir within one working day (simultaneously for four sample runs).

12 Extract solutions decanted with washings into small (500 ml) flasks.

13 Further solvent stripping achieved individually over an electric mantle set at 80°C and through a distillation column (40 cm x 2 cm ID) packed with Fenske helices (Plate 5). (Joints in 5, 6, 10 & 13 all lubricated with the least quantity of high vacuum silicone grease and relevant flask necks wiped clean before any decantations).

14 When reduced, extract solution filtered into pre-weighed glass tube (10 cm x 2.5 cm ID) together with flask and filter paper washings.

15 Sample tubes placed in an oven under a draught of air at 50°C until bulk of solvent appears to have evaporated (Plate 6).

16 When appearing 'dry' the extract sample weighed every 24 hours until a penultimate weight differs from a final weight by not more than 0.0005 grams.

17 When dried, the extract stored in cork stoppered tube for subsequent analysis.

TABLE 18. ELUTROPIC SERIES.

TRAPPE 1940 (in Stock & Rice, 1974)	SWAIN 1951 (in Bonnet, 1958)	WILLIAMS et al 1954 (in Stock & Rice, 1974)	BONNET 1958
Pure water.		Pure water.	
Methanol.	Methanol.	Methanol.	Methanol.
Ethanol.		Ethanol.	Pyridine.
Propanol.		Acetone.	Ethanol.
Acetone.	Acetone.	Propanol.	Acetone.
Ethyl acetate.	Pyridine.	Diethyl ether.	Ethyl acetate.
Diethyl ether.		Ethyl acetate.	
Chloroform.	Heptane.(?)		Chloroform.
Dichloromethane.			
Benzene.	Benzene.		Benzene.
Toluene.		EGLINTON et al, 1964	
Trichloroethylene.		N-hexane. (3% Benzene)	
Carbon tetrachloride.			Carbon tetrachloride.
Cyclohexane.		Cyclohexane.	
Hexane.		N-heptane. (0.03% Benzene)	Light petroleum.
DECREASE IN ELUTING POWER, DIELECTRIC CONSTANT & POLARITY			

5 FRACTIONATION

a Introduction

Bonnet (1958) has recorded that chromatography was first applied in the petroleum industry by Mair and Streiff around 1940 and that the first application in petroleum geology was by Smith in 1952.

Figure 6 (Loose) relates the methods, histories and brief details of chromatographic techniques in general, and improved technology has caused such an explosive growth of techniques that a more detailed review is beyond the scope of this presentation. Fractionation of organic materials, such as extractables, into broad classes of compounds is easily and readily achieved, notably by either column or thin-layer (TLC) chromatography. These two methods as applied in organic geochemistry relevant to petroleum exploration geology are therefore discussed.

Before however it is essential to understand that all chromatographic methods rely upon the fact that the substances to be separated can distribute themselves between a mobile phase and a stationary phase in proportions which vary according to their respective distribution/partition coefficients. Thus, small differences in sorptive behaviour of components are translated into large differences in migration. The greater the number of times of exploitation of such behaviour the greater is the separation and/or the less need be the differences in order to obtain improved separation. Such distribution coefficients will of course depend upon the nature of the mobile and stationary phases as well as the chemical structures of the substances (Stein & Moore, 1951). For example, different retention values (R_F) for various components arise in (analytical) TLC where

$$R_F = \frac{\text{distance moved by component}}{\text{distance moved by solvent (front)}}$$

Rubenstein et al (1975) have separated aromatics and sterenes according to the differences in R_F values (0.0-0.9 and 0.9-1.0 respectively) using silica gel TLC.

The desorptive power of solvents (mobile phases) are tabularised in Table 18 and the adsoption of various organic compounds can be classified after Bonnet (1958) in order of high to low adsorption:

Acids & Bases > Alcohols & Thiols > Aldehydes & Ketones > Esters Unsaturated hydrocarbons > Olefins & Aromatics > Saturated hydrocarbons.

In particular, it is advisable to exercise vigorous storage control for adsorbents since they may 'age' or deteriorate and cause difficulties in reproducing their properties for successive separations. Generally, heating to 200°C for 4 hours is a safe precaution for most materials (Stock & Rice 1974). However, Eglinton et al (1964) activated alumina at 200°C for 2 days after washing it with solvent, whereas Connan (1974) activated alumina and silicagel at 180°C for 2 hours and 400°C for 5 hours respectively. Acidity variations will especially affect R_F values of acidic and basic components and are likely to be encountered more often with alumina (Stock & Rice 1974). As silica gel is often supplied in plastic bags, serious contamination can result especially from gel which has been in close contact with the plastic.

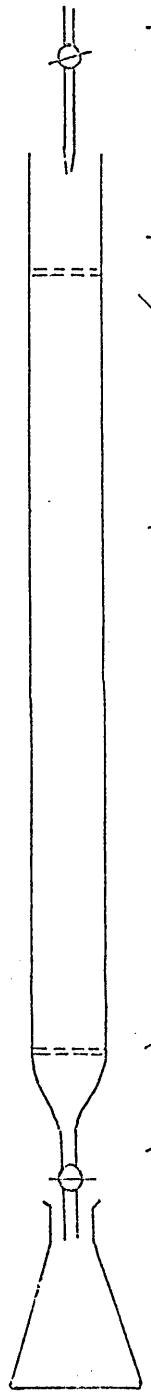
Washing with solvent can be done in soxhlets if the adsorbent is being used in a column whilst elution with a polar solvent (e.g. ethyl acetate) followed by activation of a prepared plate is appropriate for TLC prior to use (Solli pers. comm. 1977).

The progress of separation involving non-coloured components often necessitates means of identification and techniques such as UV light, chemical staining (e.g. I_2) and radioactive staining can be applied (Stein & Moore 1951, Stock & Rice 1974).

Now, adsorbents are usually efficient catalysts (Stock and Rice 1974) and Stein and Moore (1951) have noted that "occasionally compounds alter chemically during the procedure". In fact Blankenship and Nelson (1961 in Degens and Reuter 1964) suspected hydrocarbon generation from a pheophytine source when passing an organic extract along activated alumina. However, documented cases of alterations and synthesis in chromatography are rare amongst source rock evaluation studies and do not appear to deter extensive use of column chromatography or TLC. Stein and Moore (1951) have actually concluded that the chromatographic "method is a mild one".

b Column Chromatography

Since this process of fractionation was not used in this study



Generally the slower the passage of eluate through the column the sharper is the seperation.(Eglinton et al 1964 used one drop/second under slight air pressure.) Gradient elution devices are optional (first noted by Alm et al 1952).

SAMPLE applied for example via a small pipette which is rotated around the column wall. Any adhering sample is washed down with mobile phase applied in the same way.

A piece of filter paper or thin layer of clean sand can be used to protect the top of the column packing.

ADSORBENT must be uniformily packed and activated for maximum efficiency. 100-200 BSS particle size is usually suitable and once packed the adsorbent is always kept wet to prevent cracking. Channeling will occur if air bubbles are included during packing. Tswett tried more than 100 materials as column packing which is usually washed with the first eluate prior to sample loading.(Eglinton et al1964, Mathews et al 1970.)

COLUMN may be glass tubing or transparent nylon.

SUPPORT for packing can be a sintered glass disc, a plug of glass wool or a porous plate.

DETECTOR SYSTEM ideal (eg.UV) to allow automatic collection of successive fractions.

NON-ELUTED FRACTION can either be noted seperately or incorporated in the asphalt fraction. (Ferguson 1962, Bloxam 1971 & Palacas et al 1972.)

(Compiled mainly from Stock & Rice,1974)
Not to scale.

FIG.7 An annotated diagram to illustrate the BASIC PRINCIPLES OF AN ADSORPTION COLUMN.

the essentials of the experimental method are summarised in Figure 7. Known applications of relevance are reported in Table 19 and with regard to these, Nagy and Gagnan (1961 in Degens and Reuter 1964) reported that the elution characteristics of alumina and silica gel were similar but not identical.

In addition to such usage, Shibaoka et al (1973) employed "liquid chromatography" to fractionate extracts whilst Bray and Evans (1961) had earlier applied "elution chromatography" in some instances for the same purpose. Koons et al (1974) more recently declared fractionation of a C_{15+} fraction via "adsorption-liquid chromatography" whereas Milner et al (1977) distinguished the compositional classes of saturates, low ring aromatics (4 or less rings), high ring aromatics ($>$4 rings), asphaltenes and NSO compounds for the same fractions of oils using "liquid-chromatographic separation". However, none of these authors elaborated further.

The views that column chromatography needs relatively large quantities of adsorbents and sample and is a relatively slow process have been counted as disadvantages by Gill et al (unpub.) who further maintain that such separations still require further purification. Whatever, the technique of packing a uniform efficient column does require a lot of patience and practice to perfect (Solli pers. comm. 1977).

In fact, Baker and Claypool (1970) used UV light to estimate contamination in saturated fractions as less than 3% and probably as 1% by aromatics and heterocyclic non-hydrocarbons. The same authors used elemental analyses to illustrate that the aromatic fraction contained less than 10% non-hydrocarbon heterocyclics. Similarly Burns et al (1970) remarked that "no significant" UV absorption in the 270-280 microwave range was shown by their saturate fractions.

Also, the laborious recovery procedure necessary in TLC does not arise here since successive eluates merely need evaporation to leave the respective fractions. For example, Reed and Kaplan (1977) reduced the solvent to about 2 ml for each fraction by rotary evaporation and transferred each fraction (with a glass syringe) to a tared vial for final solvent removal under a stream

TABLE 19. USAGE OF COLUMN CHROMATOGRAPHY.

AUTHOR(S) & DATE.	ELUANT. SATURATES.	AROMATICS.	ASPHALTICS.	ADSORBENT/SUBSTRATE:SAMPLE RATIO
Smith,1954*	Pe	B	M	Al
Bonnet,1958	Hp	B	Py,M	Al
Ferguson,1962	Ch	B	B-M	Si,32Å pores,100:1
Gunn & Cooper,1962	Hp	B	Ac,M	Al
Degens & Reuter,1964	Hp	B	Py,M,Ac	Al,250:1
Eglinton et al,1964	Hp or Hx	?	?	Al,20-100:1
Henderson et al,1968	Hx	B	?	Al,c.300:1
Schenck,1968	?	?	?	Si-Al
Baker & Claypool,1970	Ch	B	B-M	Si
Mathews et al,1970	Hp	B	M	Al
Bloxam,1971	Hp	B	Py,M	Al
Henderson et al,1971	Hp	?	?	Si
Vuchev et al,1971	Hx	B	Cl,B-Cl-M	Al,80-200 mesh.
Wszolek et al,1971	Hp	B	M	Al
Palacas et al,1972	Ch	B	B-M	Si
Connan,1974	Hp	B	M	Al-Si
Powell et al,1975	Pet.E	B	M	Al
Allan et al,1975	Pet.E	B	M	Si,60-120 mesh
Rubinstein et al,1975	?	?	?	Si,c.60:1
Foscolos et al,1976	Pe	?	?	Al
Albrecht et al,1976	?	?	?	Si
Ishiwatari et al,1977	Hx	B	B-M(1:1)	Si
Reed,1977a,1977b.	Hp	B	M	Si,c.100:1
Reed & Kaplan,1977	Hx	B	M	? ,200:1

*Hobson,veb.comm.1972.

Pe: Pentane. Hp: Heptane. Ch: Cyclohexane. Pet.E: Petroleum ether (40°-60°C).

B: Benzene. M: Methanol. Py: Pyridine. B-M: Unspecified Benzene-methanol.

Ac: Acetone. B-Cl-M: 1:1:1 Benzene-chloroform-methanol. Cl: Chloroform.

Al: Alumina. Si: Silica gel.

TABLE 20. COLUMN DIMENSIONS.

Eglinton et al;1964:	? x 2.5cm/1.0cm. D.
Baker & Claypool,1970:	26cm. x 8mm. ID.
Mathews et al,1970:	36" x ½" or 10" x ¼"
Vuchev et al,1971:	7cm. x 2cm.
Wszolek et al,1971:	27.5cm. x 4.5cm. ID.

of purified nitrogen. Bloxam (1971) dried such fractions under vacuum.

Actual column dimensions are often lacking and from the (24) applications in Table 19 only five can be related in Table 20.

c Thin Layer Chromatography (TLC)

This method was adopted for fractionation of the extracts in this study and has been extensively employed by Gill et al (unpub.). TLC is 10-100 times more sensitive than equivalent paper chromatography (Degens and Reuter 1964) and can also permit seperations which do not work on paper (Stock & Rice 1974). In fact TLC combines some qualities of both paper and column chromatography (Hodgson et al 1967) and Albrecht et al (1976) used silica gel sometimes impregnated with silver nitrate to isolate "total alkanes" by TLC either as an alternative to or in conjunction with column chromatography.

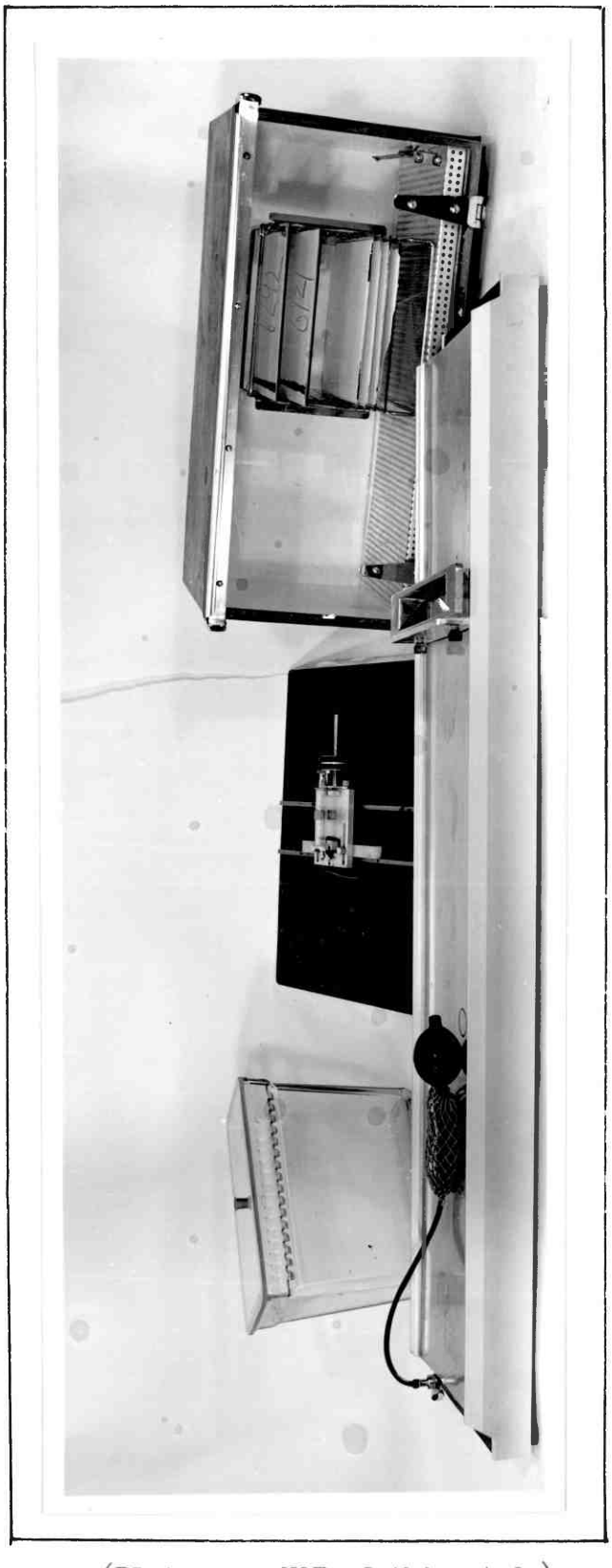
ci Plate preparation

Several methods of applying a substrate to an inert rigid support have been used (e.g. spraying, dipping or pouring) but spreading appears to be the most advantageous especially to effect an even uniform coverage of adsorbent. Today, most commercial apparatus (developed after Stahl's work in the late 1950's) generally caters for 20 cm x 20 cm or 20 cm x 5 cm (glass) plates although 'do-it-yourself' apparatus can still be devised.

A moving plate spreading device has several disadvantages since it necessitates the plates to be of equal dimensions and each plate has to be moved immediately after being covered to make room for the next plate. In contrast, a moving spreader in conjunction with a plate holder can eliminate problems caused by unequal thicknesses and widths of the glass plates. It can also allow the freshly covered plate to remain still until the applied adsorbent has had some time to become firm or dry.

For this study plates were fixed in between and below two parallel rails and held rigid by the inflation of an air bag lying beneath the plates. Incorporation of a quarter plate to lie below the hopper whilst it was filled with slurry allowed five 20 cm x 20 cm plates to be covered on evenly pulling the loaded hopper across their faces (Plate 8). The front edge of the hopper rests upon

PLATE 8 SHANDON COMMERCIAL TLC EQUIPMENT.



(Plates are NOT of this study)

the glass plates but the trailing edge was adjusted to give a film of adsorbent of a standard thickness of approximately 250 μm.

Here it is relevant to note that thin films often cause erratic R_F values whilst thick films tend to crack on drying. Also, as on drying shrinking occurs and during development expansion happens, the precise thickness of adsorbent is incalculable. Wedge adsorbent applications or grooved plates do, however, afford substrates capable of holding greater quantities of sample.

On drying the freshly covered plates in air (to allow the adsorbent to settle) the plates were then carefully removed from the holder and stacked in racks which when fully loaded were placed in an oven for two hours at 110°C. After drying, the prepared plates prior to actual use were stored in a dessicator as traces of water must be avoided because partition effects will occur.

The hopper itself was filled with a homogeneous slurry of Merck Kieselguhr G nach Stahl type 60 and distilled water. The slurry was made from its constituents in the ratio of 75 grams:120 mls respectively by vigorously shaking for about 90 seconds. In fact the diatomaceous earth from its standard nomenclature (Stock and Rice 1974) contained a calcium sulphate binder to about 10% by weight. Alternative adsorbents used in TLC embrace a wide variety (such as alumina, silica gel, cellulose powder, celite, calcium sulphate, polyamide powders etc) and, for example, Schmidt-Collerus et al (1976) used water and acetone (95:5) to make a slurry of silica gel for plates of 0.5 mm thickness.

Of course ready-made plates of better reproducible properties can be purchased but here prior to use and re-use the glass plates were cleaned with detergent, rinsed thoroughly, air dried and then degreased for approximately ½ hour.

cii Sample application

Actually, spotting via a (micro-) pipette (Eglinton et al 1964), loop or syringe, or streaking with a mechanical device (Plate 8), are methods to permit reproducible sample application upon an adsorbent depending upon the purpose of the TLC.

In this study the latter method was utilised. A segma durex

5 ml glass syringe connected to a 26G bent needle with an attached fine but not too flexible tube was used in conjunction with a trolley. Two plates per sample were streaked to provide adequate material for each of the fractions during recovery. (Between streaking and developing, streaked plates were stored in a dessicator).

Initially, the extract was (re) weighed and (re) dissolved in fresh benzene-methanol azeotrope to give a representative sample solution which was as concentrated as possible. Excess material together with washings was returned to the sample tube after streaking in accordance with Figure 8. The syringe components were washed in solvent and degreased between successive sample applications as an additional precaution.

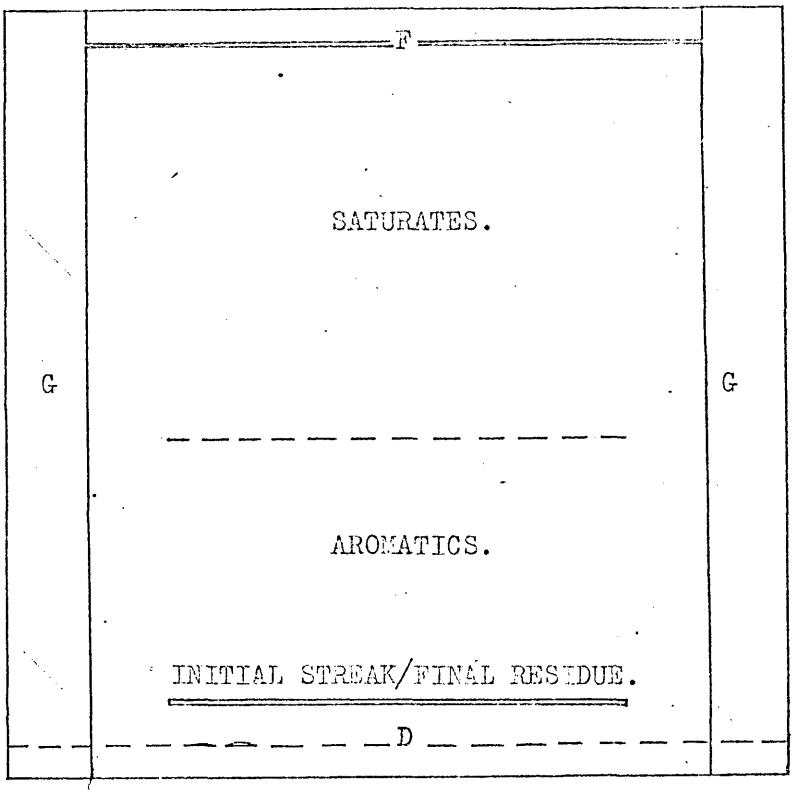
Advantages which can be mentioned here are that, according to the aim of the TLC, minute quantities of sample can be used (Hodgson et al 1967) or conversely sample application using a very volatile solvent (chloroform or carbon disulphide) and blow drying can allow additional loading without an unacceptable fattening of the streak (Solli pers. comm. 1977).

ciii Plate development

With TLC a mobile phase can be made to ascend, descend, or radiate through the adsorbent. For this work loaded plates were developed in a one-dimensional vertical sense by placing them in a commercial 'chromo-tank'. A single mobile phase/elutant was employed and n-heptane was redistilled from IP specification heptane at 98.4°C for the purpose.

The time taken for the mobile phase front to reach within about ½ inch of the top edge of the plate was about 1½ hours and unlike column chromatography the actual development period requires no attention from an operator. For an identical separation, TLC is about 4 times as fast as paper chromatography (Stock and Rice 1974).

Upon development it is not advisable to leave the plates in the tank for too long as diffusion and evaporation will occur. In this study, the respective fractions were delineated according to Figure 8 using UV light (Hanovia Model II 3660°A) whilst the adsorbent was still solvent-wet (to limit any diffusion) and the



F: A finish line can be drawn across the top of the plate and cut in the adsorbent at a fixed distance to prevent any chance of over-running and help to standardise successive operations.

G: An inert rigid support; in this instance provided by 20 x 20 cm. glass plates.

SATURATES: Colourless and non-fluorescent; hence front/rear can not be detected within ordinary substrate. Whole section taken for recovery.

AROMATICS: Generally colourless but fluorescent. Here sometimes faint red/yellow broad diffuse bands but usually diffuse/homogeneous mauve fluorescence under (brief) 3880A UV radiation.

INITIAL STREAK denotes site of major portion of relatively immobile ASPHALTICS (when using n-heptane single phase development) at end of elution. Streak applied at constant distance like F.

D: Depth of immersion standardised by using the same quantity of mobile phase in the tank for successive seperations; generally between 0.5 - 1.0 cm.

NB: Stahl suggested running a standard with every seperation; e.g. 'Butter Yellow'/p-dimethylamino-azobenzene (Stock & Rice, 1976), but only Schmidt-Collerus et al (1976) reported doing this.

FIG.8 A diagrammatic sketch of a DEVELOPED PREPARATIVE TLC PLATE with annotated details.

divided plates were then allowed to dry prior to recovery of the fractions. Eglinton et al (1964) used 254 nm to define 'aromatics' whilst Schmidt-Collerus et al (1976) specified the same radiation to distinguish polycondensed aromatic hydrocarbons.

With a one-component mobile phase, Stock and Rice (1974) have reported that a $\pm$ 10°C temperature change does not much affect the TLC separation. Another factor to observe during development is the maintenance of a homogenous atmosphere within the chromotank. To assist this the lid must fit as securely as possible and the tank should be as small as practical. One sign indicative of an unsaturated atmosphere is a concave solvent front and to avoid this the tank walls can be lined with solvent-saturated filter paper (Stock & Rice 1974).

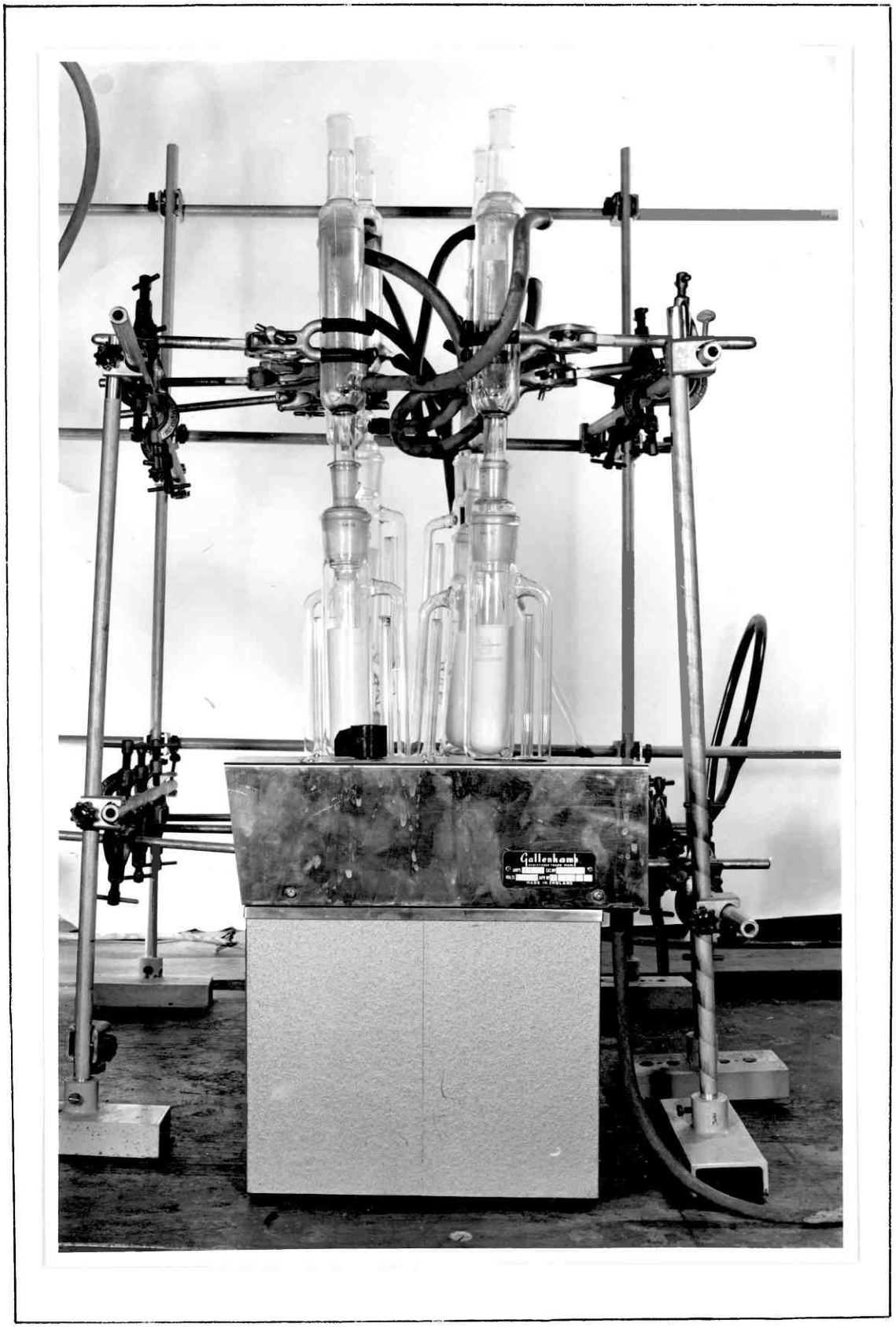
A means of documenting developed plates is through photography and Schmidt-Collerus et al (1976) used polaroid film. By employing benzo-(a)-pyrene as a test material, these authors estimated the total loss from the streaking stage to specto-photometric identification as about 6%.

civ Fraction recovery

Each respective fraction from both plates per sample was placed in a separate compressed filter paper thimble ($7\frac{1}{2}$ cm x 2 cm ID) and plugged with glass wool. The adsorbent with products was manually transferred by scraping the glass plate with a glass slide-cover plate ($7\frac{1}{2}$ cm x $2\frac{1}{2}$ cm) and using a paper flute. A six-fold small scale soxhlet apparatus was them employed (Plate 9) to extract each fraction with 150 ml of distilled benzene-methanol azeotrope for a total 'standard' time of 18 hours. The duration included the time needed for the waterbath to warm up to 80°C (approximately 1 hour) but on switching off the bath was evacuated and refilled with cold water for an immediate cooling down.

In this case, the contents of the thimbles were always completely saturated with solvent (owing to the small scale) and the soxhlet siphoning capacity was about 110 ml. On completion of extraction any residual solutions in the soxhlets were added to the respective (250 ml) round bottom flasks with washings and the solutions then reduced individually using the apparatus in Plate 5.

PLATE 9 SMALL SCALE SOXHLET ASSEMBLY FOR TLC.



Five reductions could usually be achieved within one working day and each was filtered through No.1 Whatman filter paper into preweighed tubes (10 cm x 2.5 cm ID). The ultimate solutions were then evaporated to 'constant' weight according to the previously established criterion for the rock extracts. When dry, the isolated fractions were stored in stoppered tubes, mainly in the dark at room temperature. Simoneit and Burlingame (1971) did, however, store such fractions in a refrigerator, in solution form prior to subsequent analysis.

With the exception of the water condensers, the remainder of the glassware and the thimbles were recycled after cleaning and degreasing. At least 30% of the solvent was estimated to be lost during the complete process.

For all the asphaltic fractions (of both the Kimmeridge Clay and Wealden samples) the adsorbent always remained stained. A brown hue when wet was seen to fade to a pale skin colouration on drying. An attempt to remove the strongly adhering material with acetone left a slightly more clean looking adsorbent but any recovered material was negligible in weight. In this respect, Constantinides and Arich (1967) have mentioned that "the chromatographic method leads to far better results but is usually slow and has the disadvantage of incomplete recovery for the sample; this being particularly true for non-hydrocarbons". Such material is presumably analogous to the 'non-eluted' NSO compounds often computed by difference in column chromatography. (Ferguson 1962, Bloxam 1971, Palacas et al 1972, Reed 1977) and for a comparative study where the fractions are expressed qualitatively dismissal appears justified. Further, it seems relevant to recall that Richardson (in Cunningham-Craig 1916), in filtering a Trinidad asphalt through argillaceous matter, could not recover all of the bitumen from the clay and "nothing short of distillation could remove it". Degens and Reuter (1964) did insist that TLC was not accurate enough for quantitative determinations and an accuracy in the order of 10% appears to be generally accepted (Russell priv. comm. 1976).

Subsequent to the work of this study, a semi-automatic 'fail-safe' TLC recovery and distillation plant was installed within the section to cope with 18 simultaneous soxhlet recoveries (overnight

for 22 hours) and perform 6 solvent recovery distillations at any one time. It is recorded here that the two different procedures did in fact give a very similar result for an identical sample (W12) and of course the latter introduction excels in efficiency and convenience.

Ratio:	Saturates	:	Aromatics	:	Asphalts
18 Hr waterbath	39.6	:	7.2	:	53.2
22 Hr electric mantle	35.8	:	8.0	:	56.2

d Conclusions

Casual designation of fractions with loose terminology is wrong and misnomers could be adopted in a literal sense by an unsuspecting reader. To avoid any misconceptions, Baker & Claypool (1970) suggested using the terms 'saturate' and 'aromatic' for the respective fractions of an extract.

Accordingly these names are adopted here together with the terms asphalt(ic)s/non-hydrocarbons which apply to the residual non-migrated fraction; more so the latter terms embrace component types such as asphaltenes, eluted NSO compounds and non-eluted NSO compounds which were not distinguished here.

It is rather surprising that although very sophisticated tools are now well established for detailed studies of the various fractions (GLC, MS, NMR, etc) relatively little attention is evident for the advancement of actual fractionation techniques themselves (certainly within academic organic geochemistry orientated to source rock studies.

However HPLC (Done et al 1972), for example, which can handle small samples, offers a way for more accurate and fast fractionation but, owing to its current expense, appears largely restricted to commercial circles. Schmidt-Collerus et al (1976) have remarked upon its strong promise to separate polycondensed aromatic hydrocarbons. (Figure 6, loose).

Another tool which may also start to gain wide application for accurate fast and highly reproducible determinations of extract fractions is C-13 NMR spectrometry (Budde 1976). A duration of one hour with very little sample preparation are attractions of this process which concentrates the C-13 adsorption for saturated and aromatic (naphthenic, polar and pentane-insoluble compounds)

hydrocarbons into two well separated regions (10-50 ppm and 120-150 ppm with respect to TMS) and permits their integration (since olefinic compounds are present to only a very small extent).

Constantinides and Arich (1967) have mentioned the use of liquid SO_2 for separating heterocyclics from hydrocarbons (?).

6 GAS-LIQUID CHROMATOGRAPHY (GLC)

a Introduction

The first commercial instrument became available in 1955 and Keller (1961) has since attributed the explosive growth of GLC to the petroleum industry. The literature about GLC can now be described as especially "staggering" (Stock and Rice 1974) and with regard to rapidity ($1\frac{1}{2}$-2 hours) and sensitivity (ppb) Boyle and Garrett (1970) have noted GLC is the most significant development for hydrocarbon analyses.

In this technique (as previously noted under fractionation) components of a mixture separate themselves between a mobile gas phase and a stationary liquid phase according to their distribution coefficients. The plate theory of Martin and Synge (as modified by Glueckauf) or the rate theory (as advanced by van Deemter et al) are applicable to thoroughly explain GLC (Stock and Rice 1974) and owing to its importance a flow diagram with explanation for a generalised GLC instrument is included in the Appendices.

Here, a theoretical plate can be defined as a small section of the column in which equilibrium is established between the mobile phase and the dissolved phase of the solute before the mobile phase passes onto the next stage of the column where the process is repeated. It is possible to estimate the number of theoretical plates from a peak width and the time taken to elute the peak maximum:

$$n = 16\, x^2/y^2 \text{ where,}$$

n = number of theoretical plates

x = horizontal distance between injection point and component maximum

y = width of component peak

Thus, n is seen to be a measure of the efficiency of a column and could be increased by simply lengthening the column. However, the analysis time and the ratio of the inlet to outlet pressure will also increase and reduce efficiency. Therefore the concept of height equivalent to a theoretical plate has arisen where:

$HETP = L/n$ L = Length of column
n = number of theoretical plates

The smaller the HETP the better is the efficiency of the column.

In fact, columns of more than 30,000 theoretical plates are possible although such ordinarily packed columns operate well below their theoretical performance (Stock & Rice 1974). Coated capillary columns (see later) are a great improvement but it should be realised that they can not replace ordinary-packed columns for many types of separation. Also, GLC in its usual sense can not handle all organic compounds since, for example, proteins and dyestuffs can not be volatilised or even heated without decomposition (Figure 6).

However, for most source rock evaluation studies, GLC currently finds the most popularity in its appliaction for alkane analyses where the distribution, CPI and pristane-phytane ratios are often sought. It could of course be extended to allow study of other extract fractions and the pyrolysis condensates whilst its use to check solvent purity has been mentioned.

Generally speaking saturate fractions of rock extracts can not be resolved in a very meaningful way by ordinary packed columns and pre-column separation of the normal, branched and/or cyclic components of such concentrates is required. This can be achieved to varying degrees of success by either urea or thiourea adduction or with molecular sieves; the latter technique for this purpose first being reported independently in 1958 by Brenner and Coates and Whitham (Schenck and Eisma, 1962). Conditions of ordinary packed columns used susequently to any of the following three separative methods are summarised in Table 21.

b Urea adduction

Urea adducts with straight chain alkanes whilst thiourea adducts with branched alkanes but exceptions to such rules do occur (Eglinton, 1968). It has been claimed that such separations are never completely thorough (Eglinton 1968) and in fact up to 30% non-normal alkanes have been observed in urea adducts (Schenck and Eisma 1962). Clathration with urea has been employed by Haug and Sever (1971) and Wszolek et al (1971) specified the experimental procedure for thiourea adduction.

Basically, the saturate fraction is dissolved in a solvent and a saturated solution of urea added. The resulting mixture can be warmed and shaken until homogeneous and then cooled. The crystalline adduct which precipitates out from solution can be

TABLE 21. ORDINARY-PACKED GLC COLUMNS.

AUTHOR(S) & DATE.	COLUMN TYPE.	COLUMN PACKING.	CARRIER GAS.	COLUMN/INJECT-DETECT TEMPS.
Schenck & Eisma, 1962.	60cm/2m x 6mm ID.	60%Al_2O_3 40%NaOH 50 mesh support with SF96 in 100 :30 ratio resp.	H_2 3.6 l/hr.	205°C isothermal.
Eglinton et al, 1964.	5/10 ft x $\frac{1}{8}$" D.	?	N_2	3°/min or 10°/min over 100° - 300°C; inject - c.220°-300°C detect - 150°-240°C. (FID)
Mathews et al, 1970.	5ft x $\frac{1}{8}$" St.Steel	Chromosorb W with 5% SE90.	N_2 60ml/min.	50°-325°C at 8°C/min. (FID)
Palacas et al, 1972.	5ft x $\frac{1}{8}$" OD. St.Steel	100-200 mesh Chromosorb W with 1% OV-1	?	100°C for 1 min; 100°C -250°C in 15 mins. & 250°C for 10 mins (FID)
Albrecht et al, 1976.	1.5m x 3mm	1% SE30.	?	?
Powell et al, 1976.	20ft x .04" St.Steel.	Supasorb 100-120 mesh. with 3% Apiezon L or 3% OV-1.	?	?
	50ft x .08"	Varaport 30 100 -120 mesh with 3% OV-101.	?	?
Ishiwatari et al, 1977	5ft x $\frac{1}{8}$" St.Steel	100-120 mesh Gas Chrom Q with 3% Apiezon L.	?	70°-290°C at 8°C/min.
Gill et al, unpub.	10ft x $\frac{1}{8}$" OD. or 12ft x $\frac{1}{4}$"-OD St.Steel.	Chromosorb 9 80 -100 mesh with 2-6% OV-1 or 5% Dexsil.	N_2 80psi.	120°-290°C at 5°C/min with 290°C for 20 mins. inject & detect both at 350°C (FID)

TABLE 22. MOLECULAR SIEVE SEPERATIONS.

AUTHOR(S) & DATE.	SIEVE TYPE & SIEVE :SAMPLE RATIO;SOLVENT	OCCULATION	SEPERATION	N-ALKANE ISOLATION
Eglinton et al,1964.	5Å " pellets dried in vacuo (Hg pump) for 12 hrs.at 200°C over P_2O_5 & stored in dessicator 20-100:1 Dry benzene.	Sieve refluxed with solution for 1-3 days under dried system. (Drierite)	Soln.removed with pipette & sieve washed with hot benzene in all-glass soxhlet for several hrs. Wash-ings added to soln. & evaporated to give b/c alkanes.	Washed sieve treat-ed with 24% HF under benzene with stirring for c.1hr. to dissolve sieve. Benzene soln. filt-ered thru short column of pre-wash-ed Na_2CO_3 & evap-orated to dryness
Henderson et al,1968	5Å $\frac{1}{8}$"pellets. Iso-octane.	Sieve refluxed for 100hrs.in all-glass soxhl-et.	Supernatant & wash-ings combined to give b/c alkanes.	?
Mathews et al,1970.	5Å activated. Benzene.	Sieve refluxed for c.60-70hrs.	Washings & solution evaporated under vacuum to give b/c alkanes after sieve washed with benzene in soxhlet for c.8 hrs.	Sieve dissolved in 24% HF under benze-ne;free n-alkanes seperated & dried over anhydrous $MgSO_4$
Reed & Kaplan 1977.	5Å 100-200 mesh. c.50:1 Benzene.	Sieve refluxed for 24hrs.After decantation & washing,reflux repeated for 24 hrs.	All solutions & washings comoined to give b/c alkanes.	Sieve treated with HF under benzene & agitated for 6hrs. Liquid-liquid extr action with benzen-e repeated 5 time-s. Combined solns. dried over anhydr-ous Na_2SO_4 & solve-nt removed by RFE.

filtered off and washed. The process can be repeated with the supernatant and washings which themselves can be collected together for a similar precipitation with thiourea. In this way, the normal, branched and cyclic fractions can be separated (Maxwell et al 1971).

c Molecular sieves

5Å molecular sieves can be used to occlude normal alkanes and exclude branched and cyclic alkanes (Eglinton et al 1964; Henderson et al 1968, Mathews et al 1970; Allan et al 1977; Allan and Douglas 1977; Reed and Kaplan 1977) whilst 7Å sieves have been employed to occlude branched alkanes but not cyclic alkanes (Eglinton 1968).

In the first instance, Eglinton and Calvin (1967) have explained that normal alkanes can be regarded as smooth flexible rods of approximately 4.5Å diameter and thus be adsorbed by such 5Å alumino- silicate sieves. On this scale branched and cyclic alkanes are pre-cluded simply because they can not enter the pore throats of the sieve. Yet, with regard to the stearic effects which dictate the principle of sieving, Palacas et al (1972) noted difficulty in removing all of the HMW normal alkanes from saturate fractions. Schenck and Eisma (1962) mentioned that small amounts of iso-alkanes are always absorbed by 5Å molecular sieves and Reed and Kaplan (1977) have specified the presence of 3-methyl and 2-methyl alkanes within the occluded normal alkane fraction. For recovery of occluded normal alkanes by soxhlet extraction with n-hexane, Eglinton et al (1964) observed a bias towards LMW alkanes (with respect to those isolated by dissolution with hydrofluoric acid) and declared the slow process incomplete after two days.

The preferential occlusion of 'odd' members of a n-alkane (C_{15}-C_{38}) series has been investigated by Lee (in Douglas & Grantham, 1973) and no odd/even predominance was found to be induced during the procedure.

Overall, the general application of molecular sieves to effect such separations is quite a lengthy procedure and some are annotated in Table 22.

Finally, molecular sieves have also been incorporated directly

with ordinary-packed GLC columns (Schenck and Eisma 1962; Schenck 1968). Dual columns one with (A) and one without (B) a precolumn sieve allowed substraction of the resultant chromatograms (B-A) to determine the normal alkanes, and the life of the sieve was, of course, dictated by the degree of saturation by occluded normal alkanes.

d Capillary GLC

Alternatively and more conveniently total saturate hydrocarbon fractions can now be resolved by direct injection upon a capillary column or highly efficient packed column (Douglas and Henderson, 1972) as a result of the advances in GLC. In specific studies pre-column separation is still often carried out as well (Maxwell et al 1971) and Wszolek et al (1971), for example noted that the minimum efficiency (achieved only with capillaries) to separate steranes and triterpanes was of the order of 100,000 theoretical plates. Some capillary column conditions as applied in petroleum geology studies are given in Table 23 and such GLC has also been used by Schenck (1968) and Powell (1975). Constantinides and Arich (1967) have emphasised the high resolution of capillaries and Henderson et al (1968) calculated efficiencies for their long and short columns as 50,000 and 30,000 theoretical plates using 5α-cholestane.

e Identification of components

The most reliable way of identifying components of a mixture separated by GLC is in fact to trap them as they emerge from a column and feed each of them separately into a mass spectrometer (e.g.Henderson et al 1968, Burlingame et al 1969, Haug and Sever 1971, Simoneit and Burlingame 1971, Douglas & Grantham 1973, Albrecht et al 1976, Ishiwatari et al 1977, Reed and Kaplan 1977).

In the absence of such a costly piece of equipment most individual peaks are identified either by comparison of retention times with authentic standards run under (as nearly) identical conditions (as possible) and/or by co-injecting a standard and observing an increase for the relevant peak height (Dunton and Hunt 1962; Palacas et al 1972; Stock and Rice 1974 and/or Palacas et al 1972,

TABLE 23. CAPILLARY GLC COLUMNS.

AUTHOR(S) & DATE,	COLUMN DIMENSIONS & COATING.	SPLIT RATIO	CARRIER GAS	COLUMN/INJECT-DETECT TEMPS.
Eglinton et al, 1964.	150ft x .01" Apiezon L	500-5000:1	N_2 20ml/min	?
	200ft x .01" Apiezon L	100:1	N_2 15ml/min	(Argon ionisation detector)
Henderson et al,1968.	200ft x .01" Apiezon L 150ft x .01" 7-ring poly-phenyl ester	30:1	He 2ml/min	250°C isothermal.
Powell et al, 1975;Foscolos et al,1976.	50m x .25mm ID	?	N_2	100°C-250°C at 4-6°/min & held at 250°C
Albrecht et al, 1976.	45m x .25mm ID Apiezon L/ SE30	?	?	?
Reed,1977.	15m x .5mm OV-101	?	He 3-4ml/min at 100°C.	110°C-280°C at 4°C/min. inject - 210°C detect - 310°C (FID)
Allan et al, 1977.	20m x .25mm ID OV-101 (Glass) 50m x .25mm ID Dexsil 300 (Glas) 100m x .25mm ID OV-101(St.Steel)	?	N_2 1.5ml/min	80°C-300°C at 4°C/min.

TABLE 24. NET, SPECIFIC & RELATIVE VOLUMES.

$$V_N = JV_R = \frac{3(P_1^2/P_o^2 - 1)}{2(P_1^3/P_o^3 - 1)} f.t_1.t_2$$

where,

V_N = Net retention volume.

J = Compressibility factor.

V_R = Uncorrected retention volume.

P_1 = Pressure of carrier gas at inlet.

P_o = Pressure of carrier gas at outlet.

f = Flow rate of carrier gas at outlet pressure & column temperature.

t_1 = Time taken for air peak maximum to elute

t_2 = Time taken for solute peak maximum to elute.

$$V_g = V_N \frac{273}{T.W}$$ where,

V_g = Specific retention volume.

T = Temperature of column in degrees Kelvin.

W = Weight of stationary phase in grams.

$$\text{Relative retention volume} = \frac{V_N \text{ Standard}}{V_N \text{ Substance}}$$

Douglas & Grantham 1973, Allan et al 1975, Albrecht et al 1976, Allan et al 1977 respectively). (The qualification of 'nearly identical' conditions results in a pedantic sense from the fact that conditions for a subsequent injection will be strictly different, although to an infinitesmally small amount, due in particular to the progressive volatilisation of the stationary phase and slight adsorption of components from the previous material; such a deterioration eventually becoming apparent with usage). In general, net specific and/or relative retention volumes may be used to characterise a component peak (Stock and Rice 1974) and these are defined in Table 24. Specifically normal alkanes of increasing chain length emerge from a column in regularly spaced intervals which parallel their increasing boiling point (Eglinton and Calvin 1967). However there does appear to be some confusion in the order of elution of certain particularly important branched saturate components. Eglinton (1968), Powell et al (1975) and Powell and McKirdy (1975) have given an order pristane, $n\text{-}C_{17}$, phytane, $n\text{-}C_{18}$ whilst Eglinton and Calvin (1967), Albrecht et al (1976) and Reed (1977a, 1977b) have illustrated the sequence $n\text{-}C_{17}$, pristane, $n\text{-}C_{18}$, phytane (?).

f Measurement of components

Actual peak measurement can be achieved via

1 PEAK HEIGHT assessment where tall and narrow peaks give more accurate values but require very accurate flow rates and temperature control (Stock and Rice 1974).

or

2 PEAK AREA determination (Schenck and Eisma 1962; Albrecht et al 1976).

2a by multiplying the peak height by the peak width at half the peak height to give 94% of the true area for symmetrical peaks (Stock and Rice 1974) although Keller (1961) believed that an area reflects the fractional amount to within 2%.

2b by cutting out and weighing the actual peak or still more accurately cutting out and weighing a photocopy of the peak to exclude any printed lines (Stock and Rice 1974).

2c by planimetric determination (Palacas et al 1972) although additional instrumental error may be introduced (Stock and Rice 1974).

2d by electric integration; although additional instrumental error may be introduced (Stock and Rice 1974).

However, it should be remembered that linearity between peak height and/or peak area and the amount of injected material becomes less likely with greater concentrations of components (Stock and Rice 1974).

Finally, calibration can, of course, be achieved by introducing an accurately known amount of standard component.

g This study

Chromatographs for (22) Wealden (33) Kimmeridge Clay and (14) Oxford Clay total saturate fractions were run using a 39 metre x 0.5 mm ID glass support coated open tubular capillary column with methyl silicone SF96 and a recommended efficiency of 30,000-40,000 plates.

The column was housed in a Perkin-Elmer F30 Gas Chromatograph and temperature programmed from 100°/130°C to 270°C at 3°C per minute. A final time of 45 minutes was necessary for the elution of n-C_{36} alkane and nitrogen at 100 KN/m^2 pressure was used as the carrier gas. Both the injection block/sample splitter (3:1) and flame ionisation detector were maintained at 300°C; the recorder chart speed was 5mm/minute. Identification of the eluted components was achieved by comparison of their retention times with those of authentic compounds in a standard solution (the order of elution of ....n-C_{17}, pristane , n-C_{18}, phytane ..... was observed).

As the n-C_{32} alkane was not eluted during the linear temperature programming, peak heights could not be used for CPI determination (Allan and Douglas 1977) and peak areas were approximated by method 2a.

The Organic Geochemistry Unit of the University of Newcastle-upon-Tyne (as mentioned in the acknowledgements) was responsible for the provision of 14 Kimmeridge Clay and 10 Wealden saturate fraction chromatographs. These were run on a 20 metre capillary

column containing OV-101 and the column was housed in a Perkin Elmer F17 Chromatograph; being temperature programmed from 50-255°C at 4°C/minute. Nitrogen at 5 psi was employed as the carrier gas and the chromatographs were recorded with a chart speed of 15 inches/hour through a flame ionization detector. (All have been utilised for determination of CPIs, pristane/phytane ratios and pristane/n-C_{17} alkane ratios and are designated by the letter 'N' under the results).

7 QUANTITATIVE ELEMENTAL ANALYSIS

a C, H, N, S, O etc

For determinations of C,H,N, S and O in a material little has appeared in literature relevant to this study with regard to classical 'wet' methods of evaluation.

Beers and Goodman (1944) found total carbon and hydrogen in a (sediment) sample gravimetrically on a semi-micro scale (after Niederl and Pregle) when dry catalysed combustion (CuO, Ag wire or Pt asbestos) allowed collection of carbon dioxide and water by selective U-tube absorption with ascarite and dehydrite respectively.

Total nitrogen in a (rock or kerogen-concentrate) material has been measured almost invariably by Kjeldahl's method (Robertson 1911, Down 1939, McIver 1967). A known weight of sample is treated with a mixture of concentrated sulphuric acid and (potassium) sulphate. All the nitrogen is thus converted to ammonium sulphate and this is made alkaline with excess (potassium) hydroxide. On heating the evolved ammonia is passed into a measured volume of standard acid and estimated by titration with standard alkali.

More recently Muller (1977) used a slight modification of Kjeldahl's method (after Hartman et al 1971) where the sample is heated with hydrogen peroxide, selenium digestion powder and sulphuric acid for four hours. On cooling the residue was diluted with ammonia-free water and the suspension steam-distilled with (sodium) hydroxide to allow evolving ammonia to be trapped in standard acid.

Constantinides and Arich (1967) have noted that the Dumas method (N_2 measured) and the Ter Meulen method (NH_3 measured) are alternatives.

In 1911, Robertson estimated total sulphur by heating a sample (1 gm) with sodium carbonate (5 gm) in a muffle furnace until all the carbon had been destroyed. Digestion with warm water and acidification then allowed precipitation of the sulphate with barium chloride.

Down (1939) and Dunn (1972) followed the methods of Eschka and Grove respectively whilst Reed and Kaplan (1977) have determined

the quantity of insoluble sulphate gravimetrically via a Parr oxygen bomb technique. Alone, Reed (1977) has reported the use of an elemental analyser (Hewlett Packard Model 185 CHN) in conjunction with a standard Parr bomb procedure and McIver (1967) estimated sulphur (in kerogen) iodometrically.

The oxygen of a material is usually approximated by difference (Down 1939) although McIver (1967) reported oxygen determination (in kerogen) by "Unterzaucher's method". (?)

Specifically organic nitrogen (in sediments) has been estimated by the difference between total nitrogen and inorganic nitrogen (Muller 1977) whilst nitrogen in oils has been found by reaction with sulphuric acid in closed tubes, since evolved nitrogen gas can then be measured volumetrically (Reed and Kaplan 1977 after Brenner and Edwards 1965; Cline and Kaplan 1975).

Aromatic sulphur (of extract fractions) has been assessed by element-specific flame photometric detectors attached to capillary GLC columns and with flame ionisation detectors as well simultaneous but qualitative (aromatic) hydrocarbon distribution can be observed (Albrecht et al 1976).

UV spectrophotometric methods with iodine complexes have allowed aliphatic sulphur compounds to be analysed (Ho et al 1974).

Finally, mention of the recently developed (1976) sustained helium microwave-plasma detector is justified here since incorporation with GLC now allows a total element analysis of a gas chromatographic peak and consequently, by approximating the boiling point of the compound (from its retention time), the empirical or molecular formula can be calculated (Shell International Petroleum, 1977).

b Organic carbon

In contrast to C, H, N, O, etc several 'wet' methods of evaluating organic carbon in a (sediment) sample have been documented.

Knevolden (1962) utilised chromic acid to oxidise organic carbon (Schollenberger's method as modified by Purns and Hugson 1939) and found the extent of acid reduction by titration with ferrous ammonium sulphate whilst Cosgrove (1970) attributed his evaluation to Hanna's 1964 chromic acid digestion method.

With specific regard for kerogen carbon determination Long et al (1962) treated extracted rock samples with dilute sulphuric acid

to eliminate carbonate carbon, oxidised the organic matter with acid dichromate and measured the volume of evolved carbon dioxide by absorption on ascarite.

The method where orthophosphoric acid is used to destroy carbonate carbon and chromic acid is then allowed to oxidise organic carbon to carbon dioxide, which is collected in barium hydroxide solution, has been tried by Gill et al (unpub.) who referred to Bush (1970) in support of their conclusion that the method is slow and erroneous as well as expensive.

Gill et al (unpub.) have also noted that atmospheric oxidation of organic carbon to carbon dioxide allows measurement of the latter either via its pressure or thermal conductivity (e.g. Grouvermeur 1965, Barefoot and Foscolos 1970 or Badakashan et al 1969). In fact, Baker and Claypool (1970) placed acid treated samples in an induction furnace and measured the volume of evolved carbon dioxide and more recently Schmidt-Collerus et al (1976) used a (Leco) gasometric analyser to determine organic carbon in ½ gram 270 mesh samples.

Muller has given a very detailed account where a (1-2 gram) sample was treated with distilled water (17 ml) and phosphoric acid (5 ml 88%) for a few hours at room temperature prior to three minutes of boiling. After the complete removal of carbonate carbon (as carbon dioxide) potassium dichromate (2.5 grams) and sulphuric acid (30 ml 18M) were added to the cooled suspension and an apparatus for the volumetric assessment of carbon dioxide immediately attached. The suspension was then boiled for 30 minutes to oxidise the organic carbon and the evolved gas was determined as the difference between the maximum gas volume attained and the residual gas volume left after absorbance in (5N) potassium hydroxide (with corrections being made for slight variations in temperature and pressure).

Sometimes authors record organic carbon values which were found by difference. Baker (1962) secured total carbon values via a standard combustion method and subtracted the carbonate carbon figures which were determined by an 'acid-evolution' method. Similar approaches have been recorded for other workers by Frankenburg and Giles (1970) who specifically mentioned carbonate carbon assessment via weight loss after acid treatment or by measuring the evolution of carbon

dioxide during acid treatment (as above). A gravimetric determination of carbonate carbon by absorption in ascarite after acid attack has been performed by Long et al (1962). Powell et al (1975) actually recorded organic carbon figures from an unspecified determination after 'digestion with hydrochloric acid'.

Finally, an (Amco C/H) analyser was employed by Dunn (1972) to check his estimates of organic matter whilst Bode and Connan (1974 in Muller, 1977) favoured a (Leco) dry combustion method after acid treatment.

Now, as the removal of carbonate carbon by acid treatment is a standard technique (after Krumbein and Pettijohn, 1938 in), Frankenberg and Giles (1970) investigated the effects of dilute acids with regard to an ultimate estimation of organic carbon. Nitric acid was found to increase such values whilst 10% hydrochloric acid and phosphoric acid generally gave lower values. Acetic acid was found to give variable results and the most consistent figures were achieved with 1-5% hydrochloric acid. Here it can be noted that Powell (1975) alone 'corrected' results for organic carbon evaluations (after carbonate removal) but did not explain the correction.

c This study

Total C, H and N values were determined for whole rock samples (753-8,852 µg) and their soluble extracts (803-4,686 µg). Organic carbon was measured for rock samples before (775-7,220 µg) and after (307-7026 µg) pyrolysis (and of course after acid digestion in either case).

All evaluations were achieved with a Perkin Elmer Model 240 elemental analyser through a Perkin Elmer Model 56 0-1 mV bar recorder in conjunction with a Beckman-R11C LM500 microbalance (Plate 44). Illustrations with a composite diagram and instrumental explanation have been included under the Appendices since the principles of the mechanism appear to be mirrored by many other rival commercial instruments and these tools seem to be gaining almost complete acceptance for such elemental analyses. The samples were weighed out in small platinum boats (approximately 190-230 mg) and kept in a dessicator; since, although rock samples

from the field were not dried, micro-quantities of a sample were felt to be especially susceptible to additional adsorption of moisture. Anyway, an enclosed container prevented draughts (particularly breathing) from spilling the weighed samples. Ideally at least two measurements per sample should be made to assess such parameters but by computing for a large number of samples it was thought that any existing trend should become apparent.

For single measurements, the microbalance in an absolute sense should be zeroed and calibrated before every weighing. Here, such an operation was repeated every three weighings unless of course the balance itself was noticeably upset.

When responding ideally, a working condition for the analyser to be ready for sample analysis was assumed within about $1\frac{1}{4}$ hours (unweighed, three blanks and a standard usual) and only if the machine remained on stand-by for more than one hour was it reconditioned. Once in a working condition, an analysis could be completed in about 15 minutes which compares extremely favourably with alternatively known (wet) methods. The analyser itself was calibrated daily before use with a standard material and the quoted specifications adhered to. Examples of a standardisation and a total C, H, N determination are given under the Appendices and throughout such work a Lloytron Accumatic 20 electronic calculator was used.

Generally the reduction tube packing which converts from copper to impervious hardened copper oxide with use could cope with approximately 5 working days or a theoretical 150 samples. Deterioration of the copper from experience can be indicated by a sinusoidal trend in nitrogen read values for blank runs, an ever increasing drift in the nitrogen read signals for sample runs and/or prolonged to almost infinite fill times.

In conclusion, any mechanical break-downs although momentarily frustrating are worth tolerating because once restored to a working order the speed and accuracy is apparently unsurpassed.

The boats were recycled by removing the majority of a spent sample with a pipe cleaner and briefly roasting the boat in a bunsen flame at red heat for about one minute; subsequently taking care not to

to contaminate the clean boat before usage.

For organic carbon values, acid digestion after weighing a sample was achieved by applying 10% hydrochloric acid with a syringe (The strength of acid and technique of application conformed to previous work in the section and served the necessary purpose for a comparative study).

Carbonate rich rocks, where a vast excess of acid with respect to the small quantity of sample is necessary to ensure complete reaction, do not facilitate easy disposal of the unwanted type of carbon. Reaction and subsequent effervescence can be frustratingly unpredicatble and uncontrollable. Consequently any sample which spat and ejected material outside the boat was rejected and re-attempted. In this respect, Powell et al (1976) have confirmed that "accurate organic analysis is difficult in limestones which contain a low organic carbon content because of the necessity to remove substantial amounts of carbonate by acid digestion prior to analysis".

After successful acid treatment, the samples usually in batches of 20 were oven dried at $50^{o}C$, and conveniently this drying period was standardised overnight to 15 hours prior to analysis. Kerogen carbon (as a percentage by weight) was estimated as the difference between total organic carbon of the whole rock and the carbon content of the soluble extract (with respect to the rock weight).

Subsequent to this study a 'bulk' acidisation method followed by drying and subdivision for pre- and post-pyrolysis organic carbon determinations was tested by Solli (priv.comm.) to try to dismiss the need for separate acidisations and thus save time, and also improve the accuracy.

Here it can be mentioned that Baker and Claypool (1970) claimed a precision of 2-15% for their organic carbon determinations (to within the first standard deviation) depending upon the actual amount of organic carbon present. Generally better than 5% precision was maintained for samples with more than 0.5% by weight organic carbon whilst 10-15% precision was held for those with less than 0.5% by weight. Baker (1962) had earlier expressed his error according to Figure 9.

In summary it does seem necessary to argue a sense of perspective

in connexion with this parameter (and correspondingly total carbon values). Such determinations although probably accurate with respect to the micro-sample are really 'order of magnitude' assessments with regard to the natural distribution of organic matter with a sedimentary facies (and correspondingly to the distribution of carbonate minerals). Attempts to homogenise a rock do not always seem as successful as they appear and disparity on a microscale between the distribution of organic carbon seems to be especially highlighted by lignitic rocks (Madani pers. comm. 1977 and this study).

Although the PE Model 240 analyser can be converted to measure sulphur it is necessary to reconstruct the analysing and detecting systems (to remove interference by water, oxygen and halogens). Once set up for sulphur measurement the apparatus is restricted to this element only. Hence, in the absence of duplicate facilities and in view of a machine committment to others, the presence of sulphur was sought qualitatively (on a presence or absence basis) using X-ray fluorescence.

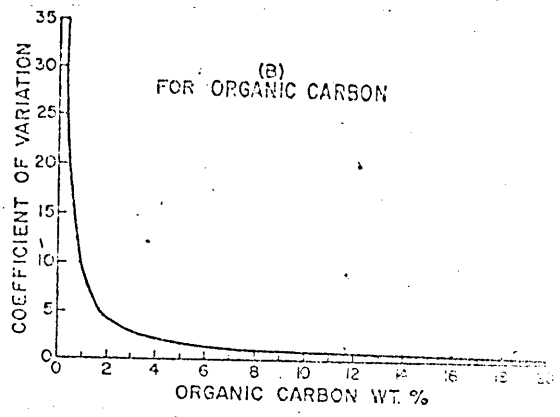


FIG 9 ANALYTICAL ERROR IN ORGANIC CARBON DETERMINATION; the standard deviation is expressed as a percentage of the mean of the parameter measured. (Baker, 1962.)

8 PYROLYSIS

a Introduction

The current main uses of pyrolysis with respect to petroleum exploration are to allow estimations of the degree of evolution of kerogen (Gransch and Eisma 1970 in Barker 1974) and thus assessment of the hydrocarbon potential of a given formation in the buried parts of a sedimentary basin by using surface samples for a simulated degradation (Tissot et al 1974).

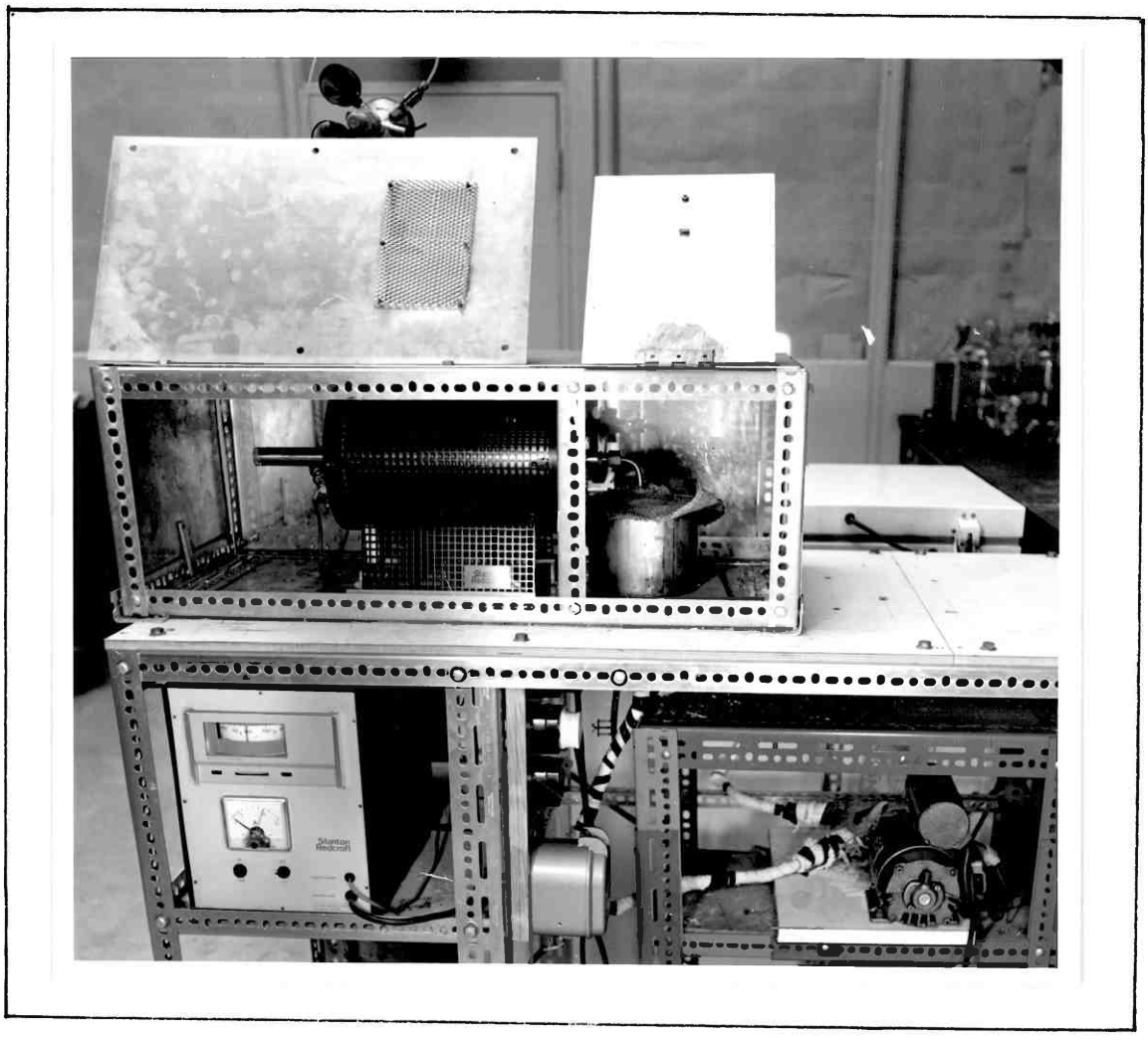
The use of higher temperatures enable appreciable reaction to occur within a short time and (as noted under the introduction, 'hydrocarbon generation') attempt to parallel changes in the subsurface (Bajor et al in Barker 1974) that would occur over a long period of time. Inert atmosphers with helium (Girand, 1970) or nitrogen (Gill et al unpub.) have been used to imitate the "reducing" conditions within a sediment;especially when they are deeply buried.

Barker (1974) did observe that possible factors affecting the products of pyrolysis embrace temperature, pressure, duration, quantity of product and catalytic effects of clay minerals. Although, it was noted that with regard to latter, products from samples of kerogen rich in montmorillonite, illite and chlorite all contrasted very little with products from the respective isolated kerogens, it is felt by some that whole rock pyrolysis is affected by mineral catalysis (Solli pers. comm. 1977). Finally, laser-micropyrolysis has been employed by Given (1966 in Hobson, 1966) whilst pyrolysis-GLC studies have been documented by Girand (1970), Claypool and Reed (1976) and Larter et al (1977).

b This study

In all about 135 whole rock Kimmeridge Clay and Wealden shale samples (of approximately 1 gm) were pyrolysed in a platinum tray (4 cm x 1 cm x ½ cm 1.b.h) individually within a Stanton-Redcroft low mass horizontal furnace (Plate 10). Each sample was injected and retrieved through a stoppered end of a 50 cm x 2 cm (dia) stainless steel cylindrical combustion tube with a quartz glass fish. The sample was held within an approximate 10 cm x 2 cm (dia) 'hot zone' which was maintained at 900°C, via a Eurotherm isothermal temperature control unit for 1½ hours. An inert atmosphere was

PLATE 10 PYROLYSIS UNIT.



created by the steady flow of oxygen-free nitrogen (80-84 ml/minute at R.T) through the apparatus. (The temperature and time compare with those of Gransch and Eisma, 1970 in Barker, 1974).

Attempts were made to condense and capture the issuing degradation products by bubbling them through a cold solution of benzene-methanol azeotrope in a (10 cm x 2½ cm dia) sample tube. The tube was placed in an insulated bath containing a stationary volume of 3:1 water-antifreeze solution and within a cooling coil through which the water-antifreeze was circulated from a cooled reservoir (Grant refrigeration unit). A trapping temperature of $-8^{o}C$ was thus achieved.

However, as an outlet to atmosphere was necessary to permit the flow of gas and hence effect the removal of products (to limit secondary cracking, to prevent inhibition of reaction because of a concentration of products and to eliminate any back reactions), considerable loss of products was observed. Of course an improved trap such as a multiple packed U-tube and/or a cooler trap (liquid nitrogen) may have improved the capture (Barker, 1974).

Such a measure was not implemented as the prime reason for pyrolysis was to achieve "C_R" ("the carbon content relative to the non-volatile part of the insoluble organic matter") with "C_T" ("the carbon content relative to the total insoluble organic matter") ratios (Feugere and Gerrard, 1970) and at present an "online" pyrolysis-GLC system is being developed. The trapping though, did suffice to allow sample differentiation in a reproducible and qualitative manner.

9 SPECTROSCOPY

Conventional spectroscopic techniques are used to observe three main types of molecular transitions. Electronic transitions are observed in the UV region of EMR whilst vibrational-rotational transitions occur in the IR. Pure rotational transitions are recorded in the Far-IR and microwave region (the boundaries here being loosely defined).

a Infra-red spectroscopy

ai Introduction

The first IR spectrophotometer was invented by Herschel in 1800 and actually lead to the discovery of IR radiation itself by Maxwell (theoretically) and Hertz (experimentally). In 1903 Coblenz started an IR study and in 1905 published 131 spectra for pure substances. However the first commercial machines did not become available until 1943.

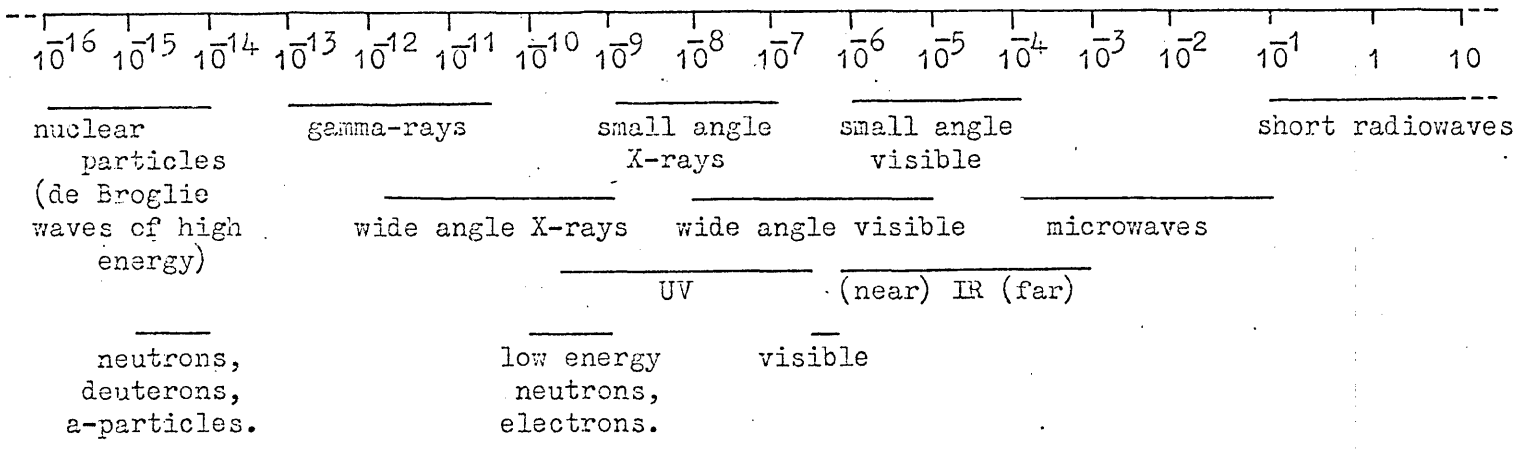
As seen in Figure 10, IR radiation lies between the visible and radiowave radiations within the EMR spectrum; having a wavelength of 10^{-3}mm - 1 mm. In fact, the vibrational region of 25 x 10^{-4}mm - 15 x 10^{-3}mm λ is the most useful (c. 4000-650 cm^{-1} $1/\lambda$).

Now the absorbance, emission and reflectance of such energy by a molecule is related to the contortions of its constituent atoms and such vibrations are characterised by the kind and number of atoms, the bonding between the atoms and their geometrical arrangement (Low 1967). The IR spectrum of a molecule is a unique characteristic.

Bjernum in 1914 invoked the concept that atoms within a molecule can be treated as small masses attached to one another by springs. However for interaction with (the electric vector of) EMR a displacement of charge (that is an oscillating dipole arising out of the differences in electronegativities of the constituent atoms) is necessary. Molecules such as chlorine and carbon dioxide (Cl-Cl, O = C = O) give no IR absorption but fortunately most chemical functional groups are not centro-symmetric and hence are IR active.

Actually, a non-linear polyatomic molecule having n-atoms has (3n-6) fundamental (simple periodic) vibrations where (n-1) are longitudinal along the axes of the bonds and (2n-5) are

FIG 10 THE ELECTROMAGNETIC RADIATION SPECTRUM.



Ranges are approximate.Compiled after Brumberger et al,1968;Garret,1965 & Meoly,1966.Wavelength is in metres.

deformational and perpindicular to the plane of bonding (Taylor, 1968). The possible vibrations for a molecule (3n-5 in the case of linear molecules) can therefore include localised symmetric and asymmetric stretching, bending or scissoring, rocking, twisting and wagging whilst the molecule as a whole can 'breathe' and overtones and combinations are also possible. Not all fundamental vibrations though are active in the IR region.

IR spectral studies are being utilised more and more in work upon kerogen isolates; usually with potassium bromide pellets containing ½-1% by weight of sample (Girand 1970, Durand and Espitalié 1976, Ishiwatari et al 1977, Wichramasinghe 1977). As early as 1958 Brenneman and Smith (Bray and Evans 1965) noted that there was little relationship between hydrocarbons in an oil and the corresponding fractions from a presumed source except for the IR spectral similarities of the heavy aromatics. More recently Williams (1974) used IR in conjunction with other techniques to correlate oils with extracts.

For this type of work Eglinton et al (1964) used a Perkin Elmer 137 and PE 237 spectrophotometer (with a Beckman IR-7 for high reduction studies on micro-samples) whilst Lynch and Brown (1973) employed a PE 521 model. Rubenstein et al (1975) used a PE 177 apparatus whereas lately Ishiwatari et al (1977) had recourse to a PE 421 model. Douglas & Grantham (1973) confirmed the hydrocarbon nature of a polythene closure extract and its (TLC) fractions using IR spectra.

In conclusion, the IR method is fast, simple, indestructive and where detailed high resolution studies are involved, unambiguous (Mattson 1971, Lynch and Brown 1973).

aii This study

IR spectra (4000 cm^{-1} - 650 cm^{-1} $^{1}/\lambda$) were run on all of the Kimmeridgian extract fractions to allow inspection of their respective functionality. Also, the Kimmeridgian and Neocomian total extracts were examined in an attempt to 'fingerprint' (Eglinton 1968) for similarities and find their functionalities (Reed 1977).

As sodium chloride (480 - 1102) prisms were available, samples were presented to IR radiation as smears within a 8 mm thick sandwich or window (25 mm dia.). Similarly potassium bromide, calcium fluoride (Taylor 1968) and silver chloride (Matteson 1971) prisms have also been used but mulling agents (Nujol 700-2000 cm^{-1} and hexachlorobutadiene 2000-4000 cm^{-1} after Brown 1959) were not used. Ideally, spectra from solution in a non-polar solvent are desireable (Williams and Fleming 1973) since they are normally better resolved.

Very careful handling, with enclosure in an atmosphere of low humidity when not in use (Taylor 1968) was observed to help preserve the life of the discs. Between each run the discs were wiped with a clean paper towel, washed sparingly in a 3:1 chloroform-ethanol solution and dried by rubbing gently on a muslin cloth over a glass slab. Samples were applied with a micro-spatula and smeared in a locking cradle. The disc edges only were touched and blank runs indicated the absence of impurities and particularly moisture.

Throughout a PE Model 157 IR spectrophotometer was employed (containing a ceramic 1200°C IR source and a thermocouple detector) and automatic (programmed cam) self-adjusting 'monochromator' slits maintained constant intensity (and noise level) for the energy of different wavelengths during a sweep. (Normal slit width and slow scan speed). Calibration against polystyrene was practised before running any batch of samples (to determine the sites of absorptions at 2924 cm^{-1} 1601 cm^{-1} 1028 cm^{-1} and 907 cm^{-1} $^{1}/\lambda$).

b Ultra-violet and Fluorescence (emission) spectroscopies

bi Introduction

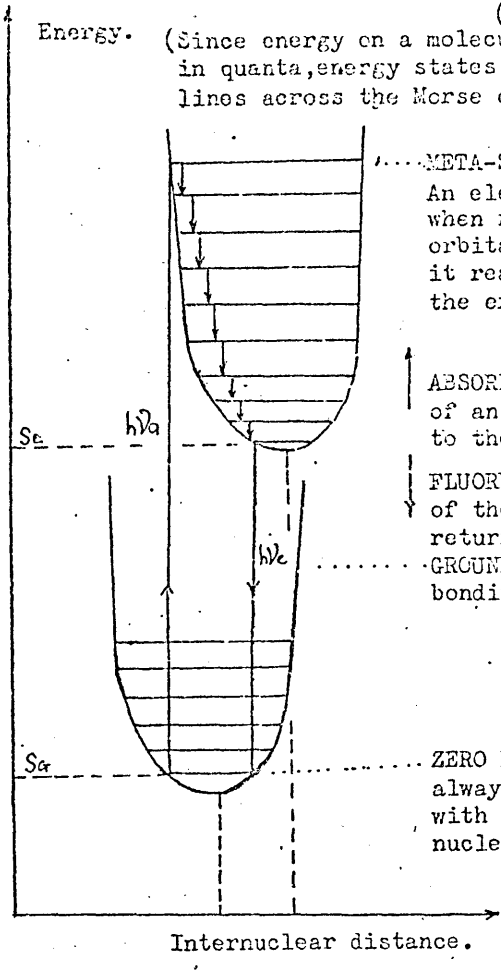
Historically one of the earliest observations of fluorescence can be traced back to about 1600 AD when Cascanola saw a barite coal fused mass glowing in the sunlight. One of the earliest documented cases seems to have been in 1565 when Monardes noted the unusual luminous appearance of an aqueous extract of wood (lignium nephriticum). At about the same time Stokes deduced that the emitted light causing fluorescence was of a longer wavelength than the incident light. In 1871 von Bayer prepared

fluorescein which is such a powerful fluoresceer that it is detectable at concentrations of 1 part in 40 million (Taylor 1970).

With regard to petroleum geology, Witherspoon and Winniford (1967) recorded the UV spectral studies of Rosenbaum who worked with asphaltenes in 1958. Meinschein (1961) related UV spectra of recent sediment extracts and crudes whilst both Gunn and Cooper (1962) and Wickramasinghe (1977) have applied UV spectroscopy to soluble extracts. Many organic substances have been found to give UV spectra whereas many inorganic water-soluble constituents rarely absorb (Hanya and Orgura 1964). Rubenstein et al (1975) reported the use of a Varian Cary 118 UV spectrophotometer and Schmidt-Collerus et al (1976) referred to fluorescence emission spectroscopy when noting it was more 'sensitive' than UV studies.

Both UV and visible light (Figure 10) can cause excitation of a molecule by altering the distribution of electrons amongst permissible energy states and without removing them from the molecule entirely. Fluorescence can be explained here simply and with 'scientific adequacy' by reference to Taylor (1970). Figure 11 is a diagrammatic summary to illustrate the principle. Incident radiation is seldom strictly monochromatic and if the frequencies as a group are of the right order wherever the nucleus may be at the time of impact energy capable of lifting the molecule ('s electrons) to a higher state is available. However, the transitions of an electron are themselves governed by the Franck-Condon principle which states that "nuclei maintain their position relative to one another during excitation". Thus a collection of molecules will absorb a range of frequencies and an absorption curve indicates a maximum at the medium nuclear position. Band spectra not line spectra are therefore observed. Similarly, the energy of the emitted light will depend upon the position of the nuclei when the quantum is ejected and hence a population of fluorescing molecules will produce a band of energies rising to a maximum at the medium nuclear position. However, not all molecules apparently capable of fluorescence will actually fluoresce and the intensity of fluorescence will depend upon the proportion of the total number of molecules

(Compiled from Taylor,1970)



(Since energy on a molecular level can only increase in quanta, energy states are represented by parallel lines across the Morse curves.)

META-STABLE EXCITED STATE
An electron is not in equilibrium when raised to an upper anti-bonding orbital and it dissipates energy until it reaches the zero point energy for the excited state

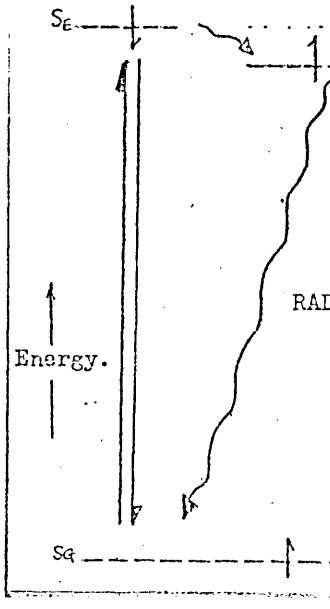
ABSORBANCE of energy causes promotion of an electron from the ground state to the excited state.

FLUORESCENCE, the emission of the bulk of the absorbed energy accompanies the return of an electron to the STABLE GROUND STATE, where electrons reside in bonding orbitals.

ZERO POINT ENERGY LEVEL. There is always a vibrational energy associated with a bond between two oscillating nuclei under normal conditions.

Nuclei are more often than not at the mid-point of vibration when radiation is absorbed or emitted but they can be elsewhere. Although a shift in equilibrium distance for nuclei occurs with absorbance the transitions obey the Franck-Condon Principle. (See Text).

FIG. 11 THE BASIC PRINCIPLES OF FLUORESCENCE.



Electron in pi* bond; opposed spin ('singlet state')

Electron in pi* bond but 'flipped'; that is with parallel spin ('triplet state')

$S_E \rightarrow T$ is radiationless transition; the closer S_E & T are, the more are such transitions enhanced.

FLUORESCENCE intensity is proportional to the number of molecules whose excited electrons do not 'flip'

RADIATIONLESS DEGRADATION $T \rightarrow S_G$

FIG. 12 NON-FLUORESCENCE PATHWAY.

(Compiled from Taylor,1970)

Electron remaining in pi bond.

whose electrons do not "flip over" (Figure 12).
In the molecular orbital theory, pi electrons are the least strongly bound electrons in a molecule and are more and more loosely held with increasing conjugation or 'delocalisation'. They can absorb energy more easily and readily than electrons involved in bonding orbitals and practically speaking fluorescence involves pi-bond to pi-antibond transitions (pi→pi*) since n→pi* transitions give only weak fluorescence. Conjugated systems include structures of the type C = C-C = C, C = C-C = O C = C-C = N and C = C-C ≡ N. (Pi-pi conjugation with p-pi conjugation where heteroatoms ("lone pair" electrons) are involved cause pi→pi* and/or p→pi* transitions accordingly). The most important example of course is the benzene ring itself. As mentioned increasing conjugation generally shifts the phenomena to lower and lower energy causing a transition from the UV part of the EMR spectrum into the visible region and planarity of a molecule is a condition necessary to permit this.

bii This study

Ultra-violet spectra for 16 Kimmeridge Clay and 10 Wealden aromatic extract fractions, randomly chosen, were obtained through a Pye Unicam (PU) AR25 Linear Recorder which was connected to a PU SP 1800 UV spectrophotometer.
Confirmation of the grouping of the UV spectra was achieved by a detailed investigation of one randomly chosen matching pair from one group (KC 1 v KC 32; 3 excitations with subsequent analyses and 3 analyses with subsequent excitations) followed by a restricted investigation for two (randomly chosen) representatives of each of the remaining groups (1 excitation with subsequent analysis and 1 analysis with subsequent excitation). For this purpose, a PE 150 Xenon Power Supply fed a PE 204 Fluorescence Spectrophotometer and results were traced through a PE 165 recorder at 20 mm/minute .
For both the UV and FES work, spectroscopically pure cyclohexane was employed as the solvent. In the UV work the absorbance of energy which is required to cause such transitions is recorded whilst in FES work the absorption of particular energies which create fluorescence of a specific energy or the fluorescent energies resultant from a specific excitation energy can be measured.

10 MACERATION - OPTICAL MICROSCOPY

a Kerogen isolation

Down (1939) recorded that McKee and Goodman made the first attempt to isolate kerogen and subsequently many variations for the destruction of mineral matter have been advanced.

With particular regard to elemental analysis of kerogen, many laborious routes have been tried and usually in such cases the the rock and/or isolated kerogen is extracted to remove any soluble organic material (Burlingame et al 1968, La Plaute 1974, Durand and Espitalié 1976, Ishiwatari et al 1977). Also, treatments have evolved especially to remove pyrite. Zinc dust and hydrochloric acid (Forsman in McIver 1967, Burlingame et al 1968), lithium aluminium hydride (Shibaoka et al 1973 after Saxby 1970) and sodium borohydride (McIver 1967, Powell et al 1975) have been tried chemically as well as physical (density-floatation) separations. La Plante (1974) and Powell et al (1975) used ultrasonics and slurrying-decanting processes respectively with an aqueous solution whilst chloroform (Powel et al 1975, Durand and Espitalié 1976) and zinc bromide (McIver 1967, La Plante 1974) have also been employed. Usually, hydrochloric acid (McIver 1967, Djuricic et al 1971, Karkanis 1975, Powell et al 1975) is used to dissolve carbonates as well as oxides (Ishiwatari et al 1977), exchangeable cations from clay minerals (La Plante 1974), sulphates and small amounts of silica (Down 1939). Hydrofluoric acid is often employed for the dissolution of silicate minerals but the formation of sparingly soluble fluorosilicates and complex fluorides necessitates inhibition by hydrochloric acid (Karkanis 1975) although Down (1939) removed insoluble fluorides by boiling with sodium carbonate. Hence, different ratios for HF:HCl mixtures and various deviations for treatment have arisen but Karkanis (1975) did observe that French in 1964 used boric acid to remove silicates and alumino-silicates. In summary, Down (1939) recalled Franks and Goodier in concluding that the separation of kerogen from mineral matter is impossible and Powell et al (1975) agreed with this more recently. Karkanis noted that further demineralisation would require "drastic conditions" although Down (1939) claimed no more than 0.5 - 1.0% of the original mineral content persisted in kerogen isolated by his method. With respect to elemental composition La Plante (1974) conceded that free

kerogen with 80-90% organic matter was suitable for analysis. However, only Gavin (1925 in Down 1939) appears to have shown concern for possible alteration of kerogen during isolation and he claimed that determination of constant C/H ratios at various stages indicated his derived kerogen was unaffected.
Finally, Pusey (1973a) has emphasised that the expense and labour of kerogen isolation makes ultimate analysis uneconomic on a large continuous scale.

b Kerogen description

"Strewmounts" (Peters et al 1977) allow microscopic inspection of kerogen isolates to discern the type, colouration and physical nature of the phytoclasts.
Kerogen components can in fact be described in terms of vitrinite, inertinite, spores, acritarchs, cuticles, bitumens,etc and point counting (on polished sections - Powell et al 1976) can be used to distinguish the category of organic matter present.
With regard to colour, the primary objection (especially to its use as an indicator of maturity) is "subjectivity" (Peters et al 1977). The thickness of the prepared slide affects efforts to deduce colour and only phytoclasts of about the same size and thickness (focusing) should be used. For a sophisticated study constant filtered illumination, with measurement, after transmittance, by a light meter/microphotometer and reference to standards are all necessary.

c This study

Whole rock random cut thin sections for about 120 of the Kimmeridgian samples were inspected to assist in the description of lithologies whereas a selected number of macerated Kimmeridgian Clay samples totalling 26 were studied (two slides per sample) to enable kerogen descriptions.
The isolation of kerogen for the purpose of visual description only was achieved slowly by initial washings of rock chips ($\frac{1}{4}$" dia. or less) with 10% hydrochloric acid until effervescence ceased and then by attack with fresh aliquots of 40% hydrofluoric acid (and decantations) until the silicate matrix had dissolved. All the residues were washed thoroughly with distilled water (until neutral to litmus) so as to prevent any residual acid from etching the glass slides. The kerogens were stored under distilled water until mounting in glycerin jelly between glass plates.

11 X-RAY DIFFRACTION (XRD)

a Introduction

From Figure 10 X-rays can be seen to have wavelengths of the same order as interatomic distances and thus a rigid array of atoms in a crystal can serve as a diffraction grating and produce an X-ray spectrum (Taylor 1968). In fact, X-ray diffraction began under von Laue in 1912 although Hadding is attributed with the first analytical application of XRD for mineral identification (Jenkins 1974).

If a uniform wavelength of X-rays is applied to a crystal, the spatial distribution of atoms in the (i.e.the size and shape of the unit cell) and, in particular, the 'd' spacing (i.e.the interlayer spacing between succsessive layers of atoms) can be determined via the reknown Bragg equation ($n\lambda = 2\ d \sin \theta$) through measurement of the reflection angle (θ usually expressed for convenience as 2θ). Accordingly a mineral can be identified from its XRD pattern.

For this presentation, the reader is assigned to Nuffield (1966) who has furnished a good explanation of the nature and generation of X-rays and experimental technique.

Such a tool has been applied for diagenetic studies of kerogen (Shibaoka et al 1973, Karkanis 1975, Ishiwatari et al 1977). (Increasing metamorphism causes an increased graphitisation and thus the accompanying increased crystal ordering produces a sharpening in peak resolution). Also XRD has been used in the structural investigations of asphaltenes (Yen et al 1961 and Barth 1962 in Witherspoon and Winniford 1967) whilst Vuchev et al 1971 actually used XRD upon soluble organic extracts and Robinson and Lawlor (1961) applied XRD to selected derivatives of kerogen oxidation products.

XRD studies of whole rock mineralogies and their associated detailed clay mineral investigations appear to warrant inclusion amongst the tools of an organic geochemist. The relationship of clay(s) with organic matter may offer solutions to the mechanistic problems of concentration (Cunningham-Craig 1916, Grim 1947 in Johns and Shimoyama 1972, Grim 1968 in Cordell versus Philippi 1972, Dunn 1972), (catalytic) generation (Johns and Shimoyama 1972) and expulsion (Weaver 1960 in Long et al 1962, Gill 1962, Powell et al

1975) experienced for petroleum source rocks. Further, such studies may help in deciphering the source of the sediment (Weaver 1958 in Long et al 1962), the environment of deposition (Vuchev et al 1971, Cordell 1974) and the degree of diagenesis (Cordell versus Philippi 1974, Albrecht et al 1976) although Pusey (1973a) has mentioned clay mineral changes are restricted to, at the least, eometamorphism.

b This study

With the above in mind and also with the aim to illustrate the distribution of the major mineralogic phases for the Kimmeridge section, about 160 whole rock XRD spectra were run for both the Kimmeridge Clay and Wealden samples. All the samples were crushed with an agate pestle and mortar and sieved to -200 mesh to help reproduce cavity mounting (20 cm x 15 cm x c.3 mm) and reduce background radiation values. An exception to the rule occurred with the very rich oil sands only; these were mounted as closely as possible but without crushing or sieving.

A selected number of Kimmeridgian samples totalling 17 were investigated in detail. Such clay fractions ($< 2\mu$) were isolated from distilled water suspensions of the whole rock powders by centrifuging for 12 minutes at 500 r.p.m.

For the work, a Phillips X-ray Powder Diffractometer was used and cobalt K_α radiation (generated at 34 KV and 28 mA) was employed after passage through an iron filter. A 1° divergent slit, 0.1 mm receiving slit and a 1° scatter slit were incorporated and diffracted radiation was detected by a proportional counter; being traced through a recorder at a speed of 1 cm/minute. The goniometer ranges for the various sample types are tabulated in Table 25.

TABLE 25. XRD GONIOMETER RANGES.

Whole Rock:		$5^\circ - 75^\circ$
Clay Fraction	Dessicated.	$2^\circ - 46^\circ$
	Glycerated:	$2^\circ - 16^\circ$
	400°C /1 Hr:	$2^\circ - 16^\circ$
	550°C /1½Hr:	$2^\circ - 16^\circ$

12 X-RAY FLUORESCENCE

a Introduction

Qualitative identification of elements by X-ray spectrometry has been utilised since the early 1900's and present-day tools differ little in principle except for the fact that a primary X-ray source is now used to excite secondary X-rays from a sample and hence necessitate the qualification by "fluorescence" (Jenkins 1974). The excitation principle has been attributed to von Hevesey (1925) or Glocker and Schreiber (1928) and, in contrast to UV and FES phenomena which are molecular features, XRF is an atomic phenomenon of accordingly higher energy involving ionisation.

In the simplest incident, and using the Bohr theory for atomic structure in accordance with the Pauli exclusion principle, excitation can cause the removal of an electron from a shell (K, L, M, etc) of an atom in its ground state beyond the Fermi level and create an ion (K+ L+ M+ etc+). An electron from an outer orbital may 'fall back' to fill the vacancy created in a shell closer to the nucleus and a succession of back-transitions is caused until the atom regains its ground state; when ultimate electron transfer is from the low energy extremities of the atom where changes are almost continuous (conductance or valence bands).

Such de-excitation is usually always accompanied by the emission of X-ray radiations although autoionisation can occur (Auger Process). In fact the relative efficiency of the two opposing routes for a return to ground state dictate the quantity of radiation from a certain level (Figure 13). "In practice, millions of atoms are involved in the excitation of a given specimen and all possible de-excitation routes will be taken . What will differ from element to element, however, is the distribution of the total de-excitation over the various routes" (Jenkins 1974) and consequently, individual characteristic fluorescence will be shown by each element.

b This study

As mentioned earlier, recourse to XRF equipment was made for the prime reason of detecting the presence of sulphur in the soluble extracts. With consideration of the available machine time and its versatility the majority of the Kimmeridgian extracts were treated qualitatively for S, Mn, Fe, Cl and Br. This was achieved

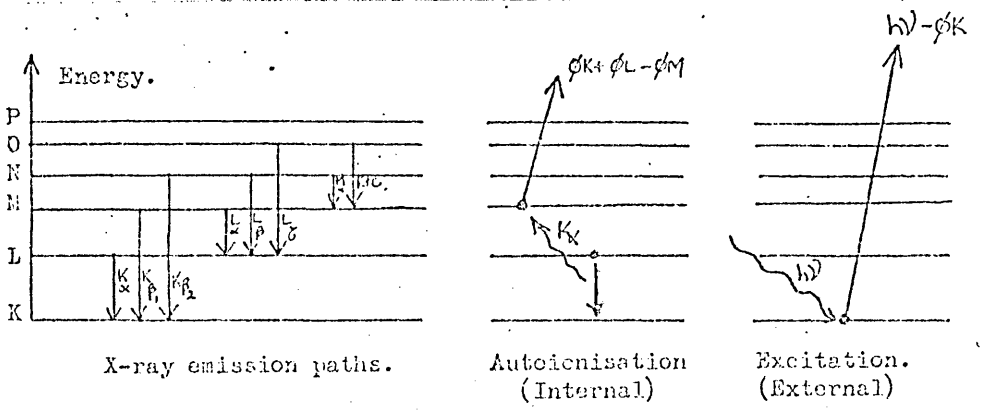


FIG 13 X-RAY FLUORESCENCE PRINCIPLES (compiled from Jenkins,1974.)

TABLE 26 XRF MACHINE SETTINGS.

ELEMENT.	X-RAY EMISSION.	DIFFRACTION ANGLE (20°).	RECOMMENDED K_a/K_b RATIO.
S	K_a Peak	75.92	1:13
	K_a Bkgrd	73.00	
	K_b Peak	70.30	
	K_b Bkgrd	72.50	
Fe	K_a Peak	85.75	1:8
	K_a Bkgrd	87.50	
	K_b Peak	76.22	
	K_b Bkgrd	78.00	
Mn	K_a Peak	95.27	1:8
	K_a Bkgrd	97.50	
	K_b Peak	84.31	
	K_b Bkgrd	83.00	
Cl	K_a Peak	65.55	1:9.7*
	K_a Bkgrd	67.00	
	K_b Peak	60.55	
	K_b Bkgrd	59.50	
Br	Bkgrd	28.00	1:9
	K_a Peak	29.91	
	Bkgrd	32.00	
	Bkgrd	26.00	
	K_b Peak	26.73	
	Bkgrd	27.50	

*From actual machine measurement on KCl powder; otherwise from White & Johnson,1970.

by counting the K_α and K_β spectral emissions lines (with respective backgrounds) for each element and determining the ratio of the intensities (Borley priv.comm. 1976). Ho et al (1974) used XRF to determine sulphur in crudes but did not elaborate upon experimental technique.

The brief study here was hampered by the absence of containers appropriate for solution work (which would have allowed better reproducibility of sample presentation) and also because of the impossibility to make a standard equivalent material. An inability to (independently) calibrate a certain number of samples contributed to the total lack of quantification.

Consequently, the problematic inhomogeneous extracts were spread in central cirular cavities (1 cm dia. x 1 mm depth) of circular perspex discs (3 cm dia. x 3mm thickness) and covered by a thin film of mylar (25μ thick).

A Phillips 1212 XRF Analyser was used with X-rays being generated (60 KV, 32 mA) from a tungsten anode for Mn, Fe and S and from a chromium anode for Cl and Br. In all cases, a fine collimator was employed and the analysing crystals were Pentaerythritol (P.E.T.), LiF (220) and LiF (200) for S and Cl, Fe and Mn and Br respectively. Detection was with both flow and scintillation counters and the machine settings are recorded in Table 26 with recommended ratios. All countings were for 100 seconds automatically with a teletype ('Addo-X') except for the background values to the bromine peaks which were averaged after 40 second counts as tracing showed the noise was not constant ("sloping background").

13 GAMMA-RAY LOGGING

a Introduction

An appropriate explanation of the types (α, β and γ) and nature of radioactivity together with the law ($N = N_o e^{-\lambda t}$) and concepts ($T_{\frac{1}{2}} = \log_e 2/\lambda$) has been given by Moorbath (in Smales and Wager 1960).

In addition, it can be noted that grain size reduction causes an increase in the (β) activity of a sample (Beers and Goodman 1944). Ideally, it has been maintained that the sample should be reduced to the original intrinsic particle size (compare with preparation for solvent extraction and XRD) but of course there are difficulties in realising this. After grinding Beers and Goodman (1944) stressed that it was essential to store the (20-100 mesh) sample for at least 30 days to allow the thorium and uranium equilibriums to be re-established. (For rocks older than one million years the potassium, thorium and uranium decay series are each in secular equilibrium (Adams and Weaver 1958, Haji-Vassiliou and Kerr 1973) and the total number of particles emitted per unit time by particular series is directly proportional to the concentration of any individual member of the series (Beers and Goodman 1944). Similarly, Moorbath (1960) has stressed that a steady state must be assumed when the rate of formation of each individual member of a series equals the rate at which it decays and the time needed for this depends upon the half-life of successive members of the series.

As for sample presentation, Beers and Goodman (1944) poured an ethanol suspension of ground rock over a copper or aluminium disc and evaporated it at room temperature to leave a uniform distribution of finely divided particles. Adams and Weaver (1958) mentioned that homogenisation was important and they thoroughly mixed their samples ($\lesssim$ 100 mesh) to avoid preferential concentration of heavy minerals at the base of any sample.

For rigorous quantification, adsorption of background radiation by the sample needs to be known and therefore the effective density and degree of packing have to be considered. Ideally background values should be measured before and after each sample count and averaged. Such radiation can be attributed to cosmic ray activity, collision products, slight impurities in the construction materials

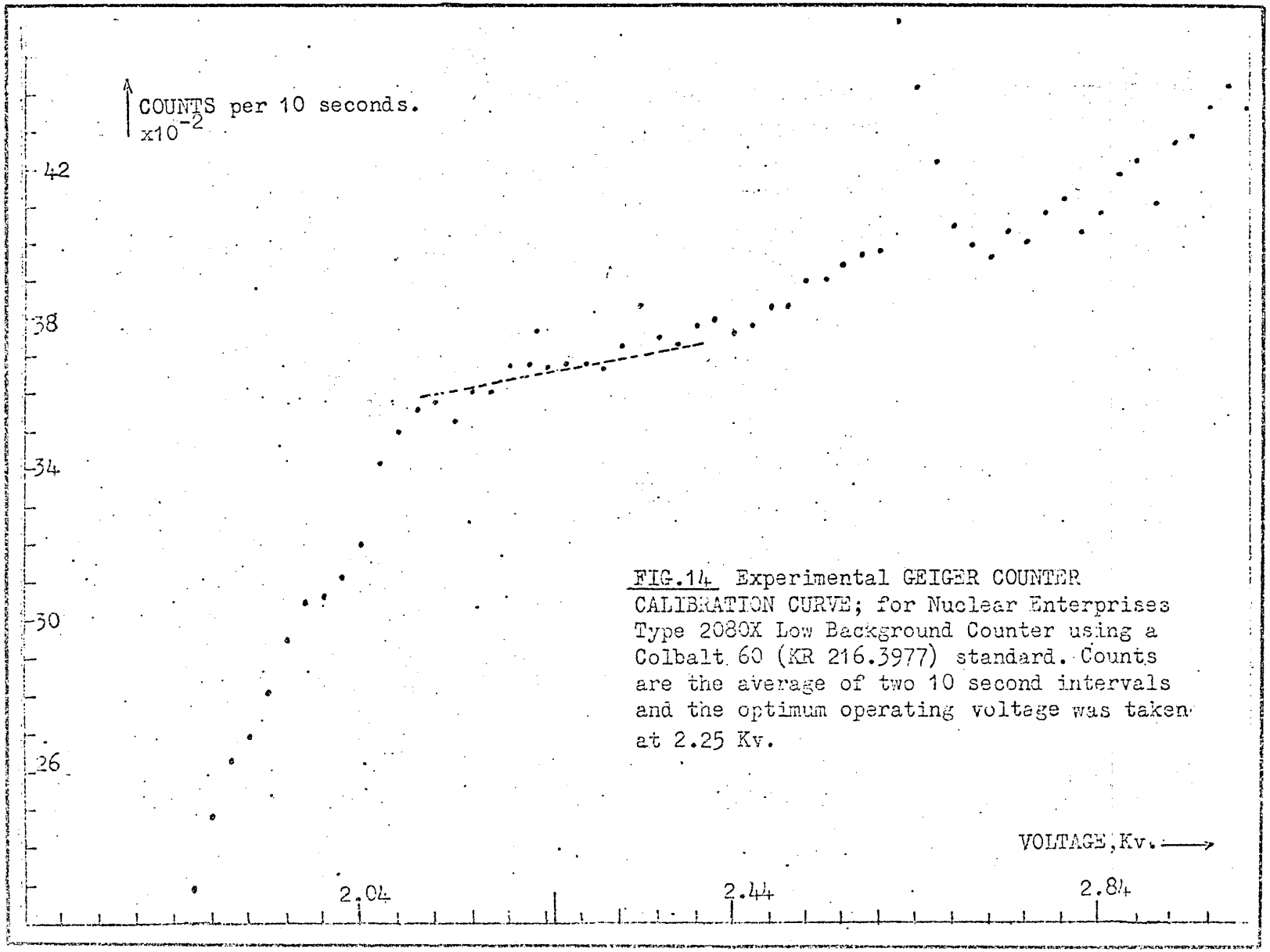


FIG.14 Experimental GEIGER COUNTER CALIBRATION CURVE; for Nuclear Enterprises Type 2080X Low Background Counter using a Colbalt 60 (KR 216.3977) standard. Counts are the average of two 10 second intervals and the optimum operating voltage was taken at 2.25 Kv.

of the apparatus and 'permanent' contamination inside the device due to sample spillage (Moorbath 1960).

A strict comparison of different rock types also necessitates activity-density curves to account for self adsorption (Beers and Goodman 1944) since the weights of uniformly active material versus activity does not give a straight line (Moorbath 1960). Thus, in a general comparative study samples of different weights but of the same surface area can be used providing their physical form can be reproduced.

Due to the random nature of decay, counting should be protracted over a sufficient length of time to obtain truly representative average figures for the number of disintegrations occurring in unit time (Moorbath 1960). In fact, it should be remembered that the standard deviation is given by $N^{\frac{1}{2}}$ where N is the number of events recorded and the probable error is $0.6745N^{\frac{1}{2}}$; being a function of N and not time.

b This study

As a comparative study to measure any residual gamma activity within the Kimmeridgian outcrop samples was made, samples were presented as identically as possible. Aluminium planchets (2.4 cm dia.) were filled with sediment powder ($\leqslant$200 mesh and $>$30 days old) and the surfaces were flattened with a glass slide until the planchet could take no more material. The loaded planchet was then covered by a film of cellotape to facilitate easier handling and to reduce the risk of 'permanent' contamination within the counter. Also α and β radiations were eliminated by the cellotape and the planchet was not in a raised position inside the apparatus during counting.

The geiger counter was calibrated using a Cobalt-60 (KR 216 3977) source to allow experimental counting at the optimum plateau voltage (2.25 KV from Figure 14) and the duration of counting was standardised to 10,000 seconds per sample or blank. The optimum voltage was chosen to ensure the least variation in the count rate for a small fluctuation in the geiger operating voltage. Background values were assessed at intervals throughout the exercise and averaged.

Initially, a more typical geiger counter in a lead chamber was

found to be insensitive (about 0.4 counts/second; Bland pers. comm. 1975) and a counter with a lower background noise (about 0.2 counts/second Evans, H.D. priv. comm. 1976) was sought. The actual counter (Figure 15 , Nuclear Enterprises type 2080X) was tied to a Harwell power unit, incorporating a scaler ($x10^3$ used), timer and adaptor, and was connected to a filtered/noiseless earth 240 volt supply. The geiger was housed in an 'aged' lead castle which stood 10.7 inches high (9.25 dia.) and the whole appartus weighed about 190 lbs.

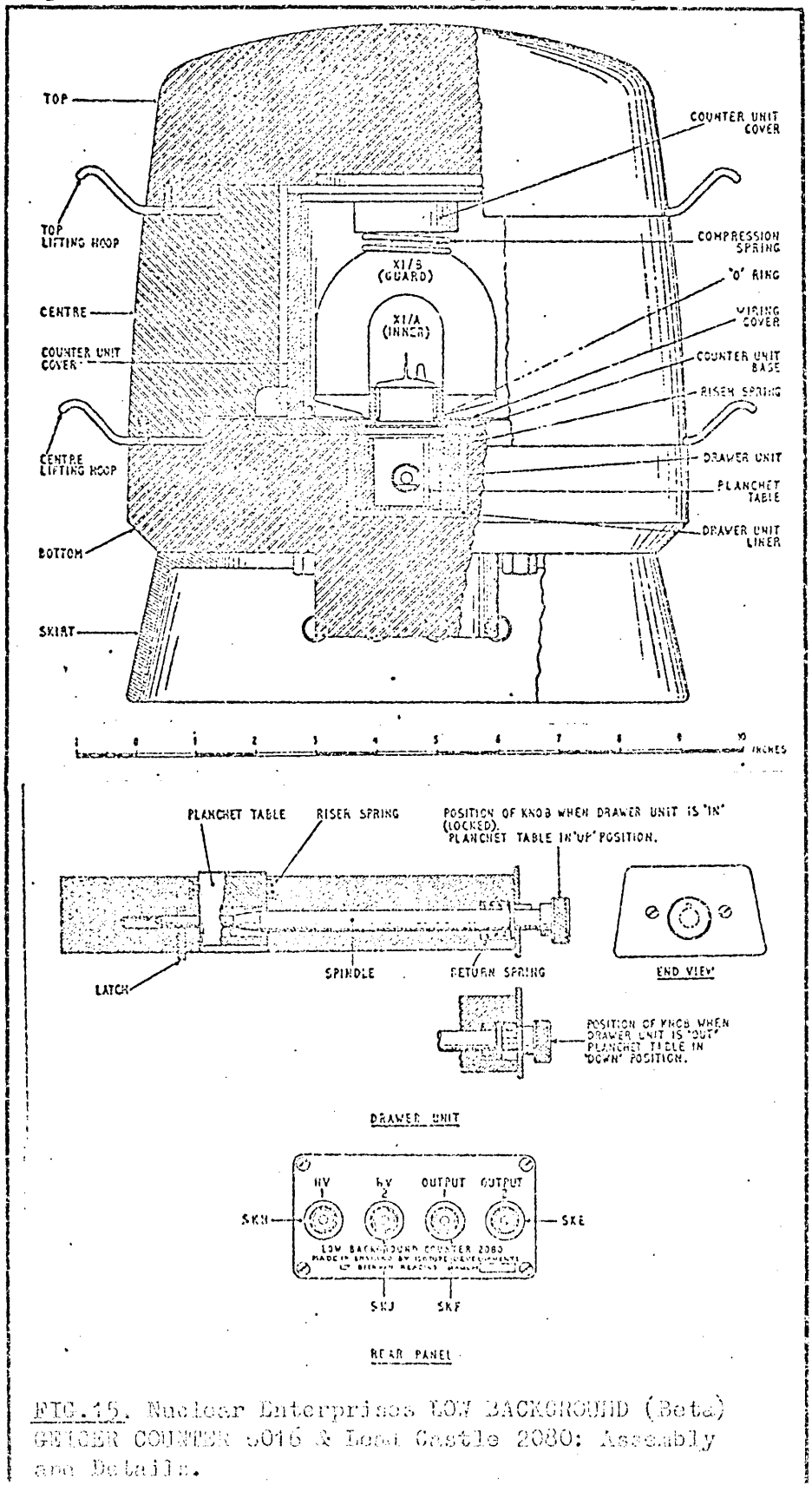


FIG.15. Nuclear Enterprises LOW BACKGROUND (Beta) GEIGER COUNTER 5016 & Lead Castle 2080: Assembly and Details.

SECTION ONE

ORGANIC GEOCHEMISTRY

PART THREE

GENERAL RESULTS AND CONCLUSIONS

1 SOLUBLE ORGANIC EXTRACT (SOE)

Baker (1972) observed that "the absolute amount of extractable hydrocarbons from non-reservoir facies may provide a quantitative basis for the assessment of petroleum source rock potential". However, he did point out that if migration is grossly efficient rocks with a low SOE are sources whereas those with high SOE are likely sources only if migration is grossly inefficient. Indicating the latter case, Fuller (1975) has stated that only about 5-15% of the total generated oil is given up by a source.

In fact, many 'source rock quality scales' have appeared since Philippi apparently documented the first in 1957 and they result from arbitrary division of the natural range of 'extractable hydrocarbon concentrations' in a non-reservoir facies. Table 27 summaries several classifications and the average distribution of rocks (from more than 1000 analyses) is shown.

McIver (1967) has remarked that "if it (any shale or fine grained rock) contains a few tenths of a percent of organic matter it is a potential source of commercial gas and oil". More seriously, Porifir'v (1974) noted that "the situation has now proceeded to the point that nearly all sedimentary rock of any composition and facies type which gives upon extraction a hundredth or thousandth percent parts of hydrocarbons is assumed to be potentially hydrocarbon generating". "Almost any sedimentary rock contains traces of organic matter" (Bitterli 1963) and "due to the low content of dispersed primary hydrocarbons it is probable to consider any sedimentary rock as a source rock" (Porifire'v 1974). For example Bonnet (1958) used the criterion of 0.03 - 0.045% soluble extract to distinguish source rocks.

Of course, in the strictest sense, "separation of non-bitumenous and bitumenous rocks is arbitrary" (Bitterli 1963) as first mentioned and "bitumenous blaes may graduate into regular oil shale in such a way that it is impossible sometimes to draw a dividing line between them" (Macleod-Mathews, 1975 cf Cunningham-Craig 1916).

Here, too, it should be emphasised that Philippi's origianl scale referred to "extractable hydrocarbon concentrations" (in Baker 1972) and not therefore to (total) SOE quantities in general.

Thus, in conclusion it is felt that a (total) SOE quantity alone can merely sometimes hint at the organic richness and source rock status

of a sample in the broadest extremes only. It should be obvious that the actual (total) SOE depends upon the type of organic matter, its quantity and its state of maturity; the expulsion factor of the host rock may even warrant consideration too. Extractability alone, therefore, can only indicate maturity *if* the type of organic matter is known or suggest the type of organic matter *if* its maturation stage is known (see crossplots).

Finally, with regard to the experimental conditions for elucidation of this parameter, it is believed that the 'total' SOE should be measured (as close as practical) since hydrocarbon generation through or from non-hydrocarbons has been thought to occur (Erdman 1961, Baker and Claypool 1970, Tissot *et al* 1974) although Foscolos *et al* (1976) have suggested high asphalt contents appear unrelated to diagenesis.

TABLE 27. SOURCE ROCK QUALITY SCALES.

	Extractable Hydrocarbons. 20	40	50	100	130	150	500	1000	1500	5000 PPM.
1	Very poor / Inadequate		Poor		Common - Adequate		Fair	Good	Very good	Excellent
										Less common - Better
2	Non-commercial				Fair		Good			
3	Poor		Fair		Good					
4	Below average		Above average		Exceptionally rich					
5	c.6% (Average value 100 ppm.)				c.29% ?					< 5%

1. Modification of Philippi,1957 by Baker,1972.
2. Philippi,1957 in Collins,1975.
3. Hunt & Meinert,1954 in Collins,1975.
4. Claypool & Reed,1976.
5. Baker,1972 from Hunt,1961 & Cenman,1962.

2 FRACTIONATION

The first fundamental subdivision of a SOE is usually into hydrocarbons (saturates and aromatics) and non-hydrocarbons (asphalts). These parameters are very useful in conjunction with others in helping to discern effects due to different sources of organic matter and/or thermal evolution. Attempts to utilise these subdivisions 'individually' have been made.

Although Foscolos et al (1976) have suggested that hydrocarbons as a percentage of the (total) SOE may be independent of organic type, environmental control has been upheld by several authors and their findings are annotated in Table 28. However, the general increase of hydrocarbons with age (maturity) does make it difficult to distinguish environmental effects in the geologic column (Tourtelot and Frost in Bloxam 1971).

Now, Witherspoon and Winniford (1961) observed that the concept of transformation of organic matter through a youthful heavy asphaltic stage into a more mature paraffinic stage has been utilised since (at least) Barton in 1937. More recently Bailey et al (1974) and Powell (1975) noted high percentages of non-hydrocarbons and low percentages of hydrocarbons respectively for immature sediment extracts. In fact, Foscolos et al (1976) put the amount of hydrocarbons within an immature sediment extract as less than 20% whilst Hunt (1977) reported a non-hydrocarbon/hydrocarbon ratio of about 6:1 for such rock extracts. Earlier, Evans and Staplin (1969) tabularised a change for the heavy (C_{15+}) fraction of an extract and showed abundant mainly NSO compounds are diluted with hydrocarbons for an immature to mature change in diagenesis whilst under dry gas metamorphism only a much reduced fraction, consisting of mainly hydrocarbons, persists.

More specifically, for increasing thermal effects upon organic matter Koons et al (1974) noticed that the saturates increase at the expense of polar compounds. Milner et al (1976) mentioned that the same effect causes an increase in the saturates whilst a slight decrease in 4 ring or lower aromatics; a marked decrease in high ring aromatics and NSO compounds and a slight decrease in asphaltenes all occur. Finally, as "processes which alter a crude after it is pooled may actually be more important than source controls" (Milner et al 1977),

TABLE 28. NON-HYDROCARBONS AND/OR HYDROCARBONS AS A FUNCTION OF ENVIRONMENT.

BLOXAM,1971	Non-hydrocarbons most abundant in non-marine and brackish water phases; high in shallow-water and peaty lagoonal sediments with biochemical metabolism (Shimada,1963) and bacterial decay of marine life forms together with some types of land plants giving hydrocarbons.(Swain & Prokopovich,1954)
PALACAS et al,1972[5]	%Hydrocarbons in Soluble Organic Extract: c.20 - Organic rich tidal marsh mud,NE Gulf of Mexico[1] c.1.1 - Organic rich algal clay, lagoonal environment 2 c.10.2 - Algal 'mück', lagoonal environment 2 23.0 - Continental shelf mud (uppermost 1 ft.) 3 11.0 - Sands and silty clays,Bering Sea 4 20.0 - Estuarine sands,Choctowhatchee Bay 5 50.0 - Estuarine mud, Choctowhatchee Bay 5 40.0 - Shallow marine sand, Choctowhatchee Bay 5
KOONS et al,1974	High wax/paraffinic crudes generated in stratigraphic sequences which contain dominant terrigenous organic matter or organic matter derived from aquatic organisms associated with waters of less than normal salinity. (Hedberg,1968)
POWELL et al,1975	Carbonates and evaporites generally give naphthenic-asphaltic heavy oils with a high sulphur content whilst shales typically produce low sulphur, naphthenic-paraffinic oils.
HUNT,1977	C_{15}- C_{40} Hydrocarbons ; Asphaltics are in approximate ratios of 1:2 and 1:10 for oxidising and reducing environments of recent sediments. (cf.Bloxam in text)

TABLE 29. PHYSICAL CHARACTERISTICS OF EXTRACT FRACTIONS.

FRACTION	UNMETAMORPHOSED:	METAMORPHOSED.
SATURATES:	Solid at -7°C; some liquid & some solid at 25°C	Liquid at -7°C;mostly liquids (some low viscosity) at 25°C.
AROMATICS:	Solid at -7°C; viscous liquids or solid at 25°C Darker in colour.	Viscous liquids at -7°C Very fluid liquids at 25°C Lighter in colour.

the quotation after Brooks (in 1948 by Milner et al 1977) that "the very heavy viscous oils, many of them free from lighter hydrocarbons such as gasoline probably represent petroleum in a very early transition stage" thus remains true (especially in view of the recognition of biodegradation) if "non-reservoir extracts" is substituted for "oils". For reservoir lithologies, the "concept of a heavy crude equating with immaturity was and still is accepted by many geologists without question but most geochemists now recognise many of the tarry asphaltic oils as the alteration products of earlier better quality oils that have been affected by water-washing, inspissation and microbial degradation" (Rogers et al 1972 in Milner et al 1977).

Therefore, "hydrocarbons in the soluble matter are of primary value in evaluating the source rock" (Collins 1975) and a high (asphaltic) non-hydrocarbon content for a non-reservoir (shale) rock extract is apparently very strong evidence in itself for immaturity. For later contrast the Kashafrud Formation, from the Iranian Kopet-dagh gas province (Madani 1977), shows dominant hydrocarbons (especially saturates) with respect to a low non-hydrocarbon (asphalt) content for the soluble extracts.

Incidentally, very little attention seems to have been paid to the physical characteristics of the various fractions of an extract since Baker and Claypool (1970) noted variations consequent from different stages of thermal evolution (Table 29).

3 a Saturates

Paraffins can sometimes constitute up to 30% of crudes (Hobson verb. comm. 1972) and in the extreme gas sources give extracts where alkanes unquestionably dominate (Madani 1977).
In fact, alkanes are now known to survive geologic time and conditions due to their strong C-C and C-H bonding and overall hydrophobic character. They can provide more information than the simplicity of their structure suggests and they harbour examples of the few types of "biologic markers" where long chains of carbon atoms are linked together (Eglinton and Calvin 1967).
Saturate fractions can be further subdivided into normal, branched and cyclic alkanes. However, since urea adduction and/or molecular sieves with conventional GLC and/or capillary GLC afford the means of detailing saturates, these subdivisions are discussed under the results and conclusions of GLC.

3 b Aromatics

Erdman (1961) has been responsible for a most informative account of the derivation of aromatic hydrocarbons which are found in (ancient) sediment extracts.
Light aromatic hydrocarbons (benzenes and lower alkyl substituted benzenes) have not been reported in animals, lower plants, bacteria, or aquatic organisms and no reference to their synthesis during autolysis or bacterial decay of plant and animal matter is known.
In fact, no LMW aromatics were detected under very sensitive analytical conditions (0.1 ppm phenyl rings and 0.01 ppm naphthyl rings detectable) and consequently Erdman (1961) suggested the precursors should include:

1) conjugated unsaturates such as squalenes, carotenes and xanthophylls; that is compounds with conjugate chains and branch methyl groups. Considerable quantities of such compounds are found in terrestrial and aquatic plants and animals and Fox et al (1937-1944 in Erdman 1961) noted their partial conversion to aromatics with time after death of the parent.
2) terpenes; whose dehydrogenation and rearrangement gives aromatic hydrocarbons. These are known to be most widely

distributed in woody plants and also sometimes occur in algal products but little is known about their distribution in aquatic organisms and their consequent fate under deposition.

and/or

3) highly unsaturated fatty acids; whose conjugation and condensation can give aromatic hydrocarbons; such acids being common to many forms of aquatic life.

Aromatic hydrocarbons of intermediate molecular weight probably have diverse origins but Erdman (1961) did note that a few had been reported as:

4) in the normal constituents of the lipid fraction of plants and animals where such aromatic hydrocarbons are stable throughout geologic time (e.g. p-cymene)

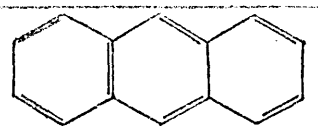
and/or

5) non-hydrocarbon material such as saturated and unsaturated fatty acids, aldehydes, alcohols and polycyclic sterols which can form such aromatics by elimination of a functional group.

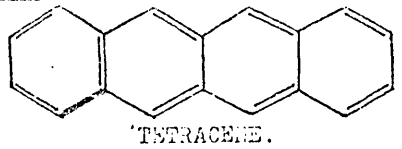
Degens et al (1962) shared subsequent support for origins via 1, 4 and 5 by stating that "isoprenoids, steroids and related cyclic constituents of the lipid fraction are the most likely sources of the arenes" with possible derivation from the aromatic-amino compounds such as phenylalanine and tyrosine. More recently Albrecht et al (1976) and Vandenbroucke et al (1976) mentioned that 'peculiar tree resin structures' (diterpenes) could easily evolve towards (tricyclic) aromatic compounds by dismutation reactions (2).

In 1976, Blumer gave a revealing account of polyaromatic hydrocarbons which consist of three or more fused benzene rings in linear, angular or cluster arrangements (Figure 16). Although unsubstituted PAHS are abundant, an extended series of substituted PAHS occurs with methyl radicals, alkyl chains and saturated 5-member rings, and consideration of sulphur containing analogues of PAHs gives an almost endless permutation (Figure 17).

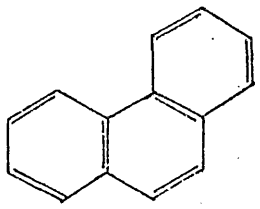
As PAHs were found to show a remarkably constant composition over a wide geographic range (continental soils to sea-bottom sediments;



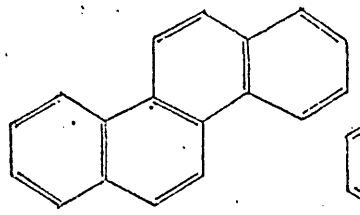
ANTHRACENE.



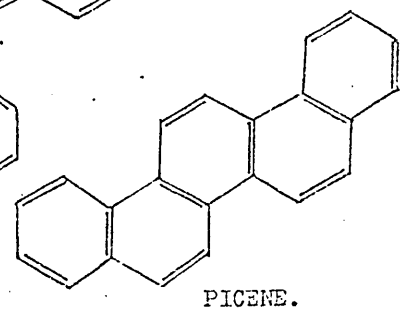
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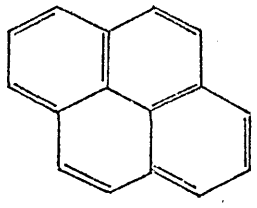
PHENENTHRENE.



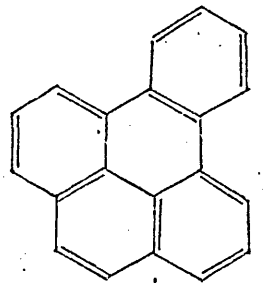
CHRYSENE.

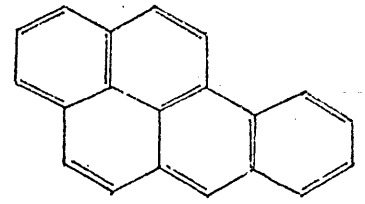


PICENE.

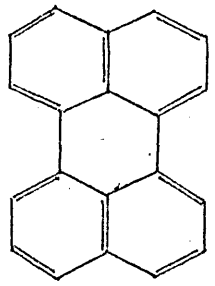


PYRENE.

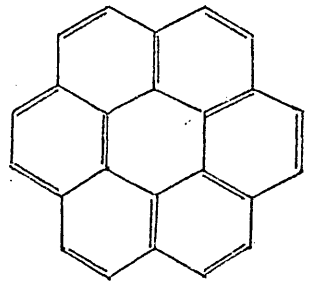




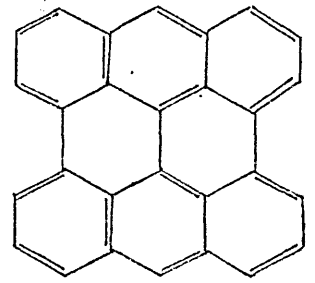
ISOMERIC BENZOPYRENES.



PERYLENE.



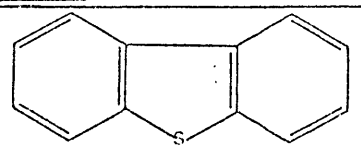
CORONENE.



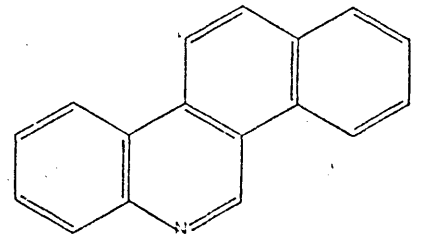
MESO-NAPHTHODIANTHRENE.

Polycyclic aromatic hydrocarbons consist of two or more rings fused together in various ways. Rings of six carbon atoms have the highest stability because they require the least distortion of the natural bond angles of the carbon atom. The rings may be linearly arranged (top row), in angular arrangement (second row) or as clusters (remainder) Order of stability is linear cluster angular. (Compiled from Blumer,1976)

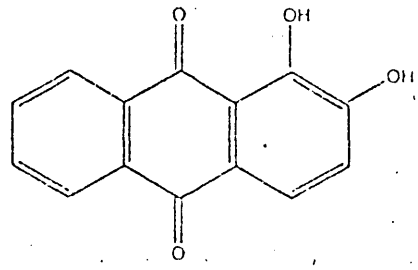
FIG 16 TYPES OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs).



DIBENZOTHIOPHENE



AZACHRYSENE



ALIZARIN

(From Blumer,1976.)

ADDITION OF FOREIGN ATOMS to polycyclic aromatic hydrocarbons greatly increases the number of structural permutations possible. Alizarin, the brilliant red pigment of Napoleon's time, has oxygen atoms and hydroxyl groups as peripheral substituents on its molecule. It bears a family resemblance to the fringelite structure shown at the bottom of preceding page.

FIG 17 STRUCTURAL PERMUTATIONS FOR PAHs.

strongly oxidising to strongly reducing deposits) a contribution of the same complex hydrocarbon series in the same proportions from a great diversity of organisms associated with such a wide variety of sites was maintained as unlikely. Instead, a thermal origin where PAHs are generated by natural pyrolytic processes was deduced (Figure 18).

In crudes, the maximum number of carbon atoms on the aromatic rings are higher than those in samples produced by high temperature pyrolysis (aromatic hydrocarbons surrounded by 5-member rings are (relatively) abundant in petroleum) and alkylated PAHs far exceed unsubstituted PAHs. Hence, during petroleum formation the time is adequate for the energetically favoured aromatisation to be accomplished but the temperature is not high enough to fragment the weaker C-C bonding of the alkyl side chains (Figure 19).

With regard to the origin of organic matter in an immature source, Bailey et al (1974) recorded that a high percentage of aromatics (within the C_{15+} fraction of an extract) commonly occurred for land derived material. Lately, Vandenbroucke et al (1976) have suggested that the relative abundance of true aromatics compared to cycloalkanes and naphtheno-aromatics may indicate whether an environment of deposition was oxidising or reducing.

Now concerning maturity aspects, Bestougeff (1961) has noted that crudes contain mono- and bi-cyclic aromatics as the main aromatic component. Polycyclic aromatics are usually in very low concentration and molecules with condensed aromatics linked by naphthenic or heteroatomic hydrocarbons are especially rare. (Specifically, Blumer (1976) cited Coleman et al in stating that PAHs constituted up to one-sixth of the 370-535°C fraction of a Prudhoe Bay crude).

Finally, in connexion with Blumer's (1976) work, it can be mentioned that Baker and Claypool (1970) attributed the colour of aromatic fractions of SOEs, in part, to nonhydrocarbon contaminants possibly in the form of complex polycyclic aromatics. They assumed the lightening of colour with increasing metamorphism indicated a transformation of the 'contaminants' into less or non-condensed LMW hydrocarbons (cf. Bestougeff 1961). However it should be borne in mind that PAHs and alkylated PAHs can persist

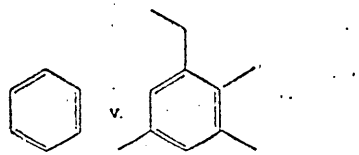
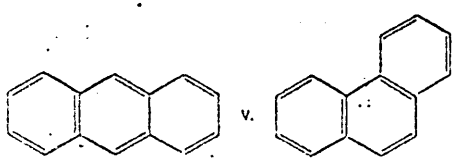
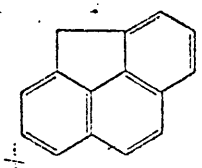
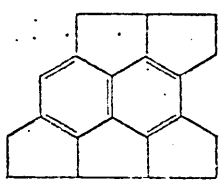
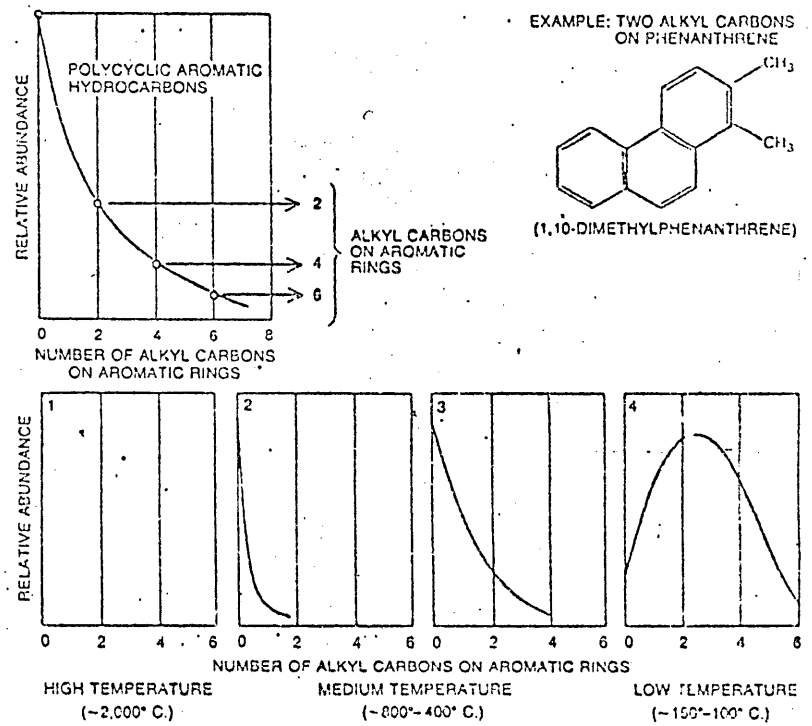
STRUCTURAL FEATURES	STRUCTURAL PREFERENCE	CONDITION OF FORMATION
 DEGREE OF ALKYLATION	LOW DEGREE OF ALKYLATION	HIGH FORMATION TEMPERATURE HIGH CARBON CONTENT IN SOURCE MATERIAL
 RING ARRANGEMENT (LINEAR, ANGULAR, CLUSTER)	ANGULAR RING ARRANGEMENT	LONG EQUILIBRATION TIME HIGH EQUILIBRATION TEMPERATURE
 STRAIN	HIGH DEGREE OF RING STRAIN	SHORT EQUILIBRATION TIME LOW FORMATION TEMPERATURE
 NUMBER OF FIVE-MEMBER RINGS	MULTIPLE FIVE-MEMBER RINGS	LONG REACTION TIME LOW FORMATION TEMPERATURE

FIG. 19 SUMMARY OF APPLICATION OF PAHs.(From Blumer,1976)
The configuration of hydrocarbon structures found in geochemical mixtures provides rich information about the conditions under which the structures formed. The type and spatial arrangement of the alkyl chains and of the saturated and aromatic rings can vary over a wide range. The presence of preferred structures in natural mixtures of PAHs reflects the composition of the source material, the temperature of formation and transformation and the duration of chemical processes involved.

FIG 18 CORRELATION OF PAHs WITH TEMPERATURE OF FORMATION.



NUMBER OF ALKYL CARBONS present as side chains on polycyclic aromatic hydrocarbons correlates closely with the temperature at which the compounds were formed. In a typical mixture (*curve at top left*) rings with no side chains are the most common; in general the more side-chain carbons there are, the lower the abundance is. An example of a polycyclic compound with two alkyl carbons is 1,10-dimethylphenanthrene. When the aromatic compounds are formed at the temperature typical of gas flames (*1*), side chains are virtually absent. At temperatures typical of wood fires (*2, 3*) abundance of side chains increases with decreasing temperature. At the low temperatures that are associated with the formation of petroleum, however, the polycyclic compounds with two or three alkyl carbons outnumber the other configurations (*4*).

(From Blumer,1976.)

in spent shale (extracts) (Schmidt-Collerus et al 1976).

3 c Non-hydrocarbons (Asphalts)

Several terms have arisen in petroleum geology-geochemistry circles notably asphalts, ONS compounds (eluted and non-eluted), resins and asphaltenes and these appear to be often applied loosely in substitution for one another. The all embracing terms of 'non-hydrocarbons' or 'asphalts' seem the most satisfactory candidates as a group name for such compounds for which many schemes of subdivision have been tried (e.g. solubility in organic solvents, molecular distillation, thermal diffusion, ultracentrifuge etc in Witherspoon and Winniford 1961).

Not surprisingly the term 'asphalt' has been described as a "somewhat nebulous entity" (Hobson 1966) and asphalts themselves do not occur in organisms (Erdman 1961, Hobson 1966). They are not identified in recent sediments (Bush verb. comm. 1973) but have been suggested to arise from condensation and/or polymerisation reactions from a wide variety of materials (Erdman 1961, Hobson 1966, Bush verb. comm. 1973). In fact, Erdman in 1964 (miscell.) proposed aminoacids and carbohydrates as precursors.

However, asphaltic compounds can comprise 0-60% of a crude (from Sachanen 1945 in Witherspoon and Winniford 1961 and extended by reference to Erdman 1961) mainly as colloidal particles (Levorsen 1954) ranging in size from 32-100Å (Witherspoon and Winniford 1961). A molecular weight range of 200-100,000 (Erdman 1961) has been given although the lowest value has been quoted as about 1200-1500 (Erdman 1964, miscell.) ? An asphaltic fraction of a crude has been defined as the residue which remains after non-destructive distillation has removed all the hydrocarbons which distill over at 350°C or less although the ASTM (D86-61) recommended a temperature of 371°C (Witherspoon and Winniford 1961). The major constituents of the asphalt fraction are O, S and N heterocyclics (Erdman 1961) and the metal porphyrin complexes occur primarily in this fraction (Hodgson et al 1961) causing a high percentage of trace elements; especially for V and Ni with respect to other fractions (Erdman 1961). Such fractions are often highly viscous liquids ('semi-solids') or apparently solids at R.T.P (Erdman 1961, Witherspoon and Winniford 1961).

FIG 20 ASPHALT(ene) STRUCTURES (From Erdman, 1962.)

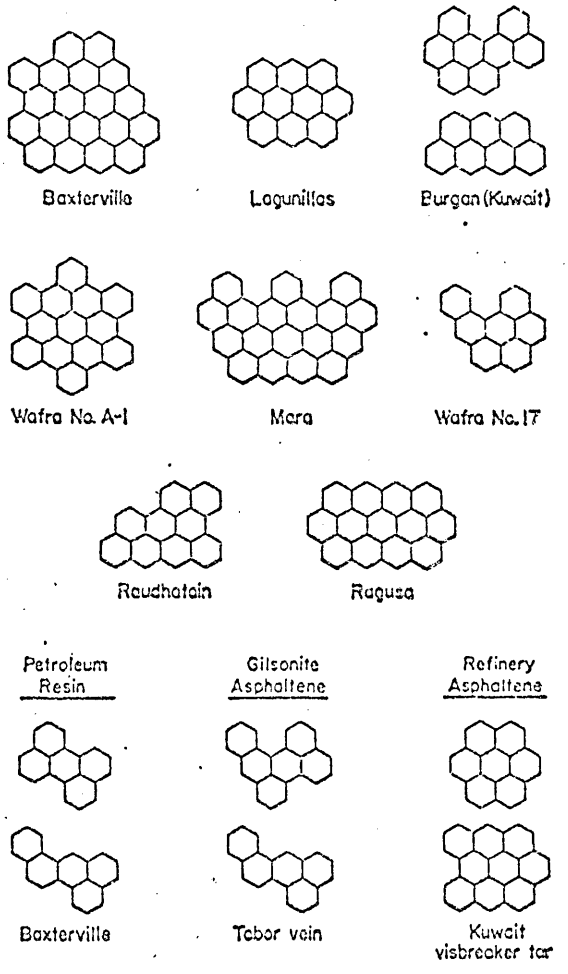


FIGURE 1.—Petroleum asphaltenes: Ring systems consistent with the average dimensional data for the aromatic sheets of petroleum asphaltene and related substances.

For a given asphaltene, resin or other asphaltic substance either the major percentage of aromatic sheets are represented by a few structures close to those in Figure 20 or no one structure represents more than a small fraction of the molecules. Although the aromatic sheets vary considerably in size, the large majority are evidently peri-condensed and from stearic considerations only a little more than half of the positions on the aromatic sheets can be substituted. A considerable amount of naphthenic structures occur within the asphaltic molecules (Erdman 1964 miscell.).

The source rock interpretation of asphalts has been discussed under the category of non-hydrocarbons and a classification is attempted in Figure 21.

3 d Asphaltenes

As noted earlier (under experiment work) at least eight authors have precipitated out asphaltenes prior to chromatographic fractionation. Yet, only Bloxam (1971) appears to have offered a geo-interpretation when it was proposed that high percentages may indicate oxidation within the depositional environment. This presumably is because asphaltenes are very resistant to oxidation and increase only preferentially at the expense of hydrocarbons which are more susceptible to oxidative attack.

More recently though, Milner et al (1977) noted that a routeway from saturated aliphatic hydrocarbons through alicyclic-naphthenic hydrocarbons to (unsaturated) aromatic hydrocarbons could allow subsequent dehydrogenation ('oxidation') and cyclisation to form asphaltenes.

It remains interesting therefore to know that the SOE of phosphorites is nearly all asphaltic (Powell et al 1975).

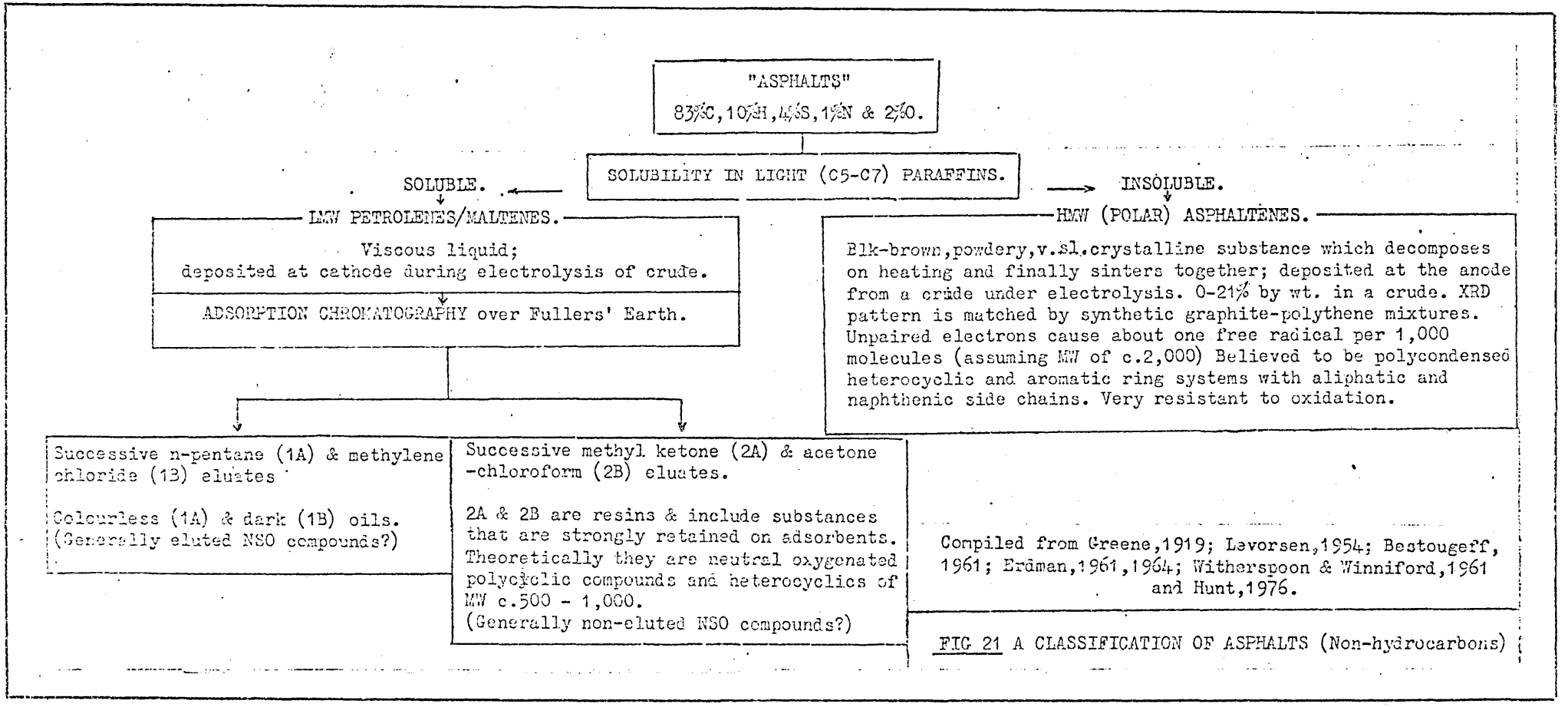


FIG 21 A CLASSIFICATION OF ASPHALTS (Non-hydrocarbons)

4 GAS-LIQUID CHROMATOGRAPHY

As mentioned before, this tool is generally applied in petroleum geochemistry, for the resolution of the saturate fraction of rock extracts and in a discussion of the (general) results and interpretations it is necessary to define the 'carbon preference index' (CPI) concept.

CPI values originally came about from (mass secptroscopic) studies by Bray and Evans (1961) who defined a CPI value as:

$$\frac{\text{summation of peak heights (areas) for odd carbon numbered paraffins}}{\text{summation of peak heights (areas) for even carbon numbered paraffins}}$$

It is therefore seen to be a mathematical expression of the odd:even dominance and is usually computed between specified limits with an allowance for effects at the ends of the distribution range. For the range nC_{24} - nC_{34}, Bray and Evans (1961) gave the formula:

$$\frac{1}{2}\left[\frac{(C25 - C33)\ ODD}{(C26 - C34)\ EVEN} + \frac{(C25 - C33)\ ODD}{(C24 - C32)\ EVEN}\right]$$

The values have generally been restricted to normal alkanes (e.g. nC_{19} - nC_{33} in Knevolden 1962, Bray and Evans 1963, Palacas et al 1972; nC_{14} - nC_{30} in Albrecht et al 1976) although it has been extended to describe branched alkanes (e.g. bC_{16} - bC_{25} in Albrecht et al 1976).

Allan and Douglas (1977) reported CPI values for the nC_{17} - nC_{31} range explaining that "alkanes below nC_{17} have not been included because of their preferential susceptibility to loss during the experimental procedures" and not recording those above nC_{31} "because of enhanced errors in peak height".

a Normal alkanes

Both the distribution and CPI are of significance in environmental source and/or thermal considerations.

Typical source rock studies usually embrace the C_{15} - C_{32} range, although the largest n-alkane in a crude is of the C_{70} - C_{80} chain length order (Martin et al 1963) and it can be remembered that marine or terrestrial organisms commonly contain only one or two dominant n-alkane components (Eglinton and Hamilton 1963 and Clarke and Blumer 1967 in Bloxam 1971; Allan et al 1975) where even numbered n-alkanes are generally absent or occur to only a very small extent (Douglas & Grantham 1973).

The CPI and distribution of n-alkanes in initial chief source

types are summarised in Table 30 but deviations to the general pattern do occur. For example, smooth distributions up to C_{35} are known in several heartwoods and many higher plants of diverse sources contain significant proportions of homologues below C_{25} (Allan et al 1975). However, with few exceptions, n-alkane distributions in (recent) sediments do not show even/odd carbon predominance (Douglas & Grantham 1973).

With specific regard to CPI values and maturation effects, the ranges of figures for recent and ancient sediments and petroleum are of the respective order 5.5 - 2.4, 2.5 - 1 and 1 (Hobson verb. comm. 1972). As an odd dominance amongst the heavy n-alkanes is typical for recent organic matter (Stevens et al 1956 in Schenck and Eisma 1962, Bray and Evans 1961, Schenck 1968), for n-alkanes of a sediment to approach those of a crude HMW (C_{18+}) n-alkanes need to change so that the odd dominance is reduced from about 3 to little or no dominance at all (Knevolden 1962).

Now as the CPI decreases a change in the distribution of n-alkanes is observed. Knevolden (1962) mentioned that the C_8 - C_{13} (intermediate) n-alkanes should be concentrated as Rossini in 1960 had given the C_8 - C_{13} : C_{18+} n-alkane ratio in crudes as about 5:1. Consequently, Cordell (1972) deduced that a high CPI indicates the lack of energy (heat) needed to break C-C bonds and thus to crack the original material to lighter ends.

In fact, Mathews et al (1970) cited Brooks and Smith from 1967 who found that the CPI decreased as accompanying coal rank increased and more recently Milner et al (1977) wrote that an absence of an odd CPI amongst heavy n-alkanes in a crude can be the result of thermal alteration.

Accordingly, Cordell (1972) noted that an oil source bed adequately mature for generation yielded n-alkanes of slight-moderate odd dominance and initially Bray and Evans (1961) insisted that the CPI had to be less than or equal to 1.2 for a rock to function as a source.

Decreasing CPIs have incidentally been detected over relatively small vertical ranges such as within a formation (Robinson et al 1977).

Here it is interesting to note that Schenck (1968) advocated the

AUTHOR(S) & DATE.	CPI/DOMINANCE.	N-ALKANE OR N-ALKANE DISTRIBUTION.	SOURCE MATERIAL AND/OR DEPOSITIONAL ENVIRONMENT.
Hobson,1966	Little odd	C_{24} - C_{34}	Algae,some corals & sponges.
Schenck,1968		C_{22}	Few algae.
Bloxam,1971		C_{12} - C_{17}	Aquatic organisms eg. bacterium Vibrio marinus & freshwater alga Anacystis nidularis
Haug & Sever,1971		C_{22}	Lagoonal sediments.
Douglas & Henderson,1972	Odd	C_{15} - C_{19}	Lower plants - algae.
Palacas et al,1972	<2	C_{17}	Brackish marine organisms Dominant in marine organisms especially algae.
Powell,1975		C_{16} - C_{17}	Primarily algal.
Powell et al,1975		C_{16} - C_{22}	Micro-organisms.
Hunt,1976	Odd	C_{15} - C_{19}	Plankton;concentrated in offshore environment.
Powell et al,1976		C_{17} - C_{20}	Marine algae.
Vandenbroucke et al,1976		C_{17}	Algae.
Reed,1977b		C_{15} - C_{19}	Lake biota; algae.
Eglinton & Hamilton,1963*	Strong odd c.10	C_{25} - C_{35}	Waxy constituents of land plants.
Eglinton et al,1964 Eglinton & Calvin,1967	Strong odd	C_{27} - C_{31} C_{29} - C_{31}	Waxy covering of leaves & pollen of terrestrial plants.
Douglas & Henderson,1972	Odd	C_{25} - C_{35}	Higher plants.
Palacas et al,1972	Strong odd c.8	C_{19} - C_{33}	Land plants.
Powell,1975	Odd	C_{23} - C_{31}	Higher plants.
Powell et al,1975		C_{23} - C_{30}	Land plants.
Hunt,1976	Odd	C_{27} - C_{31}	Land plants; concentrated in nearshore environments
Powell et al,1976		C_{23} - C_{27}	Non-marine.
Vandenbroucke et al,1976	Odd		Lipids of higher plants which contain cuticular waxes.
Reed,1977b		C_{25} - C_{33}	Cuticular waxes of vascular plants.

*In Palacas et al,1972

TABLE 30. SOURCE,DISTRIBUTION & CPI FOR N-ALKANES OF INITIAL ORGANIC MATTER.

use of n-C_{22} alkane as a maturity index from the fact that it predominated in 450 extracts but did not occur in 250 crudes. However, Reed (1977b) has observed a relative increase in the n-C_{22} alkane which he attributed to weathering effects, whilst Douglas & Grantham (1973) pointed out the coincidence of docosane predominating amongst contaminants derived from polythene closures.

Light alkanes are often analysed in commercial circles. The percentage of ethane-hexane (C_2 - C_6) hydrocarbons has been found to be low ($< 0.004\%$) for deltaic and estuarine facies where allochthonous humic material dominates but much higher (2-1 - 8.1%) for typical marine or brackish facies (Weber and Maximov 1976).

As for geothermometry, the ethane:methane ratio for immature sediments has been found to be 1000:1 whilst the ethane and propane:methane ratio for metamorphosed ('dry gas') sediments is 100:1. 'Shale gas' can in fact be as much as 50% in an oil producing area (Hunt 1977) and increasing LMW n-alkanes are a feature of increasing coalification (Leythaeuser and Welte 1969 in Allan et al 1977).

Although Erdman (1961) and Tissot et al (1974) mentioned incorporation of n-alkanes into sediments without change from higher plants and algae several authors have proposed precursors for these compounds. Actually it was Erdman (1961) who noted that with the exception of methane, n-heptane is the lowest known aliphatic constituent of living organisms.

For the generation of light aliphatic hydrocarbons, decarboxylation and (reductive) deamination of protein has been postulated as one way of formation (Erdman 1961) although more recently Philippi (1977) has suggested (low temperature anoxic) cleavage of a hydrocarbon side chain from the polypeptide backbone is followed by hydrogen transfer to form saturated hydrocarbons.

Fatty acids have been advocated as one source of n-alkanes but Cordell (1972) noted that, in 1962, Abelson and Parker objected to the idea as they maintained most free acids disappeared under reducing conditions and that the instance of free acids in modern sediments was low. Also, Mathews et al (1970) have commented

that the distribution of fatty acids within land plants was not well enough known for their assessment as n-alkane precursors. More recently Philippi has re-emphasised his 1974 view that subsurface generation of n-alkanes by the decarboxylation of fatty acids does not occur. Yet, Johns and Shimoyama (1972) maintained n-fatty acids in the lipid fraction of organic matter could serve as n-alkane precursors and specifically Powell et al (1975) proposed the n-C_{22} fatty acid of phyto- and zoo-plankton (after others) as the possible precursor of the nC_{22} alkane. Much earlier Robinson et al (1965) had suggested fatty acids with kerogen 'esters' could serve as the source of n-C_{12} - n-C_{33} alkanes.

Alternatively, the esters of fatty acids and complex alcohols could have been C_{23+} n-alkane precursors (Martin et al 1963 and Lawler and Robinson 1965 in Mathews et al 1970).

b Branched alkanes

Branched alkanes are known to usually comprise less than 10% of the saturate fraction of a recent sediment extract (Knevolden 1962) but their environmental significance and behaviour under increasing thermal maturation still appears to be controversial.

Douglas and Henderson (1972) cited Brooks et al in mentioning that an increase in the concentrations of pristane and phytane paralleled increasing coal rank and themselves observed an increase in 'acyclic isoprenoids' under an increasing geothermal gradient (Figure 22).

However, although noting several Russians had tried to use the disparity in the formation of normal and branched alkanes as a means of gauging maturation, Milner et al (1977) insisted that branched alkanes do not increase with increasing maturation. (Such an observation incidentally has been assumed to indicate the absence of catalysis during thermal hydrocarbon generation). In fact, Ishiwatari et al (1977) have stated that the pristane -nC_{17} alkane ratio actually decreases with increasing thermal alteration and suggests branched alkanes are less thermally stable than normal alkanes.

With regard to the source of the organic matter and/or environment of deposition pristane/phytane ratios have been used

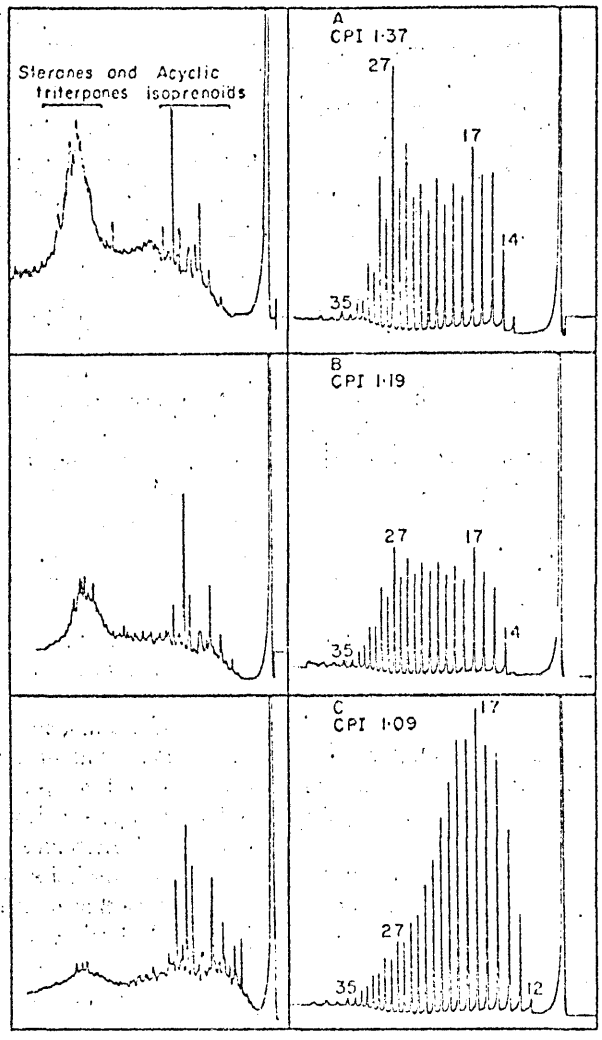


FIG 3. Gas chromatograms of normal and branched/cyclic alkanes extracted from Carboniferous shales in an East Midlands borehole. Depths, in feet, are A, 1257–1272; B, 2389–2404; C, 3539–3544. Gas chromatographic conditions: column, 3 ft × ⅛ inch containing 3 per cent OV–101 on Varaport 30, temperature programmed from 80°–300°/6° min; nitrogen 12 ml/min. (From Douglas & Henderson, 1972)

FIG. 22 THERMAL INSTABILITY OF BRANCHED/CYCLIC ALKANES.

TABLE 31. PRISTANE:PHYTANE RATIOS

> 4-5	:	Land material.
3 - 4.5	:	Mixed deltaic/marginal marine material.
(> 3	:	Non-marine material.*)
< 3	:	Marine material.

From Powell & McKirdy, 1975. (*Powell et al, 1976.)

and are given in Table 31. The reasoning for high pristane concentrations indicating a non-marine source (in immature sediment extracts) is illustrated in Figure 23. Reed (1977b) has reported low pristane concentrations with little or no phytane typify modern marine sediments whereas earlier Douglas and Henderson (1972) did note that phytane occurs in marine organisms and sediments. Pristane as a constituent in zoo-plankton, fish, whales, marine sponges and wool wax was recorded by Eglinton et al (1964).

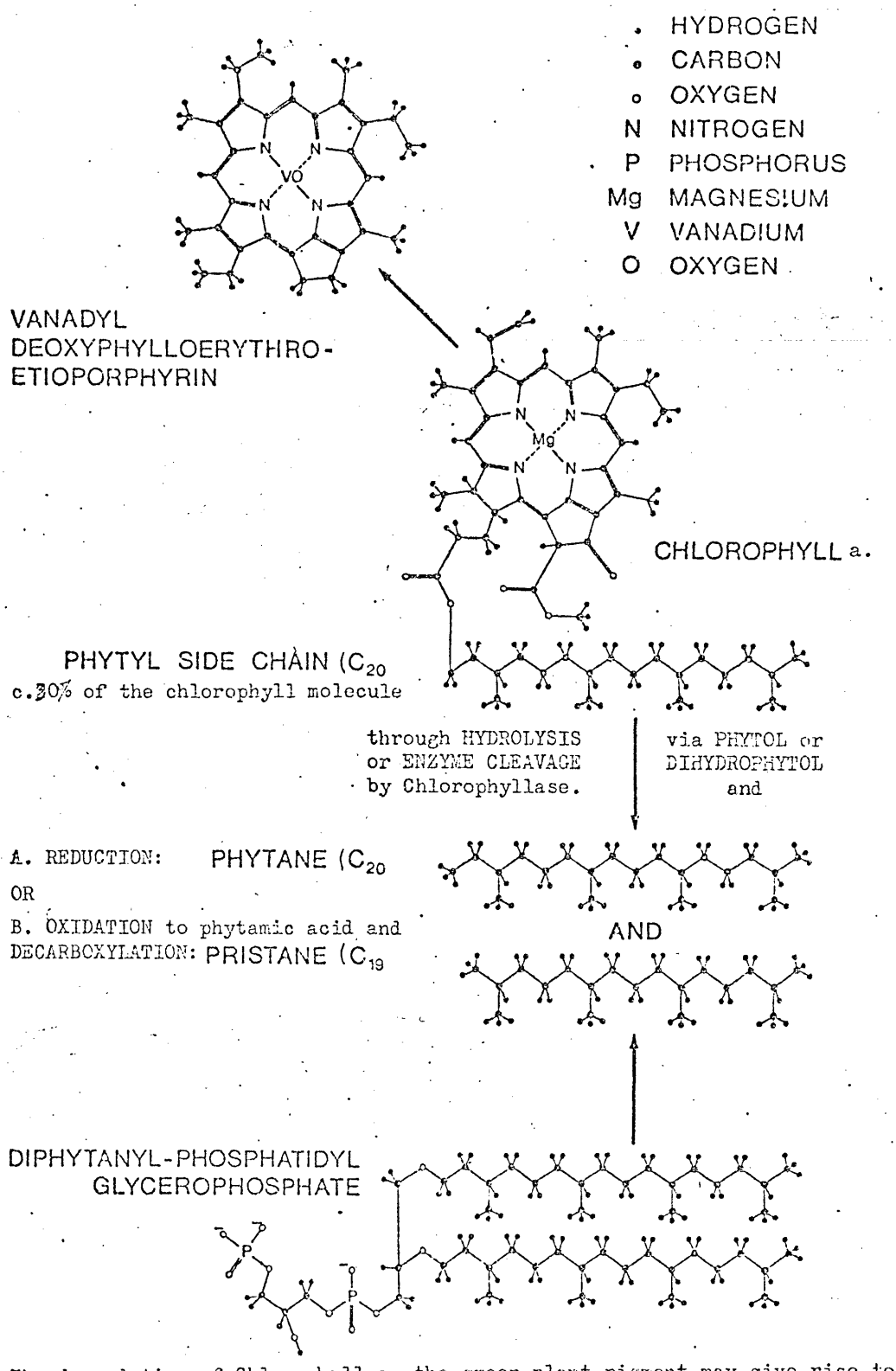
Palacas et al (1972) with reference to immature sediments did propose that the pristane :nC_{17} alkane ratio may offer a clue to the organisms providing the hydrocarbons as they recorded ratios in the range 1:0.4 - 5.0 for bacteria, algal mats, planktonic algae and one mixed phyto- and zoo-plankton sample. Here too it can be mentioned that hydrocarbons with a single methyl branch near the middle of a molecule are unusual and have only been isolated from blue green algae. Also, C_{18} and C_{19} isoprenoids appear to be forming in intensely reducing lacustrine bottom sediments of the present-day (Reed 1977b).

c Cyclic alkanes

Cyclic alkanes are in fact isomeric with alkenes (C_nH_{2n}). C_3-C_{30} naphthenes are known in petroleum and all monocyclic isomers, except C_3H_6 and C_4H_8, are liquids at RTP (Levorsen 1954). Specifically Koons et al (1974 after Martin et al 1963) noted an increase in the cyclopentane:cyclohexane ratio for increasing maturation whilst earlier Tissot et al (1971 from Allan et al 1977) had observed decreasing tetra- and penta-cyclic alkanes and increasing mono-, di- and tri-cyclic alkanes accompanied an increasing depth of burial.

With regard to environment of deposition, Vandenbroucke et al (1976) from a comparative study of sediments from one oxic and one anoxic environment found tricyclics and tetracyclics respectively more abundant.

Powell et al (1975) have cited Barbat, from 1967, in mentioning that saturated hydrocarbon fractions from phosphorites are typified by a low normal alkane content but high (and extremely complex) 'naphthenic' content.



The degradation of Chlorophyll a, the green plant pigment may give rise to two kinds of isoprenoid molecules, phytane and pristane, that have been id -entified in many ancient sediments. It also seems that both pristane and phytane can be derived from the isoprenoid side chain of a phosphate -cont -aining lipid that is a major constituent of salt loving bacteria. The porphyrin ring of Chlorophyll a is the probable source of vanadyl porphyrin that is widely found in crude oils and shales. Oxidation is of course favou -red under aerobic conditions and high concentrations have been assigned to terrestrial decay of organic matter.

FIG 23 DERIVATION OF PRISTANE & PHYTANE.(Compiled from Bray & Evans 1965, Robinson et al 1965, Eglinton & Calvin 1967, Philippi 1968 and Powell & McKirdy 1975)

d Branched - cyclic alkanes

Steranes and triterpanes (Figure 24) seem to be ideal 'biological markers' as they have not been synthesised abiogenically and although diagenesis initiates alteration and stereoisomerisation (Wszolek et al 1971), the (basic) hydrocarbon skeleton is not affected (Tissot et al 1974).

With tetraterpanes they do not occur naturally but are derived after burial from precursors (Douglas and Henderson 1972) such as their parent compounds like steroids and terpenoids which are typical constituents of the waxy coatings of leaves and pollen of land plants (Eglinton and Calvin 1967) but are also known in marine plants (Mair 1964 in Baker 1972).

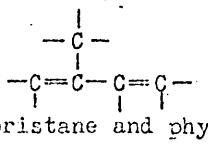
In fact, marine invertebrates, zooplankton and algae contain a wide variety of steroids (Vandenbroucke et al 1976) and actually 'steroidal & triterpenoidal alcohols' have been isolated from virtually every type of organism (Reed 1977b).

As stanols, for example, are known only to occur in sphagnum moss and in a pollen mixture almost to their total exclusion elsewhere in the contemporary plant kingdom, they are attributed to the reduction of unsaturated sterols and can themselves give steranes upon further reduction (Steel and Henderson 1972).

Tri- and tetraterpanes from continental slope and shelf sediments have been assigned to terrestrial flora whilst sterols have been found in deep ocean bottom muds that were rich in algae, diatoms, foraminifera, radiolarians and nanoplankton (Simoneit and Burlingame 1971). Sterols have also been proved for flysch sapropelites which contained abundant algae, fish and crustaceans (Hobson 1966).

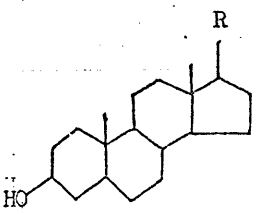
The decrease in steranes and triterpanes with increasing rank (Allan et al 1977) is illustrated in Figure 22 (Douglas and Henderson 1972).

ISOPRENOIDS are branched alkanes; derived from the basic ISOPRENE UNIT:



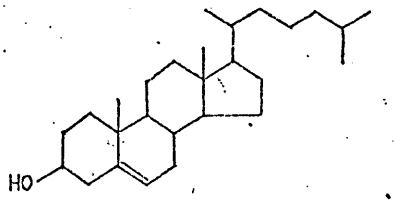
Such units are usually arranged in a regular head to tail fashion and common examples are pristane and phytane. (See Fig.23)

STEROLS are all hydroxy-derivatives of perhydro-1,2-cyclopentanophenanthrene where R is variable and may contain up to 8 carbon atoms



They are infact the solid tetracyclic alcohols in steroids and can give vitamins under radiation. The dextrorotary optical activity of most oils is generally attributed to cholesterol, $C_{26}H_{45}OH$.

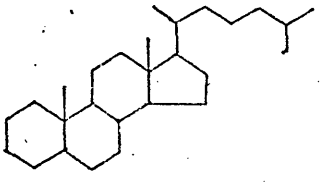
STEROIDS are the non-saponifiable, ether-soluble portion of animal and plant fats that are also partly comprised by HMW hydrocarbons.



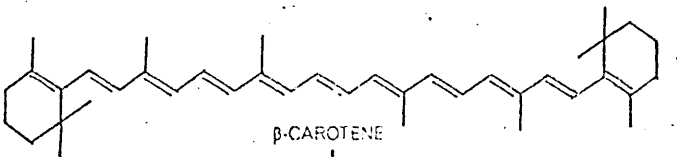
CHOLESTEROL

REDUCTION IN SEDIMENT

CHOLESTANE



TERPENES are unsaturated alicyclic compounds which can be open-chain, monocyclic, bicyclic, sesquicyclic or polycyclic and are contained in the oils of leaves, blossoms, fruits and barks. β-carotene is the red pigment in plants.



β-CAROTENE

REDUCTION IN SEDIMENT

CAROTANE

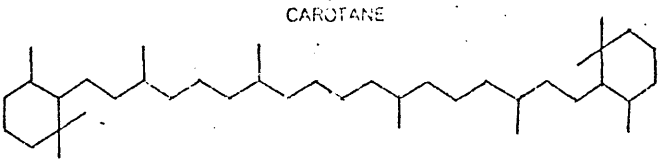


FIG 24 ISOPRENOIDS, STEROLS/STERANES/STEROIDS & TERPENES/TETRATERPANES. (Compiled from Fieser and Fieser, 1956; Eglinton and Calvin, 1967 and Hunt, 1976.)

5 QUANTITATIVE ELEMENTAL ANALYSIS

The biosphere in dealing with the chemistry of life can be defined as the 'locus of interaction' between C, H, N, O, S and P and living matter can be generalised as $H_{2960}\ O_{1480}\ C_{1480}\ N_{16}\ P_{1-8}\ S$ (Deevey 1970).

a Nitrogen

A real enrichment of organic nitrogen within total organic matter during diagenesis has been reported by Muller (1977). Much earlier Trask and Patnode found that the amount of nitrogen in sediments varies in weight almost directly with organic carbon content and, in fact, Trask tried to use nitrogen as a criterion for source rock classification (Hobson verb. comm. (1972).

However, Bloxam (1971) stated a loss of nitrogen occurred with burial and diagenesis. Certainly in a crude, nitrogen is rarely greater than 1% (Levorsen 1954; Constantinides and Arich 1961) and is generally of the order of 0.01 - 0.2% (Bestougeff 1961).

Trask's (1932) values for organic carbon/nitrogen ratios in recent marine sediments (5.3 - 13.6, av. 8.4) were taken to indicate a planktonic source of organic matter whereas Borodovsky's (1965) values for recent marine sediments (29.8 - 40.1) were said to be in the 'oil shale field' and indicate a large contribution from land derived plants (spores) and related humic-lignin derivatives (in Bloxam 1971). More recently, Muller (1977) offered figures in agreement with the earlier interpretations since values for lower plants (blue green algae, perideneans and diatoms: 4.6 - 7.5) were contrasted with those for higher plants (corn plants, Zostera and Leguminose: 14 - 30.4). For Californian marine shales, Philippi (1974) cited C/N ratios between 7 - 15.

Delwiche (1970) believed that the largest single source of nitrogen is probably terrestrial micro-organisms but he stated that the steady loss of nitrogen from the biosphere to sedimentary rocks is slight. In fact, the relationship of organic carbon/(organic ?) nitrogen and the original nature of the organic matter in sediments is still held as uncertain (Bloxam 1971)

although Philippi (1977) has concluded that the C/N ratio of marine sediments increases as the relative concentration of terrestrial matter increases.

Popl (in Gill et al unpub.) has apparently found a direct relationship between (organic ?) nitrogen and porphyrin content. Here it can be added that all oxygen-dependent organisms require porphyrins (Abelson 1956). So, it may be very relevant therefore that excessive nitrogen (in rivers and streams) leads to intensified biologic activity ('algal blooms') and the consequent depletion of oxygen kills oxygen-dependent organisms; causing eutrophication (Delwiche 1970) and conceivably a direct positive correlation of organic matter and nitrogen.

b. Sulphur

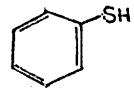
The importance of sulphur can not be under estimated since no protein can be synthesised in its absence (Deevey 1970) as sulphur links the polypetide chains and stops coiling.

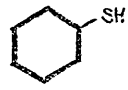
In general, carbonate-evaporitic sequences produce sour, heavy oils with a high sulphur content whereas clastics generate sweet, light oils of a low sulphur content (Bailey 1975, Powell et al 1975).

Actually Levorsen (1954) gave the sulphur occurrence in crudes (free sulphur, hydrogen sulphide or organic sulphur compounds) as 0.1% - 5.5% but Constantinides and Arich (1961) extended the range from $<$ 0.1% - c10%.

Bestougeff (1961) recorded that Smith et al (1959, 1965) isolated about 200 individual sulphur constituents from crudes. Pyrite and less well known dissolved or suspended forms of sulphur have been added to the basic occurring types of sulphur within crudes by Ho et al (1974) who felt that most sulphur compounds are introduced by secondary reactions. Figure 25 depicts organic sulphur-containing compounds identified in crudes and in fact Ho et al (1974) have suggested an immature, mature and intermediate classification of crudes based upon the relative stabilities and occurrences of such compounds. Challenger et al have given a general account of the early development of knowledge about organic sulphur compounds up to the time of their work in 1926.

c Oxygen

1. THIOLS: ALKYL: RSH. AROMATIC: 

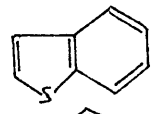
CYCLIC: 

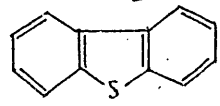
2. ALIPHATIC CYCLIC SULPHIDES: MONO,BI & POLY.



3. DISULPHIDES: RSSR. (The first type of sulphur compound isolated with more than one sulphur atom per molecule)

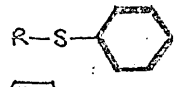
4. CYCLIC THIOPHENES: MONO: 

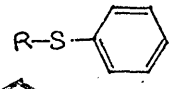
BI (BENZOTHIOPHENES): 

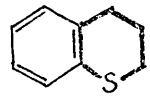
TRI (DIBENZOTHIOPHENES) : 

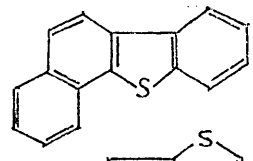
(1:2:3 ring thiophenes are in the ratio 1:9:9 and class 4 is more abundant than classes 3,2 or 1. Infact thiophenes comprise c.70% of sulphur compounds.)

5. DIALKYL SULPHIDES: RSR.

6. ALKYL CYCLO-ALKYL SULPHIDES: 

7. ARYL ALKYL SULPHIDES: 

8. 1-THIAINDANS: 

9. BENZONAPHTHOTHIOPHENES: 

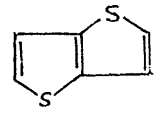
10. THIOENETHIOPHENES: 

FIG. 25 ORGANIC SULPHUR COMPOUNDS IN CRUDES. (Compiled from Levorsen 1954, Bestougeff 1961 Costantinides & Arich 1967 and Ho et al 1974)

This element has been said to occur to less than 3% in crudes (Constantinides and Arich, 1961) and usually to assume an acidic phenolic and/or ketonic habitat. Levorsen (1954) added naphthenic acids, resins and asphalts to the list of parents and ether linkages are also another abode.

O/C ratios are particularly useful in kerogen classifications based upon a 'van Krevelen' diagram (Figure 26).

d Carbon and hydrogen

The variation of carbon and hydrogen within insoluble organic matter has allowed a means of identifying the type of kerogen potential. This is utilised later under the discussion on Kerogen, although here it is interesting to note that as early as 1911, Robertson realised the lower the C/H ratio for a definite amount of organic matter the larger is the quantity of oil produced from it.

Carbon analysis alone for dry ash-free kerogen can afford an indicator of diagenesis and two similar results are given in Table 32.

For SOEs, the more 'oil-like' the ('shale') extract is the more mature is its host (Gill et al unpub.). In fact, Saxby (1977) has noted that the average chemical compositions of many crudes are similar and can be approximated to C_6H_{12} (after Levorsen 1967) where the C/H ratio is 6.

Further, Jacob (1960 in Robinson et al 1965) has offered a classification where H/C and O/C ratios for extracts may be applied and Rogers et al (1974) have recorded the possibility of calculating the aromaticity of an extract from its elemental composition (although corrections are necessarily based upon assumptions).

Finally, it should be remembered that a pure hydrocarbon structure has a higher H/C ratio than a corresponding structure containing significant sulphur or oxygen since the latter replace hydrogen (Bell and Hunt 1963 in Rogers et al 1974).

e Organic carbon

In its individual context, such a whole rock parameter has provided an indicator of the (total) organic richness of a rock apparently since Trask, in 1932, assumed organic carbon was proportional to

TABLE 32. KEROGEN CARBON AS A DIAGENETIC INDICATOR.

(Dry ash-free kerogen isolates)

PRE-OIL GENERATION.

76% C - - - - - - - - - - - -

80% C — HYDROCARBON GENERATION INITIATED.

— EARLY

82% C

— MAIN — OIL GENERATION PHASE*

86% C

— LATE

89% C

— GAS CONDENSATE GENERATION.

91% C

— GAS GENERATION.

74% C

↕

76% C — 75% C — THRESH-HOLD OF SIGNIFICANT THERMOCHEMICAL HYDROCARBON GENERATION.

— MAXIMUM OIL GENERATION.

85% C

La Plante, 1974.

Shiboaka et al, 1973.

* 85.4% C : Maximum yield of alkanes from vitrinite and/or sporinite kerogens (Allan et al, 1975.)

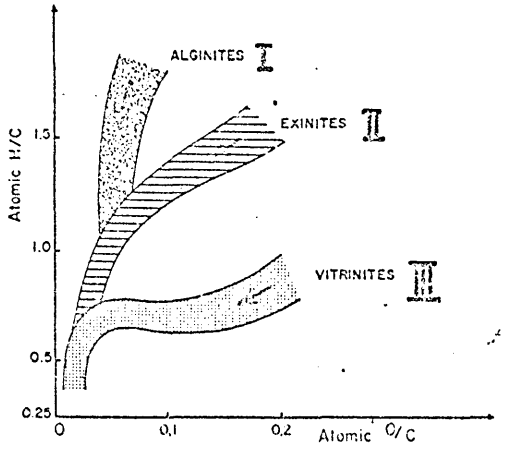


FIG 26 KEROGEN TYPE EVOLUTION PATHWAYS (After Van Krevelen from Tissot et al 1974.)

Arrows denote trends with increasing depth of burial.

the organic matter (Hobson verb. comm. 1972). World average figures have therefore been consulted to compile standards against which organic richness can be assessed (Table 33). Consequently arbitrary values have been employed as minimum criteria for rocks to have the opportunity to function as commercial sources although Dow, as recently as 1977, has insisted that it is difficult to measure the minimum concentration of organic matter which is necessary to generate enough petroleum for expulsion : to occur.

Generally for shales a figure of 0.5% organic by weight is quoted (Ronov 1958 in Hunt 1976, Collins 1975, Fuller 1975, Gill et al unpub.) whereas an 'optimistic' lower limit of 0.4% has been cited (Welte 1965 from Dow and Pearson in Dow 1977; Momper 1972 in Williams 1974). For limestones a minimum of 0.2% organic carbon has been thought necessary (Hunt 1967, Collins 1975).

However, dismissal of rocks with less than 0.3% organic carbon is practised in some commercial circles whilst rocks with more than 2% organic carbon are maintained not to realise their full potential due to adsorption (Erdman 1961, Philippi 1965). Similarly, Claypool and Reed (1976) noted that 0.5% organic carbon separates 'average' from 'above average' rocks, whilst 2% or more organic carbon indicates rocks of exceptional richness.

A classification of source rock quality based upon organic carbon is given in Table 34 and was derived from a commercial source. Of course, the better the quality of organic type (alginite) the lower is the (organic carbon) quantity needed to define a source.

Before passing on it is appropriate to note here that, apparently arising from Trask's assumption and the initial work of Forsman and Hunt (1958 in Hunt 1961), estimates of organic matter have followed due to the application of a simple "organic carbon x organic factor" concept.

Hunt (1961) recorded that it was the organic factor multiplied by the average organic carbon value (for the isolates) which allowed an average weight for (21) organic kerogen residues to

be estimated . Therefore Vuchev et al (1971) were very correct in pointing out that a more exact approximation of organic matter is achieved via the sum of the SOE and the product of kerogen (organic) carbon multiplied by the organic factor.

However, as the factor "undoubtedly varies with the type of organic matter and the depositional environment" conversion was deliberately avoided by Palacas et al (1972) and McIver (1967) in fact recorded that if "an average value of 1.24" is used an error of up to $\pm$ 20% can be expected (Table 35).

In summary it seems sufficient to appreciate that organic carbon usually constitutes 70-90% of organic matter (Dow 1977).

TABLE 33. ORGANIC CARBON DISTRIBUTION.

"CLARKE" % ORG.C.(By wt.)		
RED BEDS:	0.05	Fuller,1975.
CARBONATES:	0.24	Gehman,1962*.
	0.33	Hunt,1976.
PHOSPHORITES:	0.62	Powell et al,1975.
SHALES:	0.99	Hunt,1976,
	1.14	Gehman,1962*.
OIL SHALES:	c.35.00	Fuller,1975.

* In Collins,1975.

TABLE 34. ORGANIC CARBON SOURCE ROCK CLASSIFICATION.

Actual values.	Approx. values.	Category of Source.
0.1%C	0.1%C	
		POOR
0.44%C	0.5%C	
		FAIR
0.86%C	0.9%C	
		GOOD
1.96%C	2.0%C	
		RICH
10.00%C	10.0%C	

TABLE 35. ORGANIC FACTOR.

Hunt,1961:	1.22
Knevolden,1962:	2.00
McIver,1967:	1.12 - 1.50
Feguere & Gerrard,1970:	1.07 - 1.22
Palacas et al,1971:	1.90
Collins,1975:	1.07 - 1.22
Fuller,1975:	1.2
Dow,1977:	1.11 - 1.43
Philippi,1977:	1.25

6 PYROLYSIS

Cr/Ct values (as defined earlier after Feugere and Gerrard 1970) serve to indicate the potential of the kerogenous (organic) matter within a sediment.

Thus, an index of the present level of organic maturation (Gransch and Eisma 1970 in Barker 1974, Ishiwatari et al 1977) for known types of organics can be found. Conversely the convertibility (expressed as a percentage of organic carbon) can be paralled with weight losses experienced for kerogens and for cases of known maturity levels, the type of organic matter can be suggested. Work by Given (1962) Vandenbroucke et al (1976) and Dow (1977) has shown the maximum weight losses for (initially immature) algal and humic kerogens under pyrolysis are respectively of the order of 66-85% and 15-16%

For example, in the case of Kashafrud sediments from the Iranian Kopet-dagh gas province (Madani 1977) an average 37% convertibility was found. This value, however, referred to an induced laboratory change upon material which, from other evidences had been known to have already experienced metamorphism (dry gas) in the geologic column. As the original starting material must have been capable of giving a conversion of greater than the (residual, measured) 37% the inferred basic predominant kerogen type is algal and such organic matter was very much in evidence from a visual description of the macerated samples. (See again under crossplots, a).

Therefore, a low carbon conversion (or weak thermogravimetric loss) indicates a kerogen of strongly evolved organic matter, possibly of an originally high petroleum potential, or weakly evolved organic matter with an originally low petroleum potential (adapted from Vandenbroucke et al 1976). With increasing maturity, the Cr/Ct ratio will become closer to unity since the organic matter within the sediment will tend naturally to graphitic or inert kerogen. Very large conversion is illustrated only by immature 'algal' kerogen.

In 1972, Cordell recorded that Girand (1970) found marine type clays gave pyrolysis products rich in paraffins whilst continental type clays yielded aromatic-rich products. More recently, Vandenbroucke et al (1976) have confirmed that allochthonous terrestrial organic matter preferentially generates naphtheno-aromatic condensates whereas autochthonous marine organics provide paraffinic types.

In fact pyrograms can provide the ratio of the alkenes (dominating aliphatic kerogen products) and aromatics (dominating aromatic products) can lead to the classification of a kerogen (Solli pers. comm. from Larter Ph.D. in prep. 1978). Also perhaps an assessment of the evolutionary status can be drawn from the H/C ratio, through its linear correlation with alkene abundance and application to a van Krevelen diagram (See Appendices 16c).

Finally it should not be forgotten that the actual temperature value at which a kerogen generates the maximum evolution of gases is now realised to give indications of levels of maturity (Barker 1974, Barker 1974 in Claypool and Reed 1976).

7 SPECTROSCOPY

a Infra-red

In 1964, Schwartz concluded that exact matching of two IR spectra in the so-called fingerprint region (1400 - 650 cm^{-1}) was proof 'par excellence' of identity of the substances although it is not infallible. Further Eglinton (1968) mentioned that unknown IR spectra could be identified by comparison with those of known substances and Haji-Vassiliou and Kerr (1973) and Wickramasinghe (1977), for example, have done this.

A computerised study by Mattson (1971) lead to the conclusion that sufficient differences existed between the IR spectra of a large number of crudes to enable compilation of a catalogue of 'fingerprints' (Mattson actually normalised particular peaks against the co-occurring area of the CH vibration at 1456 cm^{-1} for each sample to dismiss thickness variations for different samples and thus allow comparison whereas Reed (1977) reported intensities relative to the 2900 cm^{-1} peak).

In consequence, Lynch and Brown (1973) reported that absorption bands within the 650-1200 cm^{-1} region (21 selected bands but rarely all present) are characteristic for an oil and can be used to identify the (pollutants) source (by comparing the ratio of absorptivities for respective bands in the unknown and known substances).

Actually, the relationship between a parent (coal) substance and a SOE was found to be the closest for the extract achieved with powerful solvents although it persisted to a marked extent in extracts obtained with weaker solvents (Brown 1959).

Recently, Vandenbroucke et al (1976) have used IR spectra to supplement their pyrolysis results in distinguishing organic matter from continental and marine sources. Relative intensities were reported to show the former was more aromatic (C = C:36.7) and less alphatic (C - H:9.4) with respect to the latter (C = C:16.8, C - H:29.6).

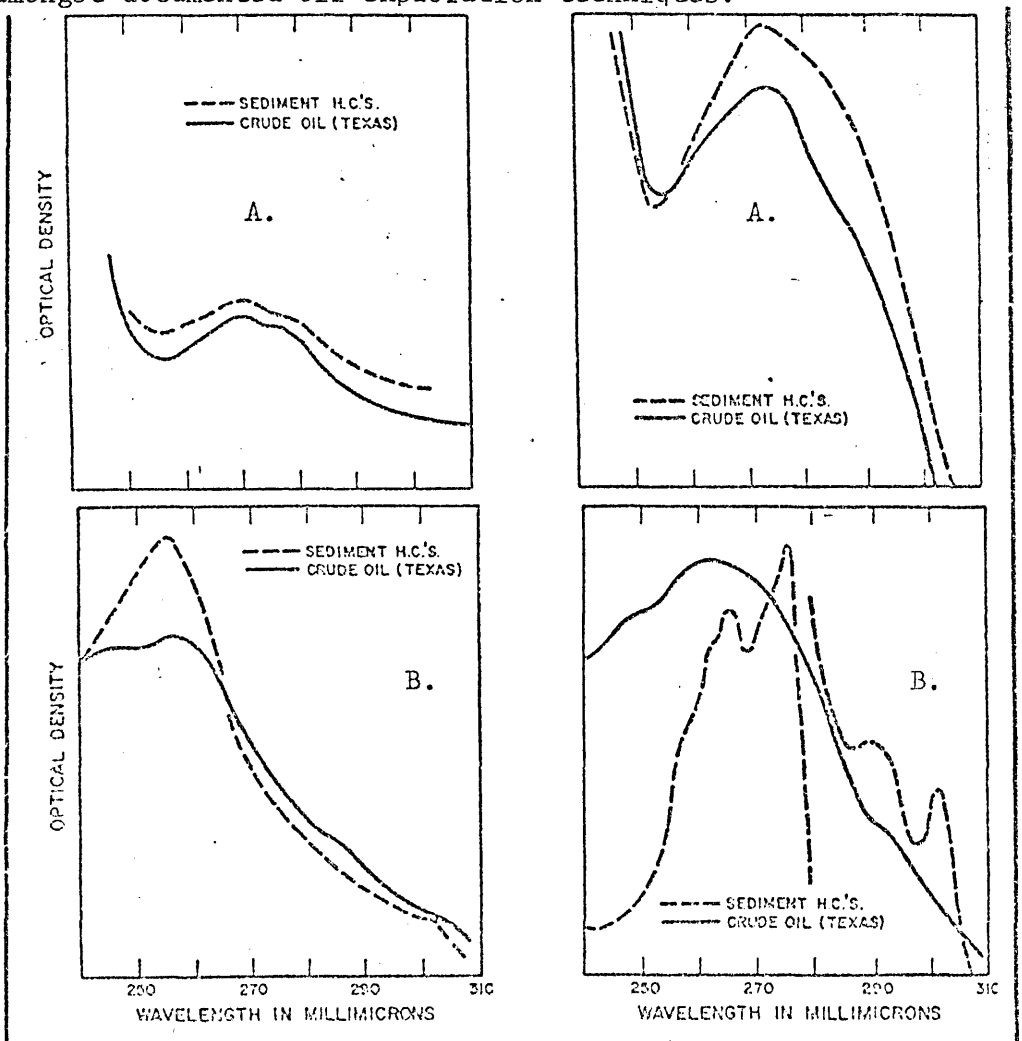
Also, the appearance of aromatic bands and the disappearance of carbonyl bands in kerogens allow a measurement of maturity (Larter et al 1977).

Finally, Fuller (1975) has placed IR third in order of priority for extract-crude correlation (following firstly light hydrocarbon analysis and then carbon isotope work).

b Ultra-violet

Meinschein (1961) appears to have first documented UV spectral characteristics in relation to petroleum geology and the results are illustrated in Figure 27.

A shift in the UV absorption for extracts was noted in 1962 by Gunn and Cooper when they reported maxima at 2550-2650Å snf 2450-2500Å for those from impure and pure limestones respectively. Allan et al (1975) assigned a broad absorption at 225 nm, for the UV spectrum of a fossil wood extract, to the presence of an 'aromatic chromophore' whilst more recently Wickramansinghe (1977) in a meteorite study assigned a 200Å wide absorption band centred upon 2,200Å to the presence of a conjugated system. In general, though, little recourse to this tool is evident amongst documented oil exploration techniques.



Structural similarities are evident for alkyl & cycloalk -yl benzenes & naphthalenes (A) of both recent sediment extracts & crudes. However, differences in distribution & complexity are apparent for polycyclic aromatics with 3 or more condensed rings. (B)

FIG 27 ULTRA-VIOLET SPECTRA OF AROMATIC FRACTIONS.

8 MACERATION - OPTICAL MICROSCOPY

a Kerogen colour

The use of spore colouration as an indicator of the diagenesis of the host rock has been used by Gutjahr (1966 in Hood et al 1975), Correia (1967 in Madani 1977), Evans and Staplin (1971) and Foscolos et al (1976) but interpretations (and experimental technique) are not always without problem.

Anomalous colour changes for the same geothermal condition may result from variations in the thermal conductivities of different host rocks. Correia (as above) has noted that micro-fossils are more readily altered in clays than in calcitic hosts whilst quartz-rich sediments yield more affected organisms than those in argillaceous mica-rich beds. (Cooper et al (1975) actually recorded the conductivities of quartzite and shale as 0.0128 and 0.0019 respectively after Lovering 1936). The recrystallisation of carbonates itself has also been proposed as a cause of the blackening of organic matter (Hunt 1976). Hot shales, over-pressured shales and oil shales are known to give palynomorphs which are often darker than predicted colours whereas red beds can provide 'bleached' palynomorphs.

Under similar conditions various types of phytoclasts may carbonise differently (spores and pollens respond faster than co-occurring acritarchs which themselves alter before co-occurring chitinozoa) and even some parts of an individual phytoclast may carbonise more readily than other parts (Correia 1971 in Madani 1977).

Recycling too presents a well known problem although reflectance histograms and staining (Wilson 1964 in Peters et al 1977) afford ways of avoiding such material.

Accordingly Peters et al (1977) have concluded that "by studying the lightest material (of approximately the same size and thickness) in each slide, data of the maximum level of organic maturity of the authigenic kerogen can be obtained" and they also noted that a decreasing regularity and lowering in the proportion of recognisable structured material accompanies increasing heat and/or time.

Table 36 offers three schemes for coupling spore colouration and the degree of diagenesis.

b Kerogen type

Kerogen is ubiquitous in sediments (Peters et al 1977) but on concentration via normal palynological preparation(s) only a fraction of the phytoclasts can often be identified microscopically (Staplin 1969 in Dow 1977); usually because the kerogen is in a finely disseminated 'amorphous' condition (Pusey 1973, Cooper et al 1975).

Identifiable isolated kerogen, similar in appearance to powdered coal (La Plante 1974, Dow 1977) contains algal bodies, spores, woody fragments and carbonised tissues (Cooper et al 1975) and thus the kind of organic matter can be distinguished via its visual description in terms of structured and unstructured components (Fuller 1975).

However, Larter et al (1977) have observed that pyrolysis experiments upon sediments yielding kerogen with a high petrological count of lignite/vitrinite material suggest an essentially 'exinitic' kerogen. Since the latter is dispersed, finely comminuted and difficult to see in white light they have cautioned against 'overweighting' during optical analysis.

Ensuing deductions arising from this type of classification should become apparent under the discussion on kerogen and Powell et al (1976) have in fact related the maceral content of a rock to both its organic carbon content and extractables.

TABLE 36. SPORE COLOURATION AS A DIAGENETIC INDICATOR.

	EVANS & STAPLIN 1969	FOSCOLOS et al 1976	HUNT 1976
GREEN	Immature		
YELLOW		Eodiagenesis	Immature
YELLOW-ORANGE		Early Mesodiagenesis	
ORANGE-BROWN	Mature	Late	Mature
BROWN			
BLACK	Metamorphosed	Telodiagenesis	Metamorphosed

9 KEROGEN

The importance of kerogen has already been hinted at under the discussion on hydrocarbon generation and "the incorporation of kerogen studies ..... into conventional exploration programmes will become essential as the search for petroleum becomes more difficult and expensive" (Dow 1977).

Here an insight into kerogen has been sought via pyrolysis and visual kerogen description but other methods have included 'wet' chenical oxidation, micropyrochromatography-mass spectroscopy, electron spin resonance, X-ray diffraction, quantitative elemental analysis, thermogravimetric analysis and infra-red spectroscopy.

In this respect chemical syntheses of (pseudo-) kerogen are also being tried (Solli pers. comm. 1977). Although the term 'kerabitumen' was proposed by the Third World Petroleum Congress (Bitterli 1963) the term 'kerogen' has been adopted in preference almost universally. Such a term appears to have first been used to describe (kerogen) material in Scottish oil shales (Cunningham-Craig 1916) which give a yellow oil and waxes upon distillation; at about 300^{o}C (Hobson verb. comm. 1972). In fact Hatch and Rastall (1965) defined a 'kerogenite' as a rock which is commonly fissile and laminated; has an ash content greater than 33% and contains 'kerogen'; the latter being a complex of vegetable and animal matter (Downs and Himus 1941, Himus 1950).

With regard to petroleum genesis Forsman (1963 from Dow 1977) applied the term to describe insoluble organic matter which can be converted into petroleum products on pyrolysis. Dow (1977), however, observed that a less rigid definition applies now and really only the criterion of insolubility remains (Hunt 1976).

In the latter respect, Schlumberger (1969) and Macleod-Mathews (1975), in a normal context, were casual in mentioning that kerogen is (respectively) "only slightly soluble" and "can be liberated ..... by solvent techniques". More explicitly Saxby (1976 in Saxby 1977), for example has defined kerogen as the "mineral free carbonaceous material remaining after the removal of inorganic components and of soluble organic compounds with a non-reactive solvent at low temperature". "Because of kerogen's insolubility and chemical complexity, little is

known about its chemical composition" (Philippi 1977) and the structure is "still almost unknown" (Albrecht & Ourisson 1971). In fact "the term kerogen is a somewhat nebulous entity" (Hobson verb. comm. 1972) since it is a complex mixture of a great variety of components (Dow 1977) of diverse origin and chemistry (Cooper et al 1975).

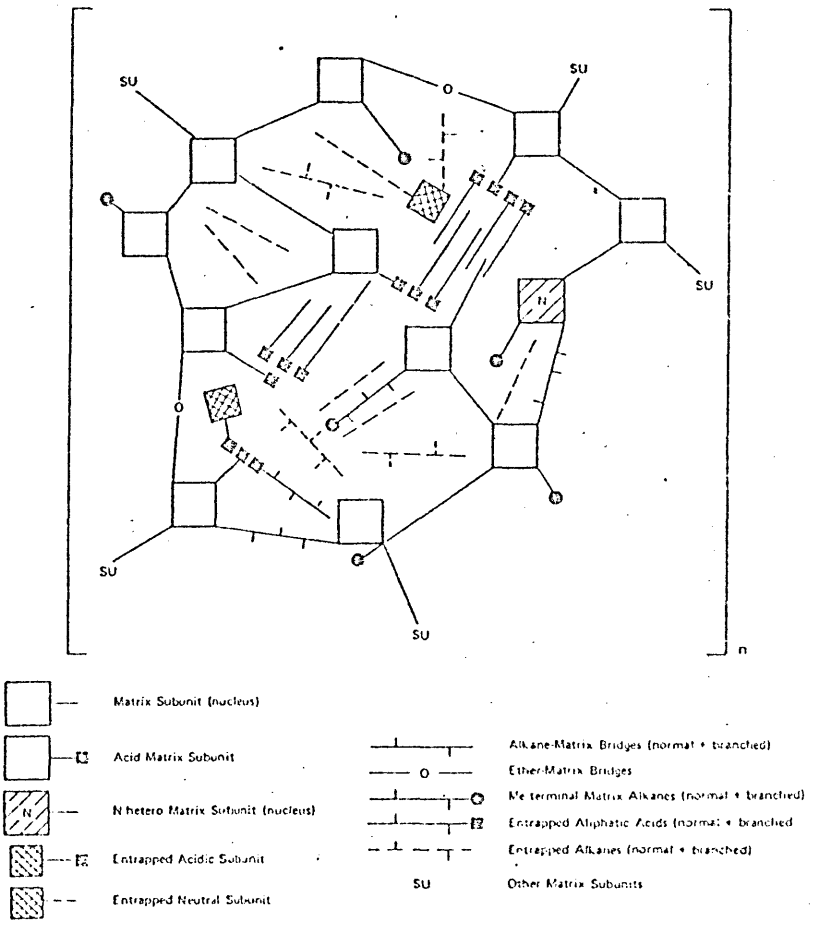
Chemically though it has been described as a predominantly lipo-humic complex (Pusey 1973a, Cooper et al 1975). La Plante described kerogen as "bitumen free" but in view of Schmidt-Collerus and Prien (1976) kerogen is now seen to serve as an insoluble molecular sieve (Yen 1976) and absorb soluble hydrocarbons very strongly. Philippi (1977) has actually suggested that the bulk of polypeptide derivatives with their hydrocarbon side chains is preserved in kerogen (referring to the relatively high nitrogen content and low C/N ratios of oil source rocks for support).

More specifically, kerogen can be compared similarly with an asphaltene (Yen 1972 in Pusey 1973a) where numerous aromatic (Yen as before) and cyclic polycondensed nuclei (Tissot et al 1974) lie in the same plane (Yen as before) linked by heteroatomic bonds, in particular oxygen (Tissot et al 1974) and have attached alkyl side chains (Yen as before, Tissot et al 1974) and functional groups (Tissot et al 1974).

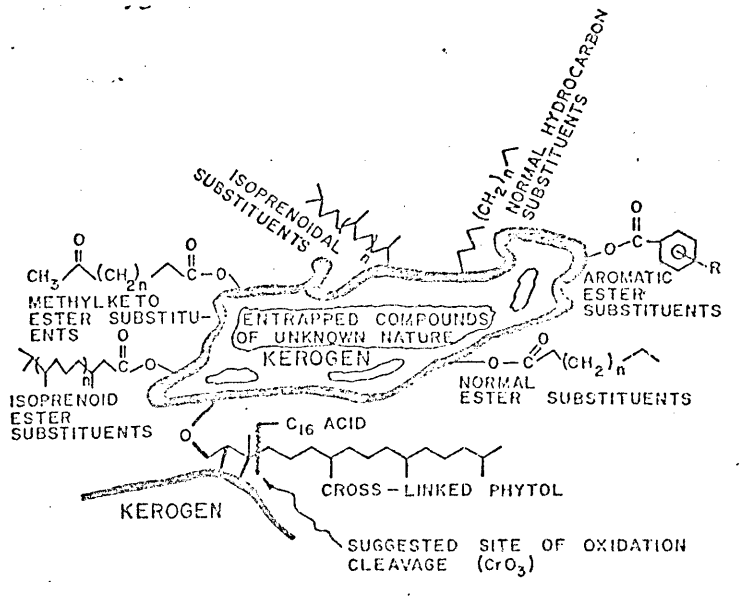
Several sheets are polymerised together to give a basic kerogen molecule (Yen as before) and a three dimensional, multipolymer, giant, diamond-like, HMW, cross-linked network of monomers results (Yen 1976). A schematic structure of a kerogen matrix is given in Figure 28 where the framework dimensions can be approximated to (39 x 27 x 25)Å together with proposed substituent structures.

Quite correctly, therefore, McIver (1967) concluded that kerogen is a single undescriptive and unsatisfactory term since materials of broad compositional ranges are included (2-12%H, 68-96%C, 1-27%O). More recently Dow (1977) emphasised that two basic categories are analogous to the vitrinite and liptinite maceral groups for coal and for the purpose of oil exploration an illustrated classification has been compiled (Table 37 ;loose). Although kerogens from lignin sources are often stated as aromatic, Nagy and Nagy (1968) did report one that is basically aliphatic.

In summary kerogen studies are hampered by the insoluble non-uniform macromolecular nature and the fact that different shales provide different kerogen (Djuricic et al 1971). Perhaps it currently remains best to describe kerogen as a 'conglomerate' of similar but varying molecular subunits (Yen 1976).



Schematic structure of kerogen matrix. (From Schmidt-Collerus & Prien,1976.)



Substituent structure of kerogen; showing various hydrolysable side chains and oxidation sites.The carbon-carbon bonded substituents should dominate over the carbon-oxygen substituents.(Burlingame et al,1968.)

FIG 28 SUBSTITUENT & MATRIX STRUCTURES OF KEROGEN.

10 X-RAY DIFFRACTION

Although nearly two hundred minerals have been identified in sediments less than twenty usually comprise more than 99% of the sediment bulk. In fact, it is rare for more than 5 - 6 mineral phases in sizeable quantities to occur in any one rock (Degens and Reuter 1964).

A 'typical shale' contains carbonates, quartz, clay minerals (kaolinite > illite > chlorite) with possibly feldspars and organic matter (Vuchev et al 1971). Clays are actually the most abundant type of sediment but because of their fine grain size ($\leq$0.005 mm) require specialised techniques for their study. Montmorillonites for example are not usually detectable in a sample unless present to more than about 15% owing to their poor crystallinity (Schmidt-Collerus et al 1976).

Sedimentologically, montmorillonites and kaolinites have been found to decrease relative to illites and chlorites with increasing distance from the shoreline (Bush verb. comm. 1972, Bjorlykke et al 1975). The modest increase in illite content near shorelines has been related to sorting phenomena or early diagenetic effects (Cordell 1974) and Hallam (1975) has specified the use of the illite/kaolinite ratios as an indicator of environment with respect to distance from shoreline. Sodium montmorillonite generally typifies oceanic clays whilst calcium montmorillonite predominates in estuarine clays (Bush verb. comm. 1972). Highley (1975) has noted that disordered kaolinite can indicate fairly fresh-brackish water conditions and agreed with illite typifying more marine sediments. Now Weaver (1958 in Long et al 1962) remarked that the great majority of clays in sediments are detrital, strongly reflecting the character of their source material and are only slightly modified in their depositional environment. Accordingly, for example, kaolinite is known to associate with more acidic environments than illite (Vuchev et al 1971) and Johnson (1975) used an increase in kaolinite to indicate derivations from an extensively weathered land surface formed by the acid leaching of alkaline crystalline material. Vermiculite has been assigned to originate from a metamorphic land source with a high percentage of biotite and chlorite (Johnson 1975) and kaolinite/illite ratios may also reflect climatic change (Bjorlykke et al 1975).

As mentioned earlier, clays are thought to assist the concentration of organic matter, the (catalytic ?) generation of hydrocarbons and the expulsion of petroleum. Grim (1968 in Cordell v Philippi 1974) has reported a low capacity for adsorption of organic matter is exhibited by illite (with respect to montmorillonite) and in fact non-source clays have been designated as illitic; since source clays are rich in montmorillonite. and mixed-layer clays (Chapman 1974 in Cordell 1974).

Most clays alter through time to montmorillonite, illite and chlorite (Schmidt-Collerus et al 1976) and both montmorillonite and illite are known to convert under burial diagenesis to illite and chlorite (Girand 1970, Cordell v Philippi 1974, Albrecht et al 1976).

Finally, identification of clay minerals from typical detailed studies can be based upon the observations summarised in Table 38 (from Shaw 1971).

TABLE 38. CLAY MINERAL IDENTIFICATION.

Air dry basal spacing	Glycerated sample	Heated at 400°C for one hour	Heated at 550°C for one hour	Boiled in 10% HCl	MINERAL
~26-29A	Expands to 31-32A with rational sequence of higher orders	May disappear or give 24A spacing	Increase in intensity of 24A spacing	-	Regular interstratified CHLORITE-MONTMORILLONITE or CHLORITE-VERMICULITE
~26-29A	Expands but gives irrational sequence of reflections	May give irrational sequence of reflections	May give irrational sequence of reflections and increase in intensity of 12-14A peaks	-	Randomly interstratified CHLORITE-VERMICULITE
~14A	No change	No change	Increase in intensity	All reflections vanish	CHLORITE
~14A.	No change or slight increase	Collapses to ~10A	No change or slight additional collapse	No change	VERMICULITE
~14A	No change or slight increase	Collapses to ~12A	Additional collapse to 11A	No change	DIOCTAHEDRAL VERMICULITE
~14A	Expands to 18A	Collapses to ~10A	No change or slight additional collapse	May dissolve in HCl	MONTMORILLONITE
⩾ 10-14A	No change	Collapses to ~10A	No additional collapse	No change	Regular interstratified ILLITE-VERMICULITE
⩾ 10-14A	No change	No change	No change or slight increase in intensity	No change	Regular interstratified ILLITE-CHLORITE
⩾ 10-14A	No change	Collapses to ~10A	No additional collapse	No change	Randomly interstratified ILLITE-VERMICULITE
⩾ 10-14A	No change	No change	No change	May dissolve in HCl	Randomly interstratified ILLITE-CHLORITE
⩾ 10-14A	Expands to higher spacing	Collapses to ~10A	No additional collapse	No change	ILLITE-MONTMORILLONITE
12-12.5A	No change	Destroyed or intenaity reduced	Destroyed.	Destroyed	SEPIOLITE
10.5A	No change	Destroyed	Destroyed	No change	ATTAPULGITE or PALYGORSKITE
~ 10A	Unsymmetrical peak with perhaps a slight shift	No change	No change except for a slight sharpening of reflection	No change	ILLITE (MUSCOVITE)
~ 7A	No change	No change	No change	No change	CHRYSOTILE or ANTIGORITE
~ 7A	Increase in spacing or possibly no change	Collapses to 7A again	Destroyed	No change	HALLOYSITE
~ 7A	No change	No change	Destroyed	No change	KAOLINITE (DICKITE, NACRITE)

TABLE 39. PERIODIC TABLE OF THE ELEMENTS (from WEAST, 1971)

1a	2a	3b	4b	5b	6b	7b	8	1b	2b	3a	4a	5a	6a	7a	0	Orbit
1 +1 H −1 1.00797 1															2 0 He 4.0026 2	K
3 +1 Li 6.939 2-1	4 +2 Be 9.0122 2-2									5 +3 B 10.811 2-3	6 +2 +4 −4 C 12.01115 2-4	7 +1 +2 +3 +4 +5 −1 N 14.0067 −2 −3 2 5	8 −2 O 15.9994 2-6	9 −1 F 18.9984 2-7	10 0 Ne 20.183 2 8	K-L
11 +1 Na 22.9898 2-8-1	12 +2 Mg 24.312 2-8-2									13 +3 Al 26.9815 2-8-3	14 +2 +4 −4 Si 28.086 2-8-4	15 +3 +5 −3 P 30.9738 2-8-5	16 +4 +6 −2 S 32.064 2-8-6	17 +1 +5 +7 −1 Cl 35.453 2-8-7	18 0 Ar 39.948 2-8-8	K-L-M
19 +1 K 39.102 -8-8-1	20 +2 Ca 40.08 -8-8-2	21 +3 Sc 44.956 -8-9-2	22 +2 +3 +4 Ti 47.90 -8-10-2	23 +2 +3 +4 +5 V 50.942 -8-11-2	24 +2 +3 +6 Cr 51.996 -8-13-1	25 +2 +3 +4 +7 Mn 54.9380 8 13 2	26 +2 +3 Fe 55.847 -8-14-2	27 +2 +3 Co 58.9332 -8-15-2	28 +2 +3 Ni 58.71 -8 16 2	29 +1 +2 Cu 63.546 -8-18-1	30 +2 Zn 65.37 -8-18-2	31 +3 Ga 69.72 -8 18-3	32 +2 +4 Ge 72.59 -8 18 4	33 +3 +5 −3 As 74.9216 -8-18-5	34 +4 +6 −2 Se 78.96 -8-18 6	35 +1 +5 −1 Br 79.904 8-18-7	36 0 Kr 83.80 -8-18-8	-L-M-N
37 +1 Rb 85.47 18-8-1	38 +2 Sr 87.62 -18-8-2	39 +3 Y 88.905 -18 9-2	40 +4 Zr 91.22 18-10-2	41 +3 +5 Nb 92.906 -18 12-1	42 +6 Mo 95.94 -18-13-1	43 +4 +6 +7 Tc (97) 18 13-2	44 +3 Ru 101.07 -18-15-1	45 +3 Rh 102.905 -18 16-1	46 +2 +4 Pd 106.4 18 18 0	47 +1 Ag 107.868 -18-18-1	48 +2 Cd 112.40 -18-18 2	49 +3 In 114.82 -18-18-3	50 +2 +4 Sn 118.69 -18-18-4	51 +3 +5 −3 Sb 121.75 -18-18-5	52 +4 +6 −2 Te 127.60 -18 18-6	53 +1 +5 +7 −1 I 126.9044 -18-18-7	54 0 Xe 131.30 -18-18-8	M-N-O
55 +1 Cs 132.905 -18-8-1	56 +2 Ba 137.34 -18-8-2	57* +3 La 138.91 -18-9-2	72 +4 Hf 178.49 -32-10-2	73 +5 Ta 180.948 -32-11-2	74 +6 W 183.85 -32-12-2	75 +4 +6 +7 Re 186.2 32-13-2	76 +3 +4 Os 190.2 -32 14 2	77 +3 +4 Ir 192.2 -32-15-2	78 +2 +4 Pt 195.09 -32 16-2	79 +1 +3 Au 196.967 32-18-1	80 +1 +2 Hg 200.59 -32-18-2	81 +1 +3 Tl 204.37 -32-18-3	82 +2 +4 Pb 207.19 32-18-4	83 +3 +5 Bi 208.980 -32 18 5	84 +2 +4 Po (209) -32-18 6	85 At (210) -32-18-7	86 0 Rn (222) -32-18-8	-N-O P
87 +1 Fr (223) -18-8-1	88 +2 Ra (226) -18 8-2	89** +3 Ac (227) -18 9-2														-O-P-Q

*Lanthanides	58 +3 +4 Ce 140.12 -20-8-2	59 +3 Pr 140.907 -21-8-2	60 +3 Nd 144.24 -22-8-2	61 +3 Pm (145) -23-8 2	62 +2 +3 Sm 150.35 -24 8-2	63 +2 +3 Eu 151.96 -25 8 2	64 +3 Gd 157.25 -25-9-2	65 +3 Tb 158.924 -27 8 2	66 +3 Dy 162.50 28-8 2	67 +3 Ho 164.930 29-8-2	68 +3 Er 167.26 -30-8-2	69 +3 Tm 168.934 -31-8 2	70 +2 +3 Yb 173.04 -32 8-2	71 +3 Lu 174.97 -32-9-2		-N O P
**Actinides	90 +4 Th (232) -18 10 2	91 +5 +4 Pa (231) -20 9-2	92 +3 +4 +5 +6 U (238) -21-9 2	93 +3 +4 +5 +6 Np (237) 22-9-2	94 +3 +4 +5 +6 Pu (244) -24 8-2	95 +3 +4 +5 +6 Am (243) 25 8-2	96 +3 Cm (247) 25 9-2	97 +3 +4 Bk (247) -27 8 2	98 +3 Cf (251) 28 8 2	99 Es (254) 29-8 2	100 Fm (257) -30 8 2	101 Md (256) -31 8-2	102 No (254) -32 8-2	103 Lw -32-9 2	104 — 32-10 2	-O-P-Q

Numbers in parentheses are mass numbers of most stable isotope of that element.

11 GAMMA-RAY LOGGING

All elements above Bismuth (in the periodic table - Table 39) show natural radioactivity but most activity in sediments is generally produced by U, Th and K; that of K being dwarfed by the activity of either Th or U (Table 40).

The ratio of the three activities together for shales, sandstones and limestones is 4 - 6:2 - 3:1 and hence γ-ray logging is usually (with few exceptions - Table 41) a measure of the shale content (Schlumberger 1969).

Although Bjorlykke et al (1975) agreed with Adams and Weaver (1958) in stating U and Th contribute (almost) equally to the activity of an average marine shale, they differed in mentioning only 13% of the total activity is attributable to K (Table 42).

Th^{232}/U^{238} ratios (measured from the differences in the energies of the ejected γ-rays; 2.62 and 1.76 MeV respectively) have been used to determine environmental conditions of deposition (Table 43). They depend upon Th having no oxidation state equivalent to the soluble Uranyl ion (U^{6+}) and hence being unable to accompany U into oceans on an equal basis. Th/U ratios therefore decrease with increasing distance from shoreline and present day respective concentrations of U and Th in oceans are <0.1 - 250 ppm and <0.1-132 ppm. Goodman (1942 in Beers and Goodman 1944) did predict high Th/U ratios for petroleum source beds.

U^{238}/K^{40} ratios can also be used in the elucidation of clay mineralogy since high ratios indicate more montmorillonite and lower ratios suggest more illite (Adams and Weaver, 1958).

K actually has three naturally occurring radio-isotopes and K^{40} constitutes 0.0118% of K; having half-life of 1.28×10^9 years (Weast 1971) and emitting β-rays accompanied by γ rays of 1.46 MeV (Schlumberger 1969) in the ratio of 100:3 respectively (Moorbath 1960).

Th in fact has twelve radioisotopes and Th^{232} creates a decay series which is accompanied by a wide array of γ-ray radiations of various energies. The initial parent decay is accompanied by γ-ray emission involving an energy of 2.62 MeV (Weast 1971).

U^{238} and U^{235} give two separate decay series which terminate in Pb^{206} and Pb^{207} respectively. U has fourteen radioisotopes (Weast 1971) and the initial (U^{238}) parent decay gives γ-ray emission where

TABLE 40. Ratio of ACTIVITIES OF THE MAIN ELEMENTS within a sediment.

RADIOACTIVITY.	POTASSIUM.	THORIUM.	URANIUM.	AUTHOR(S) & DATE.
GAMMA-ACTIVITY:	1 1	2,000 c.1,300	4,000 c.3,600	Ponsford,1955 Adams & Weaver,1958
BETA-ACTIVITY:	1	450	1,800	Ponsford,1955
ALPHA-ACTIVITY:	0	1	3	

TABLE 41. GENERALISED RELATIONSHIP FOR GAMMA-ACTIVITY & LITHOLOGY with some annotated explanations. (Compiled from Beers & Goodman,1944; Adams & Weaver,1958; Schlumberger, 1969 and Haji-Vassiliou & Kerr,1973.)

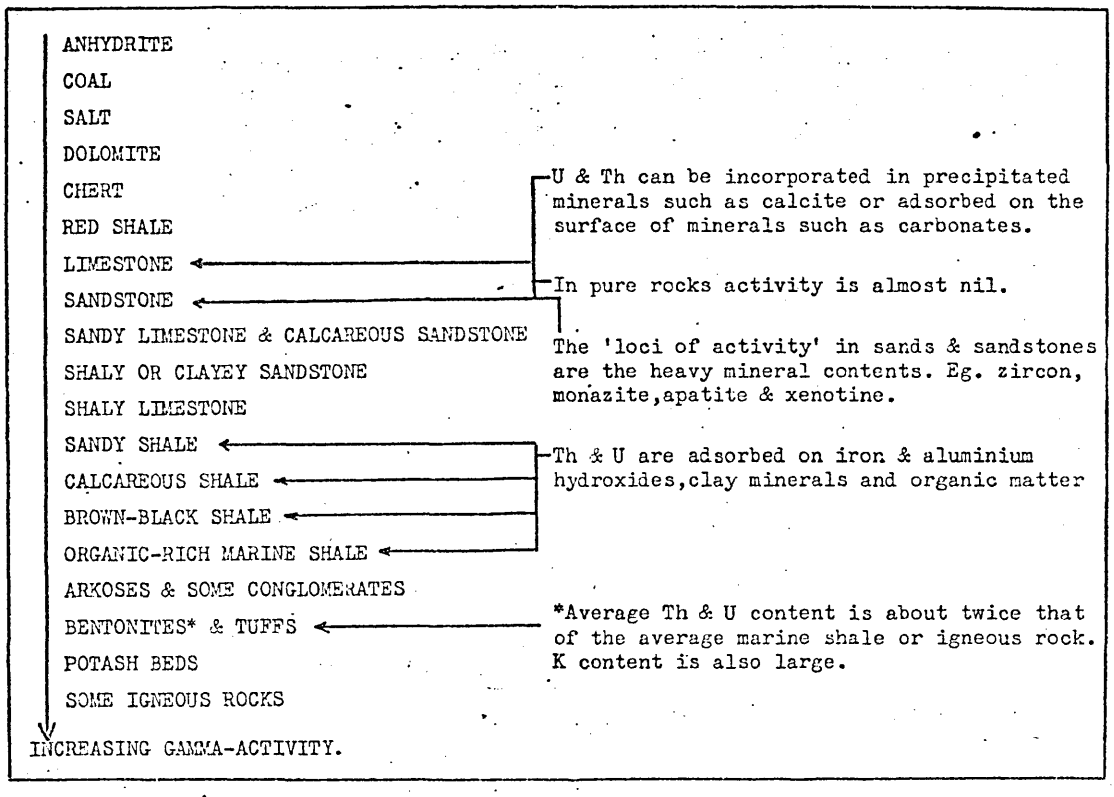


TABLE 42. DISTRIBUTION OF THE MAIN RADIOACTIVE ELEMENTS.

(Adams & Weaver,1958)	K.	Th.	U.
Relative abundance in an average shale:	7,300	3.8	1
Relative contribution to gamma-ray flux:	2.0	1.2	1

TABLE 43. THORIUM/URANIUM RATIOS.

	A	B	C
Oxidising;high Eh. ⌈Bauxites	>7	≥20	>6
Oxidising;high Eh. ⌊Continental shales		≥7	
Normal marine shales.	<7	3.8±1.1	2 - 6
Reducing;low Eh. Black shales & Phosphates.	Low	<2	<2

A: Adams & Weaver,1958
B: Haji-Vassiliou & Ker,1973
C: Bjorlykke et al,1975

the energy is 1.76 MeV. U in urano-organic rich sediments is known to be intermingled either as submicroscopic-microscopic mineral particles (uranitite, coffinite) or present as urano-organic complexes (Haji-Vassiliou and Kerr 1973). Further, U in oil shales is most abundant where organic matter is dominantly plant debris (Swanson 1955 in Haji-Vassiliou and Kerr 1973) and the Kolm black shales of Sweden is an example of an oil shale which is exploited for both its U and oil content (Hobson verb. comm. 1972).

Radioactivity has been suggested as an energy source for the conversion of organic matter firstly by Lind and Bardwell in 1926 and subsequently by Sheppard and Whitbread in 1946 and Breger and Whitbread in 1951. However, many objections have been raised against such an idea. Too much hydrogen is evident in experimental products and large quantities of hydrogen are conspicuously absent in crudes. The rate of formation of hydrocarbons also appears too slow for commercial generation. Porphyrins are known to be destroyed by α-bombardment (Knebel 1946) and Rogers in 1921 has pointed out that from energy considerations organic matter should be decomposed to oxygen and hydrogen. Further, Huntingdon in 1950 observed that the large quantities of helium, expected when α-bombardment dominates, are rarely associated with petroleum. Similarly where nitrogenous organic matter is involved large quantities of free nitrogen should be formed and these too are absent from crudes (Hobson verb. comm. 1972).

Finally, organic matter has been correlated, sometimes linearly, with total α and total β activities; Th, U and K concentrations and Th/U ratios (Beers and Goodman 1944).

12 CROSSPLOTS

a Soluble organic extract v Organic acrbon

Tissot et al (1974) used the ratio of SOE/(total) organic carbon as a measure of the transformation of organic matter into a crude. More recently, Powell (1975) stated a value of greater than 0.1 indicated a "main HC generation" (no upper ceiling offered) whilst greater than 0.05 limited diagenesis to the "early hydrocarbon zone".

However although Gill et al (unpub.) have determined the ratio of about 0.2 for a geologically defined source rock (e.g. Kazhdomi Formation of the Iranian Zagros) they have noted that values less than 0.2 are applicable to both immature and metamorposed source rock facies.

Figure 29 illustrates three main trends where for example:

a the Kashafrud Trend (Madani 1977) is a nearly vertical line indicating the amount of extract is independent of the organic matter. The explanation for this trend requires conversion and migration to the extent of "boiling off volatiles" to allow a dry gas state of diagenesis to prevail (as far as natural geothermal gradients are concerned). In fact the ratio of SOE/organic carbon shows no variation against depth of burial.

b the Kazhdomi Trend (Ala,PhD.in prep.) where a much larger SOE is observed with respect to the quantity of organic matter and the extractables increase with increasing organic carbon. Conversion and thus maturity is suggested. Here the greater values of extract per unit of organic matter for the Gurpi Formation have been linked with a lower degree of migration owing to its poor compaction.

c the Kimmeridgian Trend (of this study) where although the SOE increases with increasing organic matter the actual extract amount is small with respect to the quantity of organic matter. Hence thermal generation appears to have only just began and the trend suggests immaturity.

Finally, Powell et al (1976) recorded that the yield of extract per unit weight of organic carbon is higher in limestones and ironstones than it is in shales at similar levels of diagenesis

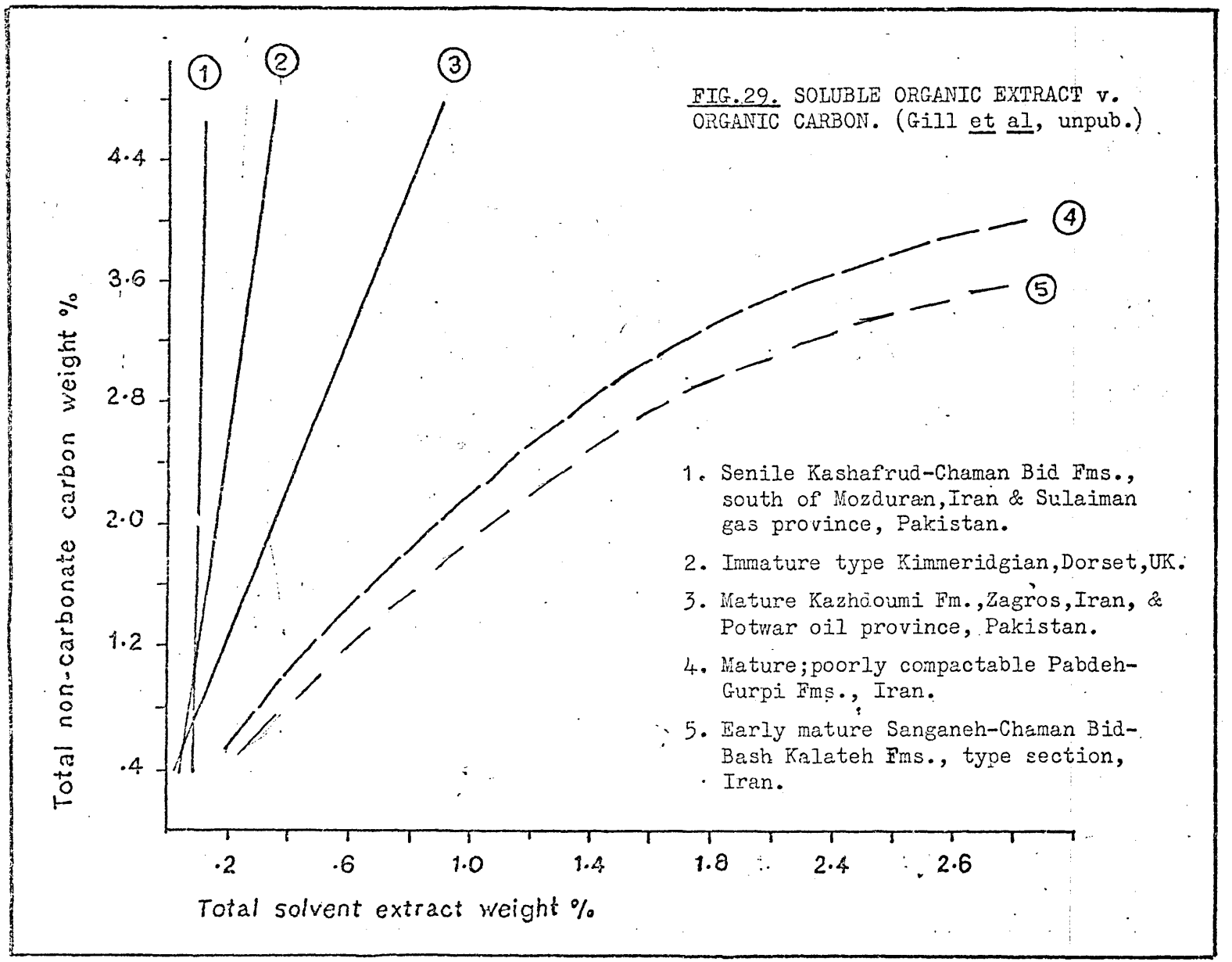


FIG.29. SOLUBLE ORGANIC EXTRACT v. ORGANIC CARBON. (Gill et al, unpub.)

and this presumably correlates with variations in the thermal conductivity of different lithologies.

b Pre- versus Post-pyrolysis organic carbon

From plots of the SOE v organic carbon (Figure 29) it is seen that the trends of immature and senile source rocks lie quite close together. Pyrolysis (as mentioned earlier) affords a means of distinguishing between the two facies types where (with respect to the dry gas trend) a separation will be illustrated by immature sources containing dominant humic kerogen but is exaggerated by those containing algal kerogen (Figure 30).
In absolute terms a Cr/Ct ratio of less than 0.6 reflects a thermal history for sedimentary organic matter which is favourable for petroleum generation. Where Cr/Ct is more than 0.6 the potential then depends particularly upon the type of organic matter present (Brooks and Thusu 1977).

c Hydrocarbon yield v Organic carbon

Foscolos et al (1976) have argued that the yield of hydrocarbons is probably a better guide to the diagenetic state of a source rock. The average shale gives a value of 0.01 for the ratio of hydrocarbons/organic carbon but since C_6 and lower hydrocarbons are not included in most detection methods Saxby and Shilboaka (1975) stated that only gross changes are significant as indicators of generation and/or migration. Figure 31 is reproduced after Baker and Claypool (1970 in Baker 1972) and the trend from an unmetamorphosed (positive correlation) state to a metamorphosed (no correlation) state can be visualised through oil, oil and gas and gas generating stages.
In 1972, Palacas et al defined a "bitumen extract ratio" (after Robinson and Dineen 1967) as:

$$\frac{\%\text{Wt. benzene-soluble organic matter}}{\%\text{Wt. organic carbon}} \times 100$$

and practically speaking hydrocarbon yield can be substituted as the numerator.
With reference to modern day sediments, they observed a higher ratio where a greater contribution of organic matter was from marine and brackish organisms with respect to plant material.
The generalised positions of lithologies have been differentiated

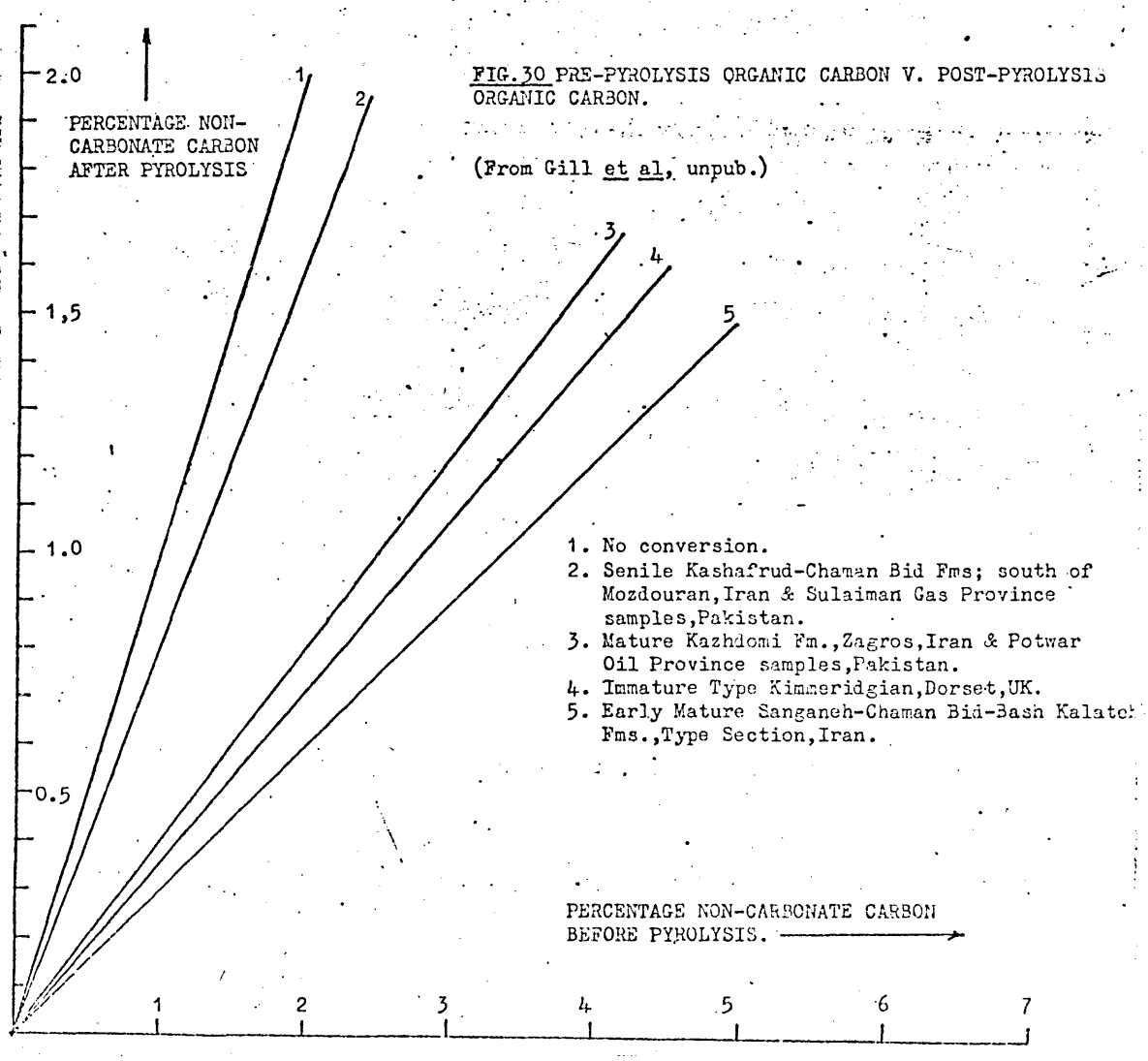
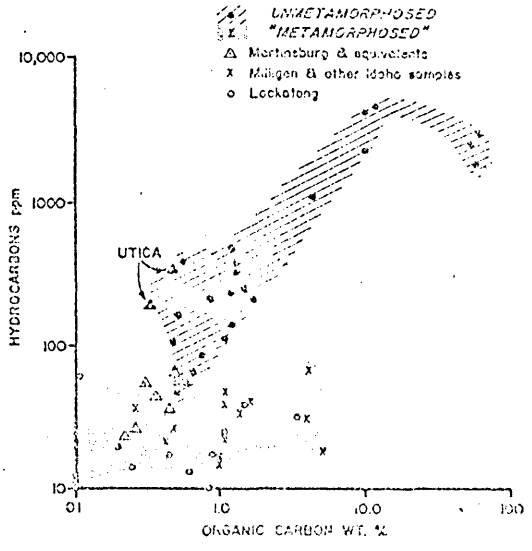


FIG.30 PRE-PYROLYSIS ORGANIC CARBON V. POST-PYROLYSIS ORGANIC CARBON.

(From Gill et al, unpub.)

FIG 31 HYDROCARBONS v.ORGANIC CARBON FOR DIAGENETIC REALMS. (Baker,1962)



No correlation for metamorphosed rocks but positive correlation for unaffected rocks.

with these two parameters by Baker (1962) and are reproduced in Figure 32.

d Saturates/aromatics v Hydrocarbons/organic carbon

Baker (1972) has shown plots, whilst earlier Baker and Claypool (1970) additionally illustrated histograms for these parameters for rocks of different thermal regimes (Figure 33). They infer that saturates increase at the expense of aromatics with increasing metamorphism whilst the amount of hydrocarbons becomes independent of the quantity of organic matter.

In fact, a generalised saturate/aromatic ratio of more than two and less than two for metamorphosed and unmetamorphosed sediments was postulated whilst the extractable hydrocarbons/organic carbon ratio was emphasised to show little variation and wide variation respectively.

In the case of individual rock types Baker (1972 from 1962) suggested that on Figure 34 coal and basinal marine shales may perhaps even be 'end-members'. Coals are seen to yield aromatic rich hydrocrabon mixtures and from their low hydrocarbon/organic carbon ratio appear inefficient sources for petroleum. Conversely black fossileferous shales and limestones yield saturate-rich hydrocarbon mixtures and seem efficient generators of crudes Owing to the principle that the distinctive properties of coal and marine shales are related to primary differences in organic source material (Baker 1972), for rocks of the same diagenetic level, an overprinted plot (Figure 34) may be applicable to serve as a hint for palaeogeographic reconstruction (e.g. James 1970 in Baker 1972).

e Interplay of alkane types

In characterising the different depositional environments for (two) sediments of similar diagenetic states, Vandenbroucke et al (1976) reported different categories of alkanes and expressed their relative variations as ratios (Table 44). However, more (contrasting) models are apparently awaiting definition before such observations can assume general application.

Table 45 briefly summaries the distribution of (light) hydrocarbon types for different levels of thermal evolution.

f CPI v Normal alkane quantity

FIG.32 HYDROCARBONS v. ORGANIC CARBON FOR DIFFERENT LITHOLOGIES.(Baker,1962)

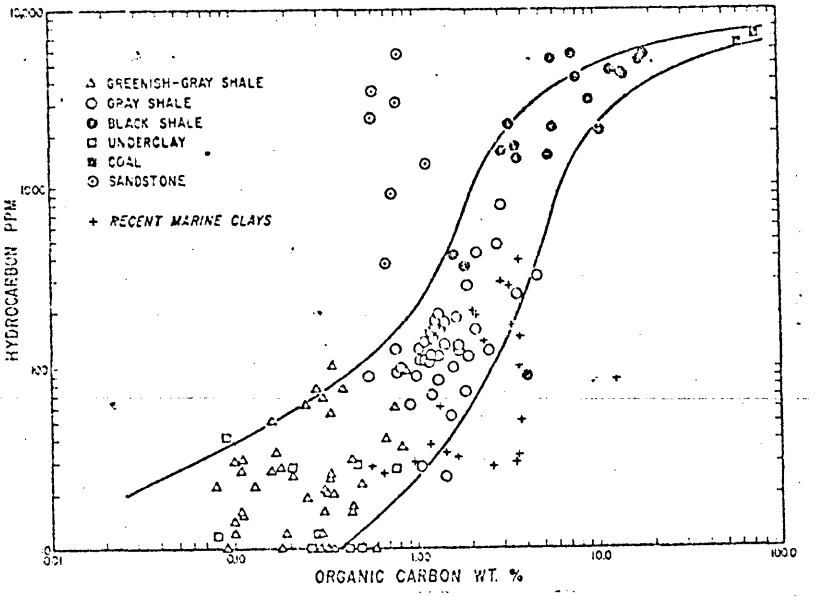


FIG. 33 SATURATES/AROMATICS v. HYDROCARBONS/ ORGANIC CARBON (WITH HISTOGRAMS). (From Baker & Claypool 1970; Baker,1972)v. DIAGENESIS.

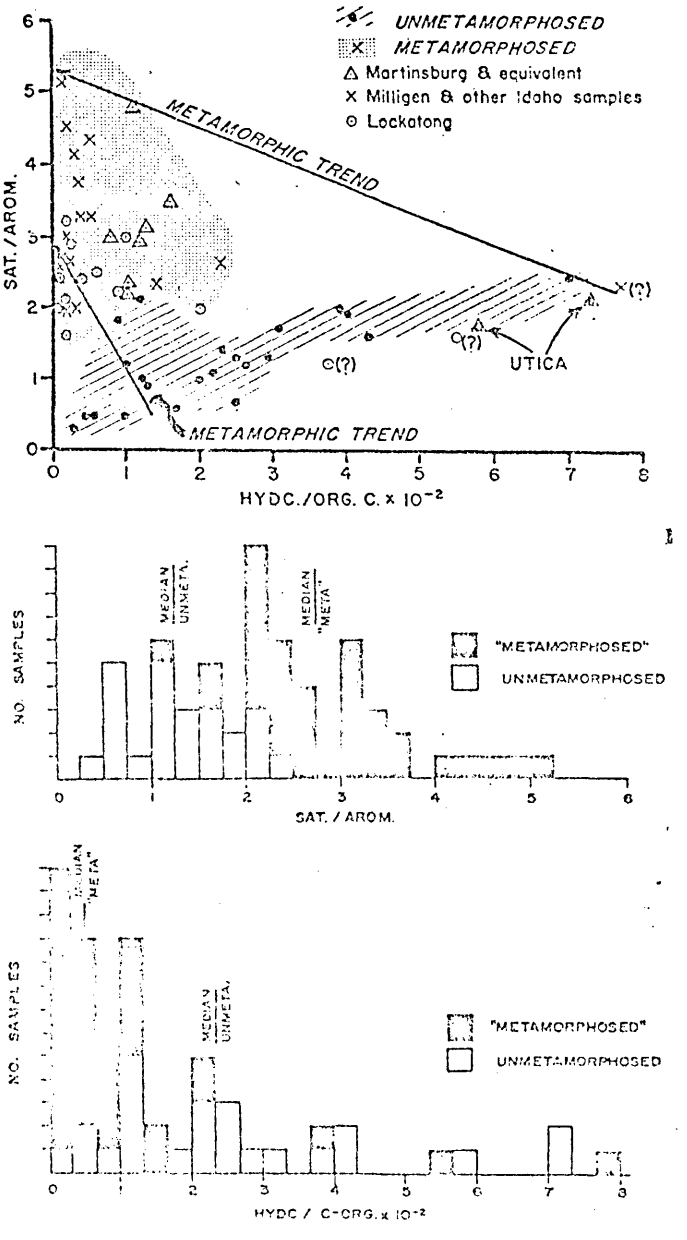


TABLE 44. ALKANE CATEGORIES VERSUS DEPOSITIONAL ENVIRONMENT.

ALKANE TYPES/RATIOS.	OXIC ENVIRONMENT. Allochthonous terrestrial organic matter of marine-deltaic environment	ANOXIC ENVIRONMENT. Autochthonous organisms such as algae, zoo- and phyto-plankton of open marine environment.
N-alkanes as % in total saturates:	31.5%	9.5%
$\frac{C_{25} - C_{30}\ \text{n-alkanes}}{\text{Total } C_{14} - C_{30}\ \text{n-alks}}$	56.0%	26.5%
$\frac{C_{16} - C_{25}\ \text{isoprenoids}}{C_{14} - C_{30}\ \text{n-alkanes.}}$	25.0%	40.0%
$\frac{\text{Cycloalkanes}}{\text{N \& Iso-alkanes.}}$	1.0	1.0

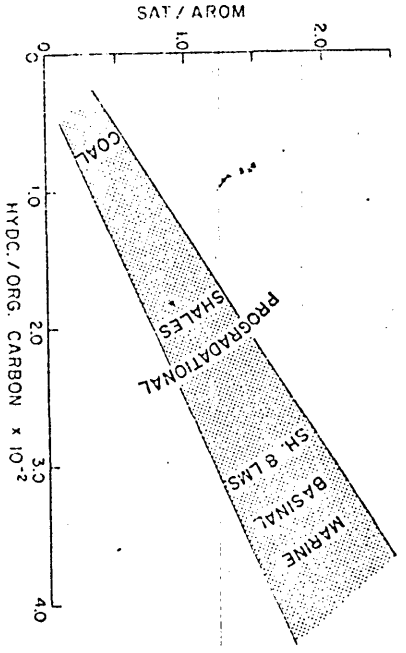


FIG 34. SATURATES/AROMATICS v. HYDROCARBONS/ORGANIC CARBON v.LITHOLOGY.(in unmetamorphosed sediments) (From Baker,1962.)

Bray and Evans (1965) and Baker (1972) have remarked that as the CPI decreases for n-alkanes, the concentration of n-alkanes increases. (Figure 35 where histograms also illustrate the deduction that the CPI indicates conversion of organic matter into hydrocarbons).

g CPI v Normal alkane distribution

Only in the cases of sediments with high CPIs and n-alkane distribution maxima high in the C_{19} - C_{35} range can a terrestrial source and immaturity be postulated with assurance (Bailey et al 1974).

In contrast, n-alkane distribution with maxima in the range C_{15} - C_{23} which show low CPIs can result from two extremes, either:

a indigenous dominantly marine derived organic matter (Milner et al 1977) which is poorly evolved (Powell 1975, Vandenbroucke et al 1976)

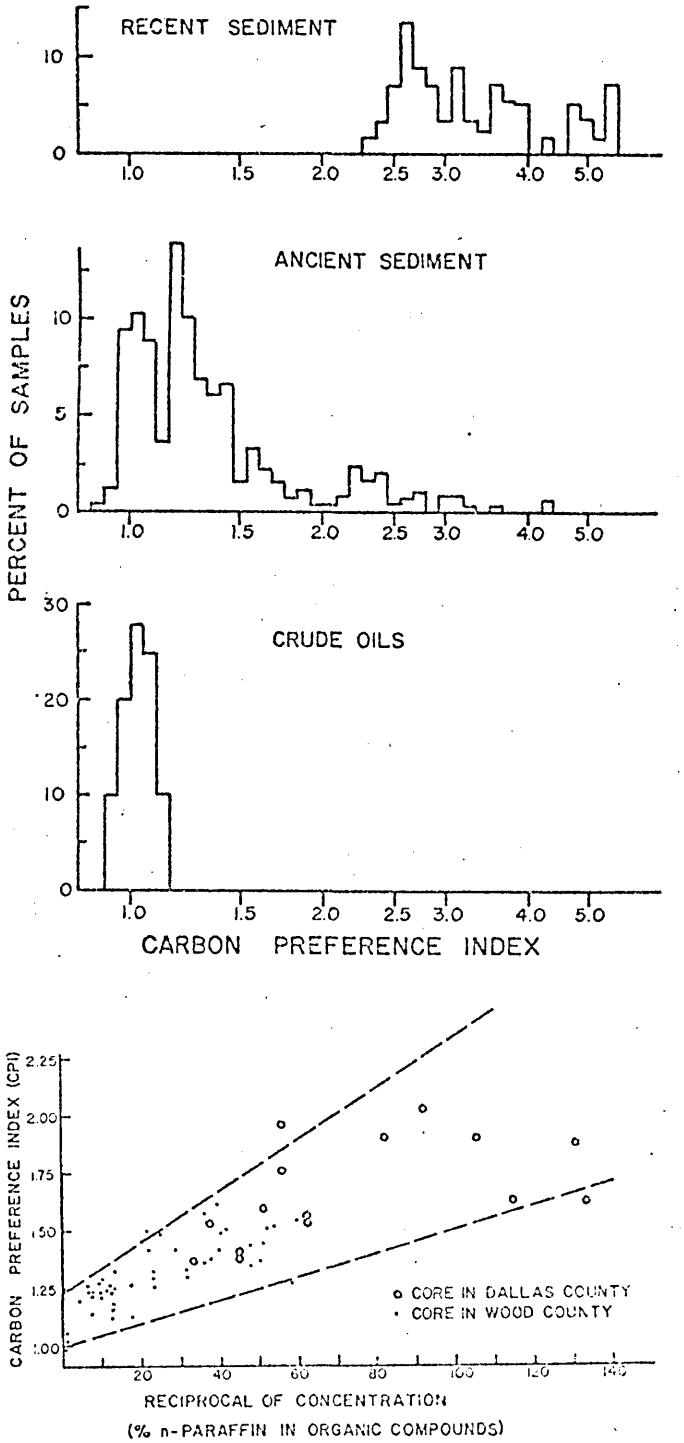
or

b thermally altered (highly evolved) terrestrial derived organic matter (Shiboaka et al 1973, Vandenbroucke et al 1976).

TABLE 45. HYDROCARBON CATEGORIES VERSUS DIAGENESIS.
(Evans & Staplin,1969.)

	GAS, C_1 - C_4	GASOLINE, C_4 - C_7	KEROSINE, C_8-C_{14}
IMMATURE.	Mainly C_1	Lean	Lean
MATURE	Mainly C_2 - C_4	Rich, C_4 - C_7	Rich
METAMORPHOSED.	Usually C_1	Lean	Lean

FIG 35 CPI DISTRIBUTION & CPI v. RECIPROCAL N-ALKANE CONCENTRATION. (Bray & Evans, 1965; Baker 1972.)



(Cores from Wood County are deeper than those from Dallas County.)

13 ORGANIC GEOCHEMISTRY: OVERALL CONCLUSIONS

Milner et al (1977) recorded the idea, that differences in source material will reflect through to an oil, has been with us for a long time. They cited White from 1915 to support the statement (the "composition of the mother organic deposit largely regulates the types of oils") although such a concept had been previously recalled by Baker (1972) who noted that "observed variations in the composition of the organic matter in ancient sediments in some cases appear to be related to differences in primary organic material". Consequently Mathews et al (1970) had argued that "the techniques used in elucidation of the structure of individual components of the hydrocarbon fractions combined with modern knowledge of biosynthetic pathways and chemical taxonomy provide a tool for identifying possible source materials of the organic constituents isolated from shales and crude oils".

However, the interplay of (thermal) generating effects came into consideration quite early as Barton (1934 in Milner et al 1977) noted "differences in the character of the mother material of petroleum and in particular conditions of generation of particular crude oils produce innate differences in different crude oils". Eventually therefore it was realised that "the use of organic matter in sedimentary rocks ..... may provide ..... a more widely applicable and more rigorous basis for the recognition and assessment of incipient metamorphism" where the facies are classified upon the molecular and compositional characteristics of the orgnaic material itself (Baker and Claypool 1970).

Thus, it has been propositioned that "an interesting problem for geochemists is to look for criteria unquestionably characterising either the nature of the organic matter or its evolutionary state" (Vandenbroucke et al 1976)

Yet, throughout the discussion of general results and conclusions it should be evident that the two chief parameters of utmost concern, notably the type and the thermal evolutionary stage of organic matter, are seldom mutually exclusive. Even upon the rare occasions where separate treatment seems permissible (e.g.fractionation of shale extracts) with regard to one of the issues (e.g.maturity) the results lack focus amidst the wide spectrum of hydrocarbon generation (e.g.

Asphaltics dominate immature sediment extracts whilst saturates major in metamorphosed (dry gas) sediment extracts but the (intermediate) boundaries are ill defined).

In conclusion, Vandenbroucke et al (1976) stated that "probably a combination of criteria should preferably be used to answer this question" and agreement must be offered since the consideration of a number of variables (as opposed to one) has already been argued as more safe and scientific.

From Table 37 some of the economic aspects of kerogen become apparent. A full appreciation of the structure of kerogen and understanding of hydrocarbon generating mechanisms will allow not only easier laboratory recognition but also the prediction of oil and gas occurrences hitherto unknown. However, the individualistic nature of kerogen in consequence of the dependence upon parameters which are variable in combination both numerically and chronologically (e.g. source types and their relative quantities versus degree and duration of diagenisis) offers a challenge to their complete understanding.

It is such a fascinating and formidable challenge which must be overcome if a successful and satisfactory exploitation of the many aspects of sedimentary insoluble organic matter is to be achieved (adapted from Davies 1973 unpub.).

Finally "the failure of organic geochemists to put enough 'geo' into the work has caused a notable absence of interpretations" (Baker 1965) and interpretations themselves also "lag ..... for the want of appropriate research" (Boyle and Garrett 1970). For example, organic geochemical data may be an additional indicator of proximity to source and thus be useful in deciphering depositional history and reconstructing palaeogeography (Baker 1972).

In the ultimate, "the increase in self criticism at all stages of the data acquisition process ... and interpretation coupled with the degree of objectivity offered by the statistical method can only improve the standard of ..... work and the quality of ..... interpretation" (Boyle and Garrett 1970).

SECTION TWO

PREVIOUS GEOLOGY AND GEOCHEMISTRY

PART ONE

THE KIMMERIDGE CLAY FORMATION

1 INTRODUCTION

Downie (1955) in his Kimmeridgian investigation noted that oil shales in general are rarely the subject of study and Bradley 1934 and Brockamp 1944 were cited for their work upon the Eocene Green River Formation (Colorado, Wyoming and Utah) and the German Lias respectively.

In 1963 Bitterli added the studies of Richter-Bernberg (1957-1960; Zechsteinvarves), Bitterli (1960;Posidonienschiefer) and Baker (1962; Cherokee Group) to his (then present study) in the list of work upon bitumenous sequencies.

Actually, the famous Torbane Hill (Bathgate, Scotland) case of 1854 seems to have begun investigations into the organic matter of fine grain sediments when experts tried to settle the issue as to whether Torbanite or Boghead Mineral was a coal or an oil shale (Robertson 1911).

More recently, with a leaning towards the 'geo' contribution Hallam (1967; Upper Domerian-Lower Toarcian, UK) warrants inclusion.

Although oil company activity in and around the Wessex Basin has been more busy than the reader may suspect (see Appendices) efforts to secure (more) relevant information have failed, (Stacey priv.comm. 1975); presumably because onshore licence awards do not necessitate the release of data after an agreed period of time. (?)

In fact, onshore the Kimmeridge oil shales have only been exploited to a very limited extent and subsurface information is not available on their occurrence to anything like that in respect of the Lothian Carboniferous oil shales (Macleod-Mathews 1975). However, renewed efforts by the Department of Energy to redetermine the onshore oil shale potential (Dickson-Mabon 1976) and the pending offshore English Channel-Western Approaches drilling activity (cf.North Sea Well Records 1976) promise to eventually improve knowledge.

The Kimmeridge Clay itself generally extends in a broad NNE-SSW trending tract from the Yorkshire coast to the Dorsetshire coast (Figure 36) although a few isolated outcrops occur elsewhere. Inland, along the main belt there are only few exposures which are usually provided by disused brick pits and these are in poor condition. (The greater variability of the Kimmeridge Clay, in particular the carbonate components, make it less suitable than the Oxford Clay for brick

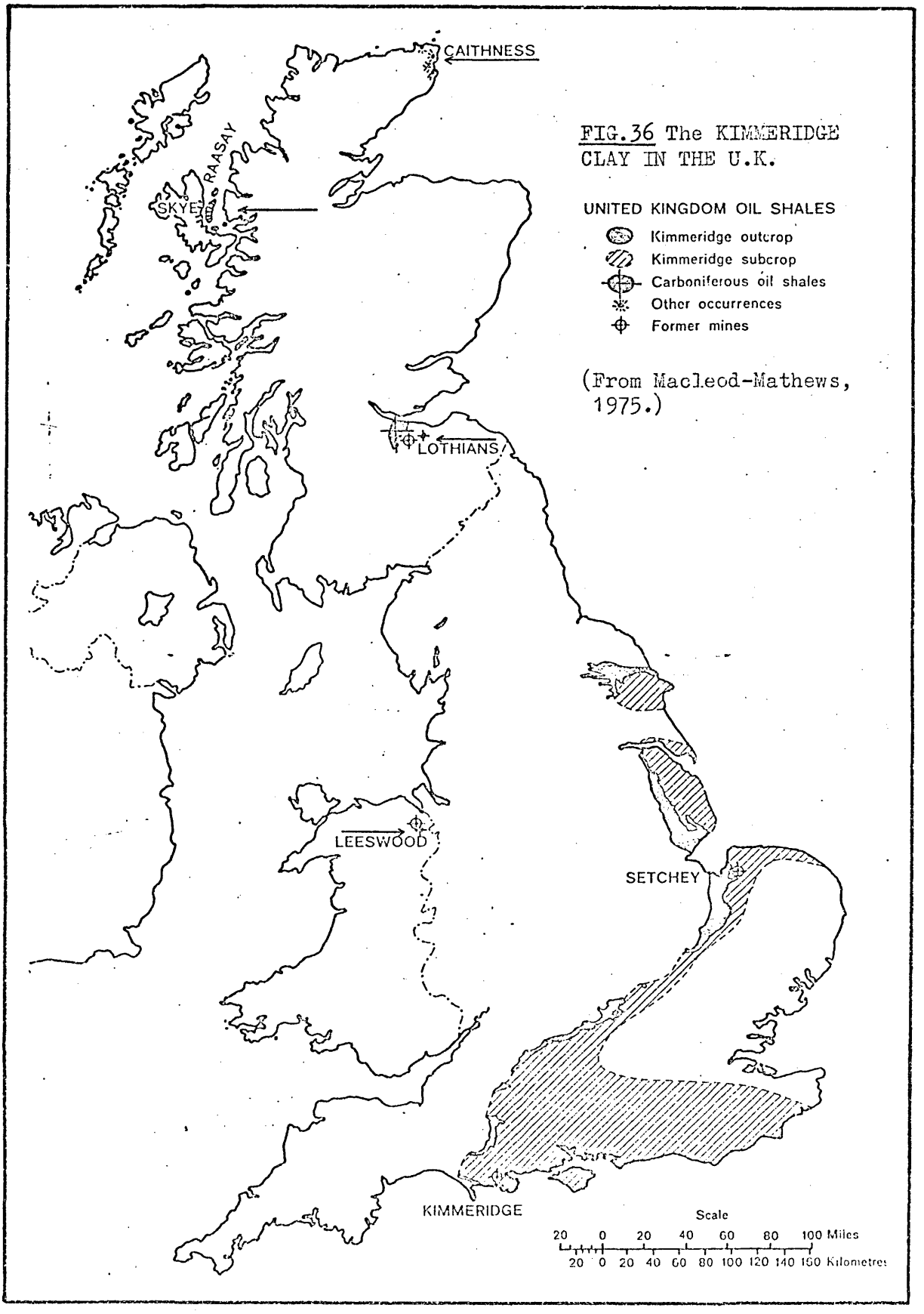


FIG.36 The KIMMERIDGE CLAY IN THE U.K.

(From Macleod-Mathews, 1975.)

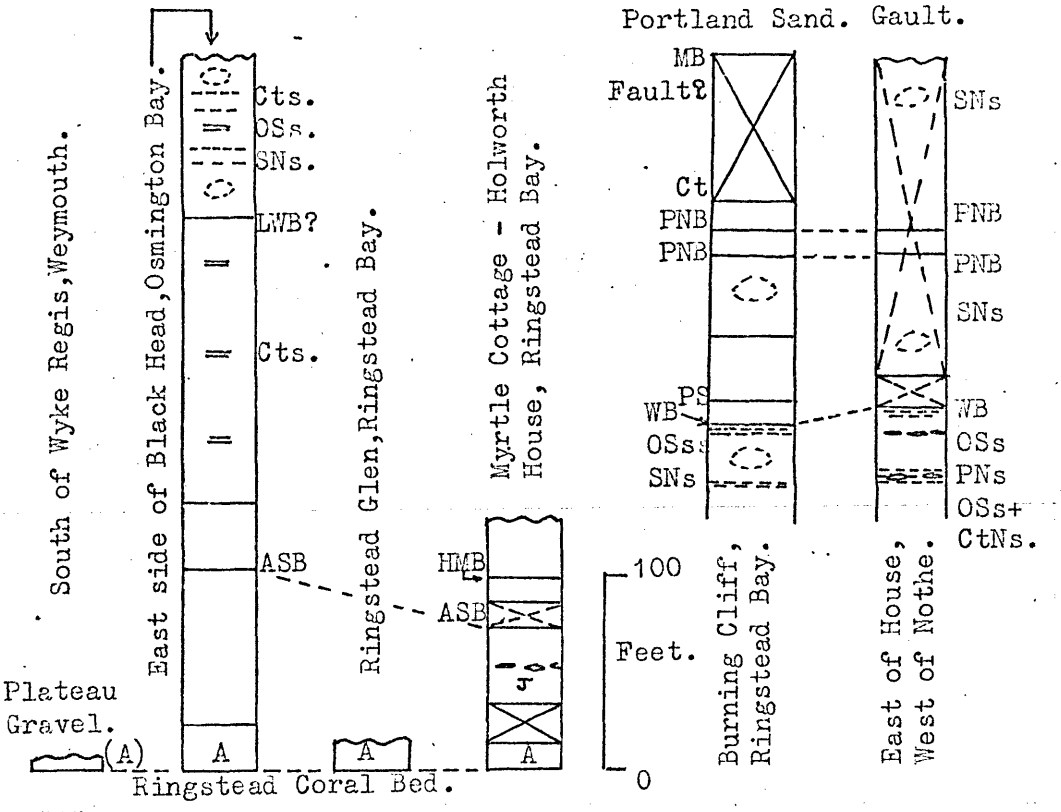
making - Rayner 1967). On the Yorkshire coast, the outcrop is almost completely hidden by a thick mantle (Lloyd 1962) and is in fact succeeded unconformably by the bluish Speeton Clay of Neocomian age; which at Speeton is about 200 feet thick (Kirkaldy and Wells 1966).

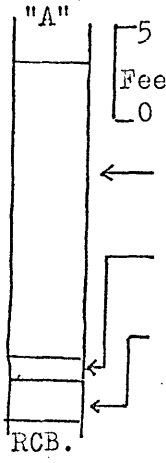
"The distribution and thickness of the Kimmeridge Clay follows the general picture of Upper Jurassic times in spite of the broadly uniform muddy facies. In the north there is the Yorkshire basin and the lesser one of Lincolnshire; in the south those of Wessex and the Weald. Between lay an unstable tract from north Wiltshire to Cambridgeshire with reduced thicknesses, non-sequences and some sandy invasion.....In particular, at Oxford the lowest clays lie uncomfortably upon Corallian limestones and the succeeeding Shotover Grit Sands (Upper Kimmeridgian Pectinatus zone) are outstanding" (Rayner 1967).

The Lower Kimmeridg Clay has been relatively neglected since the work of Blake (1875) as it is poorly exposed and rarely cored in boreholes (Brookfield 1973). For example Blake (1875) remarked that "West of Ringstead, the whole cliff however is so broken that no accurate knowledge can be really obtained of the thickness and the lie of the beds". Downie (1955) noted that the section at Burning Cliff was much harder to understand because of weathering and slippage and Kilenyi (1969) reported that the Black Head section was much disturbed by landslips. Figure 37 has been based upon earlier accounts to illustrate the sequences outside the Horbarrow Bay-Kimmeridge Bay interval.

(The burning at outcrop of the oil shale horizons has been recorded by Manfield (1916), Strahan (1920), Cunningham-Craig (1920), Arkell (1933) and Chatwin (1960).)

In contrast, the upper Lower and Upper Kimmeridge Clay is relatively well exposed along the coastal section between Horbarrow Bay and Chapman's Pool; although Hounstout is reknown for its slide on the lower slopes and its steep upper face requires agile negotiation (Figures 38 and 39 and Plate 11).



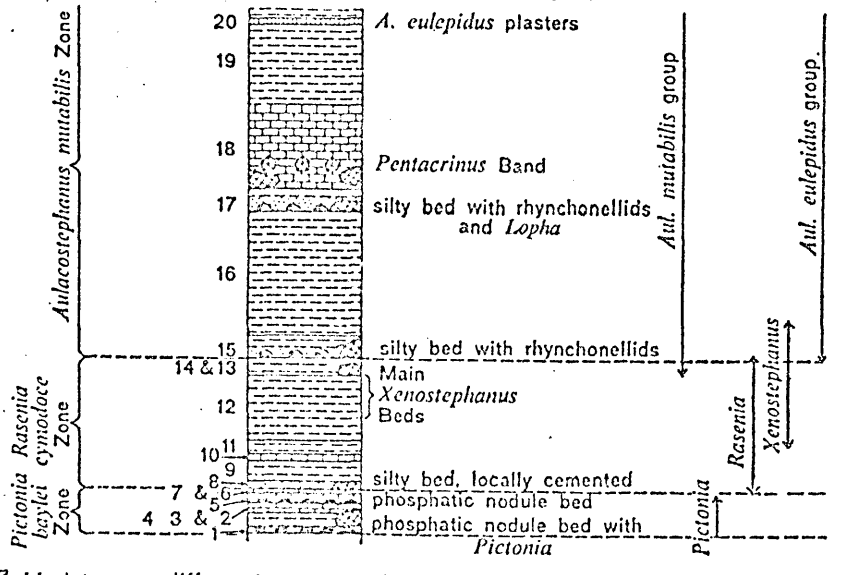


(Compiled from Brodie 1853; Blake 1875; Strahan 1920; Arkell 1933, 1947; Downie 1955; Lloyd 1959 & Mebradu 1975.)

← OSTREA DELTA CLAYS; Blue, lt.grey with crushed Raseniae sps. Soft & gypsiferous; shaly at top.

EXOGYRA NANA BED; Brown, sandy shales, locally hard & crowded with Exogyra sps. to resemble Forest Marble.

RHACTORHYNCHIA INCONSTANS BED; Purplish, lt.grey clays with many serpulids, rolled & bored phosphatic nodules iron pellets, abundant gypsum and locally hard with E. praevirgula, Modiola dumoriae & Pictonia sps.



Mudstone undifferentiated (mostly smooth dark grey but including shelly, medium grey, and burrow-mottled mudstones)

Pale grey very calcareous mudstone

Very shelly mudstone

Silty mudstone

Oil shale

Cementstone

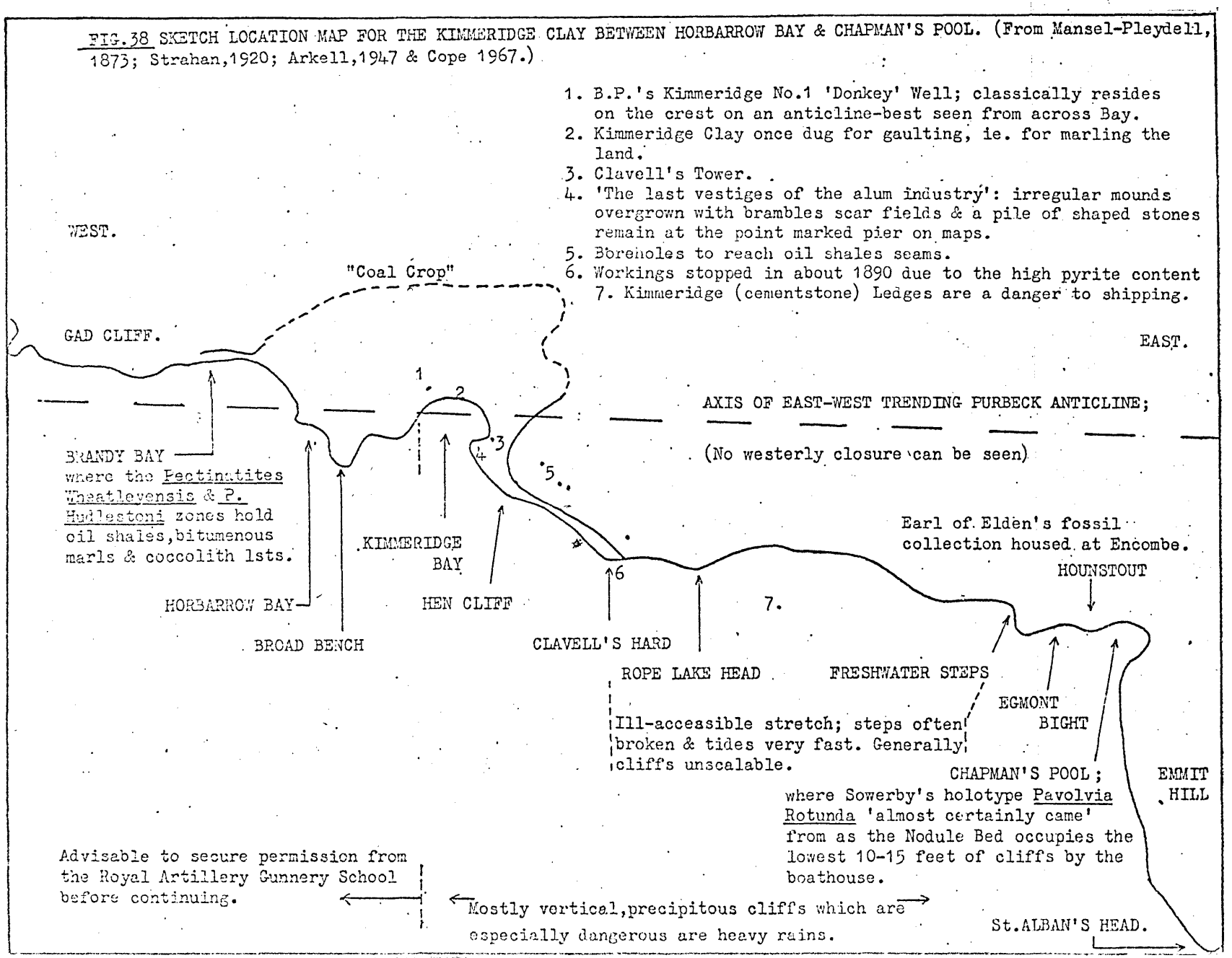
Phosphatic nodule bed

Vertical scale 1 to 300

Generalised vertical section of the Lower Kimmeridge Clay from Gallois & Cox (1976)

FIG. 37. KIMMERIDGE CLAY IN DORSET OUTSIDE HORBARROW BAY - CHAPMAN'S POOL.

FIG.38 SKETCH LOCATION MAP FOR THE KIMMERIDGE CLAY BETWEEN HORBARROW BAY & CHAPMAN'S POOL. (From Mansel-Pleydell, 1873; Strahan,1920; Arkell,1947 & Cope 1967.)



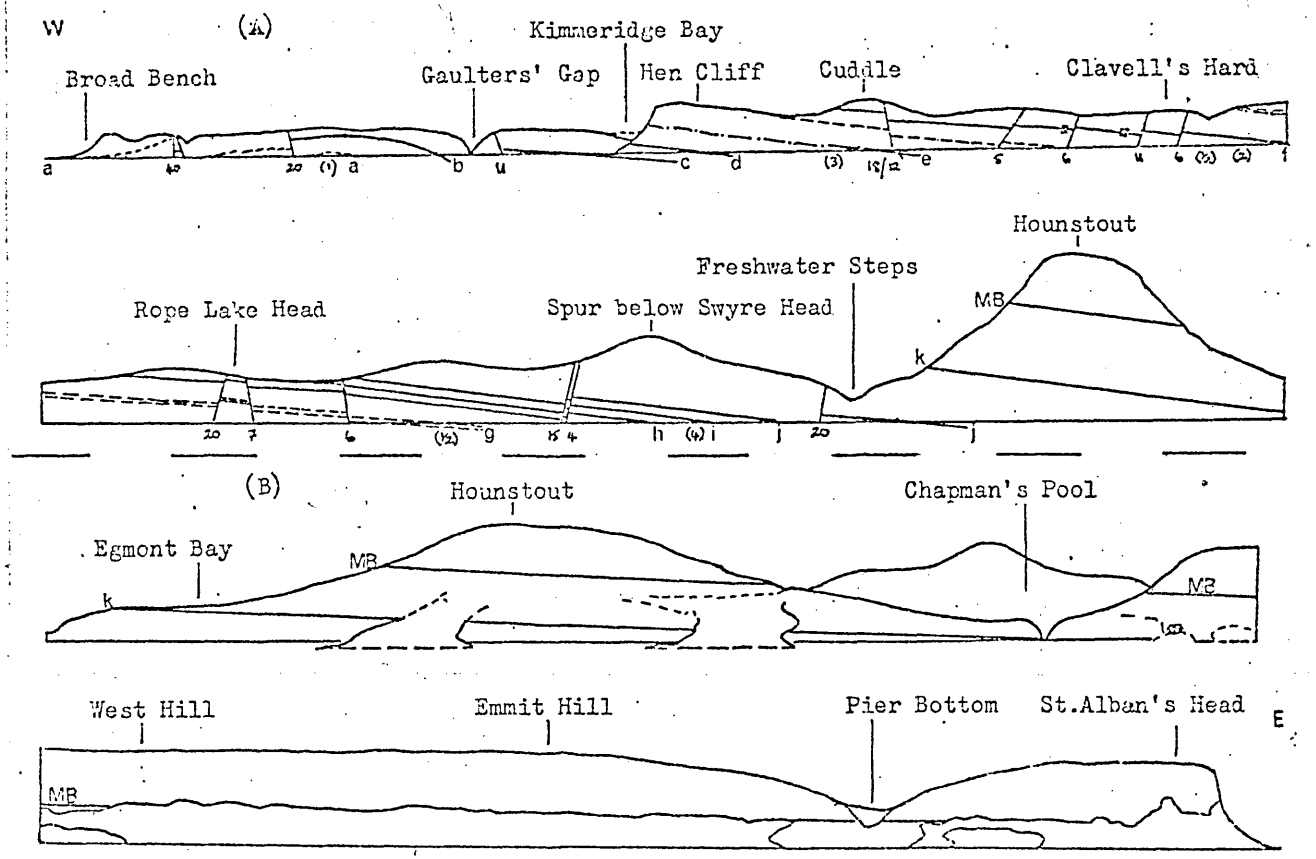


FIG.39 CLIFF SECTION BETWEEN BROAD BENCH & St.ALBAN'S HEAD illustrating the type succession for the major portion of the Kimmeridge Clay. (From Strahan 1920;Arkell 1933,1947 & Cope 1968)

The throws for the faults are given in feet (except U which is unknown). The scale of A is approximately 3.25 times less than that for B where 3.6" represents 1 mile both horizontally and vertically. The cliffs between Hen Cliff & Freshwater are seldom greater than 150 feet.

The marker horizons are respectively the Flats (a); Washing Ledge (b); Maple Ledge (c); Un-named cementstone (d); Yellow Ledge (e); Blackstone (f); Basalt Band (g); Lower, Middle & Upper White Bands (h,i,j); Hard Shale (k) and Massive Bed (MB).

PLATE 11 LOOKING WEST FROM EMMIT HILL.

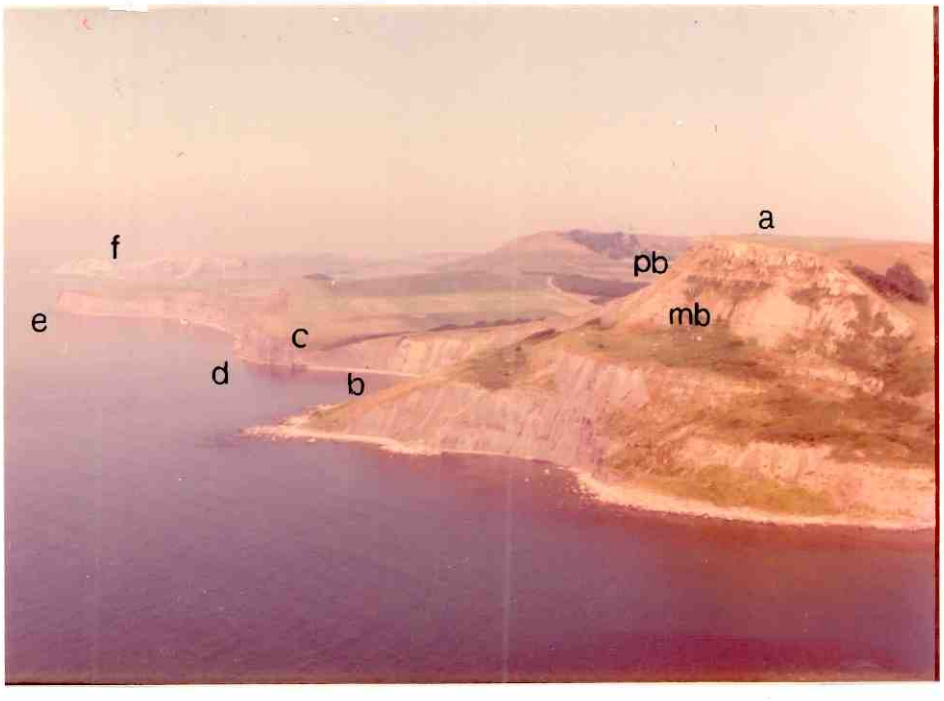


PLATE 12 LOOKING EAST FROM THE YELLOW LEDGE.

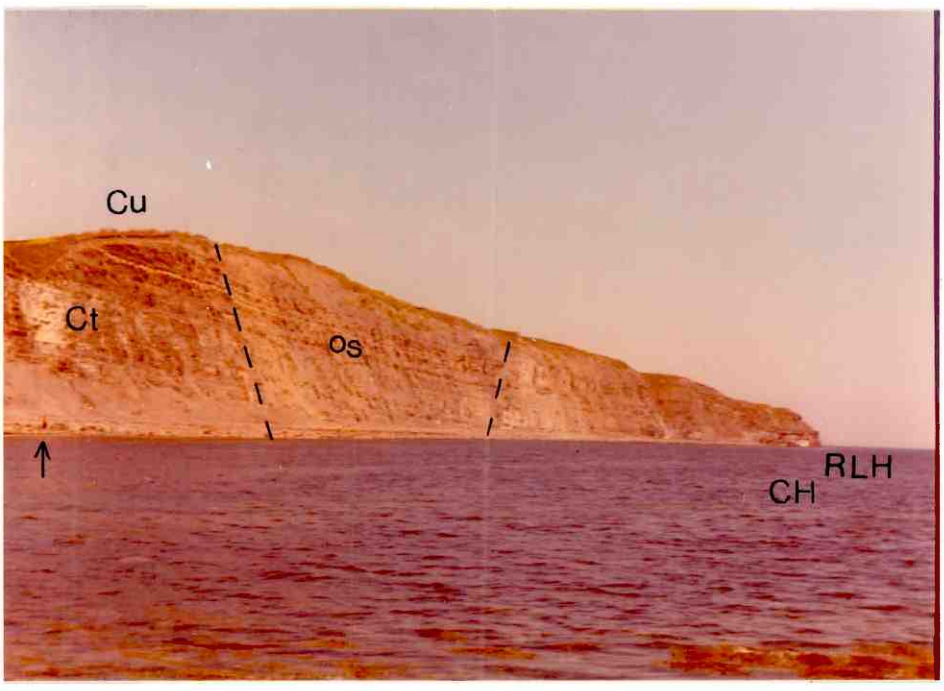


PLATE 13 DISUSED BLACKSTONE/KIMMERIDGE COAL (OIL SHALE) LEVEL.





PLATE 14 DISUSED CEMENTSTONE LEVEL.

2 OIL SHALE EXPLOITATION

With regard to present day utilisation of oil shales considerable research programmes are underway in America (e.g.'in situ' retorting) and Brazil (e.g.'Petrosix' process for the Irati shale). Operations in Russia (formerly 'Estonia') and China (formerly Manchuria) are in fact examples of successful commercial exploitation. The former uses oil shales for a fuel in electricity generation; for gas generation as a domestic supply and for a feedstock in the plastic industry, whereas the latter little publicised production probably yields the world's largest single shale oil supply in meeting one-fifth of China's current oil needs (Macleod-Mathews 1975).

In view of possible future potential the maximum gross oil reserves of the Green River Formation, for example, have been estimated at perhaps 6 (US) trillion barrels and excluding lower grade reserves, a figure 1.8 (US) trillion barrels has been deduced. These figures are $2\frac{1}{2}$ - 8 times the proven recoverable oil reserves of the world and the oil is low in sulphur with an API gravity of 26^{o} (Oxy Today, 1974).

The historic exploitation of the Dorsetshire Kimmeridge Clay has been summarised chronologically under the Appendices (Plates 13 and 14). Bearing in mind that an estimate of reserves in place is really impossible, owing to a dearth of circumstantial information, estimates for the capable yields of Kimmeridge shale oil have grown from 21 through 150 to 500 million tons with time (Macleod-Mathews 1975). Early figures for the evaluation of the shales in Dorsetshire and Lincolnshire are quoted in Strahan (1920), Cronshaw (1921) and Gardener (1963) and the question of liquid oil in Norfolk was dismissed by Thompson et al (1923). (A linear relationship between the density and yield of oil for kerogen shales has been noted by Schlumberger 1969).

"On an optimistic hypothesis regarding reserves and quality a(n) .... economic case conceivably exists that, at present levels of world oil prices .... these shales might afford a marginally profitable enterprise". Apparently, had the Scottish shale oil industry survived today on its 1962 scale it is very probable that it would have been economic (owing to the increased value of its products) although only capable of small production (50,000 - 100,000 tons per annum) (Macleod-Mathews 1975).

Resumption of a shale-oil industry in the United Kingdom embraces consideration of the future world price of oil and its products as well as environmental aspects. A tentative financial projection for eight mines to win 5 million tons of Jurassic shale each year and for 4 works to retort the shale has given a cost per ton of shale as £2.14. Here it is relevant to note that processes such as fireflooding from wells or in-situ extraction are inapplicable to UK shales because of the inadequate thickness of the oil shale seams (Macleod-Mathews 1975). A particular problem too arises from the fact that when processed a spent shale shows a 40% volume increase over its original state (Burmah Discovery 1975) but such material can be used in brick-manufacture and improving the alkalinity of podsolic soils (Macleod-Mathews 1975). In fact a good summary of the general technological advances for oil shales exploitation has been offered by Yen (1976).

Therefore, it has been concluded that "despite serious qualifications a case exists in the long term national interest for the precise extent and quality of the Jurassic shales in England to be assessed by a programme of geological investigation .... followed by ..... laboratory work" (Macleod-Mathews 1975). In this respect, Gallois (1976) has reported on the (successful) start of a programme to determine the levels, lateral continuity, oil yield and kerogen/trace metal elements of individual or groups of oil shale seams in the Kimmeridge Clay.

Out of the work a new oil shale horizon, the "Main Nannocardioceras Beds", has been found (Gallois and Cox 1976) and for correlation on Log 1 (their) beds 27 and 31 are assumed to be equivalents of the Flats and Washing Ledge stone bands respectively. Macleod-Mathews (1975) did state that the upper ("Blackstone") oil shale series contained 21 feet of shale (Plate 13) whilst the lower division consisted of seams which aggregate to 15 feet.

3 LITHOSTRATIGRAPHIC BOUNDARIES

In the type area, selected between Weymouth and Swanage by d'Orbigny (Lloyd 1959) the base can be taken at the top of the Corallian Formation which Waagen, in 1865, defined as the Ringstead Coral Bed or its lateral equivalent, the Abbotsbury Iron Ore (Arkell 1947). However Blake (1875) conceived 'passage beds' between the Corallian and Kimmerdige Clay since a major lithologic change was seen to occur at the base of the Mutabilis zone and Brookfield (1973) has recorded the members which are involved (Table 46 and Figure 40). Incidentally, although the Abbotsbury Iron Ore is exposed as a ferruginous oolitic limestone to about 11 feet (next to the subtropical gardens) by a road cutting leading to Abbotsbury Castle, the Ringstead Coral Bed is now very difficult to find and ideally it should follow the Ringstead Waxy Clay (Plate 45).

It was a lithological passage between the Lower and Upper Kimmeridge Clay coupled with an overlap of fauna which lead Hudleston et al (1896) to state that the actual line of separation is very difficult to draw. Earlier Blake (1875) had observed that Buckland mentioned "some 138 feet of clay in Kimmeridge Bay should probably be added" (to the Upper Kimmeridge Clay) and specified bed number 40 and upwards must certainly be Upper Kimmeridge Clay. Although Blake's bed number 43 occurs at/on the east corner of Kimmeridge Bay the base of the (succeeding) Hen Cliff Shales appears to have been adopted as the boundary (Arkell 1933-1947). However, Gallois and Cox (1976) seem to have taken a compromise in labelling their bed number 35 as the topmost Lower Kimmeridge Clay. If their bed numbers 27 and 31 are in fact equivalent to the Flats and the Washing Ledge, then approximately 70 feet of Kimmeridge Bay shales (c. Maple Ledge-east corner) are included in the 'Upper' Kimmeridge Clay of Arkell (Log 1).

The upper limit of the Kimmeridge Clay has received much attention and for the overlying strata, Fitton (1827) proposed the name "Portland Sands"; apparently intending the base of the sands to be a line of springs (at about 50 feet below the "Massive Bed"/top of the 'Hounstout Clay'; Chatwin 1960). The survey of 1855 utilised this level; being followed by Woodward who designated the sandy beds as 'passage beds' (Arkell 1947), but Fitton in 1836 was reported to have specified the division at the point where Pier Bottom cuts the cliff (i.e. at the 'Massive Bed' - Figure 39) and was thought to have been followed by the

N.W. European Zones	Formations in Southern England	Bed terminology Dorset Coast Type sections	Formations in Eastern England	Formations in Yorkshire	Formations in East Scotland
Mutabilis	Kimmeridge Clay	Mutabilis Zone Clays	Kimmeridge Clay	Kimmeridge Clay	Kimmeridge Boulder beds
Cymodoce		Kimmeridge Passage beds: Lower Kimmeridgian Cycles; Liostrea delta bed			
Baylei		Exogyra nana bed; Torquirhynchia inconstans bed			Allt na Cuile Sandstones
Pseudocordata	Upper Calcareous Grit	Kimmeridge Passage beds: Ringstead Coral bed; Ringstead Waxy Clay	Amphill Clay	Upper Calcareous Grit	
		Sandsfoot Grits		?	?
Decipiens	Glos Oolite Series	Sandsfoot Clay			
Coutisnigrae		'Trigonia' clavellata beds	Upware Coral Rag		
Plicatilis	Osmington Oolite Series	Osmington Oolite	Upware Oolites	Coralline Oolite Formations	Port an Righ Sandstone
	Berkshire Oolite Series	Bencliff Grit; Nothe Clay; 'Trigonia' hudlestoni bed	Elsworth Rock Series		

TABLE 46: Upper Oxfordian - Lower Kimmeridgian/Lower KIMMERIDGE CLAY simplified LITHO-STRATIGRAPHIC TERMINOLOGY (after Brookfield,1973).

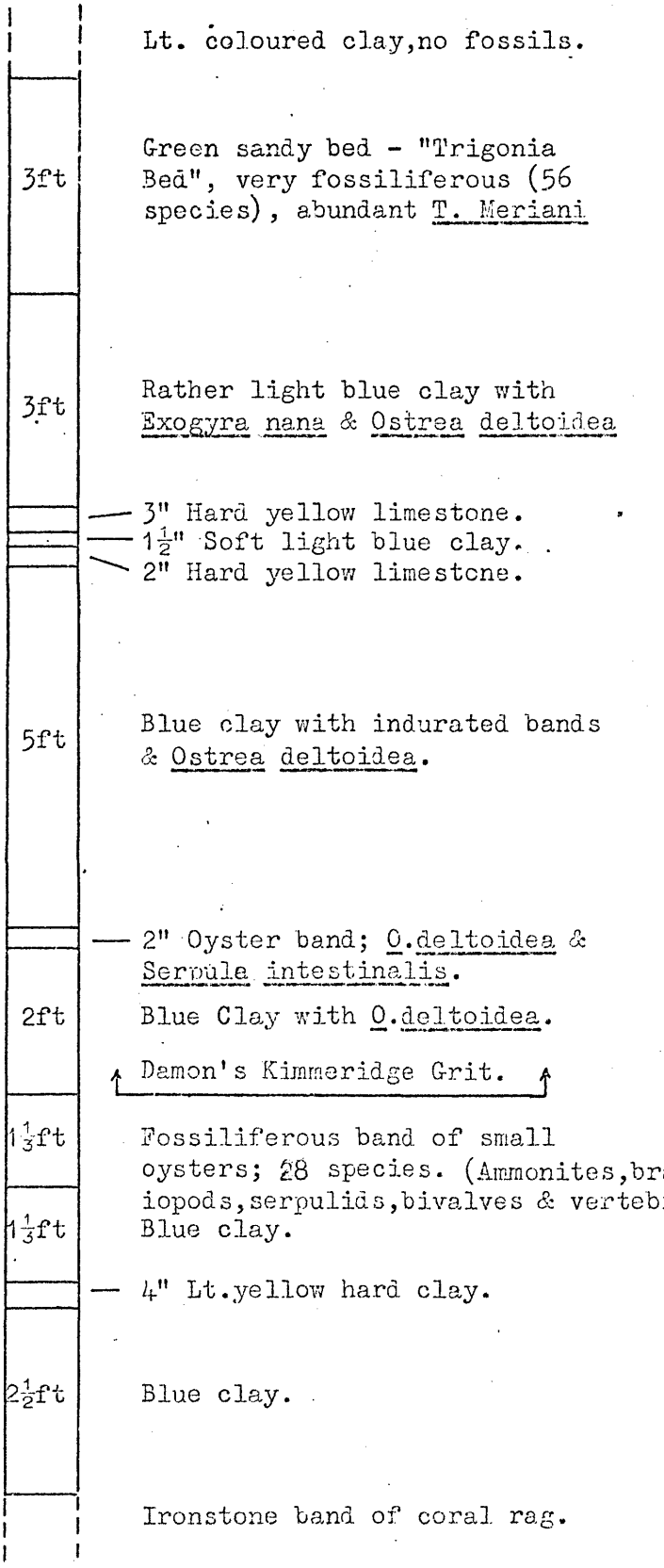


FIG. 40 LOWER KIMMERIDGE CLAY - CORALLIAN PASSAGE BEDS. (Blake 1875, Weymouth.)

Survey of 1898 (Hovenden et al 1910; Chatwin 1960). However, Blake (1875) had put the gradual change between 150 feet of unfossiliferous hard blue sandy clay (below a hard blue limestone - the 'Massive Bed') and 70 feet of blue fossiliferous laminated clay as the boundary.

In 1880, Blake commented that "we are even lead to ask what amount of justification there is for the tittle Portland Sands. If the choice lay between including these in the Kimmeridge Clay and including some more of the clays below them in the Portland Sands I should unhesitatingly take the first alternative ..... Moreover, in dividing the Portland Sands from the Kimmeridge Clay we have to draw a somewhat arbitrary line".

As mentioned, a conspicuous sandstone on Hounstout Cliff was taken as the base of the Portland Sand by Strahan (1888-1890) in agreeing with Fitton (1836) and Buckman in 1926 called the band the 'Massive Bed' (Arkell 1947). Although Hovenden et al (1910) had noted that "the exact position at which the division between the Portland Sand and the Kimmeridge Clay should be placed is a matter of doubt" Arkell, from 1933 onwards, advocated the Massive Bed as the best field datum. In doing so Arkell (1935) noted that seepages may have been pronounced in earlier times but no such line now offered itself below the Massive Bed.

Subsequently, Downie (1955), Dunn (1972) and Mebradu (1975) have all followed Arkell but Townson (1975) defined the top of the Kimmeridge Clay at the upper limit of the Lingula Shales (max. 34 metres below the Massive Bed) and in doing so. took the complete opposite direction to Neaverson (1925) who grouped the Portland Sands in the Kimmeridge Clay.

4 BIOSTRATIGRAPHIC BOUNDARIES

The Kimmeridge Clay in England is the exact equivalent of the Kimmeridgian stage (Lloyd 1959).

Ammonite zonation of the Kimmeridgian from 1913 has been attempted in Table 47 prior to which the English Kimmeridgian was apparently divided into two "intimately blended" zones (Neaverson 1924).

Here it is relevant to note that according to Neaverson (1924) Salfeld divided the formation into eleven zones; taking the upper limit at the top of the Perisphinctes eastlecottensis zone. However strata ranging from "somewhat below the White Septarian Band" to the basal Portland Sand was assigned to the P. pallasianus zone by Salfeld (1913). A new Epipallasiceras zone was established by Casey in 1967 at the top of the Upper Kimmeridgian for which Cope and Wimbledon have a detailed zonation pending (Cope and Wimbledon 1973).

In 1970, Christensen and Kilenyi divided the type section into five ostracod zones (based upon Galliaecythendea and Mandelstannia) and Mebradu (1975) gave four palynomorphological zones; but both bear little relationship to the ammonite zones.

In early international correlation Arkell (1935) apparently wrongly accused Salfeld of assigning a Portlandian age (English sense) to the bulk of the Kimmeridge Clay (Maple Ledge and above) because Salfeld (1913) actually said that the strata was equivalent to the 'Portlandian' of continental authors. In fact Downie (1955) emphasised that the Lower Kimmeridgian in an English sense is equivalent to the complete 'Kimmeridgian' of continental workers and Hallam (1969) supported this in stating that 'Kimmeridgian' in Europe refers to deposits predating the incoming of Gravesia.

The base of the Portlandian is usually accepted as the division between the Pavlova and Zaraiskites zones whilst the proposed boundary by Casey, lying between the Pectinatites and Pavlova zones, bears no relation to stage boundaries elsewhere in the world (Hallam 1975).

In 1962 Harrington (in Brookfield 1970) gave reasons for suggesting that the Jurassic-Cretaceous boundary should have been drawn between the Kimmeridgian and (Middle ?) Tithonian; this division according to Johnson (1975) being equivalent to that between the Lower Volgian (Upper Kimmeridgian) and Middle Volgian/(Middle ?) Tithonian ('Portlandian'). (? since Brookfield (1970) assigned a lower Tithonian age to the Upper Kimmeridgian).

LITHOSTRATIGRAPHIC UNITS NOT TO SCALE	SALFELD, 1913	SALFELD EMENDED BY CHATWIN & PRINGLE, 1922*	BUCKMAN, 1923*	NEAVERSON 1924, 1925 ("IN NEAVERSON")	ARKELL, 1933	ARKELL, 1947, 1956	ZIEGLER 1962 FROM BROOKFIELD 1973; GALLOIS & COX, 1976	COPE, 1968 & COPE AND WIMBLEDON IN COPE, 1968
HOUNSTOUT MARL		P. PALLASIANUS 5	P. PALLASIANUS 5	P. PALLASIOIDES E	UNFIGURED	PAVLOVIA PALLASIOIDES		UNFIGURED NEW GENUS
HOUNSTOUT CLAY								
RHYNCHONELLA MARLS	?				P. PALLASIOIDES	PAVLOVIA ROTUNDA		
LINGULA SHALES		?	?					
ROTUNDA CLAYS					P. ROTUNDA			
CRUSHED AMMONI. SHALES HS	PERISPHINCTES PALLASIANUS. 9–11	'LOMONOSSOVI' 4	'LOMONOSSOVI' 4	'ROTUNDUM' D	P. PECTINATUS	PECTINATITES PECTINATUS		P. ROTUNDA - P. PALLASIOIDES. ? SP. ?
PARKINSONITES CLAYS					V. NODIFERUS			
PECTINATITES CLAYS LWB	?	? 3	?	?	WYHEATLEYENSIS	SUBPLANITES GRANDIS		(P.) PECTINATUS
SHALES WITH NODSTS. RLH		P. EASTLECOTENSIS	? 'PECTINATUS' 3	'PECTINATUS' C				P.(A) HUDLESTONI
BITUMINOUS SHALES GL	VIRGATITES ZONES 8	VIRGATITES SP. 2	'SCRUPOSUS' 2	UNFIGURED B	'SUBPLANITES'	S. VIMINEUS.		P.(M) WHEATLEYENSIS
CATTLE LEDGE SHALES YL		VIRGATITES SP. 1	'DOROPLANUS' 1	UNFIGURED A				P.(M) SCITULUS
HEN CLIFF SHALES	GRAVESIA IRIUS? 7	?	?	GRAVESIA SPS. ?	G. IRIUS G. GRAVESIANA ML	GRAVESIA GIGAS G. GRAVESIANA		P.(V) ELEGANS
KIMMERIDGE BAY SHALES	G. GRAVESIANA 6 ML AULACOSTEPHAN -US ELOSNUS 5 A. PSEUDOMUTABILIS				A. PSEUDOMUTABILIS & A. YO	A. PSEUDOMUTABILIS		A. AUTISSIODORENSIS & A. ELDOKUS
CLAYS WITH L. DELTA.	AULACO. YO 4 R. MUTABILIS 3 RASENIA 2 CYMODOCE				'AS ABOVE' PARASENIA MUTABILIS R. CYMODOCE	'AS ABOVE' A. MUTABILIS R. CYMODOCE	'AS ABOVE' A. MUTABILIS R. CYMODOCE	
CLAYS WITH R. INCONSTANS	PICTONIA 1 BAYLEI				P. BAYLEI	P. BAYLEI	P. BAYLEI	

TABLE 47. KIMMERIDGE CLAY AMMONITE ZONATION. Type Section, Dorsetshire.

However, Johnson (1975) showed the Jurassic-Cretaceous boundary between the Upper Volgian and the Ryazanian/Berriasian (that is, within the Purbeck Formation of Portlandian (formerly 'Purbeckian') age).

Thus, it appears adequate for the purpose of this presentation to note that precise correlation of biostratigraphic intervals within the late Jurassic-early Cretaceous is the subject of extensive discussion (Casey 1974 in Johnson 1975).

5 CHRONOSTRATIGRAPHIC BOUNDARIES

With regard to an absolute time scale, the Kimmeridgian has been more recently assigned to a period between 138-143/148 million years ago (Van Hinte 1976) although Rayner (1967) and Brookfield (1970) used limits of 146-151 million years. A duration for the stage of approximately five million years has been applied by Dunn (1972 after Hartland et al 1964) and Bjorlykke et al (1975).

6 FORMATION THICKNESS

Dunn (1972) commented that "there seems little point in adding another set of measurements to those already published because variations are bound to occur depending upon the exact spot at which each worker measures the sequence and draws his line between lithologies".

However, Cope (1968) using an Abney level and/or direct measurement deduced that "some quite considerable errors are perpetuated by Arkell" who according to Downie (1955) used a stadia rod.

Figure 41 contrasts some previous results with the measurements from this study for the succession closest to the depocentre. The observation that it is easier to recognise divisions at a distance than close to the cliff face (Hudson and Palframan 1969) is applicable to the Kimmeridge Clay, but of course, contrary to Dunn's (1972) inference, there is nothing gradational about the boundaries of the classic 'cementstone' (marker) horizons.

7 SEDIMENTATION RATES

Monckton (in Hovenden et al 1910) passed the opinion that sedimentation was fast enough to cover small ammonites before the animal matter had decayed. In contrast, larger ammonites were though to be finally covered after the animal matter had decomposed. Such a gauge of sedimentation rate arose from his observation that sometimes the large outer chambers were filled with mud and unlike the inner central chambers or small ammonites, were not subsequently crushed.

More recently, Cope (1968) noted that the (sizeable) oysters preferentially sheltered on the underside of the ammonites; indicating attachment after death of the cephalopod and 'considerable time' before sediment influx killed them. Also, the views of Hudson and Palframan (1969, Oxford Clay study) can be applied here since the occurrence of infaunal and epifaunal suspension (filter) feeding lamellibranchs (see Blake's List of Fauna) implies sedimentation was not fast enough to bury the infauna and/or inhibit filter feeding.

However, for past sedimentation rates to be calculated and compared more accurately with modern day instances the compaction of the sediment must first be appreciated. Downie (1955) in assuming spheroidal bitumen globules settled upon the sea floor, derived compaction to be of the order of 80% since the 'lithified' bitumenous lenses showed

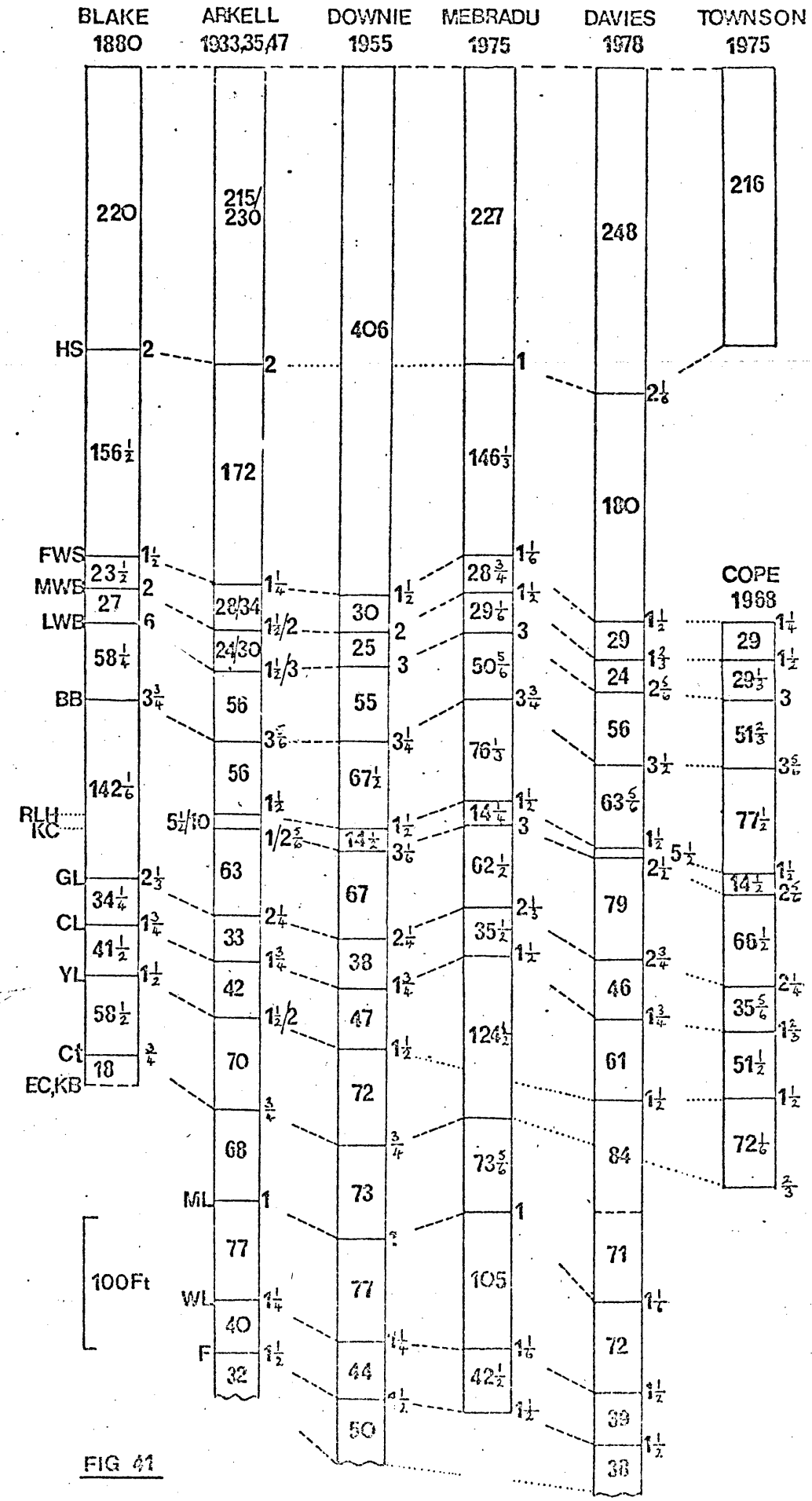


FIG 41

KIMMERIDGE CLAY FORMATION:
OUTCROP THICKNESS; Horbarrow Bay - Chapman's Pool.

vertical cross-sections of a maximum thickness $^{1}/_{5}$ where 1 is the length of the horizontal long axis. Further by analogy with coal seams, the crushing of oil shales was thought to be probably two-three times as much as that within the clays (?).

Using the degree of flattening of the ammonite tests, Dunn (1972) arrived at 'a more realistic' reduction of 60% by considering the former gas content of the chambers. He concluded the original thickness to be two and a half times the present day value.

Now, as no break in deposition was indicated for the succession in Dorsetshire (Cope 1968, Dunn 1972), inclusion of the strata concealed below the lowest beds seen (581 feet from the D'Arcy 1936-1937 Broadbench Well; Chatwin 1960) (Plate 15) and an assessment for the fault of unknown throw (probably 20 metres, Dunn 1972, Plate 16) are the only additional requirements for an estimation of the total thickness of the Formation.

Accordingly Dunn (1972) arrived at an average sedimentation rate of 25 cm/1000 years (for the section); using the duration of 5 million years as previously noted. Similarly, Bjorlykke et al (1975) have found at least 1200 metres of Kimmeridge Shale accummulated in the North Sea Basin and they deduced a very similar sedimentation rate. Here it is relevant to note that Dunn (1972, 1974) used an approximate sedimentation rate of 10 cm/1000 years in assigning 10m, 4m, 1.43m and c.1m cycle intervals to periods of 100,000, 40,000, 14,000 and c. 11,000 years respectively. In fact, in drawing coincidence with Downie's calculation of 4 ft 9 in for the average thickness of a cycle (1.45m in Dunn 1972) the lower sedimentation rate appears confined to an interval from the Flats to the Freshwater Steps which constitutes approximately between one-half and one-third of the total succession (as defined above).

Specifically though if an analogy between the present day Black Sea and past Kimmeridgian sea can be drawn for the carbonate horizons, Riley (1974) determined a sedimentation rate of 0.4 mm per year for the White Bands (4m/1000 years).

In conclusion, an overall slow clastic supply is seen to have been interrupted by occasional much faster (16-40 times) rains of coccolithospheres.

8 LITHOLOGY

PLATE 15 'LOWEST BEDS SEEN', HORBARROW BAY.



PLATE 16 FAULT OF UNKNOWN THROW, KIMMERIDGE BAY.



PLATE 17 ROTUNDA NODULE BED, HOUNSTOUT CLIFF.

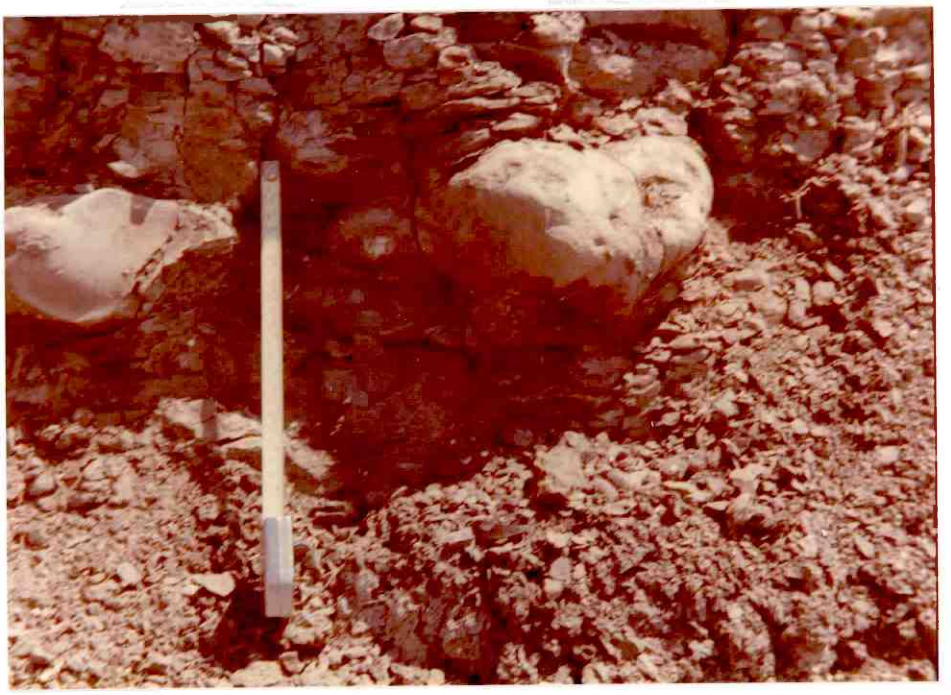
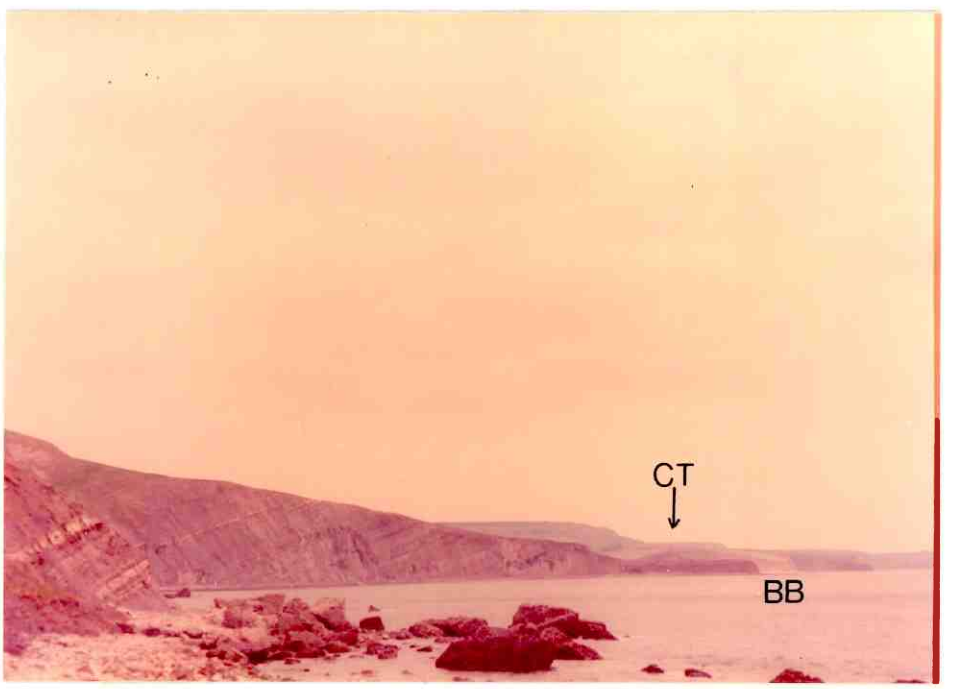


PLATE 18 STEEPLY DIPPING STRATA, BRANDY BAY.



To describe the Horbarrow Bay-Chapman's Pool Dorsetshire Kimmeridgian succession a composite log has been compiled from many authors (Log 1). For the "upper Lower Kimmeridge Clay" (lowest seen - c.Maple Ledge ?) the most recent detailed stratigraphy has been incorporated from Gallois and Cox (1976) since "all 35 sub-divisions are present in the type area". (Log 2). The single most detailed pictorial log for the section appears to be that by Downie (1955 via Wilson priv.comm. 1976) and against it characteristics of the classic 'marker' horizons have been annotated (Log 2).

The generalised features of the gross lithologic types are summarised in Table 48, and Dunn (1972) has noted that with the exception of phosphatic or pyritic nodules, the Kimmeridgian sediments lie within the compositional range of a tetrahedron between clay, carbonate, quartz and organic matter. Earlier Downie (1955) had shown that the Dorsetshire sediments lie near to the triangular face defined by clay, carbonate and organic matter. As the content of either or both of the carbonate and/or organic matter increases the rock becomes harder (Dunn 1972).

9 CYCLICITY

The cyclicity of the Kimmeridgian occurs within a host background of more major cycles reknown for the Jurassic. For example, Arkell (1956) noted that the Kimmeridge Clay is a transgressive component of a regressive sequence (Kimmeridge Clay, Portland and Purbeck Formations) which coarsens upward and shows a shallowing trend in lithology (clay-sandstones and limestones-oolites, limestones and evaporites) amidst an overall regressive Jurassic (Deep marine Lias - Purbeck sabkhas).

More specifically, Brookfield (1970) briefly discussed the major cycles affecting the Upper Jurassic. He concluded that the Lower Kimmeridgian marked the maximum extent of Jurassic sea over the shield area prior to a short-lived Upper Kimmeridgian regression (being followed by a Middle Tithonian transgression) and Mebradu (1975) appears to have deduced a similar picture.

On the most detailed lithological evidence, Downie (1955) was the first to distinguish minor sedimentary cycles and a summary is given in Figure 42 to which Riley (1974) has made some amendments. The cycles and rythmic units of deposition appear to extend over the whole

WHITE LIMESTONES: >50% Carbonate - Du. Laminated chalky limestones largely of coccoliths & coccospheres - Do/coccolithophoroids - Ri which are elongated & seperated -I by about 3% by weight of brown organic matter; the latter being composed of dinoflagellates (up to 2% of the rock weight & mostly Palaeoperidinium sps.),hystrichospheres,spores,pollen & small plant fragments but without benthos - Do./body fossils absent -Ri. Only one example of a calcareous cyst noticed in a white band which sometimes have worm tracks at their bases - Do ('bioturba -tion'-I;trace fossils-Ri) & show highly developed loop bedding (Flows are most pronounced in layers of high coccolith content) - Do. Rafted wood,plant tissue fragments & miospores presen -t in both carbonate & organic bands -Ri. Every 3/4 mm rhythmic increase in limestone laminae thickness & corresponding decrease in organic laminae thickness over 6-10 pairs occur;then rhythmic return to thicker organic laminae & very thin limestones -Do. Small-scale cross laminations (?ripples) not uncommon -I Carbonate bands are infact fairly pure calcites -I- $(Ca_{0.979}Mg_{0.002}Fe_{0.20})CO_3$ - $(Ca_{0.989}Mg_{0.04}Fe_{0.007})CO_3$
(Replacement periodically of one phytoplankton groupcoccolithophoroids-warm summer waters) by another (dinoflagellates-cool late summer/spring waters) clearly original sedimentary feature - Ri; conditions of coccolith limestone formation can be compared with those for present-day Globigerina ooze & were similar to those for Rhomb limestone formation although longer in duration - Do.)

OIL SHALES: 40-75% Organic matter & 13-35% Clay - Du. Brown streak - MM; very tough -Do,MM; resistant to weathering -G,MM in comparison to ordinary shales & give smooth pebbles -Do; conchoidal fracture especially when large kerogen content - CC/ fractures most pronounced in richest oil shales-Do;usually have low specific gravity, 1.6-2.2 & log density versus oil yield can show linear relationship - the lower the sp.gr. the greater the oil yield - S. In the field the quality is measured by the degree of facility with which it can be cut & curled up with the edge of a sharp knife.-MM. Fractures oblique to the bedding cause wedges of 15°-20° inclination; smooth slickensided surfaces often coated with calcite or less commonly with pyrite; vertical joints inveriably filled with calcite; Coker in 1732 said fresh oil shales were blue but now dark chocolate brown - Do. Black plant fragments,pieces of shale & small pyrite crystals occur throughout; calcite lenses less common & masses of bitumen lenses are the essential constituents of oil shale being seperated by streaks of clay or calcite elongated in the same direction - Do. Benthos is frequently absent -Ri. Mosaic bedd -ing occurs in very rich oil shales only whilst pellet rock textures happen in less rich oil shales.-Do.

BITUMENOUS SHALES: 20-40% Organic matter; grey-brown to dark grey - Du. Generally abundant benthos but no significant difference with that of the oil shales - Ri.

BITUMENOUS MARLS: 20-50% Carbonate, > 20% Organic matter - Du. Calcareous nannoplankton, colloidal & sapropelic organic matter abundant; negligible body fossils & material but trace fossils present - Ri.

MARLS: > c.25-30% Carbonate causes such argillaceous rocks to increase in hardness & develop a conchoidal fracture - H.

CLAYS: 5-10% Combustible matter, > 80% Clay minerals,quartz,glauconite,microcline,orthoclase, muscovite & apatite - Du. 0-20% Organic matter, 70-82% Clays & gross carbonate <10% - H. Sp.gravity 2.4-2.5 -S; least resistant to weathering & soft, being bluish grey but light grey on weathering; no lamination & quite homogeneous becoming shaly only when organic matter increases.- Du. Microplankton preserved but compression has rendered most difficult to recognise - Do. Abundant & moderately diverse benthos - Ri.

CEMENTSTONES: >50% Carbonate,>10% Clay - Du; 70-90% Lime,1-3% Organic matter - Do. Comprise the Ledges which show a uniform thickness for remarkable distances (I) & have rare macro-fossil assemblages - Du. Two types:(a) cubcidally fractured & of apparent homogeneous compos -ition & (b) vertically jointed & bedded - Do. Patches or streaks of organic matter in all except Basalt Band - Du. Very small amounts of quartz (subangular, c.20μ dia.) with specks of pyrite - Du/ small pyrite grains - Do & occassional comminuted wood fragments - Du/ plant matter -Do occur. Regions of more massive pyrite with chitinous & phosphatic matter also known - Do. Dolomite-rich bands are fine grained interlocking mosaics of sparry carbonate - Du; euhedral - subhedral - I; usually c.20-30μ dia. but up to c.50μ; often of patchy development.-Du. Loop bedding well developed; sparse fauna not completely destroyed by recry -stallisation as many coccoliths & calcispheres survive but dinoflagellates are lost because of compaction.- Do. Few uncrushed pyritised calcareous shells are preserved in the mass of rock suggesting consolidation of the cementstone before compaction had preceded as far as that in adjacent shales & clays -Do. Yet irregular tops suggest a collapse of the porosity (produced by secondary but penecontemporaneous dolomitisation) under compaction before lithification.- Du. Rhomb limestones are altered coccolith limestones - Do & infact are actually ferroan-rich dolomites or ankerites - I whose temperatures of formation varied between c.34° - 66°C. -I. *

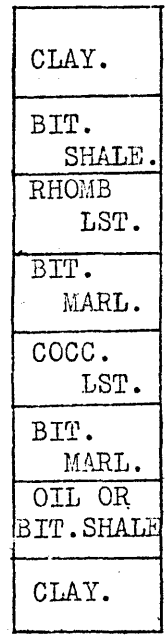
TABLE 48. KIMMERIDGE CLAY GENERALISED LITHOLOGIES. Type Section,Dorsetshire. (Key: CC - Cunningham-Craig,1916; Do - Downie,1955; Du - Dunn,1972; G - Greene,1919; H - Hallam,1975; I - Irwin Et al,1977; MM - Macleod-Mathews, 1975; S - Schlumberger,1969; Ri - Riley,1974.)
*See Bellamy,1977.Journ.Sed.Petrology.v.47.n.3 pp.973-978 for formation of Flats' megapolygons 'at a considerable depth'.

FIG. 42 SEDIMENTARY CYCLES WITHIN THE KIMMERIDGE CLAY. (After Downie, 1955 & Riley, 1974.)

6. HOUNSTOUT MARL (50ft): Clays & shales alternate to some extent.

5. CLAY NODULE GROUP: (356ft): Largely clay with bitum -enous shales occurring 9 times (between FWS stone -band & Hounstout Clay.)

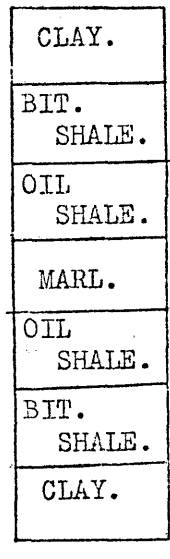
4. WHITE LIMESTONE GROUP (116ft): Above Basalt stone-band to FWS stoneband; 23 cycles, truly rhythmic.



Rapid change.
Typical benthos.
+/- Ramifying burrows.
White.
Rhomb lst may occur at base where change is rapid.
Rapid change.
Rapid change.

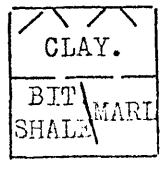
3. BASALT STONE CLAYS (74ft): Thick uniform series with no signs of any rhythms.

2. OIL SHALE GROUP (40ft): 9 cycles between the Rope Lake Head stoneband & FWS stoneband (approx).



Rapid change. (Sometimes absent)
Partings of rhomb lst. sometimes replaced by nodules.
Rapid change.

1. CLAY SHALE GROUP (455ft): 74 alternations from base to just above Rope Lake Head stone -band/base Clavell's Hard.



Rapid change; tendency for dicey fracture near top. Gradual change at base.
(Oil shales now known.)
Rhomb lsts. occassional.

area (Riley 1974).

From a trace element study, Dunn (1972) noted periodicites of 40,000, 14,000 and 11,000 years for the 'Blackstone sequence' and later in 1974 added periodicities of 200,000 and 100,000 years for the section. Several of these periods were realised to be coincident with the duration of certain astronomical phenomena which can cause climatic fluctuations (for example, 40,000 years is coincident with the period of variation in the obliquity of the ecliptic path of the Earth, whilst 100,000 years has been related to the period of variation in the Earth's eccentricity).

Downie and Wilson (unpub. from Riley 1974) have also recognised 11 year cycles within the White Bands on the basis that pairs of laminae with thick carbonate bands fluctuate with pairs of laminae containing thick organic rich layers over intervals of 8 or 16 laminae. These have been paralleled with solar radiation cycles.

10 MINERALOGY AND INORGANIC CHEMISTRY

For the Dorsetshire succession Dunn (1972) confirmed Cosgrove's (1970) statement that illite and kaolinite are the main clay minerals although it was emphasised that mixed layer (illite-montmorillonite) clays were possibly present.*

In this respect, the Kimmeridge Clay appears to confirm with general Jurassic clay mineralogy (Hallam 1975) whereas the facies equivalent from the northern North Sea Basin differs since mixed-layer clays are more dominant (Bjorlykke et al 1975). Usually for the Dorset area, illite predominates over kaolinite (Dunn 1972).

For the 'Blackstone sequence', other mineral phases include dolomite, calcite, quartz, pyrite and rare siderite (Dunn 1974). From the succession as a whole, glauconite (Lloyd 1959, Dunn 1972), garnet (Lloyd 1959), tourmaline and zircon (Dunn 1972) have been noted in thin section or macerated residues.

Sulphate sulphur was disregarded as negligble by Dunn (1972) since barytes was recorded only in a pyritised plesiosaur vertebrate and no gypsum was noted. However, Lloyd (1959) and Cope (1968) mentioned that secondary gypsum was present although Downie (1955) specified that pyrite and sulphate sulphur each remained at around the 0.5% level (indirectly relating total sulphur content to the organic matter). For the Blackstone horizon only, MacDougall and Cawley (1951), using one ton of oil shale, found that sulphur distributed itself in sulphate, pyrite and organic matter according to the respective percentages 3.3, 45.2 and 51.5. !

In 1925, Neaverson gave a detailed account of the heavy minerals for the 'Emmit Hill locality' but unfortunately no sampling horizons were indicated or can be discerned. Proximate compositions of the mineral matter are available from Himus (1951).

Generally, aluminium rich minerals were found to dominate the lower part and give way to potassic minerals in the upper part of the section. Three different suites of elements were found to be harboured in the clay minerals (K, Al, Si, Zr, Zn, Ti, Ga, Co, (Cu), (V?), (Ni)), the bitumenous fractions (Ag, Bi, Se, Mo, Ni, Cu, P, S) and the carbonates (C, Ca, Mg, Mn, (V)) whilst the 'Blackstone sequence' was seen to hold abnormal quantities of Mo, S, P, Ag and

*Bellamy (1977, Journ.Sed.Petrology, v.47, n.3, pp.973-978) has said that shales adjacent to the Flats stone-band are comprised by illite, kaolinite, and mixed illite-montmorillonite clay minerals with calcite, quartz, glauconite and often siderite.

Bi with some rare-earth elements (Table 39) concentrated in the faecal pellets. In fact a strong antipathy between elements associated with clay minerals and organic matter lead Dunn (1972) to conclude that the organic matter is not controlled by the clay content. Earlier, Cosgrove (1970) had noted that (particular horizons within) the sediments were markedly higher in Br, I and Mo as compared with an 'average' shale (Log 1).

11 RADIOACTIVITY

For the northern North Sea Basin Johnson (1975) has reported that zones of roughly equal gamma deflection bear a marked relationship to the pattern of sedimentation during the close of the Mesozoic. In fact, the highest value region shows an interesting correlation with the line of the Viking Graben and increases to the north where the maximum concentration of organic matter for the Kimmeridgian is indicated (see later; Source of Organic Matter). Inorganic trace elements such as Actinium were held responsible for the activity. (Table 39).

Although high gamma ray deflections are probable from the currently confidential borehole logs of onshore wells, Ponsford (1955) had to conclude, from a study involving Dorsetshire outcrop samples, that "the bitumenous shales such as the Upper Jurassic Kimmeridge beds" are "devoid of significant radioactivity".

12 ORGANIC GEOCHEMISTRY

Much of the early work on the Kimmeridge Clay was expressed in terms of moisture, volatile matter, fixed carbon, ash, specific gravity, 'sulphate of ammonium', sulphur in oil and oil yield per ton of rock (Table 49).

Examination of distillates was also favoured, and in fact "the process of retorting decomposes kerogen into a variety of hydrocarbons which when condensed at atmospheric temperature and pressure constitute a form of crude petroleum analogous to that occurring naturally in the reservoirs of oil and gas fields ..... The crude that results from the destruction of the shale during retorting differs somewhat in chemical composition from crude oils normally occurring in strata but it is susceptible to normal refining and disposal techniques" (Macleod-Mathews 1975).

Blacker (in Greene 1919) noted that a Norfolk Kimmeridgian oil shale distillate held 20% sulphur free saturates, 50-60% olefines and diolefines and 20% organic sulphur compounds, with the reservation that lower temperatures reduced the olefine content. "Everyone who had to do with the Kimmeridge shale oil agreed it was very highly unsaturated" and probably contained diolefines (Challenger et al 1926) although Cawley & Kingman (1944) believed much of the unsaturation and polymeric material was caused by the loss of hydrogen during retorting as hydrogen sulphide.

The high percentage of sulphur in the distillates (5-8% Challenger et al 1925) has long been a prohibitive factor in the exploitation of the Kimmeridge oil shales and many attempts to remove it have been listed (Table 50).

Yet Cronshaw did cite Forbes-Leslie (1919) in mentioning an 'upper sulphurous series' was divided by a middle practically sulphur free oil shale in the Norfolk area (?) (1920).

In fact specification of the organic sulphur compounds was attempted by Challenger et al (1926) who found very little thiophen but a considerable quantity of 2-methyl thiophen. Also 2-ethyl, 2, 3-dimethyl and tetrahydro-thiophens were noted as well as 'thionaphthen' (benzothiophene) and tetramethylene sulphide. A sulphur-ketone (possibly propylacetothienone) was observed earlier and like alkyl sulphides, mercaptans too were not held to be chief sulphur-organic

TABLE 49. KIMMERIDGE CLAY BOREHOLE ANALYSES. (From Strahan, 1920.)

Borehole.	Depth of bottom of Seam.	Description of Material.	Thickness.	Moisture	Organic Volatile Matter.	Fixed Carbon.	Ash.	Yield of Oil. Galls.	Spec. Grav. of Oil at	Sulphate of Ammonia. Lbs.	Sulphur in Oil.
	Ft. In.		Ft. In.	per cent.	per cent.	per cent.	per cent.	per ton.	15·5° C.	per ton.	per cent
Kimmeridge No. 1 B.H.	57 10	Clay	4 0	4·0	7·1	5·9	83·0	3·9	—	13·4	—
" "	60 2	Shale, inferior	2 4	2·8	13·2	8·6	75·4	13·8	—	19·5	—
" "	62 0	Clay	1 10	3·8	12·8	7·5	75·9	11·7	—	16·2	—
" "	65 0	"Short Joint" and cementstone	3 0	3·1	23·2	8·5	65·2	22·6	0·982	20·3	5·12
" "	68 0	Shale, inferior	3 0	3·7	14·4	4·7	77·2	5·6	—	7·8	—
" "	70 0	Clay	2 0	3·0	14·3	8·3	74·4	10·8	—	13·0	—
" "	71 0	Shale	1 0	2·6	18·3	9·8	69·3	19·1	—	23·4	—
" "	77 8	Shale, inferior	5 0	2·7	18·2	10·9	68·2	15·3	—	19·3	—
" "	78 10	Clay	1 2	3·9	16·0	6·7	73·4	13·6	—	21·0	—
" "	80 6	Shale, inferior	1 8	4·1	20·0	9·6	66·3	19·1	—	25·8	—
" "	85 6	Clay	5 0	4·9	7·1	4·3	83·7	3·1	—	11·6	—
" "	87 5	Shale, inferior	1 11	4·5	10·3	7·9	77·3	8·1	—	17·6	—
" "	89 11	"Blackstone"	2 6	4·2	34·6	19·3	46·1	40·6	0·987	22·7	6·16
" "	91 9	Clay	1 10	4·1	8·3	6·8	80·8	5·8	—	9·9	—
" "	96 8	Shale, clay and "pudicum"	1 9	4·2	20·7	11·7	63·4	22·6	—	18·4	—
Kimmeridge No. 2 B.H.	46 6	Shale, inferior	2 6	3·2	13·2	6·5	77·1	16·2	—	14·5	—
" "	48 3	Clay	1 9	3·8	13·6	7·3	75·3	9·9	—	17·6	—
" "	51 3	Shale and cementstone ...	3 0	1·9	22·2	12·9	63·0	15·5	—	17·7	—
" "	53 6	Shale, inferior	2 3	3·2	12·5	8·2	76·1	11·9	—	14·9	—
" "	57 5	"	0 11	2·6	18·2	9·6	69·6	19·2	—	20·9	—
" "	64 5	"	4 7	2·7	16·9	11·8	68·6	16·2	—	20·2	—
" "	65 7	Clay	1 2	3·2	12·4	7·0	77·4	10·2	—	12·6	—
" "	67 2	Shale	1 7	3·8	17·7	11·4	67·1	18·6	—	25·2	—
" "	75 1½	Shale and clay	1 11½	3·1	20·0	8·3	68·6	19·8	—	18·1	—
" "	77 4	"Blackstone"	2 2½	2·5	39·1	11·8	46·6	38·4	—	32·4	—
Kimmeridge No. 3 B.H.	24 0	Shale with "Short Joint"	2 0	2·4	23·7	11·7	62·2	23·5	—	24·7	—
" "	26 3	Shale, inferior	2 3	3·0	11·8	9·6	75·6	11·5	—	18·4	—
" "	30 6	"	1 10	2·2	16·1	9·7	72·0	14·8	—	17·8	—
" "	57 0	"	4 3	2·1	16·7	11·8	69·4	15·3	—	17·6	—
" "	40 8	"	2 4	2·8	19·6	9·5	68·1	17·7	—	23·4	—
" "	47 4½	"	0 8	3·1	14·8	10·4	71·7	15·3	—	21·6	—
" "	49 7	"Blackstone"	2 2½	2·7	31·6	13·4	52·3	34·4	—	30·7	—

Borehole.	Depth of bottom of Seam.	Description of Material.	Thickness.	Moisture	Organic Volatile Matter.	Fixed Carbon.	Ash.	Yield of Oil. Galls.	Spec. Grav. of Oil at	Sulphate of Ammonia. Lbs.	Sulphur in Oil.
	Ft. In.		Ft. In.	per cent.	per cent.	per cent.	per cent.	per ton	15·5° C.	per ton.	per cent
Corton No. 1 B.H. ...	47 11	Shale, inferior	1 8	7·2	16·2	10·7	73·1				
" " ...	50 6	"	2 7	6·3	12·4	9·8	77·8	15·0	—	3·3	—
" " ...	51 2	"	0 8	6·9	15·6	8·8	75·6				
" " ...	54 8	"Main Bed"	2 0	6·9	29·5	18·0	52·4	25·5	—	28·5	—
Corton No. 2 B.H. ...	92 8	Shale	0 8	4·1	9·5	15·2	75·3				
" " ...	95 4	"	2 8	6·5	13·9	11·1	75·0	13·6	—	11·0	—
" " ...	96 6	"	1 2	5·9	8·1	12·3	79·6				
" " ...	96 9	Clay	0 3	5·5	6·2	8·8	85·0	12·1	—	11·2	—
" " ...	98 7	Shale, inferior	1 10	7·1	13·8	8·9	77·3				
" " ...	100 0	Clay	1 5	8·4	7·2	5·6	78·8	3·0	—	9·2	—
" " ...	102 0	"Main Bed"	2 0	7·5	22·7	11·7	65·6	28·1	1·008	14·6	7·20
" " ...	103 11	Clay	1 11	7·7	4·3	5·4	82·6	2·7	—	9·5	—
" " ...	104 11	Shale, inferior	1 0	7·5	14·7	9·7	68·1	16·7	—	15·2	—
Corton No. 3a B.H. ...	16 2	Shale	0 8	8·9	15·5	11·2	64·4				
" " ...	16 9	Clay	1 7	9·0	9·7	7·3	74·0	15·6	—	13·2	—
" " ...	18 9	Shale, inferior	2 0	9·4	13·8	11·4	65·4				
" " ...	20 8	Clay	1 11	8·2	10·5	6·9	74·4				
" " ...	21 2	Shale, inferior	0 6	10·3	15·4	7·7	66·6	8·7	—	11·1	—
" " ...	23 0	Clay	1 10	9·4	7·8	5·7	77·1	5·5	—	8·8	—
" " ...	24 9	"Main Bed"	1 9	11·0	25·9	11·3	51·8	29·9	—	23·3	—
Corton No. 4 B.H. ...	85 6	Shale and clay	2 10	4·8	14·2	7·9	73·1	13·5	—	17·1	—
" " ...	88 0	Clay	2 6	4·5	11·0	7·3	77·3	7·1	—	12·3	—
" " ...	90 3	Shale and clay	2 3	4·7	12·6	8·8	73·9	7·2	—	12·4	—
" " ...	92 4	" "	2 1	4·1	11·1	9·4	75·5	7·0	—	18·1	—
" " ...	94 6	Shale	2 2	5·0	13·4	10·9	70·7	10·7	—	15·5	—
" "	95 2	Clay	0 8	4·7	8·1	5·6	81·6	4·5	—	13·4	—
" " ...	96 6	Shale	1 4	5·5	13·4	9·1	72·0	11·3	—	16·2	—
" " ...	98 4	Clay	1 10	4·6	7·9	4·9	82·6	3·7	—	11·1	—
" " ...	100 5	"Main Bed"	2 1	6·5	33·5	11·8	48·8	29·1	—	20·1	—
Domington No. 1 B.H. ...	195 3	Shale	1 0	3·59	18·88	6·74	71·36	10·4	0·959	—	4·63
" " ...	284 1	Shale, inferior	1 9	3·99	15·40	8·98	75·62	11·8	0·990	—	—
" " ...	310 9	" "	1 6	4·30	15·45	6·80	77·75	7·0	0·982	—	—
" " ...	315 0	" "	1 5	3·49	12·95	8·00	79·05				
" " ...	315 3	Shale	0 3	3·85	21·98	10·25	67·77	8·8	0·984	—	3·89
" " ...	352 8	Shale, inferior	1 3	2·99	8·70	10·61	80·69	1·3	—	—	—
" " ...	353 8	Clay	1 0	3·15	8·85	7·61	83·54	—	—	—	—
" " ...	363 5	Shale, inferior	1 10	3·40	12·67	9·81	77·52	7·0	0·990	—	—
" " ...	366 1	"	0 8	3·90	11·67	5·93	79·40	8·7	0·990	—	—

TABLE 50. KIMMERIDGE CLAY - DESULPHURISING EXPERIMENTS.

METHOD.	SULPHUR IN PRODUCT.
Distill untreated shale.	8.9%
Distil shale over red hot iron.	7.4%
Treat shale oil with mercuric sulphate.	7.4%
Treat shale oil with alcoholic mercuric chloride.	6.0%
Treat shale oil with fuming sulphuric acid.	Oil destroyed.
Hydrogenate shale oil.	30% sulphur-free spirit.
Pass shale oil over heated metallic oxides.	6.0%
Distill shale with caustic soda and lime.	6.0%
Treat shale oil with sodium plumbate.	7.2%
Distill shale oil with 8% sulphuric acid in 4:1 ratio	4.45%
Treat shale oil with aluminium chloride.	3.7%
Hydrogenate at 200 atmos. & 400°C with catalysts.	Entirely hydrocarbons.
Blend with non-sulphur oil to meet requirements.	

(Compiled from Manfield,1916; Greene,1919; Cawley & Kingman,1944 and MacDougall & Cawley, 1951.)

compounds (Challenger et al 1925). Finally, propyl-, methyl ethyl- and trimethyl-thiophens were also suspected (Challenger et al 1926).

An ultimate analysis of the 'asphaltic base oil' distillate (a high percentage insoluble in petroleum ether, 40^{o}-60^{o}C) was given as 80.9%C, 8.6%H, 1.4%N, 6.5%S and 2.6%O (Cawley and Kingman 1944) and can be compared to that for a shale oil from the St.Champ area; 77.3%C, 9.2%H, 0.04%N, 12.0%S and 1.14%O (Demeuse and Rembourg in Greene 1919).

Williams, as early as 1855, determined members of the pyridine series ($C_n H_{n-5} N$ when n = 10, 14, 16 and 18 in this case) for the sulphur free bases in the distillate of a Dorsetshire bitumenous shale and these together with the unsaturated hydrocarbons were held responsible for the horrible smell evolved during distillation (Challenger et al 1925).

It has been long appreciated that the solubility of the organic matter in the Kimmeridgian shales is low. Forbes-Leslie (1916) stated that only 1% of a rich Norfolk oil shale was ether-soluble and that carbon disulphide extracted only about 0.25%. Similarly Bitterli (1963) recorded that only 1.44% of a 'coal' sample was gas and ether-extractables whilst Bonnet (1958) and Gill et al (unpub.) for a Norfolk and Dorsetshire shale respectively cited values of 0.02% and 0.4% for soluble extracts (achieved by methods discussed under experimental work). Also, two values for bitumen extracts have been quoted after Teichmuller (1961 in Cosgrove 1970) as 'only' 4.1% and 6.8% but no technique for such relatively high figures (especially in comparison to this study) was disclosed. In 1919 Greene recorded a 5.38% bitumen extract which appears to have been won in carbon disulphide and this was possibly referred to by Cunningham-Craig (1920) who cited more than 5% free oil or bitumen (?).

A total extract/organic carbon ratio for one sample (Gill et al unpub.) is 0.06.

An analysis of a benzene extract for a Dorsetshire shale (Gill et al unpub.) has provided the data: "10% alkanes, 14% aromatics and 60% complexes" (using TLC procedures as in this study) and 63.6%C, 10.3%H and 0.2%N (by elemental analyses as described for this work).

For North Sea Kimmeridgian extracts Johnson (1975) has observed

high concentrations of zinc, copper and iron.

Organic carbon values have been reported by a small number of workers (Table 51) and Downie stated the range of organic matter as 1.6%-75.3%. Likewise Dunn (1972) recorded 'broad estimates' (Dunn 1974) of moisture, organic matter and carbon dioxide and the thermogravimetric methods of both workers entailed weight losses at 104°C/110°C, 500°C/520°C and 900°C/1000°C respectively.

Elemental analyses for organic matter in whole rock (non-deashed) samples have been offered by Downie (1955) and are reproduced in Table 52.

Kerogen isolate studies for the Kimmeridgian sediments have been fairly popular and kerogen elemental analyses are summarised in Table 53.

The colour has been found to vary from pale green to deep red brown or black but generally to be yellow or brown in transmitted light (Downie 1955). Similarly, Cosgrove (1970) agreed with Forsman, from 1963, in stating that the cellular structures were yellow-brown whilst Mebradu (1975) concluded that the Dorset palynomorphs fall into the categories 1 and 2 of Evans and Staplin (1969); being green-yellow-brown. Dunn (1972) reported a yellow-orange colour in plane polarised light with a red colour and parallel extinction under cross polarised light whereas Downie (1955) had said that the orange-yellow bitumen is pale grey with parallel extinction.

Downie pioneered the field of kerogen description in deducing (notably for the oil shales, bitumenous shales and limestone horizons) that the organic matter was dominated by dinoflagellates or coccolithospheres with a contribution of hystrichospherids and only minor wood fragments, spores, pollens and resins. In addition he found unknown bodies (*incertae sedis*, calcareous cysts, calcispheres and saccules), chitinous remains of *foraminifera*, holithurian spicules and radiolarians. However some clays were found to hold up to 90% of land-derived material and plant fragments, dominantly coniferous, were often converted to jet.

Oxidation studies upon kerogens (from different sources) have been performed by Down and Himus (1941) who found that a considerable portion of the non-volatile non-oxalic acids formed during alkaline permanganate attack are not of the type produced from coals (Table 54). In

TABLE 51. KIMMERIDGE CLAY ORGANIC CARBON DISTRIBUTION.(% By Wt.)

DORSETSHIRE.

COSGROVE,1970:

Ringstead Bay	1.1
Clacell's Hard	71.4
* 26A	39.8
$26C_1$	55.3
$26C_2$	24.5
$26C_3i$	17.9
$26C_3ii$	15.3
$26C_3iii$	34.9
$26C_4$	34.5
$26C_5$	33.9
$26C_6$	37.3
$26C_7$	33.1
$26C_8$	16.9
$26C_9$	16.7
26E	40.0
26F	20.7
35A	36.8
35B	16.3

GILL et al,unpub:

Unspecified shale	6.0

FULLER,1975:

Bitumenous shale average	3.75
Grey shale average	1.6

BITTERLI,1963:

Kimmeridge Coal	36.8

ELSEWHERE.

FULLER,1975:

YORKSHIRE.

Oil shale	30.9
Bitumenous shale average	7.95
Dark grey shale	3.4

SUTHERLAND.

Black shale average	5.5

SOUTHERN NORWEGIAN SHELF.

Amoco 2/11-1 core average		2.1
Well section	2,600ft av.	5.0
	100ft.average	10.0

*"Blake's bed numbers as listed on page 72 of Arkell's 1947 memoir" (See Composite Lithological Log; log no: 1)

TABLE 52. KIMMERIDGE CLAY KEROGEN ELEMENTAL ANALYSES.

In & after Downie,1955 From Clavell's Hard.	%C	%H	%N	%O	%S
BLACKSTONE:	74.3	8.4	1.9		
	73.3	9.1	1.9		
	71.5	8.0	2.0	10.0	8.5
	72.3	7.7	2.0	9.2	8.4
	71.3	7.9	2.0	10.6	8.2
BUBBICUM:	73.7	8.0	1.9	8.0	8.4
	72.2	8.6	1.9		
SHORT JOINT COAL:	71.3	8.0	1.8	8.7	8.4
	72.8	8.9	1.8		
SHORT JOINT CEMENTSTONE:			1.7		
	72.2	8.1	1.8	9.2	8.7
CLAY		9.0	2.1		
	67.6	7.2	1.8	15.2	8.0
BLACKSTONE, Brandy Bay:		8.5	1.8		

fact the ease of oxidation exhibited by the Kimmeridge Clay kerogen was taken to indicate a high sulphur content whilst the products suggested less than 10% aromatic nuclei within the kerogen structure.

TABLE 53. KIMMERIDGE CLAY DE-ASHED KEROGEN ELEMENTAL ANALYSES.

%C	%H	%N	%O	%S	DORSETSHIRE.
74.1	6.1	2.0		2.3	'Jet' Damon,1884 (in DOWNIE,1955.)
72.7	7.7	2.0			Blackstone
71.3	7.9	2.0			Blackstone
	8.0				Blackstone
73.7	8.0	1.9			Bubbicum DOWNIE,1955
73.1	8.0	1.8			Short Joint Coal
		1.8			Short Joint Cementstone
	7.2	1.8			Clay
72.0	7.5	1.5	10.0	9.0	"Water/ash free material" Teichmuller (in COSGROVE,1970)
69.0	7.1	1.4	13.7	8.8	Deashed oil shale, DOWN,1939.
76.4	8.4				Bitumenous shale,FULLER,1975
80.5	10.3	2.2	6.0	1.0	Smith in Eglinton & Murphy,1969 from DUNN,1972.
73.6	7.84	1.8	9.9	5.3	AVERAGE, from above. Atomic H/C=1.28;O/C=0.10
		ELSEWHERE. (Potential)			
80.1	8.7	Oil shale — Yorkshire.			(Oil)
78.9	8.1	Bituminous shale — Yorkshire.			(Oil)
78.0	5.3	Dark grey shale — Yorkshire.			(Gas/Condensate)
76.6	5.8	Black shale Sutherland			(Gas)
83.0	7.6	Amoco 2/11-1 core average — Norwegian Shelf			(Oil)
83.6	6.2	Well section, 2,600ft average — Norwegian Shelf			(Oil) FULLER,1975.

TABLE 54. KIMMERIDGE CLAY KEROGEN OXIDATION PRODUCTS.
(using alkaline permanganate) From HIMUS,1951.& DOWN and HIMUS,1941.

Percentage carbon appearing as:	Dorset.	Norfolk.
Carbon dioxide	48.8%	66.0%
Acetic acid	9.5%	1.4%
Oxalic acid	30.7%	13.4%
Non-volatile,non-oxalic acids*	10.0%	16.8%
Unoxidised	1.0%	1.6%
*Non-volatile,non-oxalic acids (40.2%C;5.3%H & 54.5%O.)		
Succinic [1]	P	P
Benzoic	P	A
σ Phthalic	P	A
p Phthalic	P	A
Mellitic (Benzene hexacarboxylic)	P	A
1,2,5,6-anthraquinone tetracarboxylic	A	P

P: Present A: Absent 1: Emended after Giedroyc.

3 SOURCE OF ORGANIC MATTER

Early ideas by Green, 1886 (1), Mansel-Pleydell, 1894 (2), Woodward, 1895 (3), Forbes-Leslie (4) and Cunningham-Craig, 1916 (5) were said by Downie to have suggested derivation by decay of animal matter (1-5) with contributions from the decay of plants (2) and a 'deeper source' (4,5) (?) whilst Conacher (1916) and Livingstone (both in Downie 1955) assigned origins to vegetable matter and 'humins, ulmins, resins and plant fragments' respectively.

The Geological Survey once subscribed to the view that the meat of cephalopods was the source (Cunningham-Craig 1920, Himus 1951) although Dunn (1972) dismissed neritic and benthonic macrofossils as quite insufficient. Cunningham-Craig (1920) himself maintained that vegetable matter was the cause and Hallam (1975) made a general observation of an abundance of vegetable matter in Jurassic bitumenous shales.

Due to a disparity in the trace element chemistry, a suggestion by Strakhov in 1969, that underwater meadows of seaweed made a contribution to the total organic matter (being deposited far from the shore), was dismissed by Dunn (1972).

Downie (1955) noted that the relatively higher hydrogen and oxygen of the organic matter did not suggest a derivation from resins or waxes and overall algal matter was actually seen to dominate. He also recorded Damon's 1884 analysis lead to the suggestion that the low hydrogen and sulphur content in jet inferred woody matter was not a contributor to the organic matter.

In 1970 Cosgrove on the basis of bromine and iodine correlations with organic matter deduced an incorporation of marine plants and Dunn (1972) agreed with the same conclusion; noting that Forsman from 1963 reported mainly phytoplankton with some plant material for the kerogen isolates. However, Riley (1974) did not believe that plankton was the prime source but Gallois (in Brooks and Thusu 1977) has assigned algal (probably dinoflagellate) blooms as the major progenitor of the hydrocarbons; although conceding limited amounts of hydrocarbons may have been generated from the associated humic and plant debris.

The most recent detailed micropalaeontological study was by Mebradu (1975) who postulated a relative increase in the number of micro-plankton and tasmanitids accompanied a decrease in miospores for both the Lower-Middle Kimmeridgian and Upper-most Kimmeridge Clay

whilst the lower Upper Kimmeridge Clay showed a converse relation. Finally it can be mentioned that the upwelling of nutrients as the cause of (in particular) the (White Band) algal blooms has been suscribed to by Downie (1955), Dunn (1972), Hallam (1975), etc. However, an episodic distribution within the succession can be related to a fluctuation in the global availability of nutrients which in turn depends upon their release from the mantle by volcanic processes. Thus, as zones of mantle upwelling have been associated with plate tectonics, the supply of nutrients is seen to be enhanced at rift margins (Valentine 1971, Irvine et al 1974 and Naylor et al 1974 in Johnson 1975).

A seasonal control, though, is superimposed upon the periods of blooming and this has been related to changes in illumination; as accentuation results from increased death due to severe inhibition of photosynthetic activity during late spring-early summer/winter periods in higher latitudes (Hallam 1972 and Reid 1973 in Johnson 1975; Hallam 1975). Such explosions ('red soups') are known to produce a jelly-like mass of bitumen globules upon the sea floor (Downie 1955) which periodically kills off the clay fauna (Rutten 1956 in Hudson and Palframan 1969).

14 PRESERVATION OF ORGANIC MATTER

On a global scale and in contrast to most other sediments vast quantities of organic matter are preserved in the Kimmeridgian succession.

Downie (1955) was the first to suggest preservation was consequent from the sheer abundance since oxidation and reworking by organisms (whose presence was indicated by the large fossil benthos) apparently proved inadequate to consume the supply of organic material. (In this respect, Reed (1977b) has estimated the sedimentation efficiency relative to the total organic productivity, for a Californian lake, as 40% since the major fraction is recycled).

More recently Hallam (1975) cited Brongersma-Saunders (1971) in declaring that restricted circulation as a control on bottom stagnation has been greatly over-emphasised at the expense of organic productivity. The Santa Barbara Basin and Gulf of California were quoted as examples where organic laminae occur in waters which contain small amounts of oxygen and it was impressed that 'stagnation' is far more widespread in shallow tropical-subtropical waters than deeper temperate-polar equivalents.

However, periodic contamination of the lower water strata by hydrogen sulphide was believed to enhance preservation still further (Downie 1955) although Forsman (1963 in Dunn 1972) later assigned preservation in general to a reducing environment. Bitterli (1963) cautiously noted that it is the degree and duration of anaerobic conditions which contribute to the factors necessary for bituminous sequences to evolve. Lately, Johnson (1975) suggested a restricted anaerobic condition, where poorly oxygenated waters inhibit the decay of organic matter, to explain the richly organic Kimmeridgian of the northern North Sea. The occurrences of infaunal and epifaunal lamellibranchs in the Dorset sections do imply sedimentation was not under truly anaerobic conditions (Downie 1955, Cope 1968, Hudson and Palframan 1969, etc).

Now, the views of "an accummulation of pyrite on the sea floor" (Dunn 1972) and "a penecontemporaneous formation of pyrite envisaged at the mud-sea interface" (Hudson and Palframan, Oxford Clay 1969) could possibly be explained by the activity of sulphate-reducing bacteria which are known to function in a wide variety of fine grain sediments deposited in oxygenated waters (Hallam 1975). Also the

formation of pyrite within the top layers of a sediment can result from the diagenetic alteration of the monosulphide hydrotroilite and thus have no direct bearing upon the conditions of bottom waters (Hallam 1975).

However, the rarity of deep infauna in the Dorset section does suggest anaerobic conditions occurred not too far from the sediment surface (Hudson and Palframan 1969).

Thus, it seems unnecessary to propose truly anaerobic conditions (and associated 'barred basin' hypotheses) for the preservation of (vast amounts of) organic matter and poorly oxygenated waters appear adequate.* To explain the overwhelming organic richness of the Kimmeridge Shales one is simply left with the logical starting point of an abnormally high quantity of initial organic matter. Although Powell et al (1975) attributed the organic matter of phosphorites to accummulation in euxinic environments, Downie (1955) did suggest that only graptolitic shales seem to exemplify genuine euxinic conditions.

(It can be recalled here, from Section I, Part 3, No.3d, that perhaps the presently available organic geochemical inference of phosphorites is one of 'oxidation' within the depositional environment. Bloxam, 1971 (and Milner et al, 1977 ?) v. Powell et al, 1975.)

* Bellamy (1977, Journ.Sed.Petrology, v.47, n.3, pp.973-978.) has stated an "abundance of organic matter, now preserved as kerogen, indicates that bottom waters were often anaerobic." !

15 TECTONISM

Kent (1949) first produced a delineation of the Wessex Basin (Figure 43); the major structures of which are inherited from Triassic times (Brookfield 1973) and very similar pictures can be interpreted from more recently available Bouger anomaly maps (Terris and Bullerwell 1965, Maroof 1974).

Specifically, Naylor and Mounteney (1975) have reported that ENE-WSW synclinal basins (roughly parallel to the south coast of England) lie in the 'Channel Basin' and are filled with rocks of Permo/Trias - Tertiary age; the western delineation of the Channel Basin being provided by the uplifted Pre-Cambrian-Palaeozoic, Cherbourg-Plymouth basement barrier.

On a global scale, the distribution of land and sea for the Kimmeridgian was very similar to that of the late Oxfordian (Hallam 1969). Although Dunn (1972) maintained that the position of outcrop with respect to the basin centre was still a matter of speculation, Lovely (1946) had stated that thinning and facies changes indicated the original northern, western and eastern limits of the basin (Mendips, Cambrian Massifand London Platform) were not "too far" from the (respective) present day outcrops (40 miles, 60 miles and c.100 miles respectively in Figure 43).

In fact, the low gradient of the depositional slope (Figure 44)has been allied to that of any stable foreland of most fold systems (Gill verb. comm. 1972) and Brookfield (1973) has emphasised that the sedimentary basin of southern England was tectonically stable throughout most of the Jurassic.

Now fine grain sediments 'far' from land show more subtle changes, with respect to their shallow fringing equivalents, for variations in the geometry of the sedimentary basin (Dunn 1972) and surrounding source areas. With the possible exception of the actual occurrence of abundant organic matter itself (see later: Environment of deposition) refined studies appear necessary to determine any consequences from 'distant' events.

Here, for example, unlike the shallow "Kimmeridgian-Portlandian" facies of the Boulonnais, the Dorset sections (surely) shows no obvious features for which a 'base level oscillation' explanation (cf. Riley, 1974) could be offered (?) Further, non-sequences such

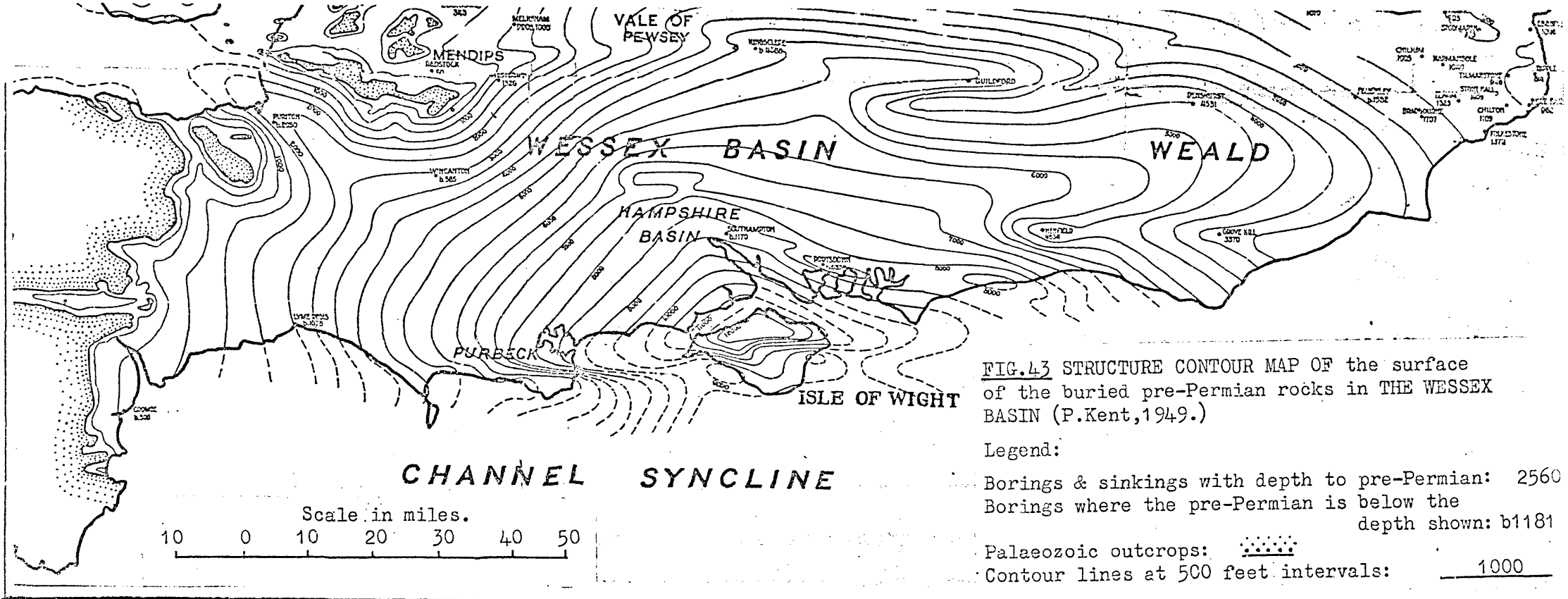


FIG.43 STRUCTURE CONTOUR MAP OF the surface of the buried pre-Permian rocks in THE WESSEX BASIN (P.Kent,1949.)

Legend:

Borings & sinkings with depth to pre-Permian: 2560

Borings where the pre-Permian is below the depth shown: b1181

Palaeozoic outcrops:

Contour lines at 500 feet intervals: 1000

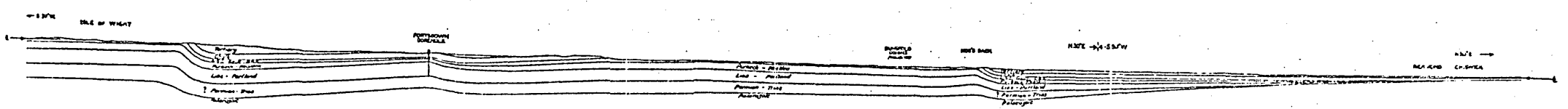


FIG 44. GENERALIZED SECTION FROM THE ISLE OF WIGHT TO LONDON

ADAPTED FROM SECTION BY K.KASHINSTORE GRAY.

SCALE: VERTICAL & HORIZONTAL

(From Lees & Cox,1937)

as those in the Oxford (2) and Swindon (1) areas have not been found in Dorset (Cope 1968).

It is not surprising therefore that the 'immediate' neighbourhood was tectonically active.

Downie (1955) noted that the Diester phase of Kimmerian movements (Arkell 1933) were most severe (in Germany) before the onset of the Upper Kimmeridgian (English sense) and a southeastward tilt of Britain was caused. (It can be recalled that (from Rayner 1967) "the lowest clays lie unconformably on the Corallian" at Oxford). More recently in agreement, Brookfield (1973) has mentioned uplift of the greater part of northwestern and western Britain occurred at the end of the Mutabilis zone; a change in the characteristics between the Mutabilis and Pseudomutabilis zones (in Dorsetshire) causing the inference of a connection with the initial opening of the Atlantic Ocean. In fact such uplift of the Scottish and Welsh Highlands was recognised as early as 1925 by Neaverson and more recently Johnson (1975) suggested a correlation with the failed 'Viking Graben' arm of the North Sea triple rift plate junction. Also, Naylor et al (1974 in Johnson 1975) proposed that a contribution to the organic shales of Dorset was made through the activity of a series of broadly trilete troughs extending along the axes of the Western Approaches - English Channel area (see earlier: Source of Organic Matter) and Downie (1955) did in fact show some nutrient supply from this direction.

A later pulse in the making of the Atlantic appears to have been recorded in the Subplanites zone (c.Basalt Band times and/or after) when increased circulation was used to explain a major change in the trace-element geochemistry of the Dorset section (Dunn 1972).

On the assumption that the Pavolvia Rotunda Nodules (Plate 17) correlate with the base of the Middle Volgian of the Russian Platform, Hallam (1975 after Casey 1971) recorded a regional uplift. Lydite pebbles were said to be derived from the (extensively exposed) Lower Carboniferous Limestone of northern England and although Neaverson (1925) thought they were absent (from the (?) Upper Kimmeridgian) in the Isle of Purbeck, Lloyd (1959) found 'minute' lydite pebbles in his quartz-type residues for the Dorsetshire succession.

Therefore, even though the London-Brabant Platform and Pennine-

Scotland areas were persistent highs (Johnson 1975), repeated tectonic disturbance occurred throughout the Kimmeridgian and effectively 'outside' the Dorset depositional area; being superbly illustrated by the 'Boulder Beds' of the Helmsdale-Brora section in Scotland (Bailey and Weir 1933).

The superficially monotonous appearance of the Dorset Kimmeridgian thus belies the surrounding tectonic regime of the time and Bitterli's (1963) remark, that favourable situations for the formation of bitumenous sequences are seen to be created at "palaeogeographic turning points", must (surely) be specifically applicable in this instance (?).

'Normal' conformable sedimentation and basin subsidence is indicated for the Wessex Basin from the close of the Kimmeridgian until the end of Wealden deposition. (Figure 45 shows the presumed position of the western land surface at the end of the Kimmeridgian). A (classic) angular unconformity then interrupts the succession as uplifting, tilting and erosion occurred before a subsequent transgression by the Lower Greensand was superseded by a more widespread Gault-Upper Greensand transgression (this area Figure 46); prior to a third successively overstepping Chalk transgression (Naylor and Mounteney 1975). The relatively small time gap between, in this case, the Kimmeridgian and the unconformable Albian sediments is typical for "basin centre" situations and contrasts with the large time intervals expressed at basin edges. (The Albian deposits sit upon New Red Sandstone at Shaldon, Devonshire; the western basin margin in this incidence). Here too, it is important to stress that the chronology and severity of the Albian unconformity (i.e. the tectonism and erosion) can assume blame for the (vast ?) reduction of the oil prospects in southern England (Gill verb. comm. 1972) (Figure 46). In fact, a pre-Upper Cretaceous uplift greater than the thickness of the Wealden sediments is indicated by the Arreton No.1 well (as derived Jurassic occurs in the Upper Cretaceous) and the Fordingbridge No.1 well shows the Lower Greensand-Upper Kimmeridgian interval missing (See Appendices).

At the end of the Upper Cretaceous (Laramide Phase) widespread uplift, tilting and erosion of the Chalk occurred prior to approximately 2,000 feet of Tertiary deposition (Eocene-Oligocene) (Naylor

FIG. 45 THE PRESUMED POSITION OF LAND AT THE END OF KIMMERIDGIAN TIMES.
(From Terris & Bullerwell, 1965)

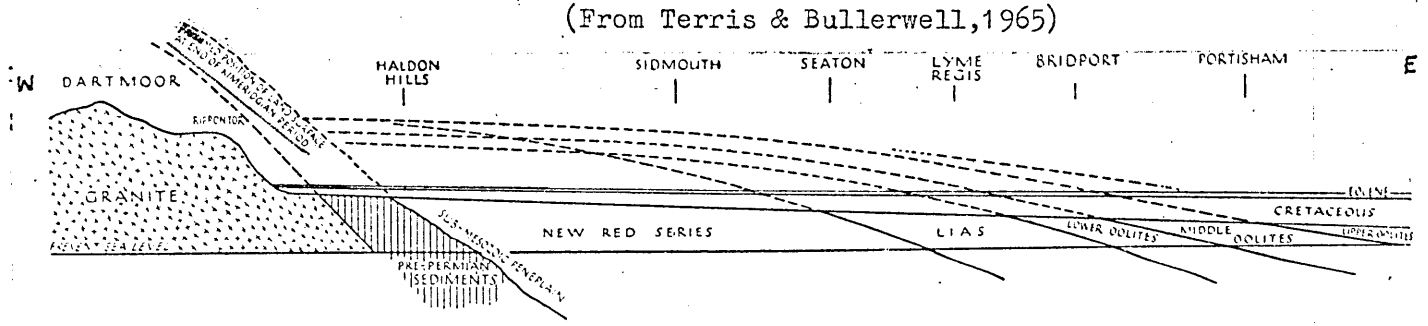


FIG. 94. Diagram to illustrate the supposed relationships of the Jurassic strata to the Dartmoor highland before the Cretaceous Transgression and erosion, assuming them to have been the same as on the margin of the London landmass, except for a deeper downcutting by the Cretaceous (here Upper instead of Lower). Supposed former positions of the Jurassic base-lines represented diagrammatically by broken lines. The highest and nearly horizontal line represents the level plain across which the Dartmoor detritus and Chalk flints from Devon were transported to the Hampshire Basin. Total distance 70 miles. Vertical scale greatly exaggerated.

FIG. 46 THE CRETACEOUS UNCONFORMITY IN LULWORTH COVE.
(From Arkell, 1947.)

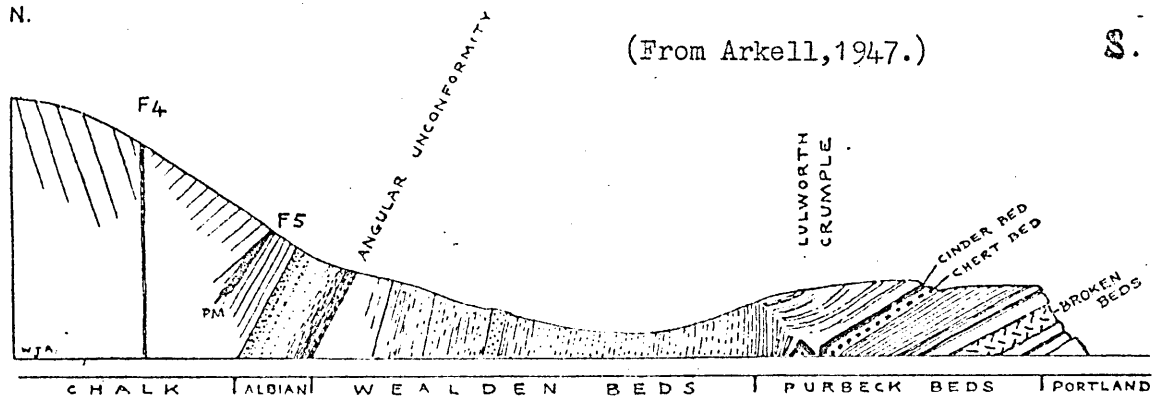


FIG. 71.—*Section in the east side of Lulworth Cove, showing the Broken Beds and the Lulworth Crumple, the angular discordance between the Lower and Upper Cretaceous beds, and faults of groups 4 and 5* (F4, F5). The hade of F4 is conjectural. P.M. = Plenus Marl. (Reproduced from *Quart. Journ. Geol. Soc.*, vol. xciv, 1938, p. 3.)

and Mountcney 1975). The Eocene does in fact overstep higher chalk divisions (Woolridge and Linton 1938 in Wells & Kirkaldy 1966). Miocene 'Alpine' earth movements then subsequently impressed the structural habit which is evident today (Figure 47). Such post-Cretaceous asymmetric en echelon folding was along parallel but not identical east-west axes; the folds being more numerous and greater in amplitude (often > 600 feet) than those in the London Basin (Figure 48) (Wells & Kirkaldy 1966). The surface expressions of such folds have played a major role in focussing early oil exploration within the district (see Appendices).

Similarly, two periods of main faulting have been suggested and the Powell Anticline (Figure 49) apparently exemplifies reversal of movement along a fault zone (Tait and Kent 1939). Elsewhere, two closely parallel faults; a normal fault of pre-Upper Cretaceous age (down-throwing to the south) and a post-Upper Cretaceous reverse fault (hading to the south) are inferred and within the Wessex Basin strike faulting is pronounced (Kirkaldy and Wells 1966). Ridd (1973), however, has offered an alternative interpretation to some of the structures witnessed today which involves a disharmonic response by the buried Kimmeridge Clay.

Consequently, the Kimmeridge Clay of Dorset is disposed in a structurally simple fashion and forms the core of the asymmetric east-west trending Weymouth-Purbeck Anticline. The Isle of Portland provides the remnant of the gently dipping (usually 5^{o}-10^{o}) south limits whilst the northern limits can dip more steeply (usually 10^{o}-15^{o}) and cause marked attenuation. (Gradients from Kirkaldy and Wells 1966). In fact the 'coal bed' is reduced to three inches in thickness at Brandy Bay (Hudleston et al 1896) and was consequently not worked there (Plate 18).

Dunn (1972) recorded fourteen faults between Broadbench and Chapman's Pool and, with the exception of the fault of unknown throw (as already noted to have a displacement of probably twenty metres - Plate 16) none were reported to have throws greater than 13 metres. However Strahan (1889-1890) did show seventeen faults for the same interval (Geological Survey, six inch to one mile) and at some horizons very closely spaced joints make it impossible to extract ammonites complete (Cope 1968).

FIG 47 CONTOUR MAP OF THE SUB-EOCENE PENEPLAIN to show the effects of subsequent earth movements (After Woolridge & Linton in Wells & Kirkaldy,1966.)

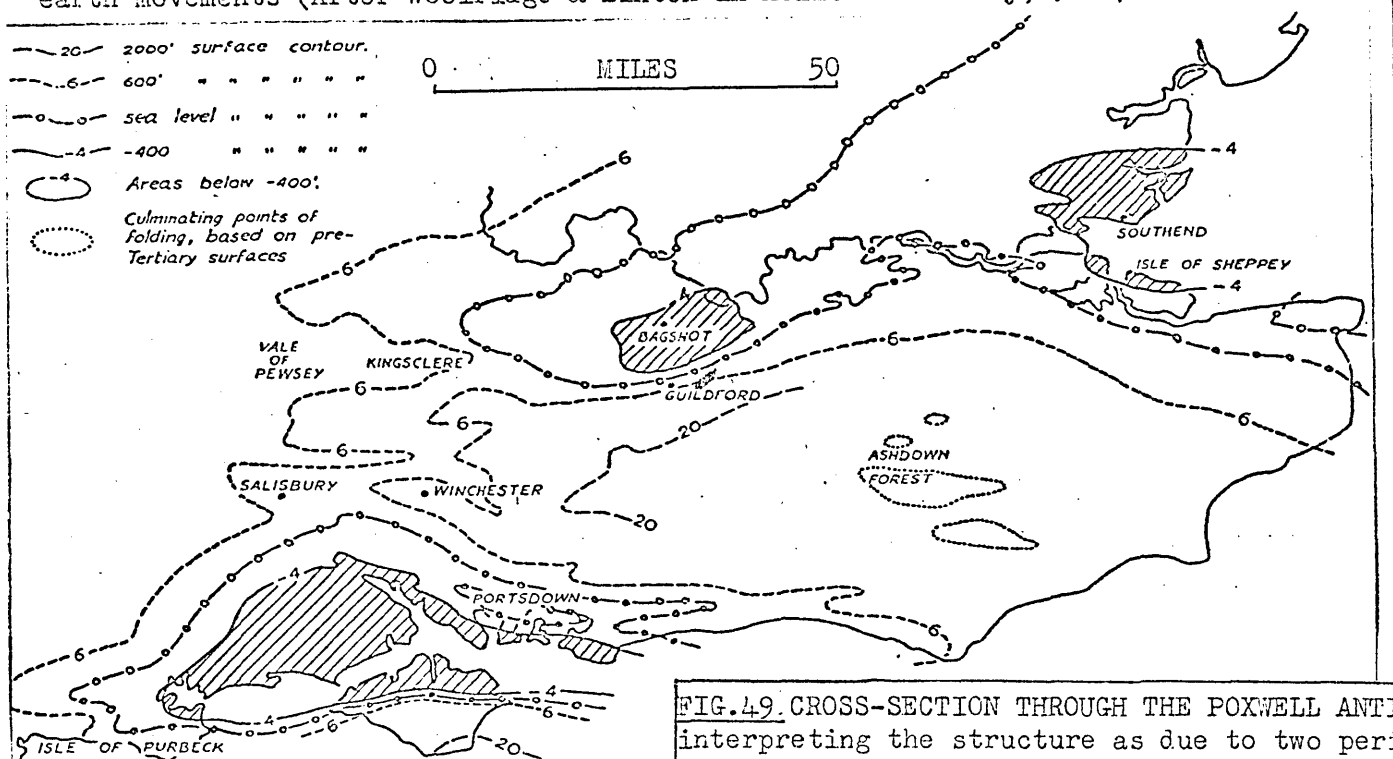


FIG.48 CROSS-SECTION (N-S) THROUGH LULWORTH COVE. (From Terris & Bullerwell,1965.)

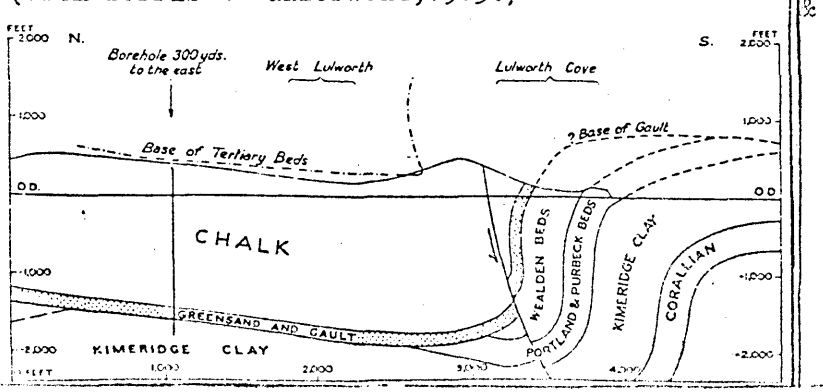
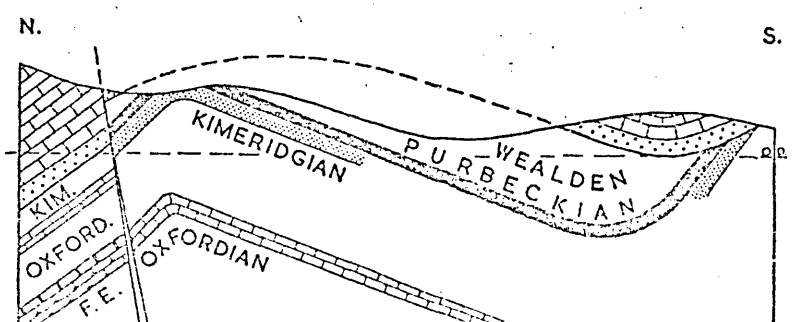


FIG.49 CROSS-SECTION THROUGH THE POXWELL ANTICLINE; interpreting the structure as due to two periods of folding: the earlier pre-Albian, the later, post-Cretaceous. (From Wells & Kirkaldy,1966 after Taitt & Kent,1939.)



16 PALAEOGEOGRAPHY

Improvement to Will's reconstruction of 1951 for the Lower Kimmeridgian was said by Downie (1955) to be unnecessary with the exception that the western channel (Figure 50) did not close so quickly, if at all.

Brookfield (1973) appears to be in general agreement by advocating a free open-sea connection between southern England and southern France; a low land area in the Western Approaches and a connection between the Wessex Basin and the Irish Sea area; especially since the latter caused some Mutabilis clays (at least) to be deposited in the Bristol Channel district (Figure 50). Sediment derivation was indicated to be from the direction of northwest France.

For the Upper Kimmeridgian Downie (1955) again employed Will's picture with the reservation that previously suspected land in northern England was known to be certain land and provide a sediment run-off to the south (Figure 51).

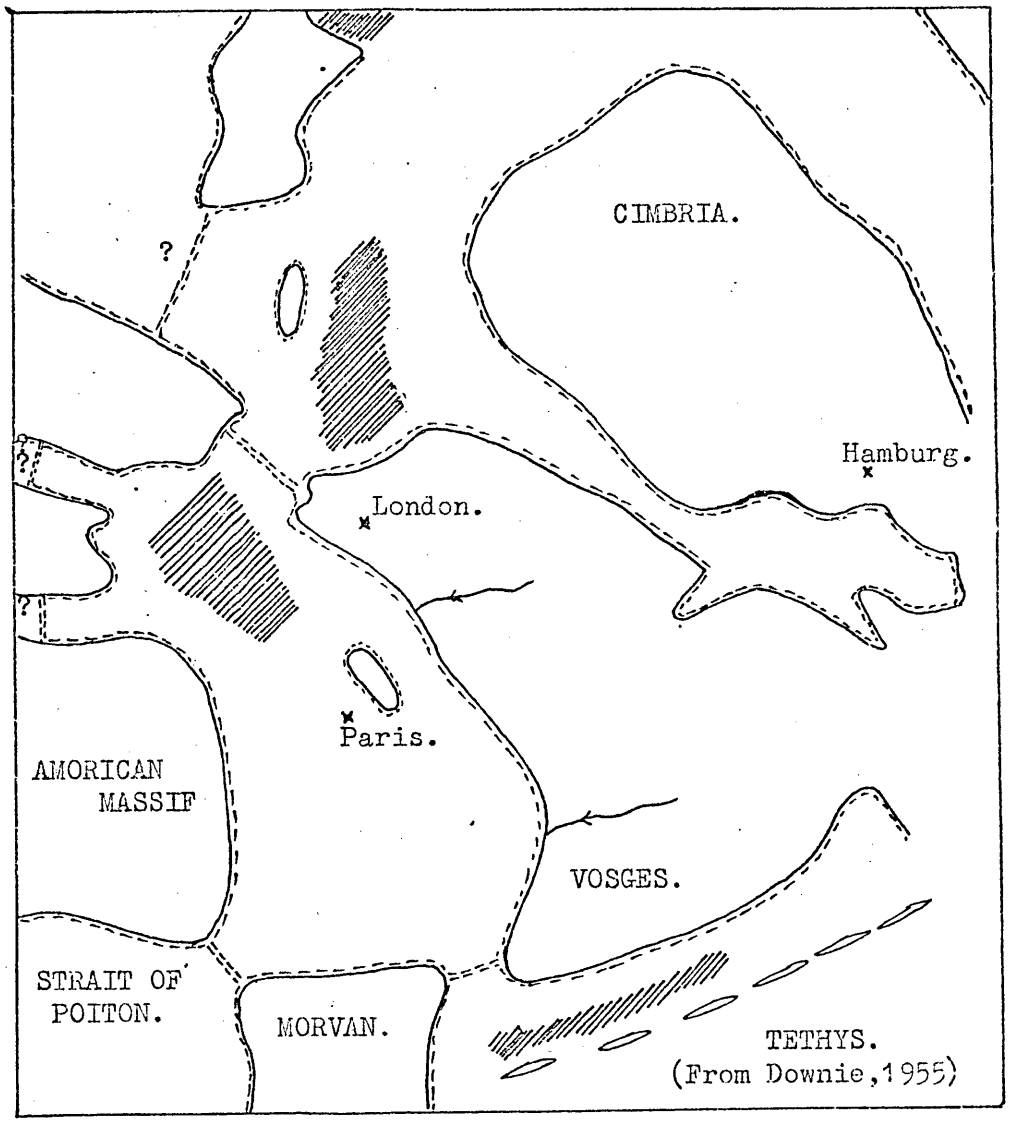
Later, Dunn (1972) modified Downie's conclusions with a rotation of 30^{o} about a polar axis situated near Paris and he suggested the nearest land mass was probably in the Swindon area (c.75 miles).

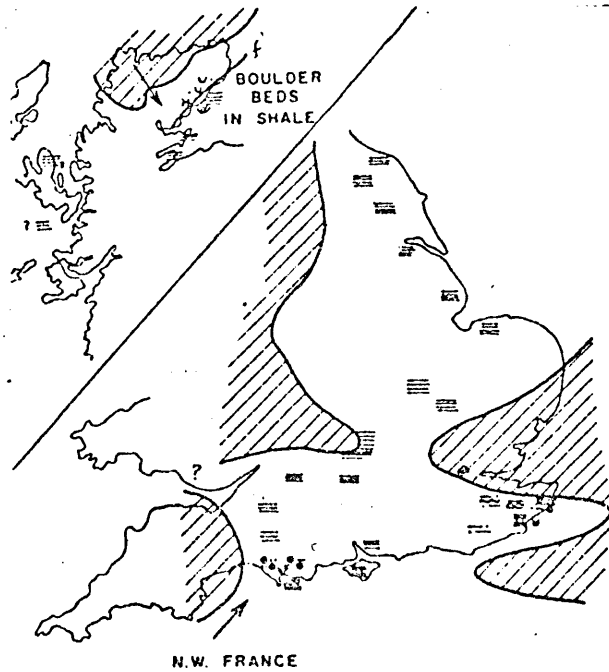
17 ENVIRONMENT OF DEPOSITION

Hallam (1967) referred to a mathematical model (of Keulegan and Krumbein 1949) where a 1:600 beach slope gradually diminishing offshore was adequate to cause little disturbance of the sea floor. Likewise, as for the Upper Domerian-Lower Toarcian and amidst an overall background of regression (Kimmeridge Clay-Wealden) such a picture seems more acceptable for the Kimmeridgian as no very pronounced deepening for a short time (end of Oxfordian-start of Portlandian) is suggested by field evidence.

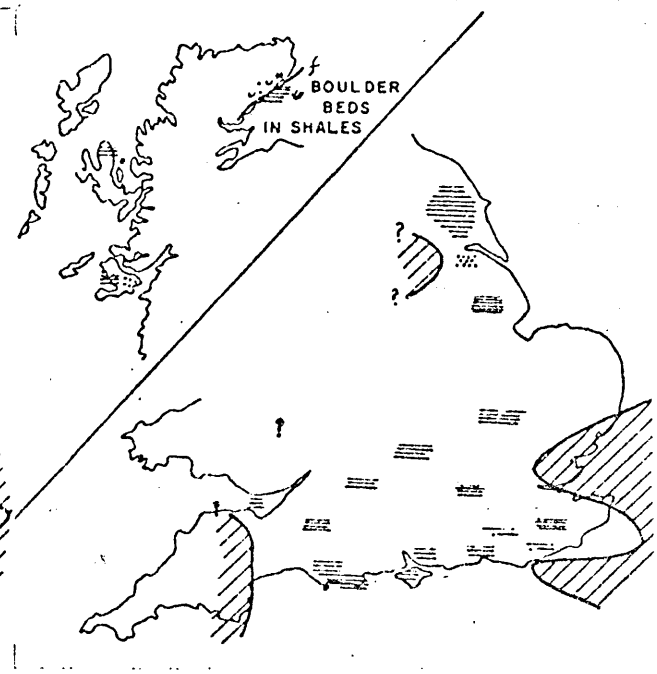
Thus, with the exception of the carbonate bands as noted earlier (Riley 1974), conditions of deposition contrary to Dunn's (1972) view do not seem similar to those of the present day Black Sea and analogy as an example of barred-basin sedimentation seems inappropriate. As any minor topographic high would impede circulation still further in the 1949 model, there seems 'no good reason to doubt that bituminous shales are relatively shallow water deposits' (Hallam 1975) and it is "highly improbable that the term 'deep water' can be applied to this (or any other British) Jurassic Formation" (Rayner 1967).

FIG. 50 LOWER KIMMERIDGIAN PALAEOGEOGRAPHY.





BAYLEI AND CYMODOCE ZONES. (Brookfield, 1973)



MUTABILIS ZONE.

In fact Bitterli (1963) envisaged a marginal or subsiding open marine basin in classifying the Dorset Kimmeridgian as typically neritic. An offshore, open sea environment was postulated by Mebradu (1975) whilst Gallois (in Brooks and Thusu 1977) has proposed an environment between that of an open ocean and an enclosed basin. *

Most recently, Irwin et al (1977) described a relatively deep basinal area within a widespread epicontinental sea although an interaction with wavebase would follow if their suspicion of possible ripples within the White Bands is verified.

Actual estimates of water depths have ranged from Dunn's (1972) moderate-shallow 200-800 metres to 15-30 metres which Hallam (1975) considered as a 'reasonable guess' and Downie, by reference to Durand's (1932) oyster study in the Paris Basin, proposed a depth of 100-120 metres in 1955.

In fact, the Jurassic as a whole had a more equable climate than the present day and thus reduced wind circulation created less oceanic currents consequently lowering the effective wave base (Hallam 1975), discouraging storms and promoting restricted circulation (Bitterli 1963).

A warm climate (Bitterli 1963, Dunn 1972), a subtropical climate (Hudson 1968 in Hallam 1975) and an arid climate (Downie 1955) have been applied or are applicable although a temperate climate (Mebradu 1975) or even a pronounced moist climate (Bitterli 1963) may have prevailed (!). Dunn (1972) even specified less than 80 cm of rainfall per year.

However Irwin et al using isotopic compositions have deduced a temperature of formation for the coccolith limestones as about 26°C. (the diagenetic nodular calcites and cementstones show subsequent subsurface values of 15°C and 34°-66°C).

The proximity of the Dorsetshire deposition to a land source has been described as "far" by Mebradu (1975) whilst Downie (1955) and Bitterli (1963) inferred "closeness". * In fact Downie gave a figure of thirty miles whereas Dunn (1972) estimated one hundred kilometres (c.75 miles) and envisaged a low lying area drained by sluggish rivers. Application of the model cited by Hallam (1967) does necessitate a "topographically subdued region".

Whatever, a picture of slow sedimentation (Cope 1968) within a sea of

no extreme salinities (Dunn 1972) can be visualised where the calm conditions promoted unprecedented spasmodic planktonic blooms (Dunn 1972). The concept of 'subsequent redistribution of bitumenous matter accummulated in coastal swamps and lagoons under periodic earth movements' (Riley 1974) appears untenable (see earlier: (Syndepositional) Tectonism).

*The sediments "were deposited in relatively deep water,at some distance from shore, in a basin that was receiving dominantly clay-grade clastics." (Bellamy,1977.Journ.Sed.Petrology,v.47,n.3,pp.973-978.)

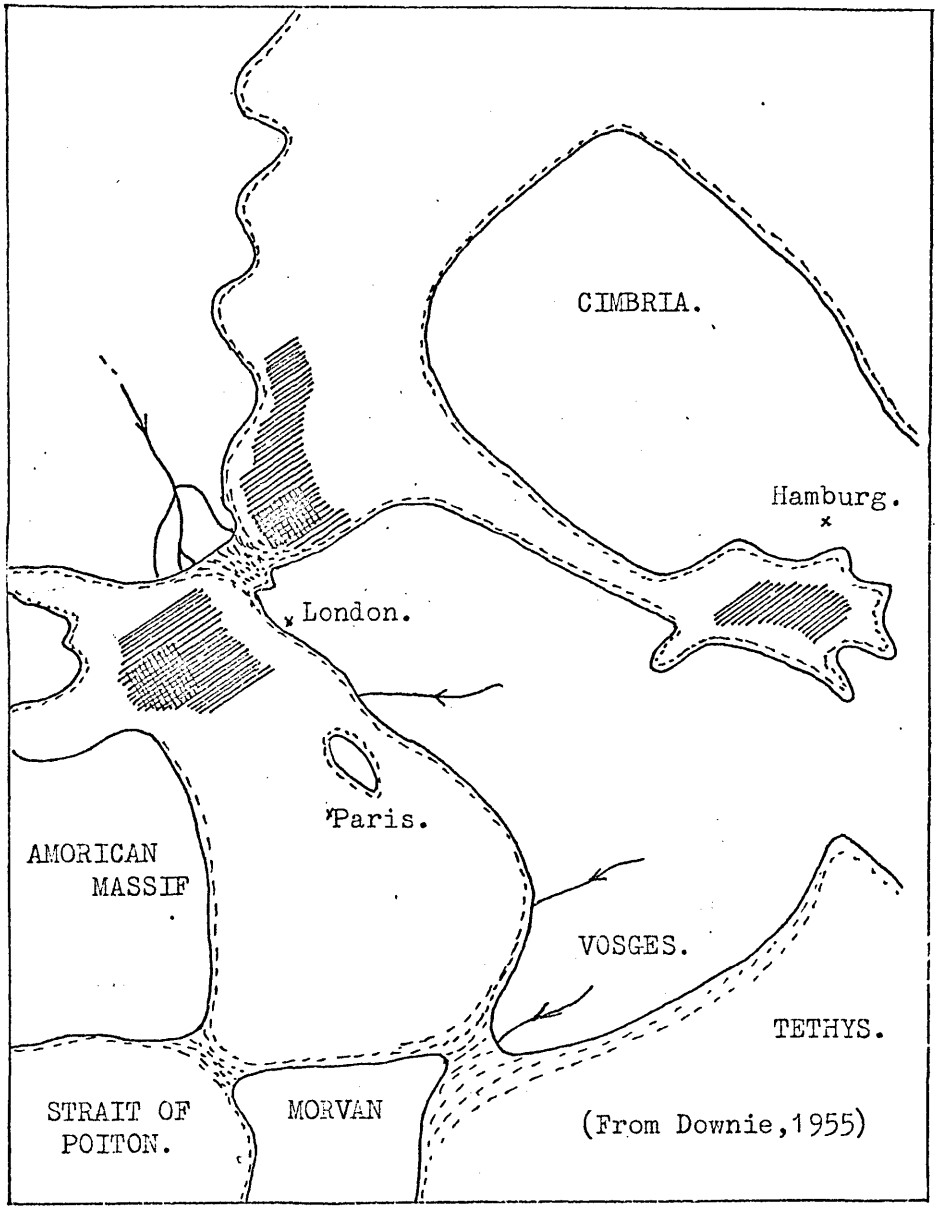


FIG 51 UPPER KIMMERIDGIAN PALAEOGEOGRAPHY.

SECTION TWO

PREVIOUS GEOLOGY AND GEOCHEMISTRY

PART TWO

THE WEALDEN FORMATION

1 INTRODUCTION AND ECONOMIC EXPLOITATION

With the exception of Lees and Cox (1937) and Lees and Taitt (1945) the Wealden Formation, outside the type area, has received little original contribution in a petroleum geology context. Similarly geological study in general is preferentially orientated to the type area: the Weald of southeast England.

Accordingly the economic geology of the Weald has been discussed by Highley (1975) where the Wealden Formation has provided paving stones and roofing tiles (Horsham Stone) and still yields brick clays (from the Ashdown Sand, the Wadhurst Clay, the Tunbridge Wells Sand and most notably the Weald Clay). A brick clay (which usually contains disordered kaolinite or illite or a mixture of the two as the main clay mineral) was once won from the Wealden on the east side of Lulworth Cove at approximately 225 feet up from the base of the Formation (Arkell 1947).

2 LITHOSTRATIGRAPHIC BOUNDARIES

In the type area, the Formation is traditionally divided into two subdivisions: an upper Weald Clay and a lower Hastings Beds to which three and six members are respectively assigned (Rayner 1967) and Kirkaldy (1975) has briefly indicated their historical origin (Table 55).

However, in the Wessex Basin the Formation is usually divided into an upper Wealden Shales and a lower Wealden Marls (Rayner 1967) and further segregation is difficult (Arkell 1947).

Webster and Fitton observed conformity between the Purbeck and Wealden Formations in both the Weald and Wessex Basins and united the two as a single unit (Arkell 1947) whilst Lamplugh et al (1923) have noted similar conformity in Kent.

In fact "no line can be drawn which does not either include beds of Purbeck type in the Wealden or beds of Wealden type in the Purbeck; the two Formations being absolutely inseparable" (Strahan in Arkell 1933).

However, although Chatwin (1960) subscribed to the view that no definite line could be drawn on lithological and/or palaeontological grounds, the Wealden was noted to overstep the Purbeck and older strata to the west.

Accordingly, the top of the Purbeck (i.e.base of the Wealden) has

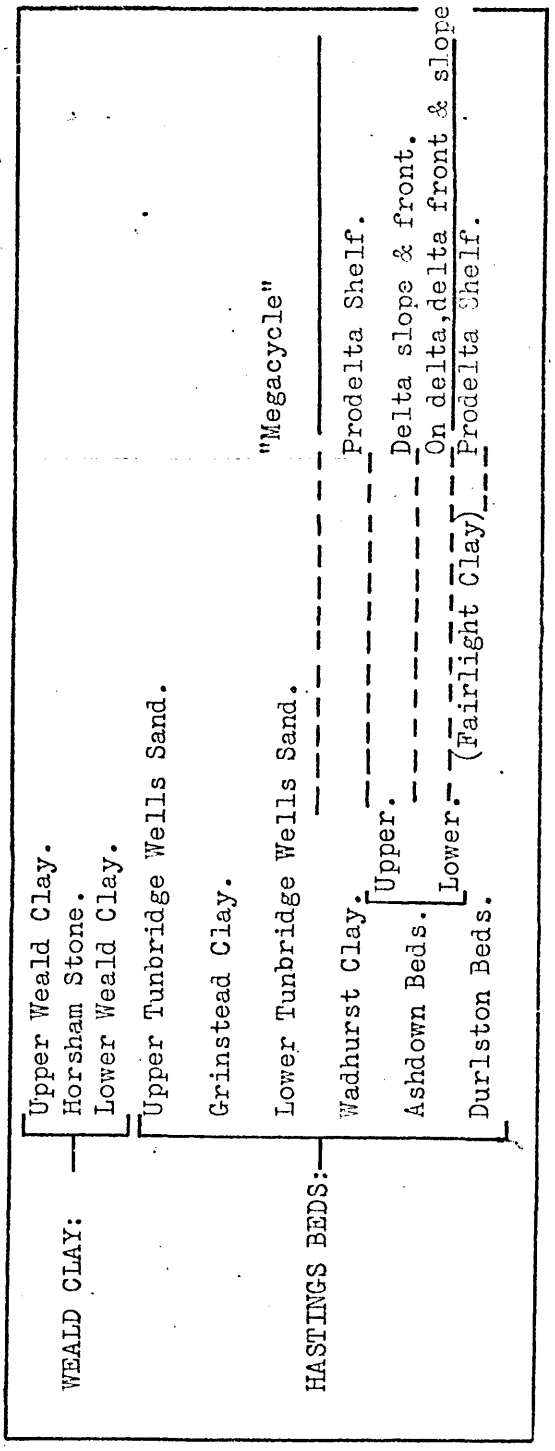


TABLE 55. WEALDEN FORMATION SUBDIVISIONS (TYPE AREA) Compiled form Hatch & Rastall, 1965 Rayner, 1967 & Allen, 1975.

Upper Greensand & Gault:	Albian.	106
Lower Greensand:	Aptian.	112
Unconformity.		
Weald Clay:	Barremian.	118
	Hauterivian.	124
Hastings Beds:	Valanginian.	130
Middle & Upper Purbeck:	Ryazanian.	136

Compiled from Rayner, 1967 & Allen, 1975. Age in millions of years to base of stage.

TABLE 56. WEALDEN FORMATION: BIOSTRATIGRAPHIC & CHRONOSTRATIGRAPHIC SUBDIVISIONS.

been approximated at the top of the Upper Cypris Clays and Shales (Evans, WE. verb. comm. 1973).

In contrast the upper boundary in Dorset is marked by the unconformable transition to the lithologically different Upper Greensand-Gault (which has already been mentioned under Kimmeridgian (post depositional) tectonism).

It is interesting to note here that if the 'Neocomian' transgression had not caused an unconformity to cut strata (at least) as old as the Kimmeridge Clay (in Yorkshire, Lincolnshire and Norfolkshire) Arkell (1933) proposed siting the Jurassic-Cretaceous boundary at the top of the Wealden. Nowadays, the Cinder Bed (Purbeck Formation) is generally taken to mark the transgression throughout Europe which initiated Cretaceous deposition (Naylor and Mounteney 1975).

3 BIOSTRATIGRAPHIC AND CHRONOSTRATIGRAPHIC BOUNDARIES

Through a lack of macrofauna the (continental) Wealden Formation of southern England and its subdivisions have been approximated to the (marine) Neocomian stages of northeast England, (Table 56); on the strength of the micro- and megaspore content (Hughes 1958).

Radiometric dates for the bases of approximately equivalent Neocomian stages have been applied to Table 56.

4 FORMATION THICKNESS.

As early as 1873, Mansel-Pleydell recorded a marked westward attenuation for the Wealden strata in the Wessex Basin by noting 1800, 725, 660, 462 and 172 feet of sediments at Swanage, Worbarrow, 'Mewps', Lulworth Cove (east side) and Man O'War Cove (Durdle Door, east side). Arkell (1933) in fact recorded the disappearance of the Wealden 'before Bridport is reached' and in particular the Wealden Shales thin westwards from 34½ feet at Swanage through 12 feet at Corfe and are missing at Worbarrow (Arkell 1947).

As Cunningham-Craig (1937) recorded as much as 2,200 feet for the thickness of the Wealden Formation in Kent boreholes, only 785 feet of equivalent strata at Portsdown (Arkell 1947) has lead to the concept of a swell separating the Wessex and Weald depositional basins (Dingwall 1971).

5 OUTCROPS

Owing to the parallel juxtaposition of the rock formations with the

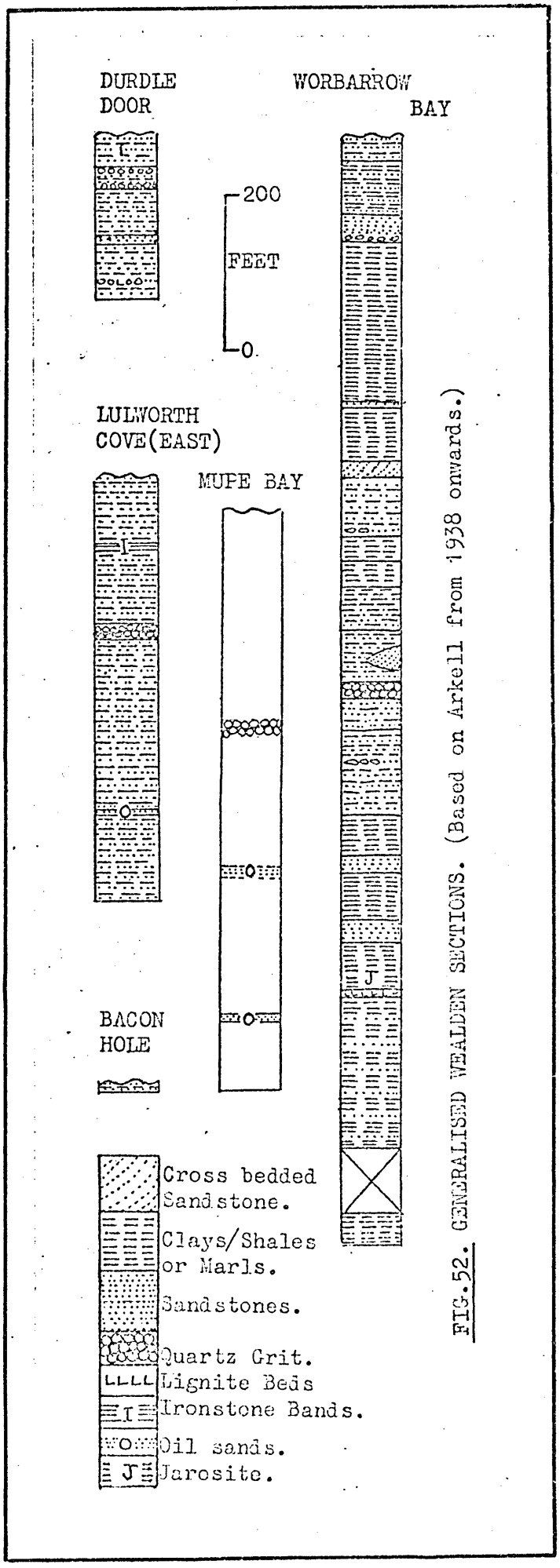


FIG.52. GENERALISED WEALDEN SECTIONS. (Based on Arkell from 1938 onwards.)

coastline and their differences in resistance to weathering, a spectacular 'Dalmation' type coastline has been developed in the Isle of Purbeck; where, in particular, marine erosion has successfully attacked the 'soft' Wealden in relative preference to the 'hard' Portland rocks. Thus, the Formation provides six (main) outcrop sites where its narrow strike is cut by the coastline and generalised sections (based on Arkell) for the steeply dipping and sometimes (strike) faulted exposures are given in Figure 52. (A location map is given under the Appendices). Today, like (too) many of the Mesozoic exposures along the south coast, the outcrops are in a very poor, slipped and often concealed condition. (Here in particular see Plates 19, 20, 21 and 23).

6 LITHOLOGY AND CYCLICITY

In the Wessex Basin, the upper Wealden Shales include grey, locally shelly limestones, clay ironstones and sandstones within a host of evenly laminated dark shales and contain gasteropods and abundant ostracods.

The lower Wealden Marls are a series of variegated marls and sandstones alternating with mottled clays; where bands of quartz grit and conglomerate, usually with a ferruginous cement, wedge out laterally (Rayner 1967).

Megacycles for the type area have recently been listed by Allen (1975) but are not recognisable in the Wessex Basin (Rayner 1967). (A 'megacycle' as explained by Hatch &Rastall (1965 after Allen 1959) is annotated on Table 55.

7 HYDROCARBONS

Upper Purbeck-basal Wealden gas shows are reknown historically for the type area (especially Sussex) although, with the notable exception of the rich Chilley oil sand (Table 57), minor oil stains are sometimes found and/or chloroform solutions are readily coloured.

(Adcock 1957, 1963; Bromehead 1923; Buckman 1967; Daily Graphic 1902; Dawson 1898; Edmunds 1923; Hewitt 1898; Highley 1975; Lees and Taitt 1945; Milner 1922, 1964; Reeves 1945, 1948; Roberts 1938; Strahan 1920; Warman et al 1956). Details are annotated in the Appendices.

The presence of oil sands in the Wealden of the Wessex Basin was first realised by Lees (in Lees and Cox 1937) and all the strike outcrops, with the exception of Durdle Door (that has now been trampled into

PLATE 19 WEALDEN OIL SAND, DUNGY HEAD.



PLATE 20 WEALDEN OIL SAND, STAIR HOLE.



PLATE 21 WEALDEN OIL SAND, LULWORTH COVE.



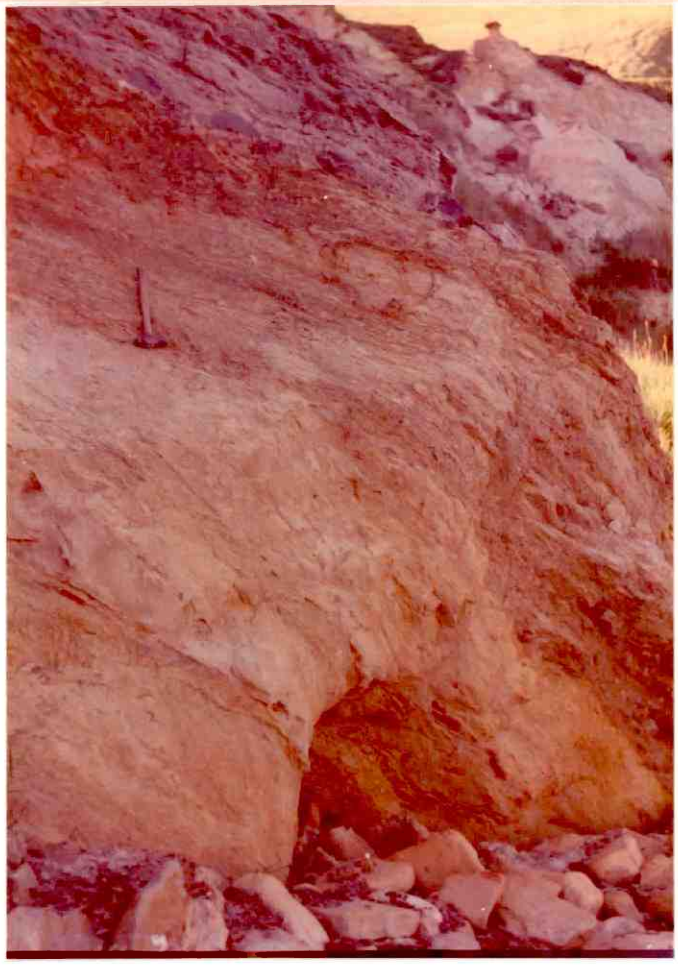


PLATE 22 WEALDEN OIL SAND, MUPE BAY.

PLATE 23 WEALDEN OIL SAND, WORBARROW BAY.



TABLE 57. PREVIOUS DETAILS OF THE WEALDEN OIL SANDS.

CHILLEY :	Approximately in the middle of the Tunbridge Wells Sand. Reknown since Mantell,1833. About 8 feet thick; 25% by volume or 12% by weight black viscous oil,of 0.995 specific gravity, achieved by benzene extraction. Sulphur content in oil is c.0.66%
LULWORTH COVE:*	0.15% Benzene extract; 1.85% Benzene-methanol azeotrope extract; 3.73% organic carbon. Benzene extract = 53.44%C,8.61%H & 0.43%N ; 17% Saturates,38% Aromatics & 44% Asphaltics by tlc.
MUPE BAY:	Coarse sandstone boulder from the conglomeratic oil sand contained 7.9% by weight of oil.
WORBARROW BAY:	An oil sand approximately two-thirds up from the base of the Formation showed 2.83% of oil which has a specific gravity of 0.96
*From Gill et al,unpub. Otherwise after Lees & Cox,1937.	

oblivion under the feet of tourists), still reveal the saturated sands (Plates 19-23 inc.).

Initially the discovery of the oil sands stimulated the prospects of oil exploration in the Wessex Basin and even as late as 1966 it was thought that "Cretaceous accummulations may be awaiting discovery" (Brumstrom). However, the early drilling activities (Lovely 1946) have continued to be unsuccessful for such targets (Falcon and Kent 1960).

Organic geochemical data for the Wealden Formation is summarised in Table 57 and it can be mentioned that " a lignitic phase dominates the Wealden Clays" (Cunningham-Craig 1937). The hydrocarbons usually have less than 1% sulphur (Miscell.).

8 TECTONISM

Pre- and post-depositional tectonism can be derived from the discussion for the 'Kimmeridgian' situations; the latter (with its ensuing erosion) being responsible for the drastic (westward) thinning of the Formation.

Syn-depositional tectonism has more recently been acclaimed as a major control of sedimentation within the Weald Basin where faulting, not warping, has been suggested; with eustatic, geomorphic and/or sedimentological influences achieving only secondary status. In fact, vertical movements in southern England, Germany and Spain (during the Osterwald phase of the Kimmerian) were considerable but uncc-ordinated and the final decay of horst topography happened earlier in the London-Kent area than in south-west England (Allen 1975).

Thus, an active hinge line between a gentle basinal subsiding foreland slope (Figures 43 and 44) and the horst block source areas must have existed and there is now some evidence for this (Allen 1975).

9 PALAEOGEOGRAPHY

A reconstruction is offered in Figure 53 from Rayner 1967 (after Allen 1965) who said the postulated "Portsdown Swell" not only explains the thinning of sediments within this area but also accounts for the more marine influence in the Wessex Basin (Lamellibranchs from the Isle of Wight show a 'Spanish' affinity).

Heavy mineral studies (in east Purbeck) have suggested a derivation from Dartmoor Granite (Kirkaldy in Chatwin 1961) (Figure 45) and the Start-Cherbourg area has been upheld as positive (Dingwall 1971).

10 ENVIRONMENT OF DEPOSITION

Although a littoral-estuarine environment was postulated by Cunningham-Craig (1937), until recently, the long established unquestioned picture was one of deltaic deposition (Lovely 1946, Rayner 1967, Taylor 1963) where 'delta-switching' caused an intercalation of predominantly freshwater-brackish and marine rocks through the abandonment of and return to delta lobes. In fact, for southern England, extensive lagoonal and deltaic flats were envisaged (Kirkaldy in Chatwin 1960) "across two slowly sinking depressions" (Naylor and Mounteney 1975).

However, Allan (1975 and in preparation) has been self-critical in advancing a new model of no known modern analogue. A "demi-graben x Maracaibo Basin" with partial enclosure by active horsts is thought to have allowed high frequencies of floods on an 'Algerian or Tunisian' scale.

Thus, braided stream (arenaceous) deposition off uplifted horsts (under rejuvenated erosion) with possible confluent alluvial fans was terminated by subsequent geomorphic decay of the source blocks or their downfaulting (during periods of relative tectonic quiesence) when transgressive mudswamps reasserted themselves.

FIG 53 WEALDEN PALAEOGEOGRAPHY.

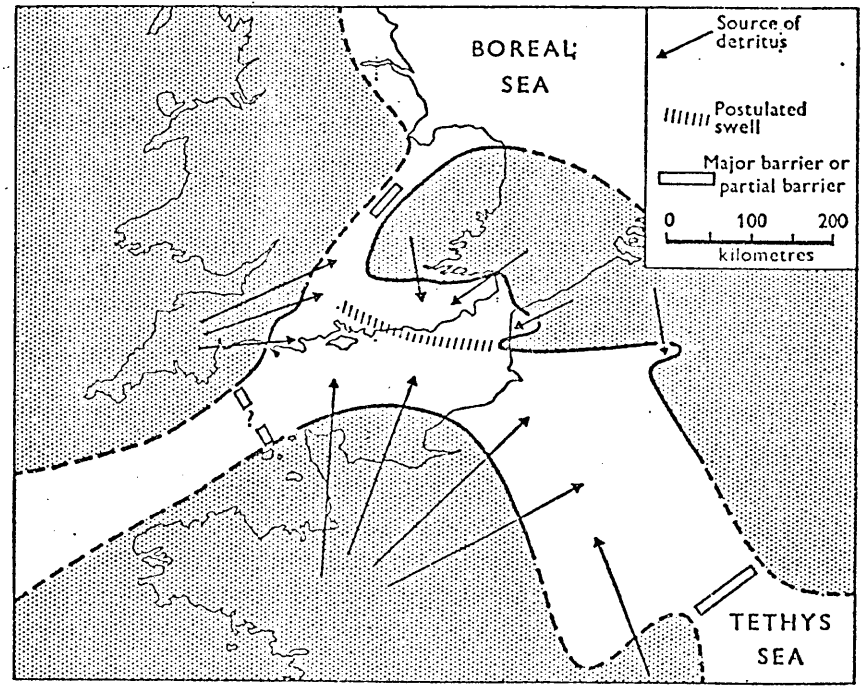


Fig. 64. Palaeogeographic reconstruction of the Anglo-Parisian Basin in Wealden times, showing the barriers separating the basin from the northern and Tethys seas and the sources of detritus. A low swell or ridge is deduced to extend eastwards from Portsdown to the French coast. Within the British sector the boundaries of the Cornubian uplands and London Platform are fairly certain but those in the midlands and north are much less so. (From P. Allen, 1965, p. 324.) in Rayner, 1967.

SECTION THREE

RESULTS AND INTERPRETATIONS OF THIS STUDY

The following interpretations of the results of this study have been made in the main by analogy to the General Results and Interpretations of established organic geochemical work described and discussed earlier (Section One, Part Three). Accordingly where all references have been previously cited they are not repeated here (only additional points are referred) and experimental data for the Kimmeridge Clay and Oxford Clay are tabulated in the Appendices.

PART ONE: THE KIMMERIDGE CLAY FORMATION

1 SOLVENT EXTRACTION

The variation in the percentage by weight of the total SOE is illustrated in Log 3 stratigraphically. Actual ranges extend from 0.02% (KC116) to 2.48% (KC67) and the loose boundary at "a few tenths of a percent of organic matter" (0.2%) has been delineated. In general the quantity of SOE falls off from above the Freshwater Steps Stoneband (KC74); the decrease perhaps being slightly more accentuated from the Hard Shale upwards. Elsewhere only a small "Basalt Band" interval (KC57-62) is equivalently low in SOE although the occasional 'isolated' cementstone and shale is conspicuously low in SOE (KC5, 12, 22, 39, 44, 69). The average extract percentage for all the section is 0.4% and the figure for KC87 (in consideration of its other characteristics) is anomalous.

The physical nature of the extracts is reported in Log 8 where mobile liquids through viscous and very viscous liquids to soft solids with or without crystalline aggregates have been distinguished at room temperature.

The colour varies from yellow (low SOE) to dark brown-black (large SOE) and the variation appears to be a 'concentration' effect.

Therefore, a little less than two thirds of the section is seen to contain more soluble organic matter alone than the minimum postulated for organic matter as whole to enable the parent rock to have source potential.

Also, the physical nature of the extracts is apparently close to that described for asphalts.

2 FRACTIONATION

For all the section, the average gross composition is 18% saturates, 11% aromatics and 71% asphalts.

The average non-hydrocarbon/hydrocarbon ratio is approximately $2\frac{1}{2}$:1

whilst the saturates/aromatics ratio averages at 1.6. Stratigraphic variation of the SOE composition is illustrated in Log 4 whilst that for each of the two ratios appear on Log 3. Excluding KC3, 43, 67, 99 and 106, the actual ranges are 4.8% (KC39) - 37.3% (KC22) saturates, 1.2% (KC112) - 28.5% (KC109) aromatics and 49.2% (KC87) - 89.6% (KC39) asphalts. The nonhydrocarbon/hydrocarbon and saturates/aromatics ratios extend through 0.8 (KC88) - 12.1 (KC43) and 0.32 (KC109) - 7.72 (KC26) respectively.

A relatively high saturate percentage occurs for KC67 (48.2%) and although the aromatic fraction is small in some other cases it is very low for KC43, 99 and 106.

The saturates/aromatics ratio is larger than 8 in the cases of KC43, 57, 58, 99, 106 and 112 whilst it is less than 1 for KC3, 10, 11, 14, 27, 32, 33, 49, 53B, 69, 82, 93, 101 and 102.

Values greater than 6 and lower than 1 for the nonhydrocarbon/hydrocarbon ratio are shown by KC39, 43, 105 and KC3, 67, 72, 87, 88 respectively.

Here it should be mentioned that throughout only a one phase/single development (n-heptane) tlc procedure has probably weighted the asphalts with a "larger-than-usual" aromatic content (especially in comparison to column elution with solvents of increasing polarity). Also, almost invariably, the aromatic fraction defined itself under incident UV light with a 'diffused' mauve fluorescence where colour banding was either very poorly developed or entirely absent. Despite filtering some silica gel managed to contaminate the fractions and due to the relatively drastic extract solution evaporation the saturate fraction in particular is preferentially low.

Accordingly an average percentage by weight yield of hydrocarbons can be derived (0.4 x 29%) as 0.12 or be expressed as 12×10^4 ppm. Now, the section is seen to fall into the category of excellent source rocks (Table 27) which even embraces the lowest hydrocarbon yield (KC116).

Although the large percentage of asphalts/low hydrocarbon content in the SOE and the low saturates/aromatics ratio (<2) suggest immaturity, the actual value of hydrocarbons is more than 20% and the nonhydrocarbon/hydrocarbon ratio much less than 6:1. Some degree of thermal evolution is perhaps suggested (?). The diffuse fluorescence

exhibited by the aromatic fractions can be attributed to a concentration of alkyl substituted polycondensed aromatic hydrocarbons whose presence in such dominance infers immaturity.

3 GAS-LIQUID CHROMATOGRAPHY

The GLC results for 47 samples of the total saturate fractions are expressed conventionally as bar diagrams (peak areas) in Figure 54 where the respective sample number, CPI, Pristane/Phytane ratio and Pristane/nC_{17} alkane ratio are given in sequence from the left hand side.

With the exception of KC116, 113 and 106 (Figure 55) and caution that even highly efficient GLC resolution without molecular sieving is not absolute, an odd dominance prevails where the average CPI for all of the samples is 1.3. Usually, a branched-cyclic/naphthenic envelope occurs; sometimes being very significant and the average pristane/phytane ratio is 0.8 ranging from 0.4 to 1.3. The pristane/nC_{17} alkane ratio extends from 0.5 to 2.6 and averages at 0.9. The n-alkane distributions are seen to be generally bimodal and centred about nC_{17-23}(ODD) and nC_{25-29}(ODD). Preference to focus over the LMW region or a tendency for a more equal distribution over both regions exist. Only in KC61, 82, 90, 92, 102, 110, 116 can a slight-pronounced bias to the HMW region be suggested or observed. Typically one or two alkane components seem to dominate a distribution.

In fact, KC127 (Figure 56) shows a (classic) focus upon the nC_{21} alkane and over the LMW region whilst KC110 (Figure 57) exhibits the bias to the HMW region centred around the nC_{25} alkane KC99 illustrates the more equal bimodal distribution (Figure 58).

From the average CPI the section is seen to lean towards an immature diagenetic condition although it is close to the upper index limit for a functioning source rock (1.2). The branched-cyclic/naphthenic envelope, however, seems typical for rocks of an immature status. The even dominance given by the three samples, which actually lie near to or at the top of the formation, could be explained by a derivation (in part) from higher plant material which do not conform to the general pattern for n-alkanes. Alternatively, a different mechanistic origin via reduction and not decarboxylation from a precursor is perhaps conceivable (?).

Assuming an immature state of diagenesis prevails, an overall dominant

FIG.54 KIMMERIDGE CLAY GLC RESULTS. C_{15} - C_{30} n-alkanes from total saturate chromatograms expressed in bar diagram form (approximate peak areas) with sample number, CPI, pristane/phytane ratio and pristane/n-C_{17} alkane ratio reading from left to right.

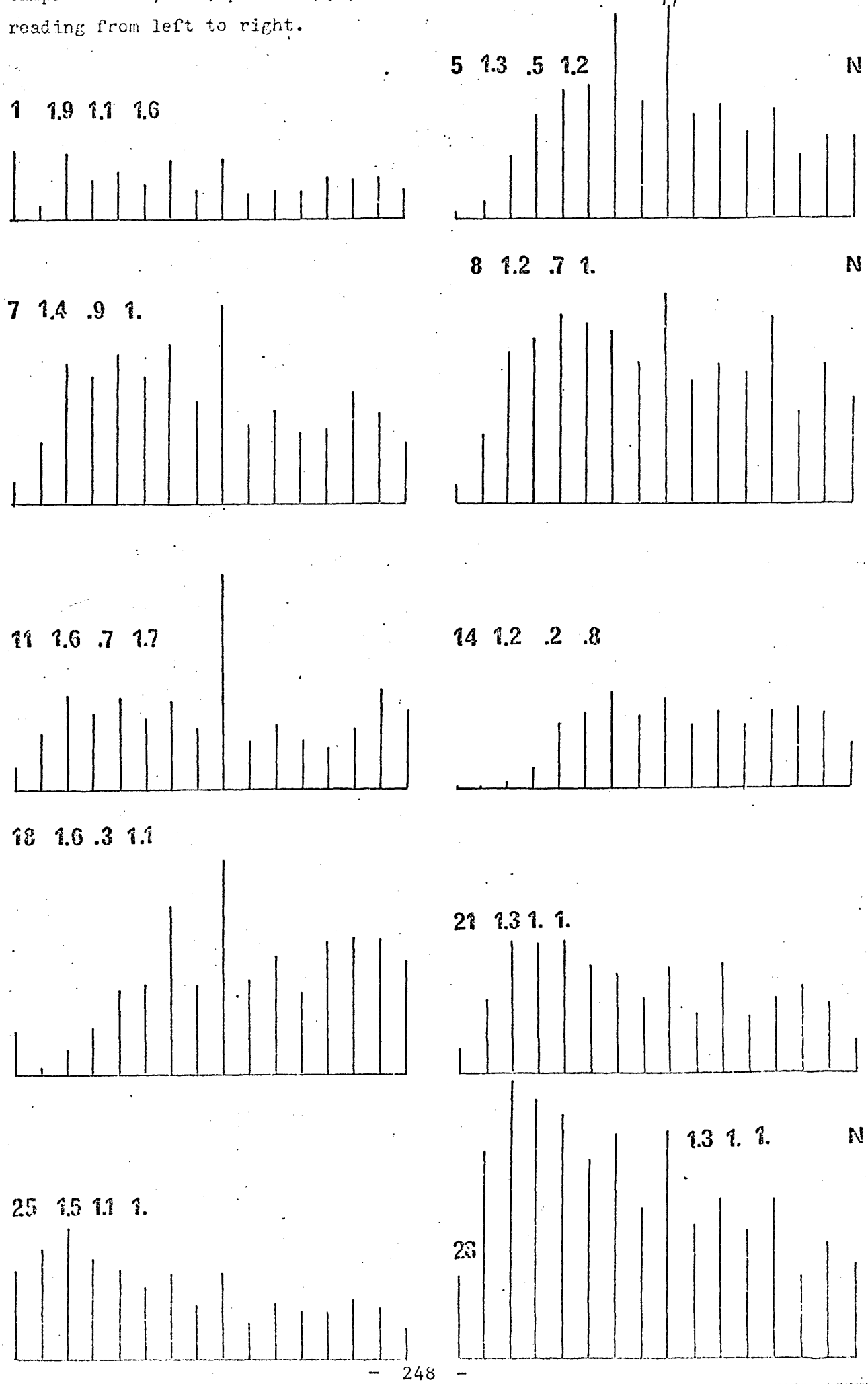
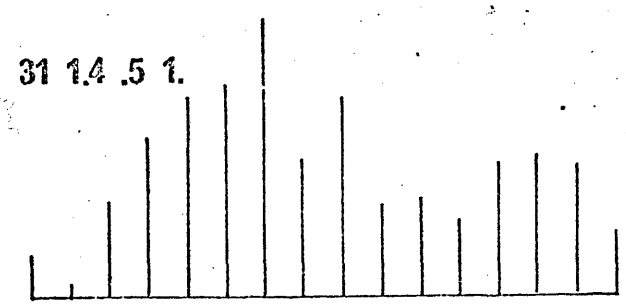
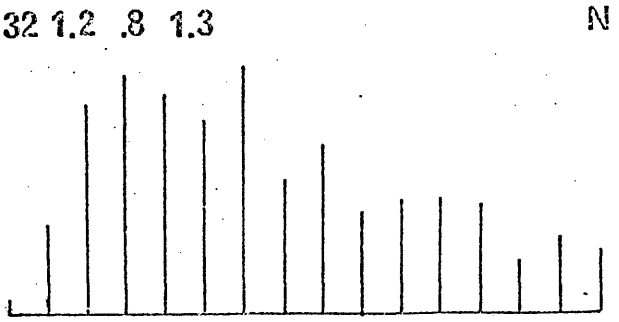
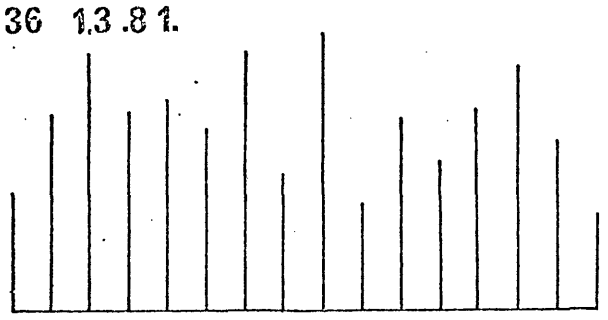
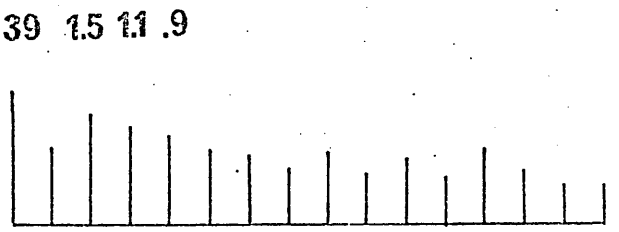


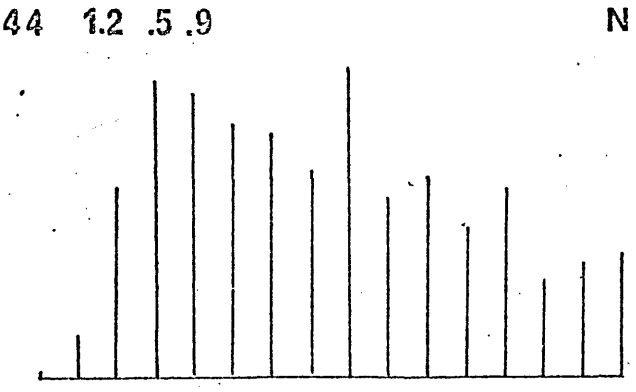
FIG. 54 cont.(2)

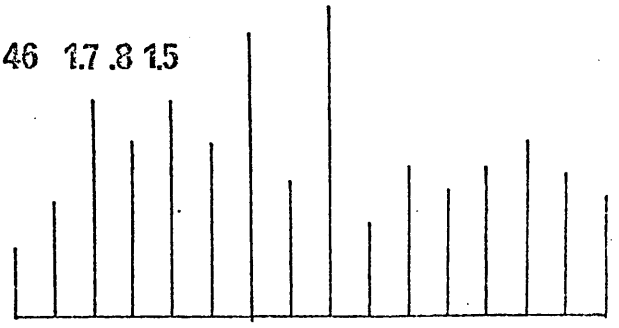

31 1.4 .5 1.

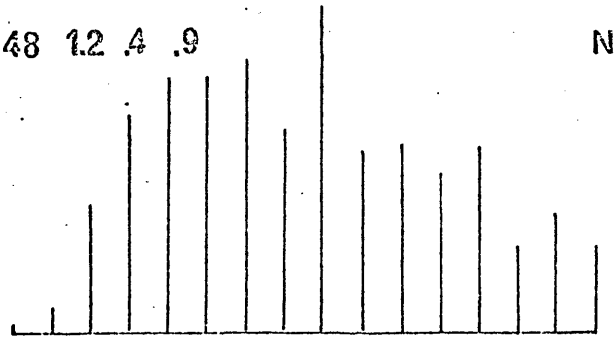

32 1.2 .8 1.3
N

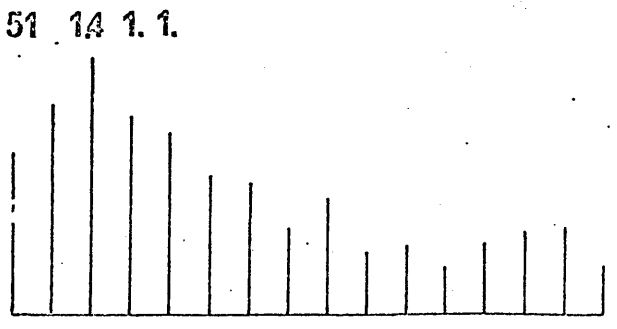

36 1.3 .8 1.

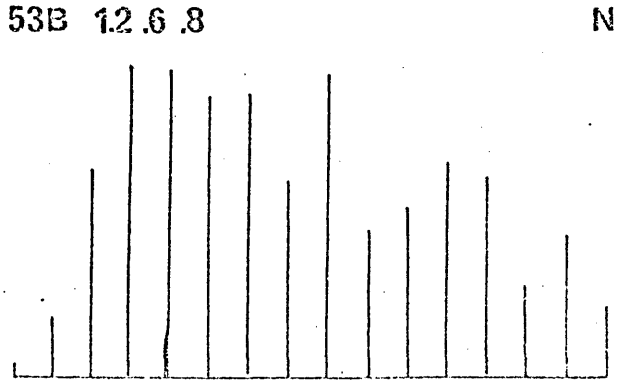

39 1.5 1.1 .9

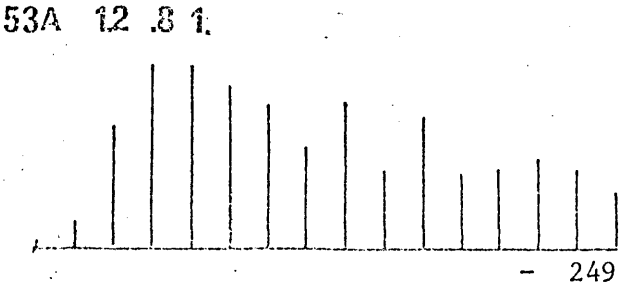

44 1.2 .5 .9
N


46 1.7 .8 1.5


48 1.2 .4 .9
N


51 1.4 1. 1.


53B 1.2 .6 .8
N


53A 1.2 .8 1.

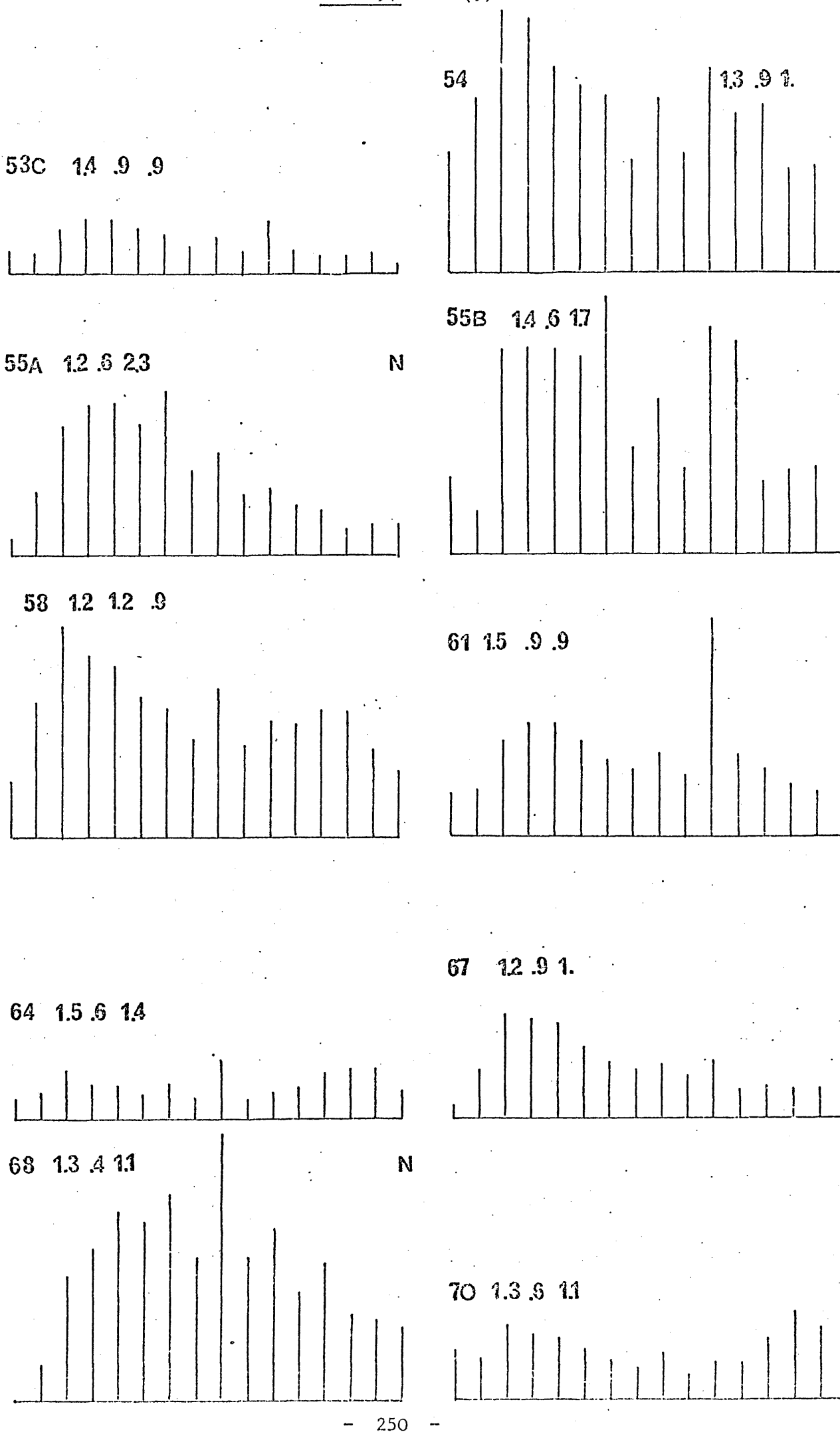
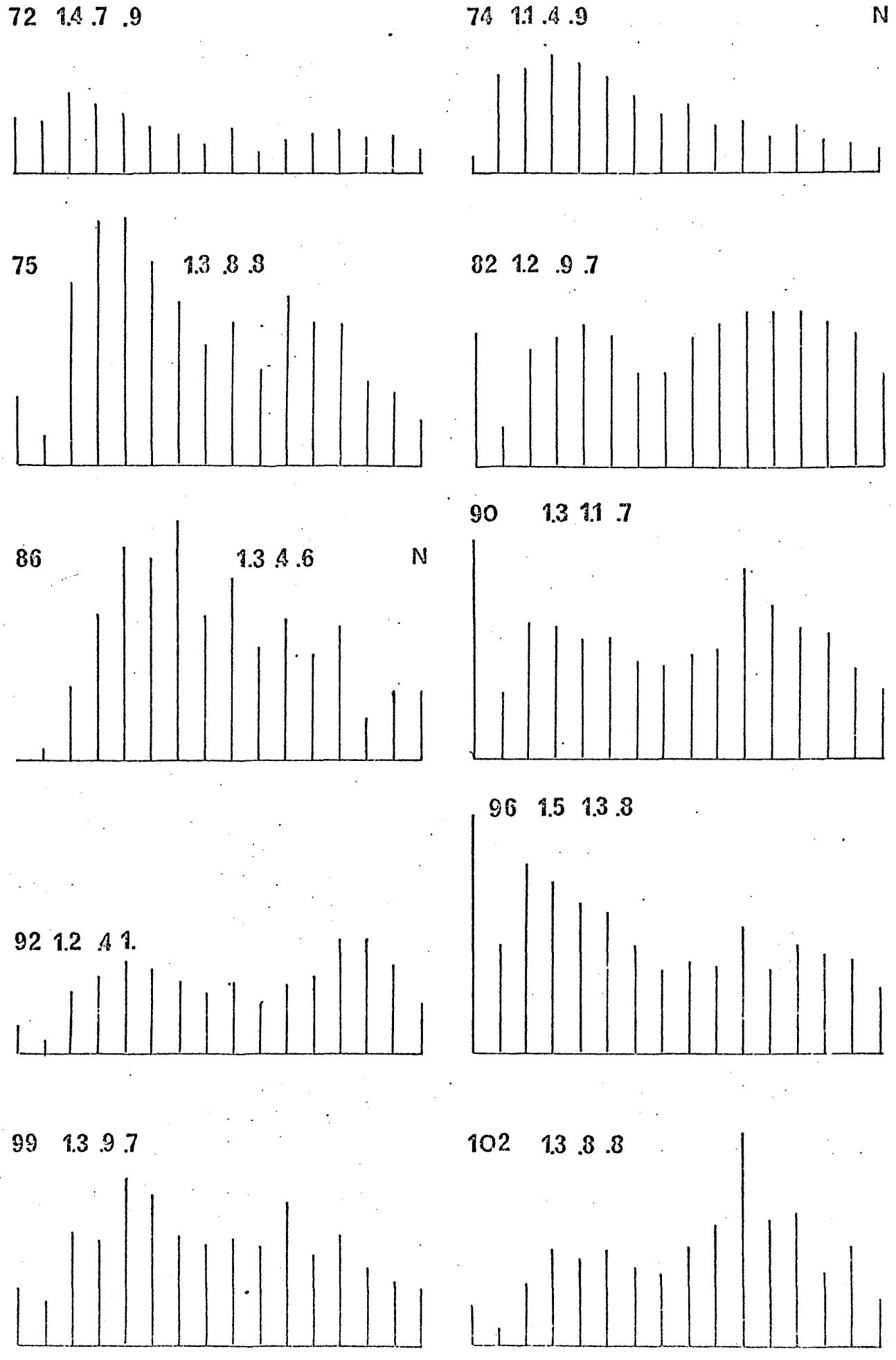

53C 1.4 .9 .9
54 1.3 .9 1.
55A 1.2 .6 2.3 N
55B 1.4 .6 1.7
58 1.2 1.2 .9
61 1.5 .9 .9
67 1.2 .9 1. N
64 1.5 .6 1.4
68 1.3 .4 1.1 N
70 1.3 .6 1.1

FIG. 54 cont.(4)


72 1.4 .7 .9
74 1.1 .4 .9 N
75 1.3 .8 .8
82 1.2 .9 .7
86 1.3 .4 .6 N
90 1.3 1.1 .7
96 1.5 1.3 .8
92 1.2 .4 1.
99 1.3 .9 .7
102 1.3 .8 .8

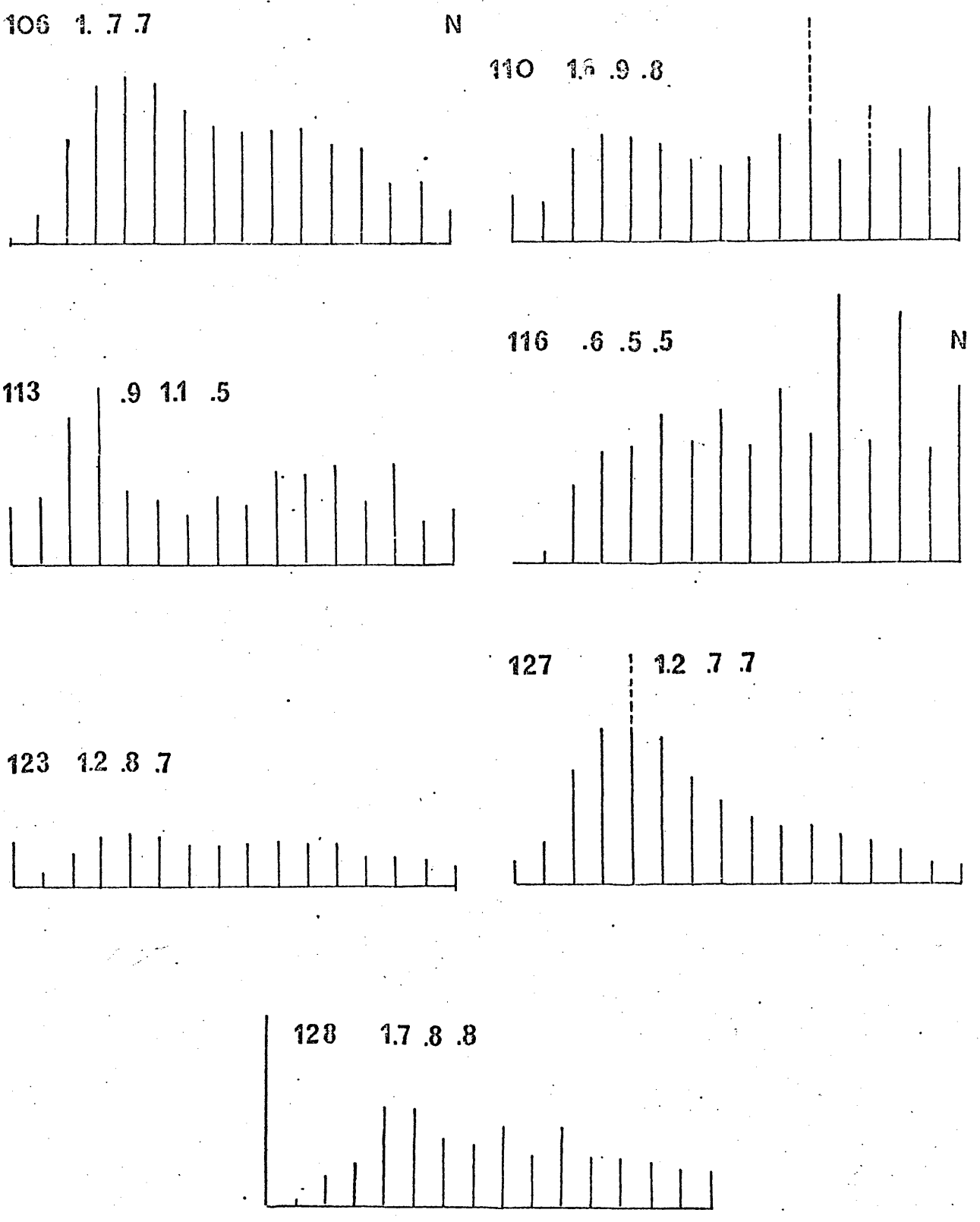


FIG. 54 cont.(5)

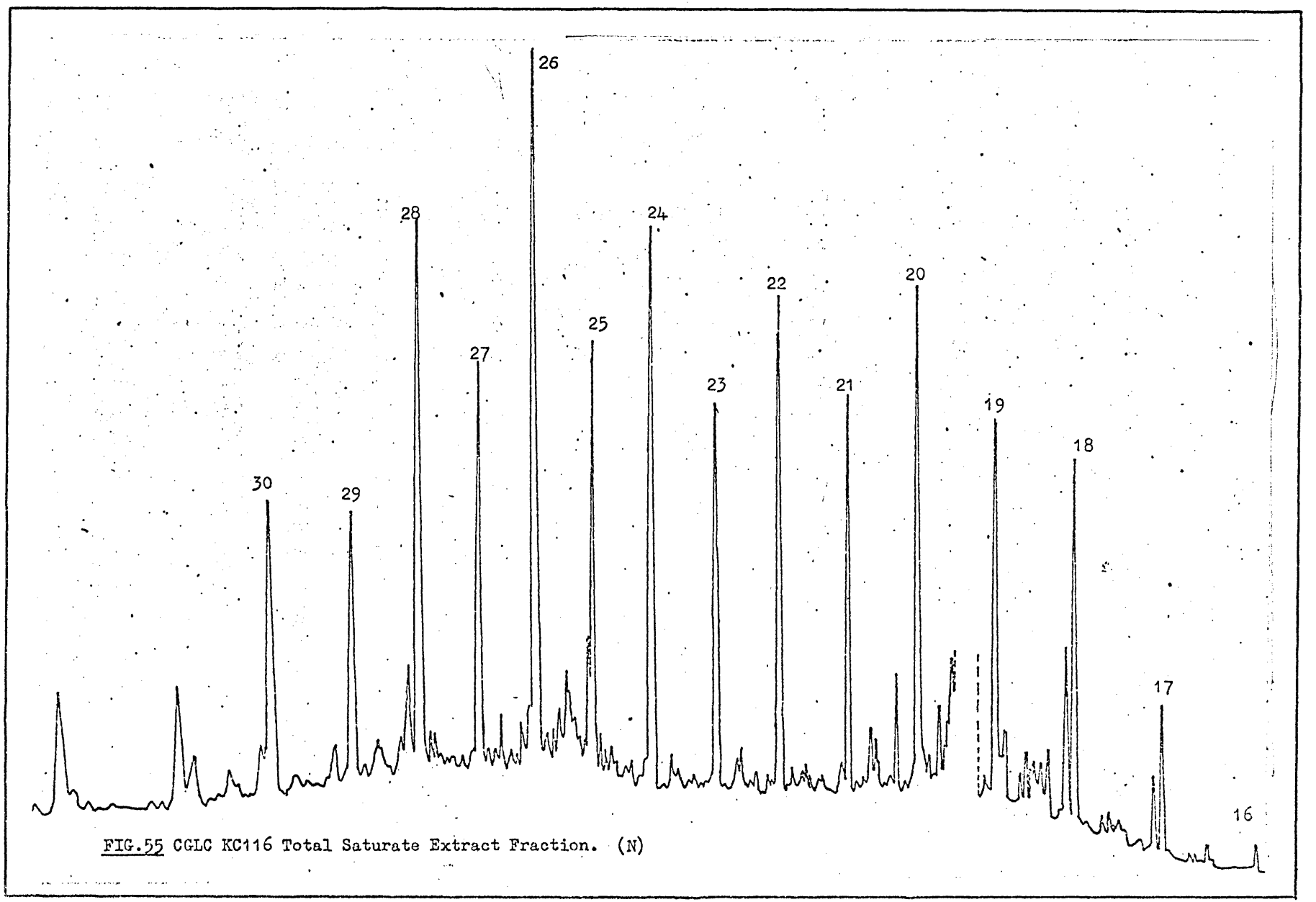


FIG.55 CGLC KC116 Total Saturate Extract Fraction. (N)

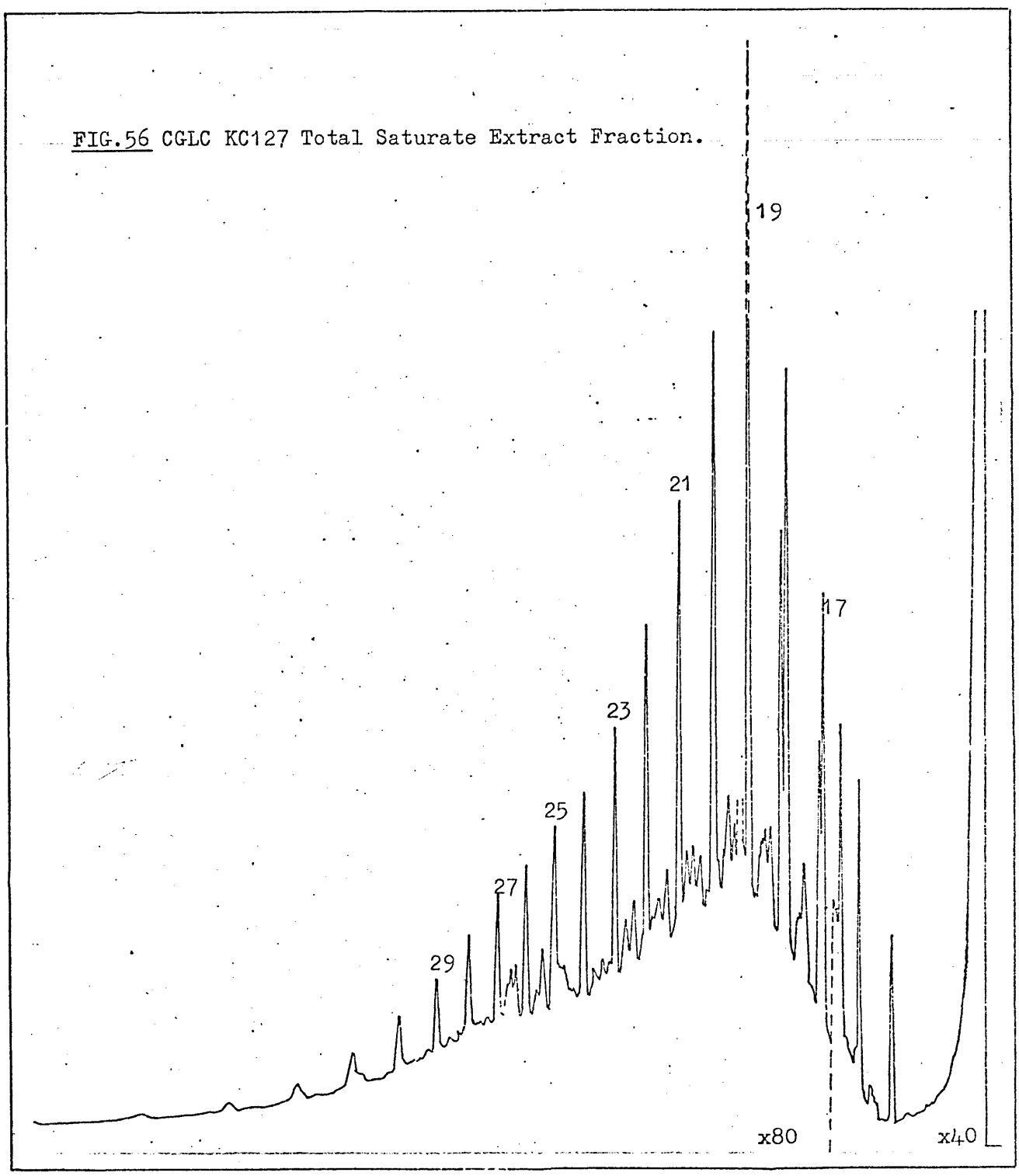


FIG.56 CGLC KC127 Total Saturate Extract Fraction.

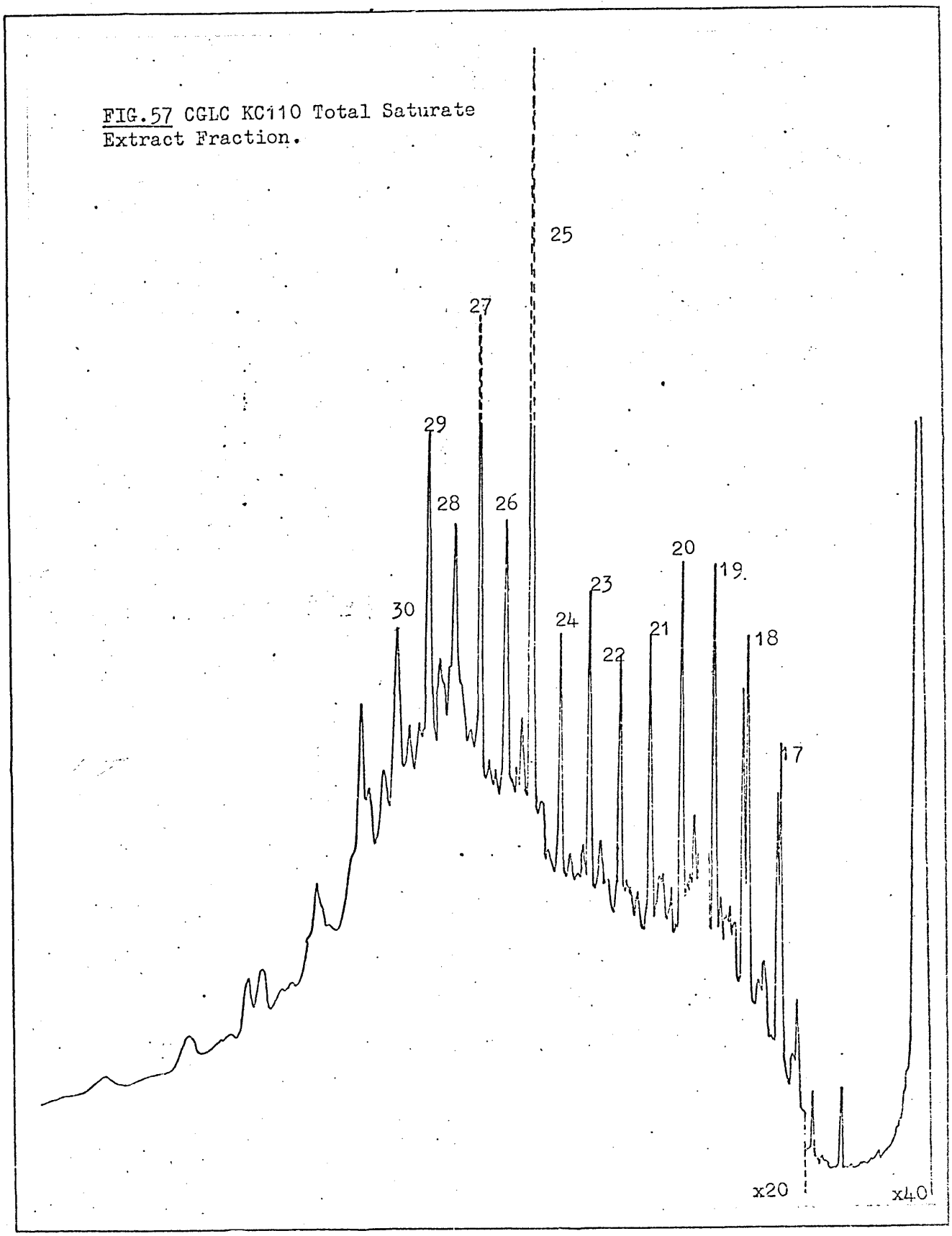


FIG.57 CGLC KC110 Total Saturate Extract Fraction.

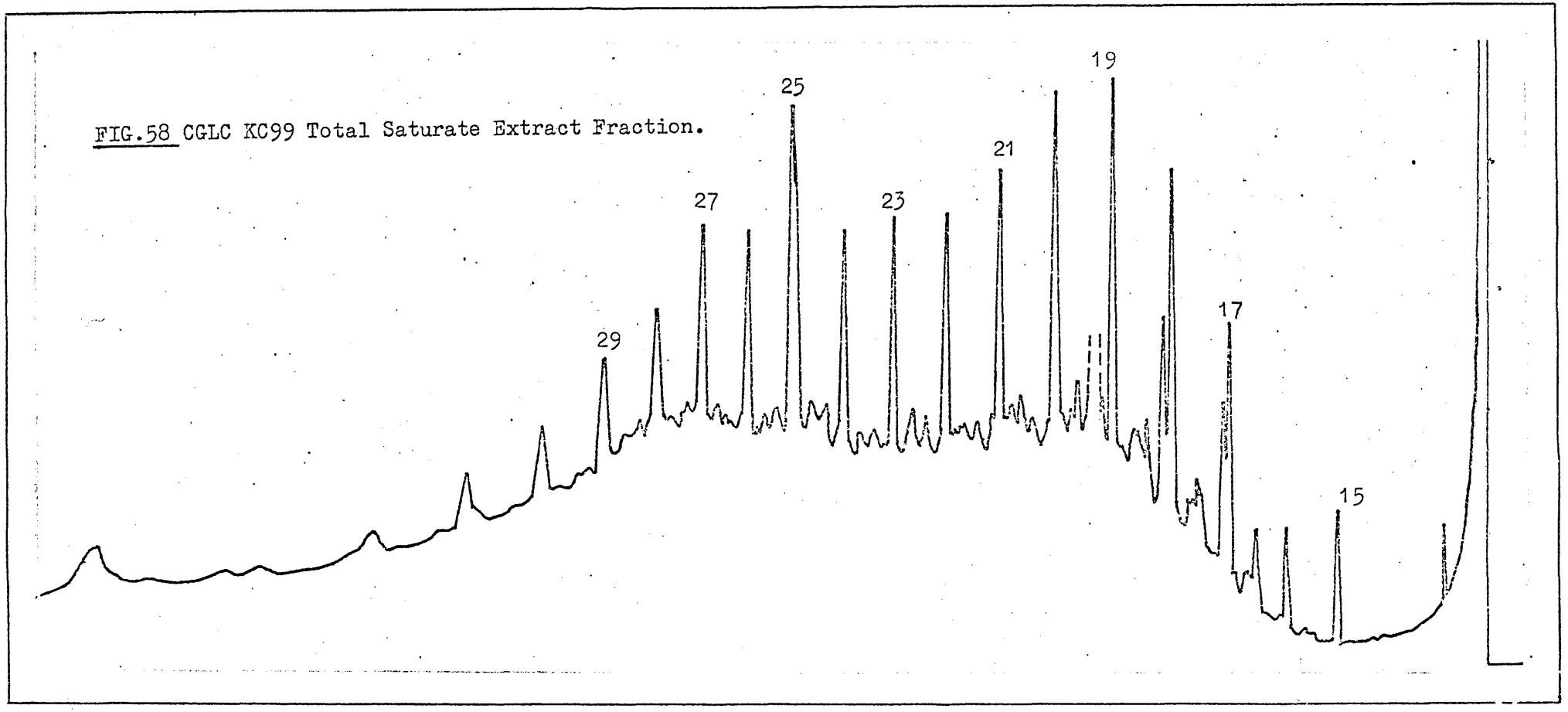


FIG.58 CGLC KC99 Total Saturate Extract Fraction.

algal distribution (KC127) or more equal bimodal distribution (KC99) (where algal n-alkanes seem slightly more pronounced) is typical with only a restricted number suggesting an increased importance or dominance of "terrestrial" n-alkanes.

The pristane/phytane ratios accord with the view for a marine environment of deposition whilst the pristane/nC_{17} alkane ratios fall within a range postulated for immature sediments with bacteria, algal mats, planktonic algae, or mixed phyto/zoo-plankton as sources.

In all samples, except 10 (KC86, 74, 51, 46, 39, 36, 31, 18, 8 and 5) a 'massive' branched/cyclic alkane concentration is evident and it elutes before the nC_{20} alkane. However it is completely missing in KC5 and varies between being 'slightly subdued' to 'very reduced' in the remaining 10 exceptions (Figure 59). KC53A is unique in giving a 'massive' b/c-alkane component before the n-C_{23} alkane (Figure 60A).

'Pre-nC_{26} alkane' b/c-alkane components occur in KC106, 75, 74, 72, 68, 55A, 55B, 53B and 48 and range from large to significant in relative peak size. The depicted peak in 55B (Figure 60B) appears to be a sum of at least two peaks, which are seen to occur in 55A under improved resolution, and the remainder seem to be variants of either 55A or 106.

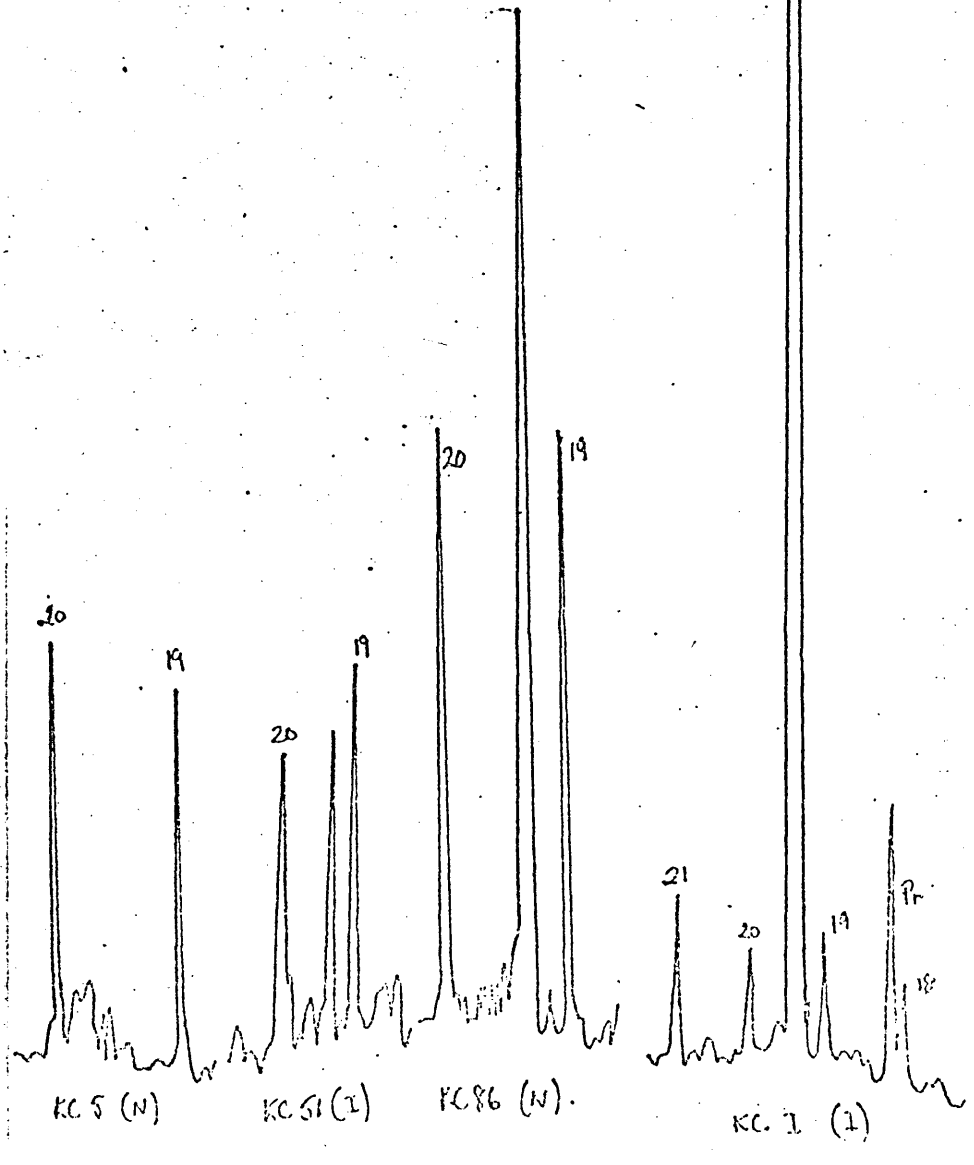
KC7 and 11 are alone in exhibiting a pre-nC_{27} alkane peak of relatively large dimension but comparison with KC5 and 8 under better resolution suggests addition of at least two of three significant b/c-alkane components is the explanation (Figure 60C).

B/c-alkane components are seen to 'crowd' in the vicinity of the nC_{28} alkane for KC86, 74, 68, 67, 55A, 54, 53B, 48, 44, 32, 28, 18, 11, 8 and 5 (15 samples) on a relatively large-significant scale (Figure 60B).

Thus, the disproportionate 'massiveness' of the pre-n C_{20} and pre-nC_{23} b/c-alkanes is an obvious indication of an anomaly and these are discussed under the Appendices.

Nowhere, though, is the n-C_{22} alkane/docosane of any relative significance. However, the relatively large/significant b/c-alkanes in the proximity of the nC_{26}, nC_{27} and nC_{28} alkanes are of an equivalent order of magnitude as the n-alkanes themselves to warrant

FIG.59 VARIATIONS IN THE PRE-nC_{20} BRANCHED/CYCLIC ALKANE COMPONENT: Missing, significant, large (subdued) & massive.



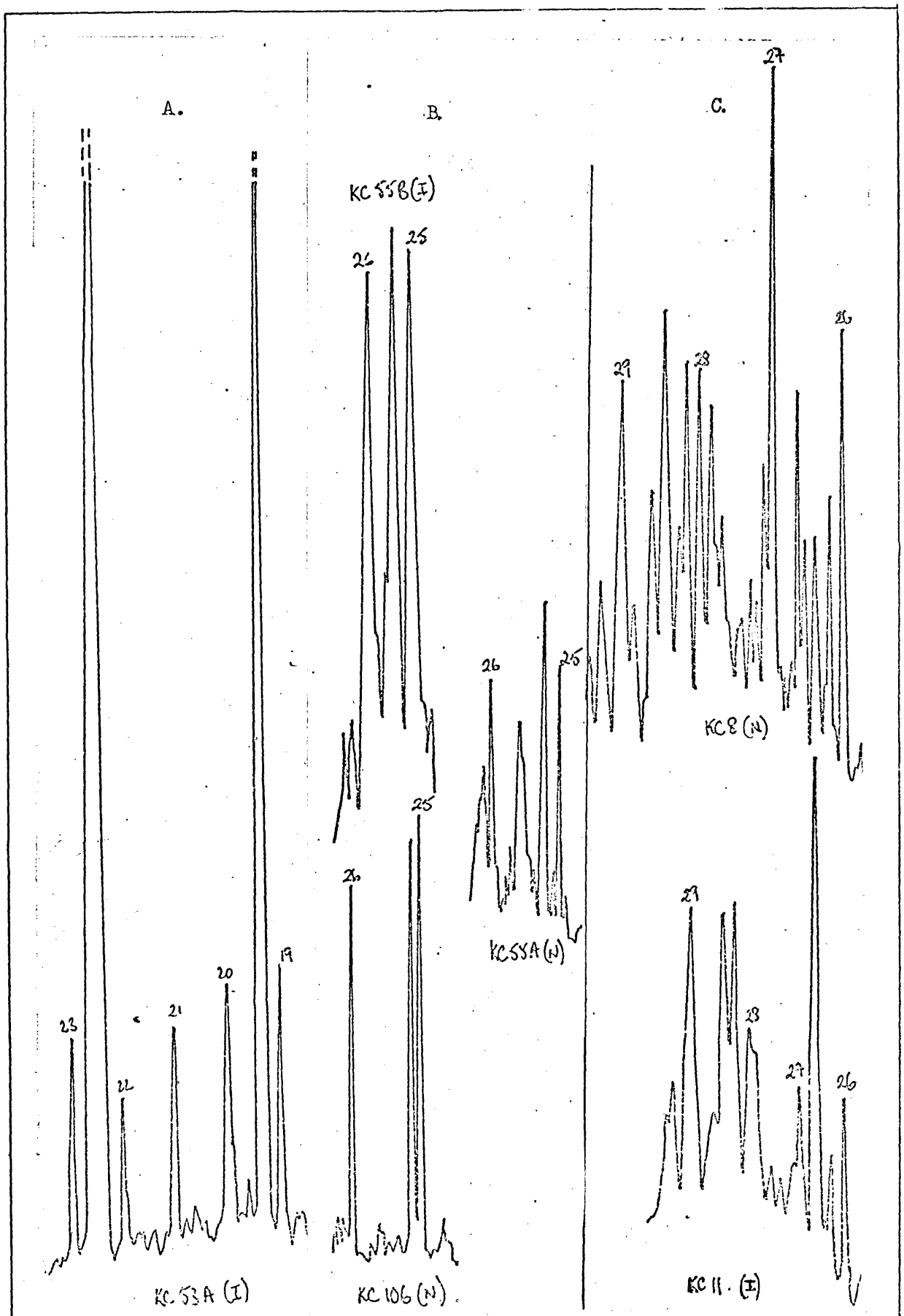


FIG.60 VARIATIONS IN THE PRE-nC_{23} (A); PRE-nC_{26} (B) & PRE-nC_{27} (C) BRANCHED/CYCLIC ALKANES WITH "nC_{28}" CROWDING amongst the Kimmeridge Clay CGLC total saturate fractions.

no immediate suspicion upon their authenticity. Their occurrence may be taken as a sign of immaturity since they are reported to diminish under an increasing thermal gradient (?).

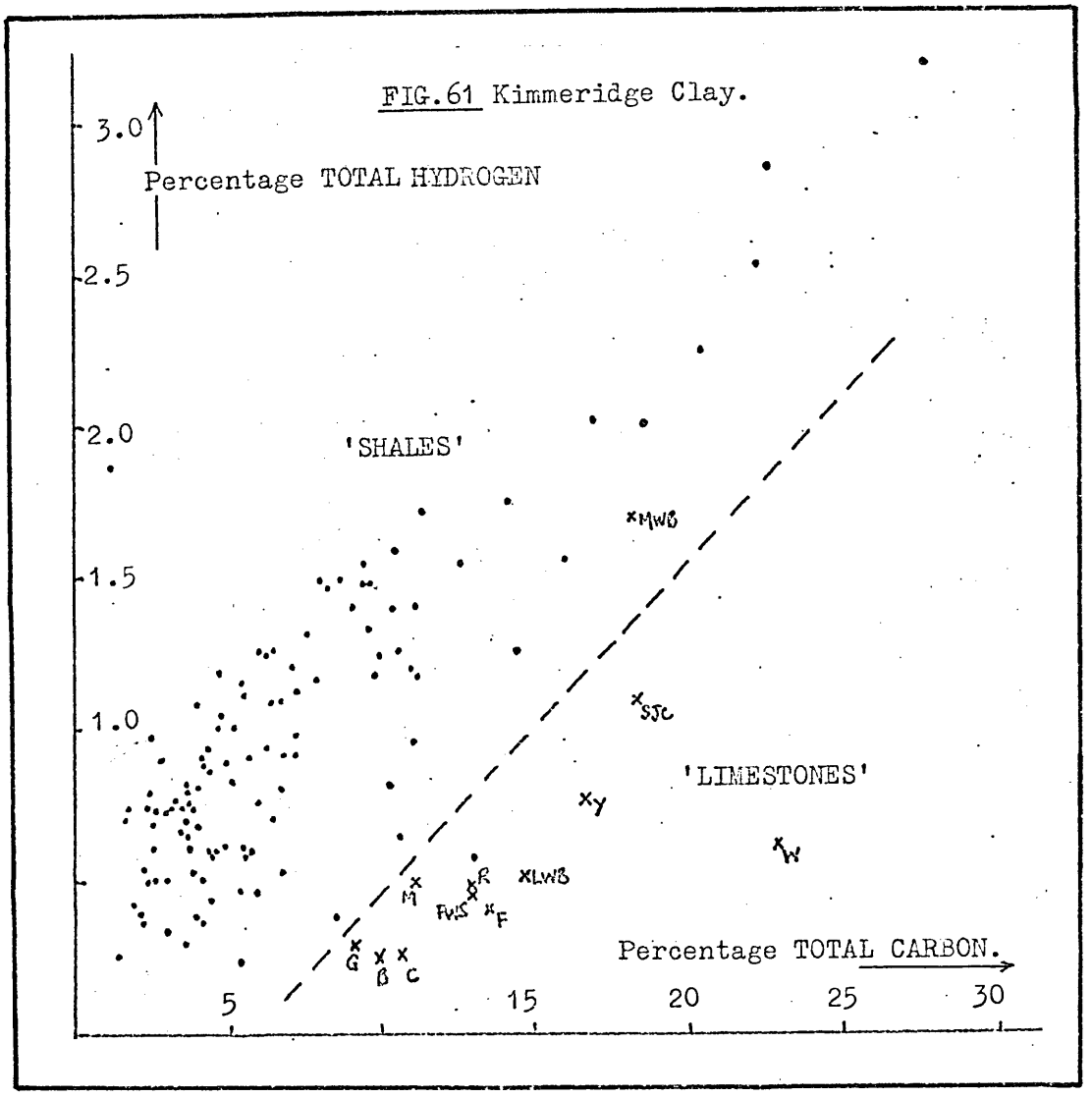
4 QUANTITATIVE ELEMENTAL ANALYSIS

Total "whole-rock" carbon (ranging from 1.32% (KC116) to 27.7% (KC55A), initial organic carbon (varying from c.0.7% (KC114) to 23.3% (KC55A) and averaging 5%) and post-pyrolysis organic carbon (covering 0.17% (KC32) - 8.65% (KC55A) and giving a median value of 1.8%) are illustrated stratigraphically on Log 5.

Total "whole-rock" hydrogen (extending from 0.28% (KC116) to 1.73% (KC30)) and nitrogen (changing from 0 (KC5, 18, 44, 54, 59-62, 66, 67, 71, 73, 75, 82, 91, 101-103, 106, 112, 113, 115) to 1.0 (KC34)) depicted vertically on Log 6. More than 2% hydrogen is shown by KC55A, 53, and 6 whilst less than 0.25% hydrogen is given by KC114, 73, 61 (44 ?, 39 ?) and greater than 1% nitrogen occurs in KC 74, 45, and 37; these values being excluded from the limits.

Elemental values for carbon, hydrogen and nitrogen within the SOEs are given stratigraphically on Log 4. Soluble organic carbon is less than 45% in KC98, 94, 90, 74, 73, 66, 48, 39 and 4 whereas it is above 81% in KC109, 87 and 67. Hydrogen shows a value of less than 5% for KC98 only whereas it exceeds 15% in KC55A, 56, 57 and 87. Nitrogen is greater than 3% in KC74, 70 and 66. The C/H ratio averages at 7.6 for the section varying between 6.12 (KC48) and 8.33 (KC78) with only KC74 below 6.0 (Log 4).

A percentage carbonate carbon (computed by difference from the elemental analyses) is overprinted upon the dolomite-calcite XRD relative intensities on Log 7. In fact, only one assessment (persistently) exceeds the theoretical maximum (c.12%) for a pure limestone (KC11) and is obviously anomalous. Otherwise the section is seen to vary from non-calcareous 'shales' (KC84, 31, 22, 21, 19, 14, 9, 8, 7, 4) to limestones (KC32, 10.59% carbonate carbon). Hence, a plot of total carbon versus total hydrogen is given in Figure 61 and in the main the 'classic' cementstones and white limestones separate from the shales because of their relatively high total carbon and low hydrogen contents. To a first approximation, the shales seem to hold total carbon and total hydrogen in a linear relationship.


FIG.61 Kimmeridge Clay.
3.0
Percentage TOTAL HYDROGEN
2.5
2.0
'SHALES'
1.5
1.0
'LIMESTONES'
Percentage TOTAL CARBON.
5
15
20
25
30

In all cases, the minimum source rock criterion of 0.5% organic carbon is seen to be well exceeded and thus the source rock potential is excellent. (Actually all except five samples yield values greater than 2% which has been suggested to indicate inhibition of fluid expulsion due to self-adsorption ?).
The relatively large range of low carbon contents in the soluble organic matter is indicative of the presence of nonhydrocarbon material in varying quantity and consequently an asphaltic nature is suggested for the SOEs.
Also, the C/H ratio of 7.6 (atomic C/H = 1.6) indicates a degree of unsaturation which is atypical of crudes and thus infers immaturity.

5 PYROLYSIS

As mentioned, residual organic carbon can be found on Log 5 where the plot of $C_T - C_R$ is also given to indicate the relative potential within the section (since C_T and C_R encompass 'total kerogen' and reflect both its type and amount together). An arbitrary division of poor, medium, good and excellent source potential has been derived and is shown on Log 8 for intraformation comparison only.
A "percentage kerogen carbon convertibility" is illustrated vertically on Log 3 where it is calculated as:

$$\frac{\text{Kerogen carbon } (C_T) - \text{Residual organic carbon } (C_R)}{\text{Kerogen Carbon } (C_T)} \times 100\%$$

and

Kerogen carbon = Organic Carbon - Soluble Organic Carbon

(All values being 'normalised' with respect to rock weight)

The average conversion value for the induced maturation is 64% for the whole section and colours of the pyrolysed rock, with a colour-based description of condensate richness, are reported on Log 8.
Clearly, such a large percentage conversion itself can only infer little diagenesis/poor evolution of (highly) productive organic matter. Accordingly the dominant "kerogen-type" can be discerned through employment of an organic factor of 1.24 as in Table 58 and Table 59 summaries the distribution of samples from the section (Log 3). The 'mixed-basic types' represent those samples embraced by a $\pm$20% error and the average conversion value falls within an algal-alginite overlap category. In the extreme conversion ranges

KEROGEN TYPE	APPROX. WEIGHT LOSS	EQUIVALENT % CARBON LOSS.	20% ERROR FIELD.	APPROX. 'PURE TYPE' % CARBON CONVERSION RANGE.
Inertinite.	0 - 5%	0 - 4%	±0.8%	0 - 3%
Humic.	5 -15%	4 -12%	± 0.8 - 2.4%	5 - 9.5%
Leiptinitic.	15-50%	12-40%	± 2.4 - 8.0%	14.5-32%
Algal.	50-85%	40-69%	± 8.0 -13.8%	48 - 55%
Alginite.	> 85%	>69%	⩾ ± 13.8%	> 83%

TABLE 58. LIMITS OF THE KEROGEN TYPE CLASSIFICATION.

INERTINITE:	(71A),87,(89A),103
Inertinite - humic:	57,102
HUMIC:	39
Humic - Leiptinitic:	114
LEIPTINITIC:	18,61,75,81,82,83,89,91,94,100,113
Leiptinitic - algal:	12,24,28,29,31,38,71,79,80,(88A),90, 92,96,97,98,99
ALGAL:	(2A),5,7,20,34,35,36,37,41,42,46,50, 52,53A,53B,56,58,59,69,73,77,86,88,106
Algal - alginite:	1 - 4,(4A),6,8 - 11,13 - 17,19,21-23, 25-27,30,33,40,43-45,47-49,51,53C,55A, 60,62-65,67,68,70,72,(72A),76,78,93,95, 101,104,105,108-112,115,116
ALGINITE:	32,54,66,74,84,107,55B

TABLE 59. KIMMERIDGE CLAY KEROGEN TYPE DISTRIBUTION.

from 0% (KC103, 87) to c.97% (KC74, 55B, 32) and the classification employed here functions only as a practical tool to the limit of published knowledge; obviously lacking control with regard to the precise ("academic") composition of kerogen.

6 CROSSPLOTS

a SOE v Organic Carbon

Figure 62 shows the graphical plot of these two parameters and the trend has been compared with those for suites of rocks from different diagenetic regimes (Figure 29) where it is seen to fall within a field occupied by senile rocks as well.

The majority of the shales give values of 0.05 - 0.1 for the SOE/organic carbon ratio and an average sectional value is 0.08. Samples KC67, 61 and 39 (LWB, BB and CL) and KC91, 89, 65, 31 give somewhat higher values closer to 0.2.

Here it can be noticed that the nonhydrocarbon organic matter together with any inorganic salts or elemental sulphur does not seem to detract too much from the linear relationship. The gradient illustrates that little SOE is available with respect to the large amounts of organic matter present and, in fact, with the exception of KC67 (2.48% SOE), the organic carbon of the whole section is nearly all kerogenous.

Specifically, the average SOE/organic carbon suggests that the section once resided within 'an early hydrocarbon generation zone' (<0.1 but >0.05). KC67, 61 and 39 are 'classic' limestones and a possible explanation for the high ratio of the other 4 samples could perhaps be a 'higher-than-usual' iron content (?).

b Pre- v Post-pyrolysis organic carbon

Figure 63 portrays the relation of these two parameters and the trend has been put into context with those of other established diagenetic regimes in Figure 30 where senile and immature rocks (can sometimes) differentiate themselves. In particular, the Kashafrud and Kimmeridge Clay Formations hold similar organic material but at different stages of maturation.

The average CR/CT ratio is 0.4 and thus the section is seen not to have experienced a thermal history unfavourable to petroleum generation (CR/CT <0.6). In gross terms (Figure 63) the trend is seen to lie quite close to that for the maximum laboratory induced

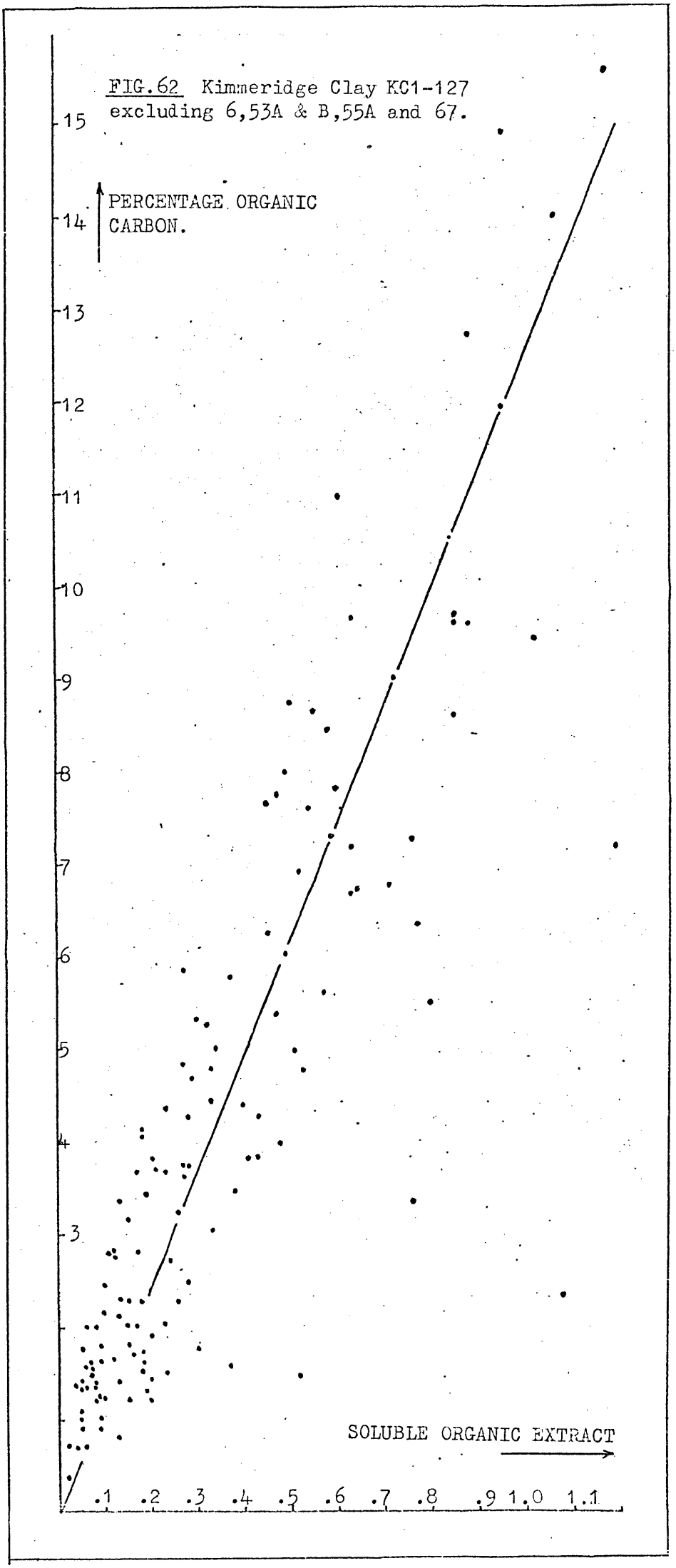
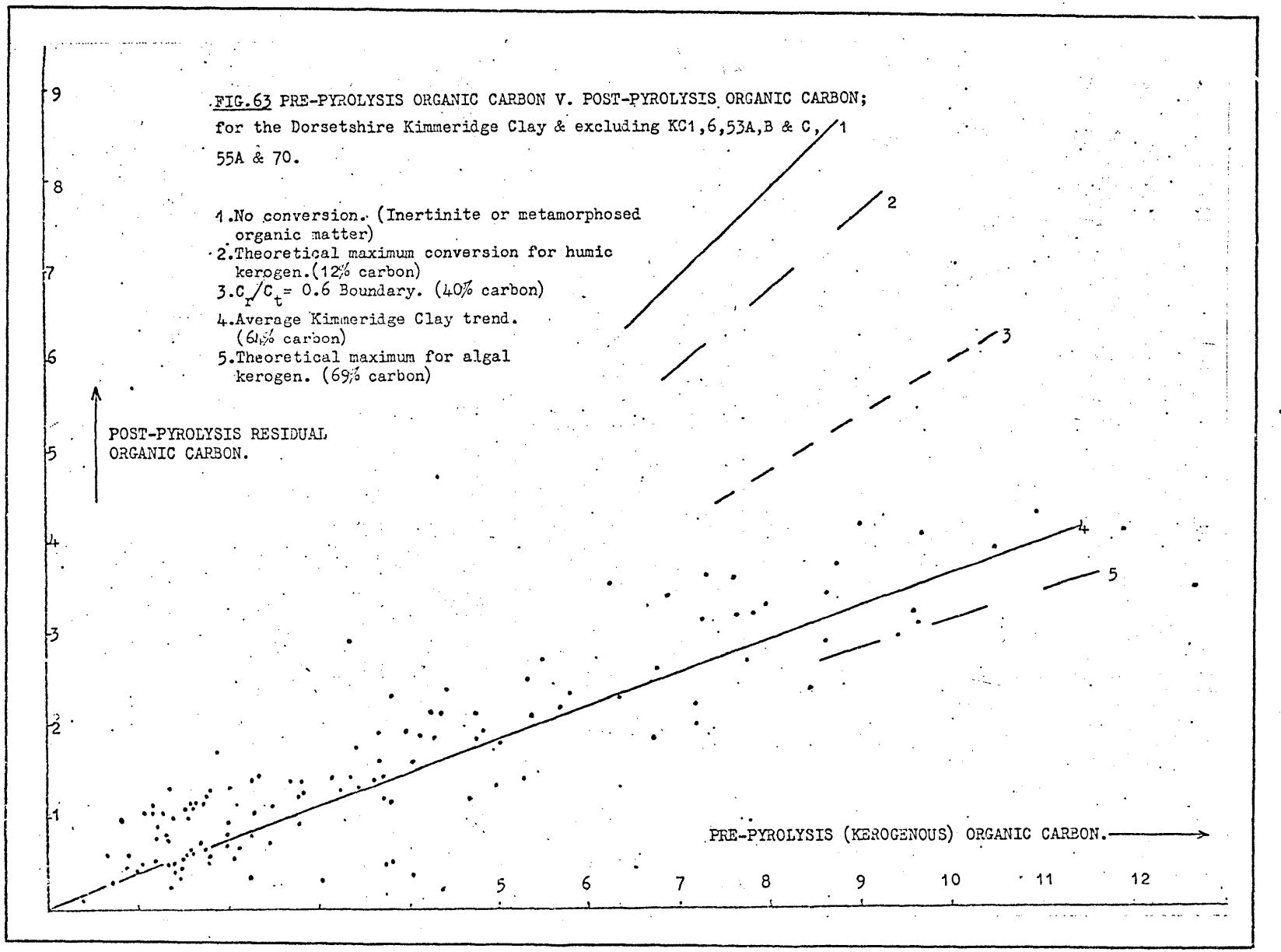


FIG.62 Kimmeridge Clay KC1-127 excluding 6,53A & B,55A and 67.


FIG.63 PRE-PYROLYSIS ORGANIC CARBON V. POST-PYROLYSIS ORGANIC CARBON;
for the Dorsetshire Kimmeridge Clay & excluding KC1,6,53A,B & C, 55A & 70.
1.No conversion. (Inertinite or metamorphosed organic matter)
2.Theoretical maximum conversion for humic kerogen.(12% carbon)
3.C_r/C_t = 0.6 Boundary. (40% carbon)
4.Average Kimmeridge Clay trend. (64% carbon)
5.Theoretical maximum for algal kerogen. (69% carbon)
POST-PYROLYSIS RESIDUAL ORGANIC CARBON.
PRE-PYROLYSIS (KEROGENOUS) ORGANIC CARBON.
1
2
3
4
5
1
2
3
4
5
6
7
8
9
10
11
12

changes experienced with fresh (immature) algal kerogens.

c GLC v Pyrolysis

From visual inspection of the bar diagrams of the n-alkane distributions a (sometimes slight) bias for the terrestrially derived material was suspected for KC61, 82, 92, 102, 110 and 116. By reference to Table 58 agreement is observed with regard to the broad predominant organic types except for 110 and 116 which pyrolysis suggests to have little/no terrestrial in-put. As their distribution bias is pronounced, they currently remain anomalous.

d Hydrocarbons/organic carbon

Using the average values for the SOE (0.4%) and the quantity of hydrocarbons within the extractables (29%) the average percentage by weight yield of hydrocarbons is 0.116% and a sectional mean for the ratio of hydrocarbons/organic carbon of 0.023 results.

Accordingly, the formation is seen to be an 'above average' shale (HC/Organic carbon $>$ 0.01).

e Saturates/aromatics v Hydrocarbons/Organic carbon

Figure 64 shows the plot for these variables and the mean of the wide spread of results does lie within the general domain of unmetamorphosed sediments.

f Optical (whole rock) microscopy v extractibility v pyrolysis

In this instance (randomly cut) whole rock sections were broadly classified into an oil shale/bitumenous-(carbonaceous) facies because of the occurrence of either subparallel wavy red-brown lammae or dispersed lenses of bitumen and a carbonaceous-(bitumenous) facies by the absence of any bitumen.

Surprisingly the 'bitumen rich' facies types have an extractibility of more than 0.2% by weight whereas those of the visually 'bitumen barren' facies provide SOEs of less than 0.2% by weight and few exceptions to this rule are observed.

(For those predicted to give little or no extractibility ($<$0.2%) excluding KC87, eight were strictly wrong with one falling on the arbitrary division. Of the eight, three lie uncomfortably close to the limit.

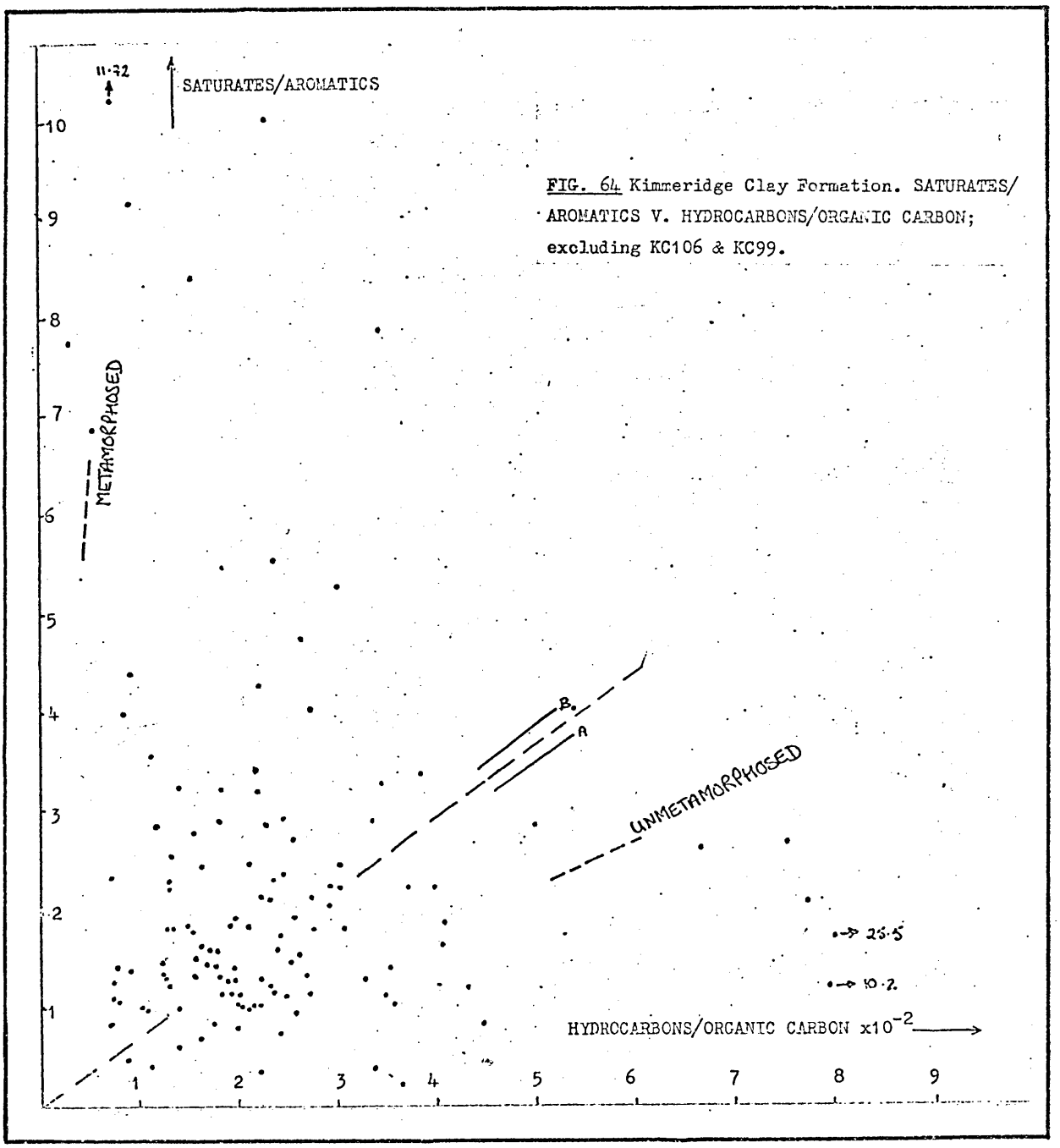


FIG. 64 Kimmeridge Clay Formation. SATURATES/AROMATICS V. HYDROCARBONS/ORGANIC CARBON; excluding KC106 & KC99.

For those thought to have more than 0.2% extractibility only four were wrongly placed and three fall on the division. Of the four samples misplaced, all in fact lie very close to the boundary.)

Using arbitrary boundaries, the extractability itself was applied to distinguish types of an oil shale facies ($\geq$0.4% SOE) from both the bitumenous-(carbonaceous) (0.4 - 0.2% SOE) and carbonaceous-(bitumenous) facies ($\leq$0.2% SOE).

Finally, the descriptive names were correlated to the respective predominant kerogen types deduced from pyrolysis, and the relative facies types are assigned on Log 8 together with an indication of the disagreeing parameter(s).

Pyrolysis is seen to cause the most frequent conflict with the chiefly optical-based classification and as noted earlier, this is because, in contrast to certain individual components, most organic matter is finely comminuted and impossible to recognise without much more sophisticated study. Consequently pyrolysis often suggests here that carbonaceous-(bitumenous) facies types should be elevated to (at least) a bitumenous-(carbonaceous) facies since algal/algal-alginite/alginite kerogen types are inferred to really dominate. (Where inertinite through to liptinitic/algal kerogen types are advocated for the carbonaceous-(bitumenous) facies members, no contradiction is annotated on Log 8).

The occurrence of bitumenous laminae, sometimes to an overwhelming abundance does reflect the vast organic richness of the host rock and certainly focuses the realm of diagenesis away from dry gas metamorphism.

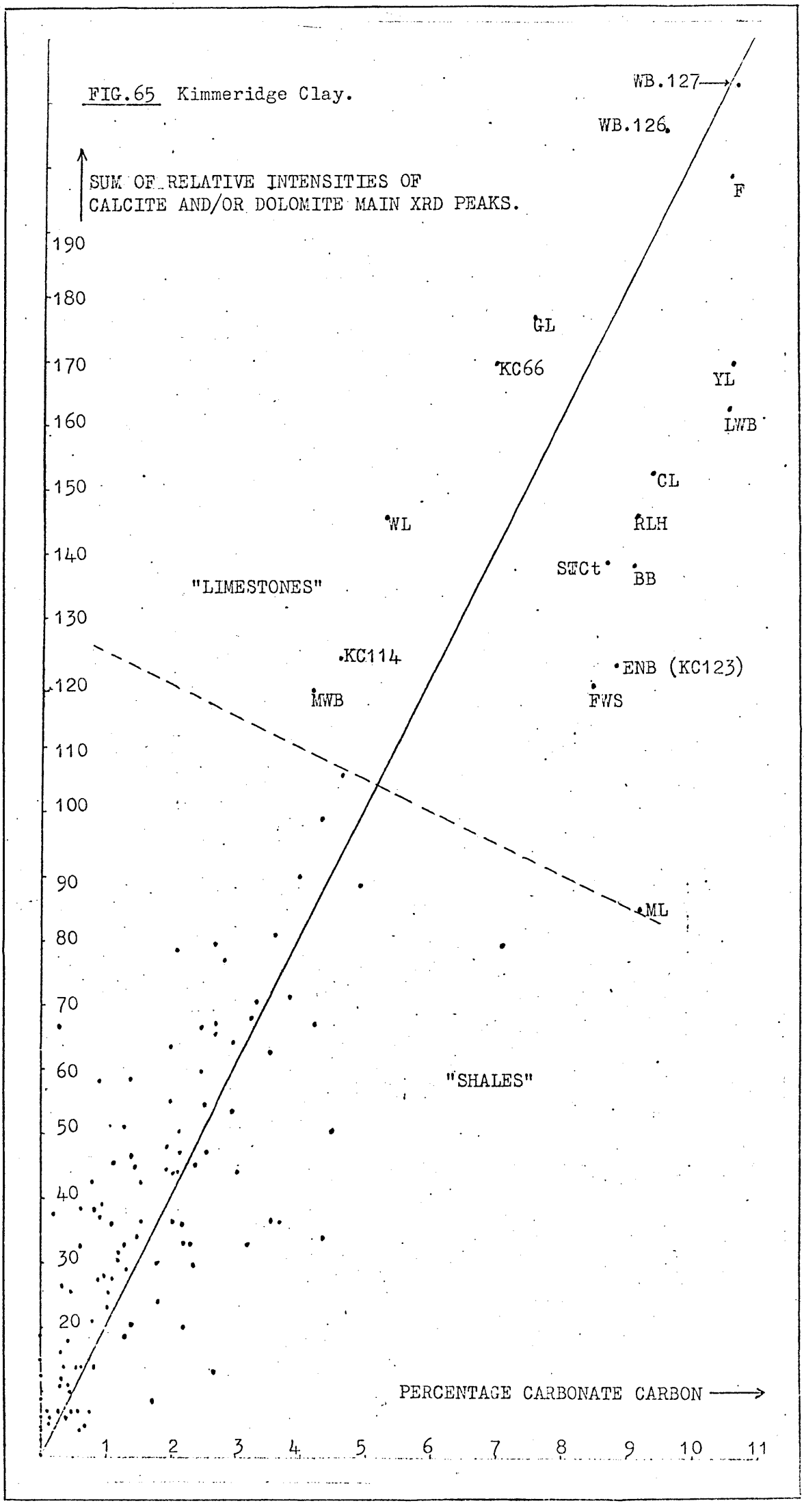
g Carbonate carbon percentage v dolomite-calcite relative intensities.

The estimated percentage carbonate carbon (deduced from elemental analysis) is plotted directly against the sum of the relative intensities for the dolomite (2.89Å d) and calcite (3.03Å d) major XRD peaks in Figure 65 where the deviations to the straight line relationship are reflections of the experimental difficulties in both techniques (Curtis priv.comm. 1977).

7 SPECTROSCOPY

a Infra-red spectroscopy

The IR spectra for the SOE and the three gross fractions are


FIG.65 Kimmeridge Clay.
SUM OF RELATIVE INTENSITIES OF CALCITE AND/OR DOLOMITE MAIN XRD PEAKS.
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
WB.127
WB.126
F
GL
KC66
YL
LWB
CL
WL
RLH
SCt
BB
"LIMESTONES"
KC114
ENB (KC123)
MWB
FWS
ML
"SHALES"
PERCENTAGE CARBONATE CARBON
1
2
3
4
5
6
7
8
9
10
11

grouped into four total (Figure 66), four saturate (Figure 67), three aromatic (Figure 68) and four asphaltic (Figure 69) main types in Table 60 where unassigned samples indicate either poor or no resolution was achieved. The majority of the total extracts give spectra of their type D whilst the asphaltic spectra are dominated by their type A. Each of these two chief types are identical to one another.

Thus, a close similarity is suggested for the functionality and therefore nature of the SOE throughout the section with few exceptions and an asphaltic nature is prevalent.

b Ultra-violet and Fluorescence emission spectroscopies

The UV spectra of the aromatic fractions are classified into five groups according to Table 61 and a representative of each group is illustrated in Figure 70. The main peaks show a shift to a lower energy (longer wavelength) in the order of 15 nm with respect to benzene.

Confirmation of the UV classification is shown by the FES results where the analyses of randomly chosen pairs from each class are summarised in Table 62 and Figures 71 and 72.

The results are jointly indicative of PAHs with three or more condensed benzene rings (Atkinson priv. comm. 1977) and their dominance in the aromatic fraction of the SOE suggests immaturity.

8 MACERATION

The findings from the microscopic examination of the macerated samples are furnished in Table 63 and some photographic illustrations are given in Plates 24-43 (incl). The tentative descriptions and/or identification are awaiting confirmation through detailed optical microscopy and scanning electron microscopy (Peat priv. comm. 1977).

Everywhere the colour of the lightest spores (in transmitted light) is yellow and although slightly degraded their structure is relatively well defined. In conclusion, a low degree of diagenesis is indicated for the organic matter which has both marine and terrestrial contributions.

9 X-RAY DIFFRACTION

For the section a stratigraphic variation in the mineralogy is displayed on Log 7 by plots of relative intensities for each mineral phase (Group names are employed where appropriate).

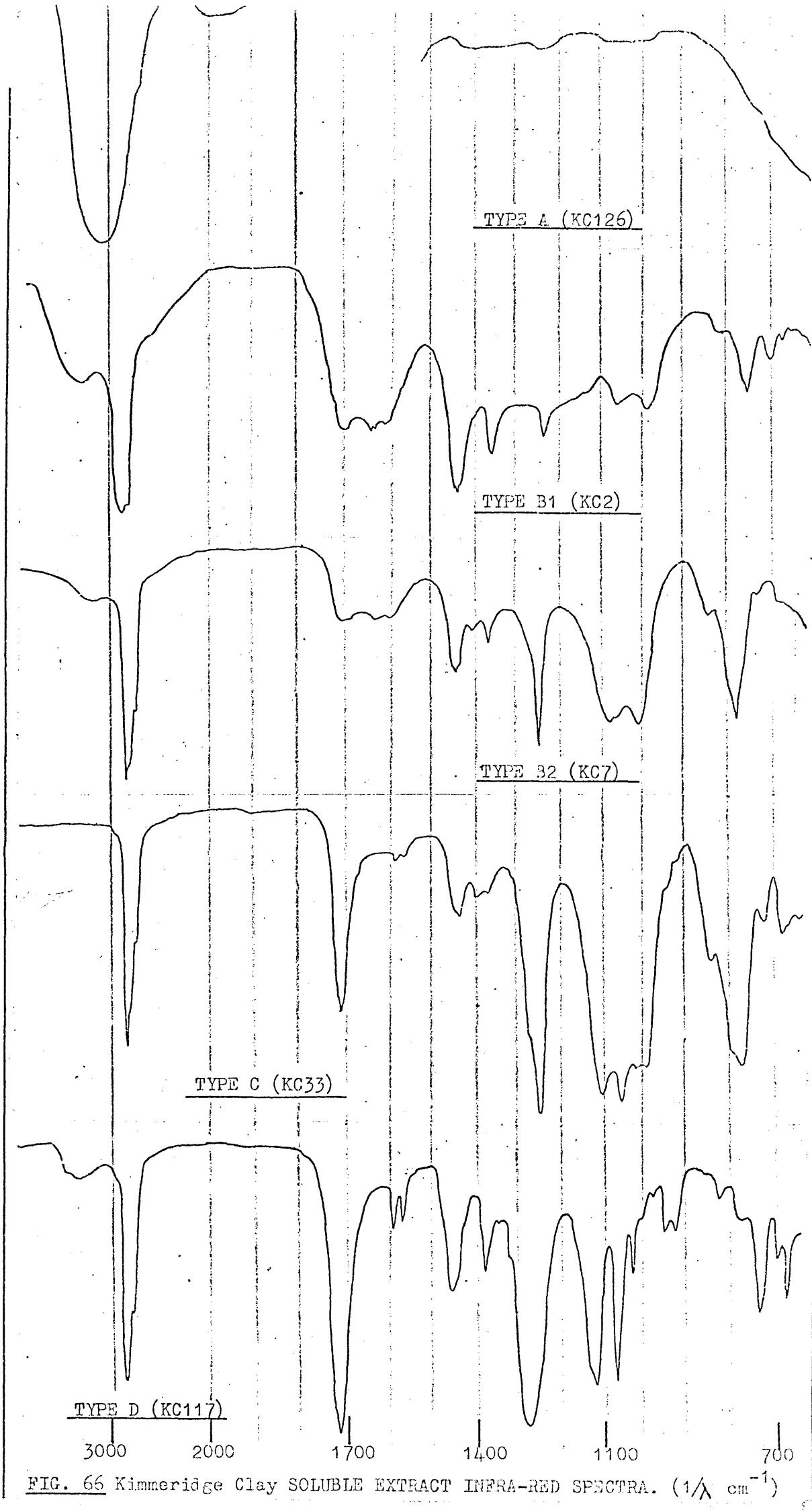


FIG. 66 Kimmeridge Clay SOLUBLE EXTRACT INFRA-RED SPECTRA. ($1/\lambda$ cm^{-1})

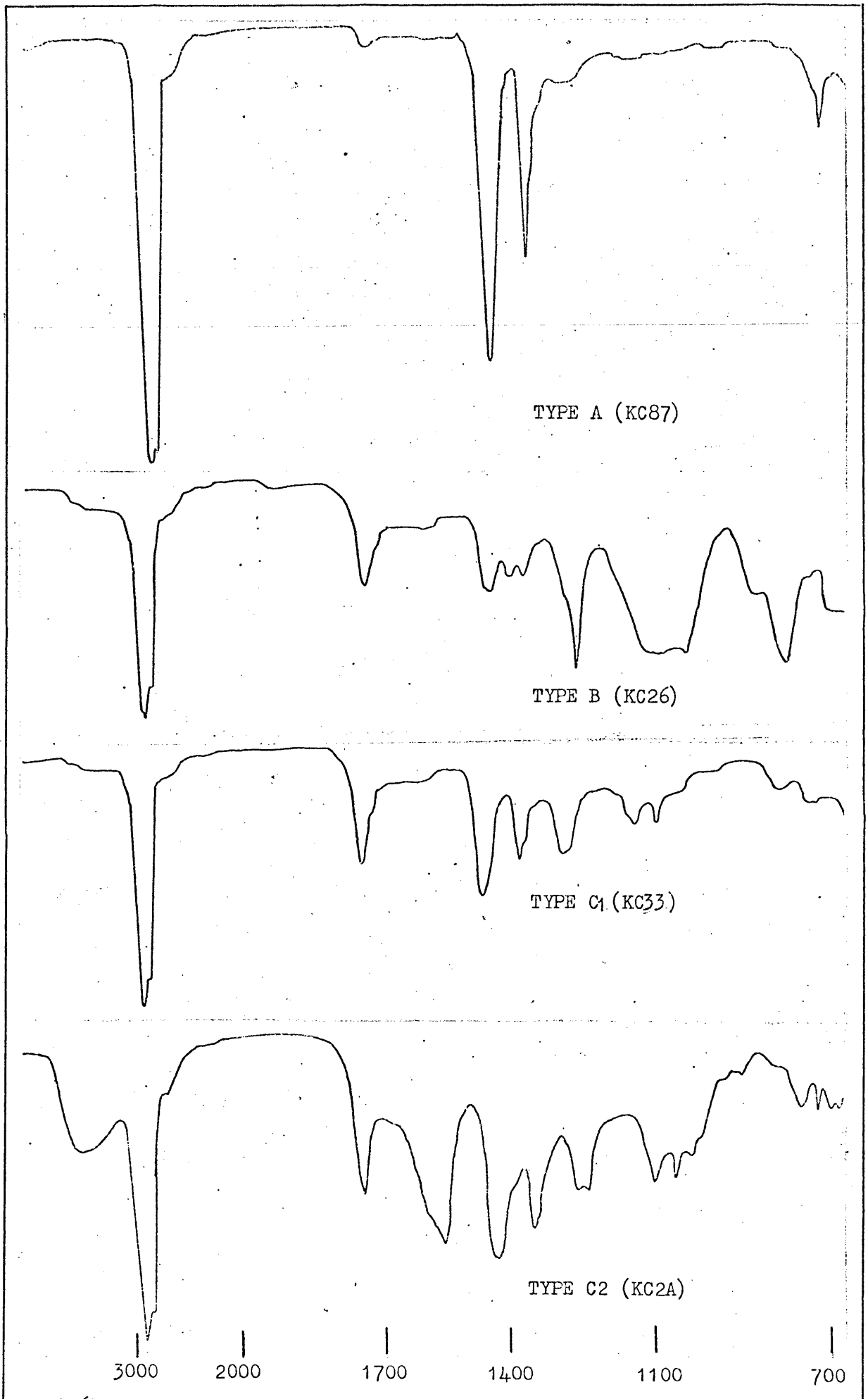


FIG.67 Kimmeridge Clay SOE SATURATE FRACTION INFRA-RED SPECTRA.
(Wavenumber cm^{-1})

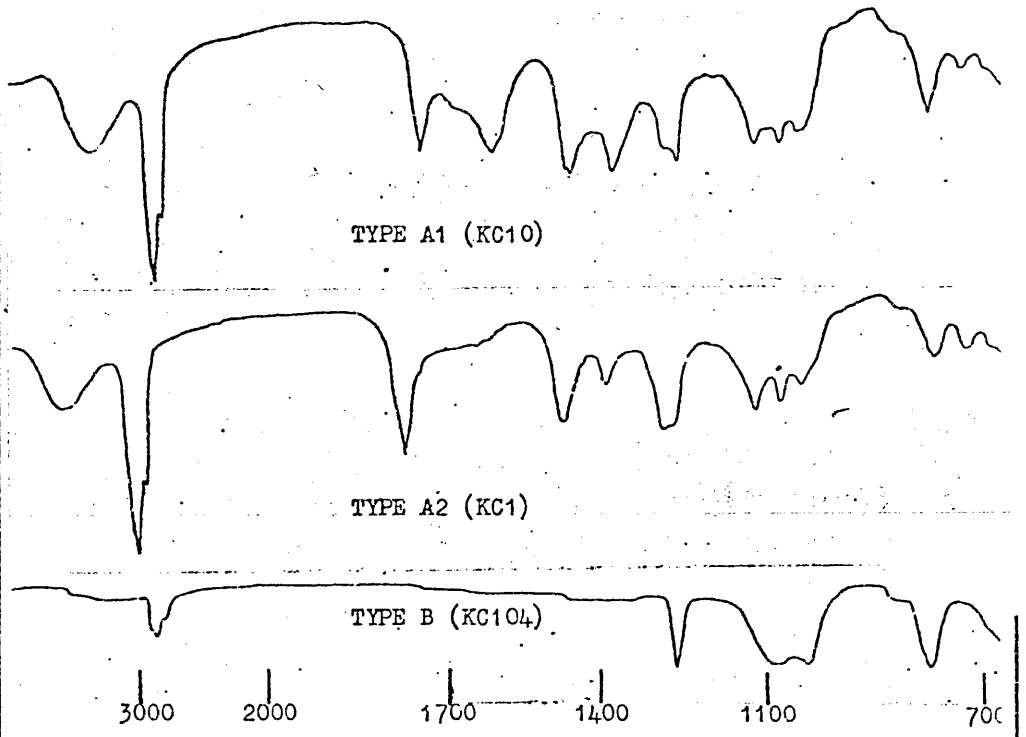


FIG.68 Kimmeridge Clay SOE AROMATIC FRACTION INFRA-RED SPECTRA. (Wavenumber cm^{-1})

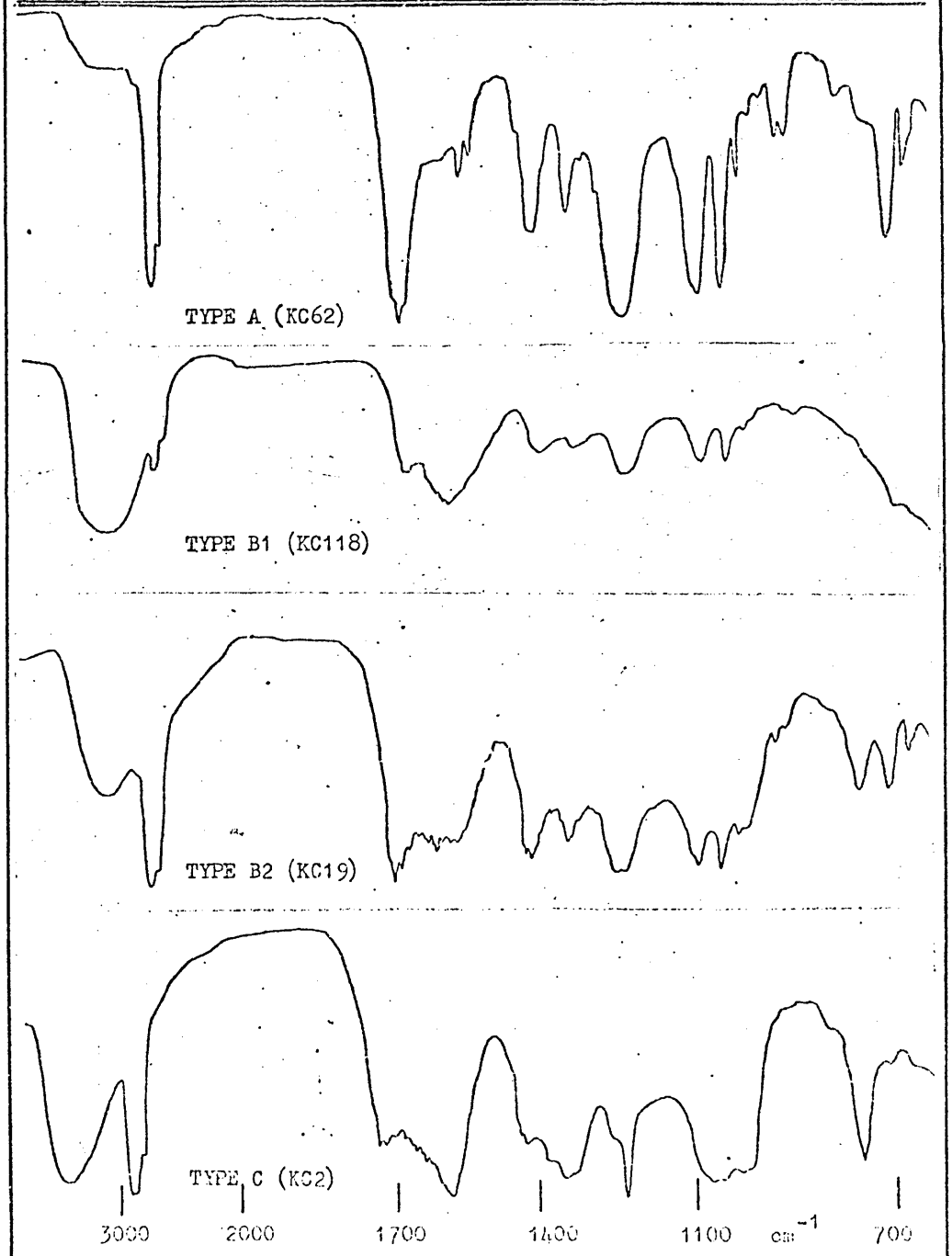


FIG.69 Kimmeridge Clay SOE ASPHALTIC FRACTION INFRA-RED SPECTRA.

TABLE 60. INFRA-RED SPECTRAL CLASSIFICATION. Kimmeridge Clay soluble extracts & extract tlc fractions. X: Omitted or no/ inadequate resolution.

SAMPLE.	TOTAL EXTRACT FIGURE 66						SATURATES FIG 67					AROMATICS F.68				ASPHALTICS FIG 69				
KC	A	B_1	B_2	C	D	X	A	B	C_1	C_2	X	A_1	A_2	B	X	A	B_1	B_2	C	X
116					x					x			x			x				
115					x				x			x				x				
114					x						x	x				x				
113					x						x				x	x				
112					x				x			x								x
111					x						x		x			x				
110					x						x		x			x				
109					x						x		x			x				
108					x				x				x			x				
107					x				x				x			x				
106					x				x						x	x				
105					x				x			x				x				
104					x						x			x		x				
103					x				x						x	x				
102					x						x		x			x				
101					x					x			x			x				
100					x						x				x	x				
99						x		x							x	x				
98						x		x					x			x				
97						x		x				x				x				
96					x			x				x				x				
95					x					x					x	x				
94					x						x				x	x				
93					x						x		x			x				
92					x					x		x				x				
91					x				x						x	x				
90					x				x							x				
89					x		x						x			x				
88					x		x						x							x
87					x		x					x.				x				
86					x					x		x				x				
84					x					x		x				x				
83					x					x		x				x				
82					x					x		x				x				
81					x						x	x				x				
80					x					x		x				x				

TABLE 60 Cont.

SAMPLE	TOTAL EXTRACT FIGURE 66						SATURATES FIG. 67					AROMATICS F.68				ASPHALTICS FIG. 69				
NO	A	B_1	B_2	C	D	X	A	B	C_1	C_2	Z	A_1	A_2	B	X	A	B_1	B_2	C	X
79					x					x		x				x				
78					x					x		x				x				
77					x				x				x			x				
76					x				x				x			x				
75					x					x		x				x				
74	?								x			x				x				
73	?									x					x					
72					x					x		x				x				
71					x						x	x				x				
70					x				x			x				x				
69					x				x			x				x				
68					x					x			x					x		
67					x				x				x			x				
66					x				x				x			x				
65						x				x		x					x			
64					x				x				x			x				
63					x				x			x				x				
62						x			x						x					x
61					x				x				x			x				
60					x					x			x			x				
59					x					x		x				x				
58					x				x				x			x				
57					x				x						x	x				
56					x				x				x			x				
55A					x				x				x			x				
55B					x				x				x			x				
54					x				x				x			x				
53C					x					x					x	x				
53B					x				x				x			x				
53A					x				x				x			x				
52				x					x			x				x				
51						x			x				x			x				
50					x				x			x				x				
49					x							x				x				
48					x						x	x				x				
47					x				x			x				x				
46					x				x			x								x
45					x				x				x			x				
44					x				x			x				x				
43					x					x			x			x				
42					x				x			x				x				
41					x				x				x			x				
40					x				x				x			x				

TABLE 60 Cont.

SAMPLE.	TOTAL EXTRACT FIGURE 66						SATURATES FIG 67					AROMATICS F.68				ASPHALTICS FIG 69				
NO.	A	B_1	B_2	C	D	X	A	B	C_1	C_2	X	A_1	A_2	B	X	A	B_1	B_2	C	X
39					x				x				x			x				
38					x				x				x			x				
37					x				x			x				x				
36					x				x			x				x				
35					x					x			x				x			
34					x				x			x				x				
33				x					x						x	x				
32					x					x			x			x				
31					x					x		x				x				
30					x				x				x			x				
29					x				x				x							x
28					x				x				x			x				
27					x				x				x			x				
26					x			x				x				x				
25					x				x				x			x				
24					x			x					x			x				
23					x			x					x			x				
22				x				x					x					x		
21					x				x				x			x				
20					x				x			x				x				
19					x					x		x				x				
18					x					x		x							x	
17					x					x		x						x		
16			x							x		x							x	
15			x							x		x							x	
14			x							x			x						x	
13			x						x						x				x	
12				x					x						x	x				
11				x					x				x						x	
10			x						x				x						x	
9					x				x				x					x		
8			x							x		x							x	
7			x							x			x						x	
6			x							x		x							x	
5			x							x		x							x	
4		x							x			x							x	
3		x								x			x						x	
2		x							x				x						x	
1			x							x			x						x	

TABLE 61. ULTRA-VIOLET CLASSIFICATION.

CLASS.	MAIN PEAK POSITION (nm).	SUBSIDIARY PEAKS/SHOULDERS (nm)	MEMBERS./ILLUSTRATION.
A.	c.228 - 238.	c.260-268; c.296.	KC 1,33 Fig.70 KC1.
B.	c.224 - 233.	c.253-258.	KC4,68,74,86 & W25,32 Fig.70 KC74.
C.	c.224 - 231.	(c.253-265); c.273-275; c.281-282.	KC55A,116 & W5,7,15,2[illegible] 31. Fig.70 KC116.
D.	c.229 - 235	c.252; c.257-258; c.262.	KC28,32,48,53B,106,128. Fig.70 KC48.
E.	c.226 - 235.	c.257-260; c300.	KC5,67 & W8,21,22. Fig.70 KC67.

FIG.70 ULTRA-VIOLET SPECTRAL STUDY: Representative spectra for 5 different classes of Kimmeridgian & Neocomian aromatic extract fractions.

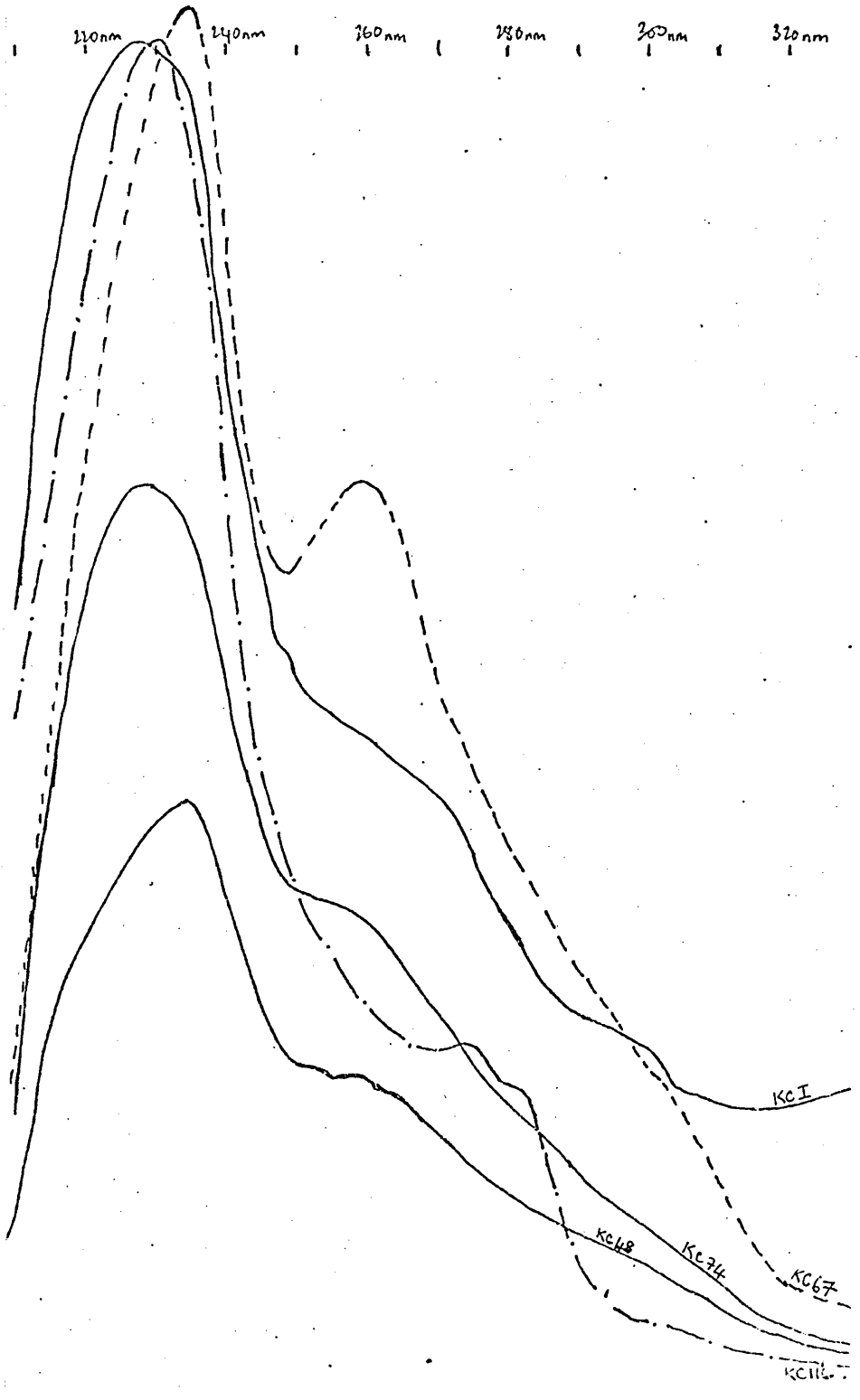
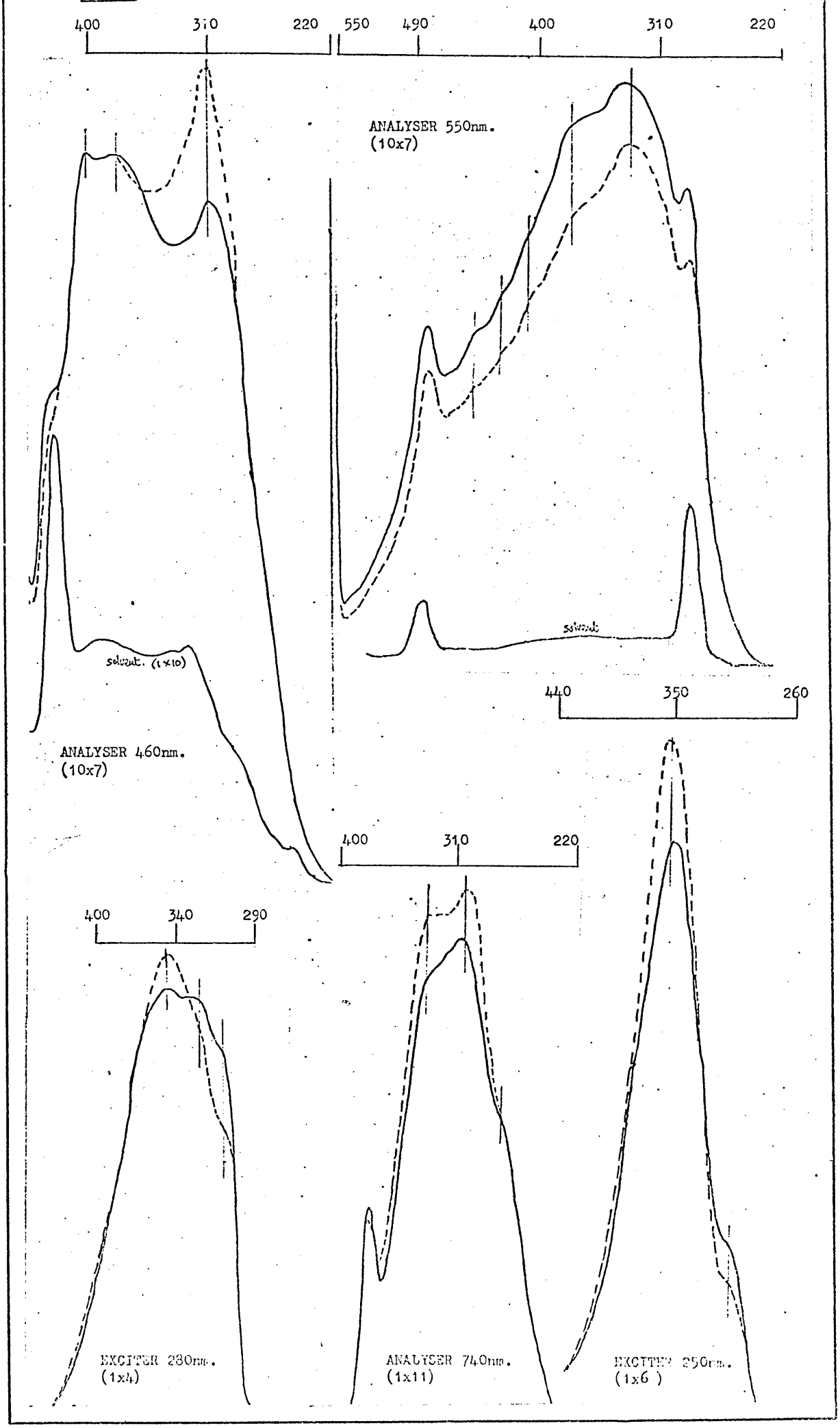


FIG.71 DETAILED FLUORESCENCE SPECTRAL STUDY for KC1——& KC33 ----



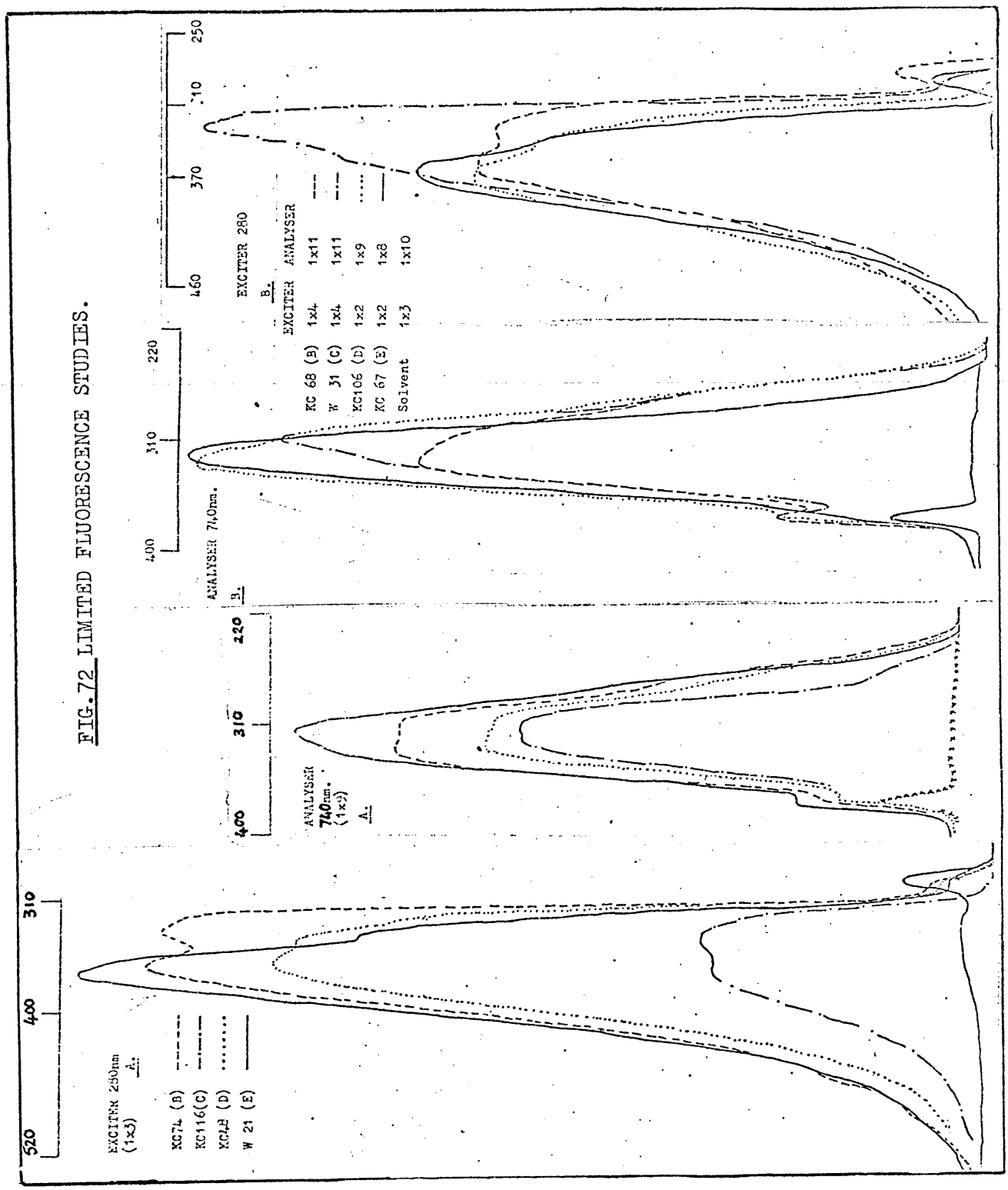


TABLE 62. FLUORESCENCE SPECTRAL CLASSIFICATION

UV CLASS.	KEEPER.	ANALYSER(nm).	FLUORESCENCE(nm).	EXCITER(nm).	ABSORBANCE(nm).
A. Fig.71 excluding 310nm * excitation	KC1	740	305,328,(280).	250	350.
	KC33	740	301,328,(280).	250	356.
	KC1	460	313,385,406.	280	328,350.
	KC33	460	313,382,400.	280	325,350.
	KC1	550	331 370,(405, 418,445.)	310*	359.
	KC33	550	328,370,(400, 418,439.)	310*	356.
B. Fig.72	KC68	740	310,(335.5),325.	280	329.5,358.
	KC74	740	310,336.5,(325).	280	333,361.
C. Fig.72	KC116	740	313,325.	280	331,358.
	W31	740	307,325.	280	326.5,352.
D. Fig.72	KC48	740	310,325.	280	340sh,358.
	KC106	740	310,325.	280	340sh,363.5.
E. Fig.72	KC67	740	319,329.	280	364,340sh.
	W21	740	319,331sh.	280	370,334sh.

KC 116:	Abund.plant fragments,spores & algal filaments. Small spherical spores often indent -ed,elongated or broken. Alisporites sp. & Tasmanites sp. identified; latter shown in Plate 24. Plate 25 shows an undetermined organic body which has an interesting suture. (Tourmaline is conspicuous amongst the heavy mineral residues)
KC 108:	Fine sapropel,common plant fragments,abundant spores & ?algal filament. Spores usually small,spherical with few broken. Tasmanites sp. identified. (Quartz aggregates common in mineral residues.)
KC 100:	Abundant fine sapropel,common plant fragments and abundant spores. Latter generally small & spherical but occassionally massive. Small,marine spore, Classopollis sp. identified. Plate 26 depicts a thin-walled sphaeroid ? acritarch
KC 92:	Common fine sapropel,sparse plant fragments,abundant spores & some algal filaments. Spores both large & small,spherical & broken. Plate 27,assuming superimposed crystal not aperture.is of a thin-walled degraded algal spore; Plates 28 & 29 show chains of algal cells (?) or more probably by analogy with KC36 uncoiled 'pectin' membranes of a foraminifera sp; Plate 30 could be either a pollen,acritarch or large pectin fragment (?) and Plate 31 records a pyritised Tasmanites sp.
KC 84:	Common fine sapropel,sparse plant fragments (usually black,some very large; one structured and some brown) abundant yellow spores and algal filament. Spores small but some large; spherical,elongated or broken. Two dinoflagellates. (Quartz aggreg -ates in mineral residues.)
KC 78:	Abundant fine sapropel,abundant black plant fragments (some brown), abundant spores with algal filaments and algal cell clusters. Spores spherical,elongated or broken with or without pyrite; one triangular spore. Plate 32 is smooth,unfrilled thin-walled ?algal spore with pyrite. (Abundant quartz aggregates in mineral residues)
KC 74:	Dominant fine sapropel,rare plant material,rare spores & algal filaments. Spores usually small & spherical. Plate 33 shows folded,ornamented algal spore,Tasmanites or Crassosphaera sp.? Plate 34 could be of carbonized plant material or contamination, particularly from incomplete diesel fuel combustion ('taxi exhaust') Plate 35 is of a degraded ?algal spore.
KC 70:	Dominant fine sapropel,rare black plant fragments,rare spores (some very round & some elongated) and algal cell clusters & free cells. Plate 36 is ?algal spore.
KC 67:	Some sapropel,rare plant fragments,rare spores (spherical) and algal filaments.
KC 64:	Dominant fine sapropel,common plant fragments (some structured),common & diverse spores with ?algal cell clusters. Spores either very large (some deformed),medium or small (spherical),eg.Exesipollenites sp. Plate 37 either algal cell or fungal spore cluster. Plate 38 is vascular/tracheid plant fragment.
KC 61:	Dominant sapropel with light brown very rare spores and one bisaccate pollen grain; latter of which could be authentic (?)
KC 58:	Dominant fine sapropel,common black plant fragments,abundant spores and rare algal filaments. Spores either large or small & spherical or deformed. Plate 58 shows ?Tasmanites sp. and obliterated/pyritised spore or pollen.
KC 55A:	Dominant fine sapropel,rare black plant fragments & rare mostly broken spores.
KC 55B:	Abundant black plant fragments in common sapropel; one broken spore.
KC 53B:	Dominant sapropel,rare plant fragments (usually black but one red-brown piece), rare spores and algal filaments. Spores either large, ?Araucariacites sp. or small.
KC 48:	Dominant sapropel,common spores and rare plant fragments. Spores small-medium,often sperical but one deformed.(Some light brown)
KC 44:	Dominant fine sapropel,rare plant fragments and rare spores. ?algal filament.
KC 39:	Dominant fine sapropel,rare plant fragments,one small,sl.deformed spore and an algal filament.
KC 36:	Fine sapropel,rare small,spherical spores and rare plant fragments. Plate 40 Pollen grains; thick walled with parallel straie across central part of body.(under higher magnification) Plate 41 Folded/creased partly degraded ?outer membrane of ?pollen grain or acritarch; partly pyritised. Plate 42 ?Fungal filament. Also diagnostic coiled pectin membrane of foraminifera sp. and diagnostic fungal filament - spores produced in acropetal succession at end of hyphae; hyphae generally have buds but rare clamp connections occur.
KC 32:	Dominant sapropel,very rare plant fragments.
KC 25:	Dominant fine sapropel,common plant fragments & abundant spores. Latter small, medium or large & spherical or deformed/broken. ?algal filaments.
KC 18:	Fine sapropel,very rare plant fragments & rare spores; latter small-medium,spherical
KC 15:	Fine sapropel,very rare spores (small,spherical) and an ?algal filament. Indeterminate body.
KC 11:	Fine sapropel with very rare small,greenish spherical spores.
KC 7:	Fine sapropel with one broken spore. Plate 43 large ?composite body - algal/pollen?
KC 1:	Fine sapropel,rare plant fragments and rare spores. Structured black matter as P13L.

NB: The foregoing is generally tentative except where clarified and is awaiting confirmation by SEM (Peat,priv.comm.1977). The occurrence of two dinoflagellates with no conclusive acritarchs (Davies,Madani & Peat independently) in view of their previous documented abundance (eg.Downie,1955) suggests (especially as they should have survived the maceration process) that weathering of the thin-walled organics has occurred in the surface samples (?)

See Appendices, 16.

TABLE 63. KIMMERIDGE CLAY MACERATION RESULTS.(with explanations for Plates 24 - 43.)

PLATE 24 : KC 116 x 165.



PLATE 25 : KC 116 x 165.



PLATE 26 : KC 100 x 103.

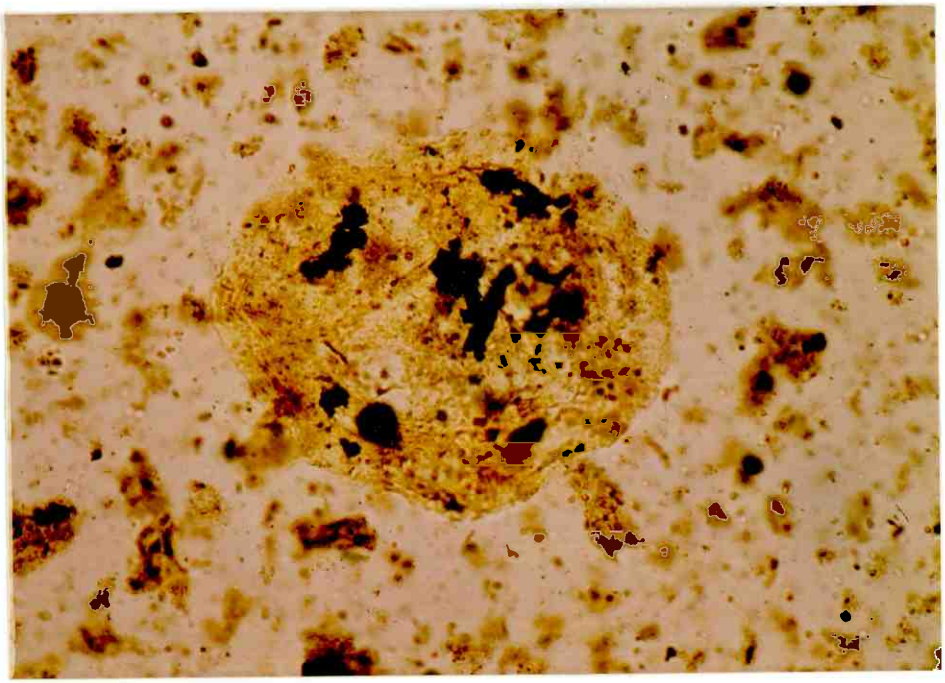


PLATE 27 : KC 92 x 165.

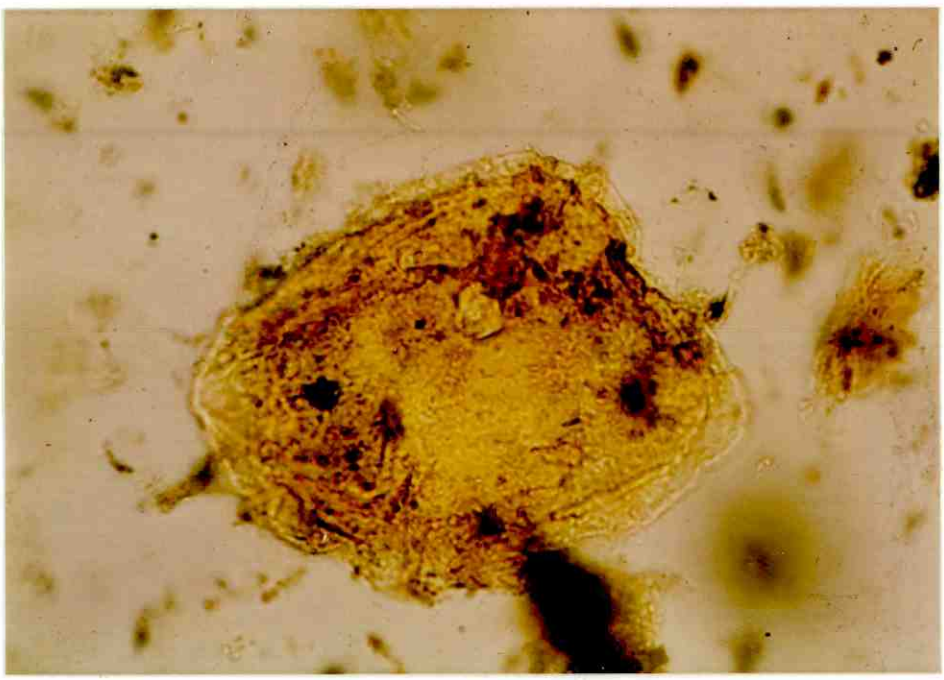


PLATE 28 : KC 92 x 103.

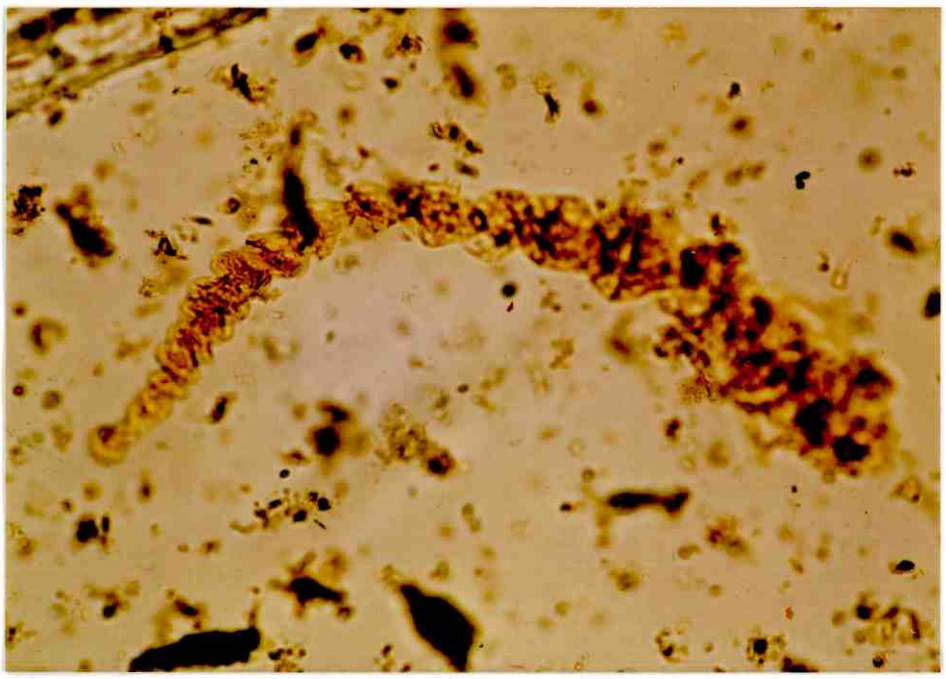


PLATE 29 : KC 92 x 103

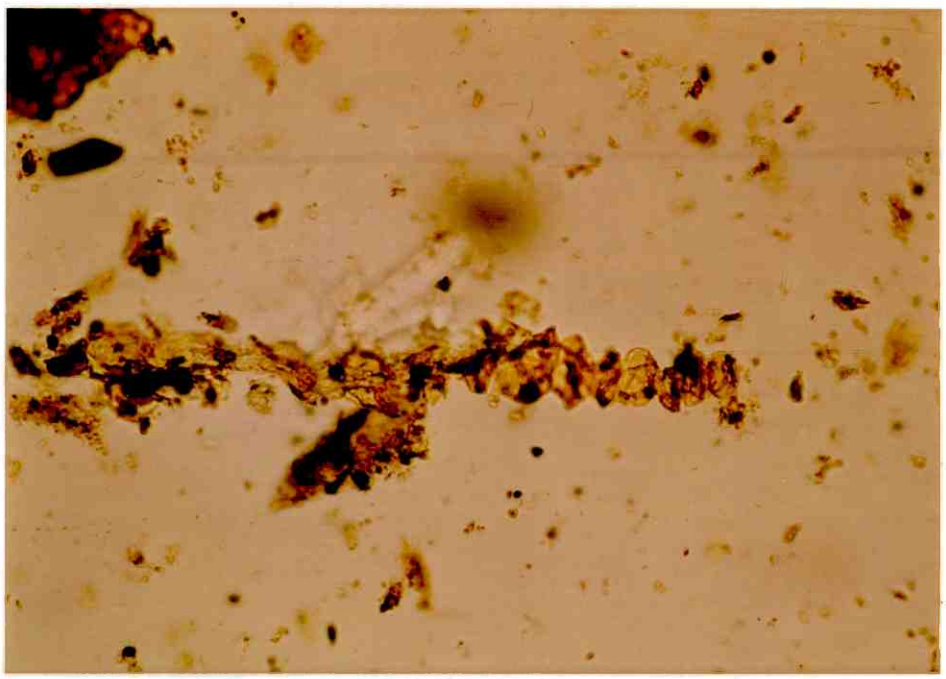


PLATE 30 : KC 92 x 103.



PLATE 31 : KC 92 x 103.

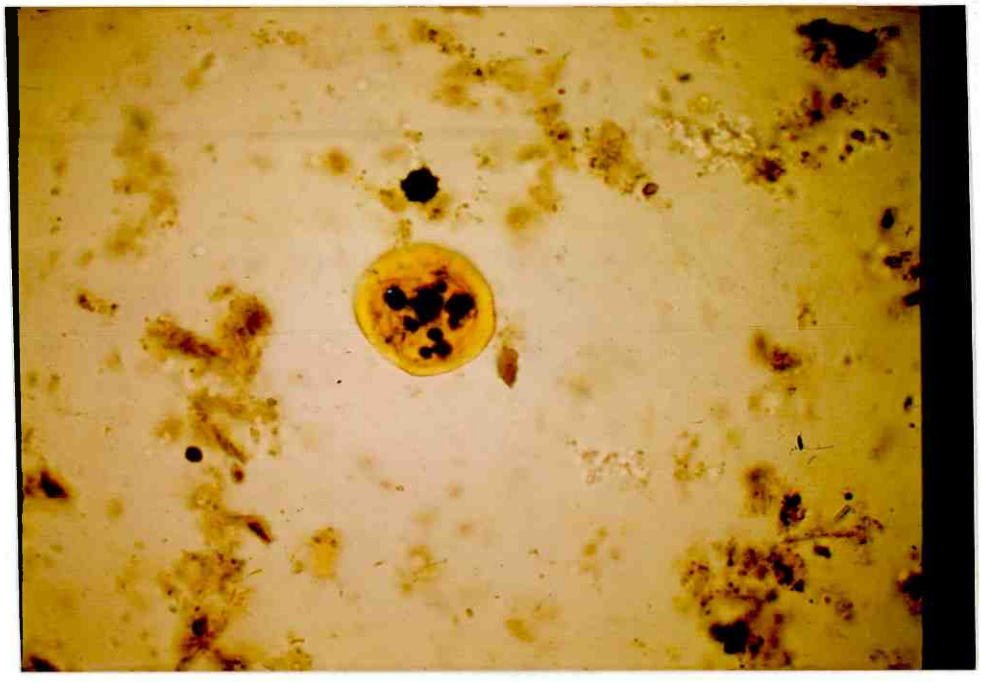


PLATE 32 : KC 78 x 165.



PLATE 33 : KC 74 x 165.

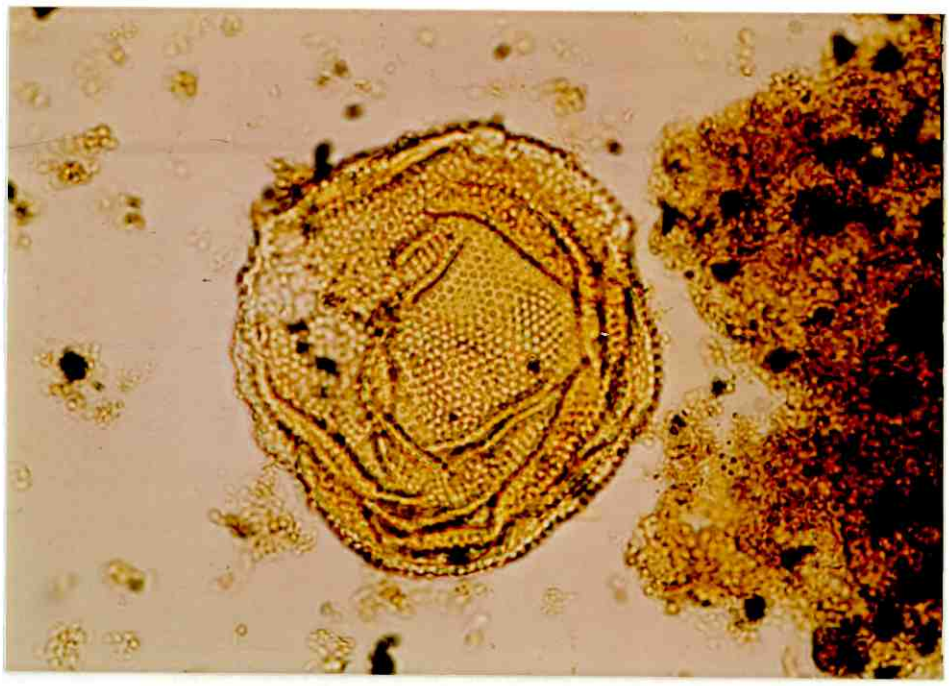


PLATE 34 : KC 74 x 165.

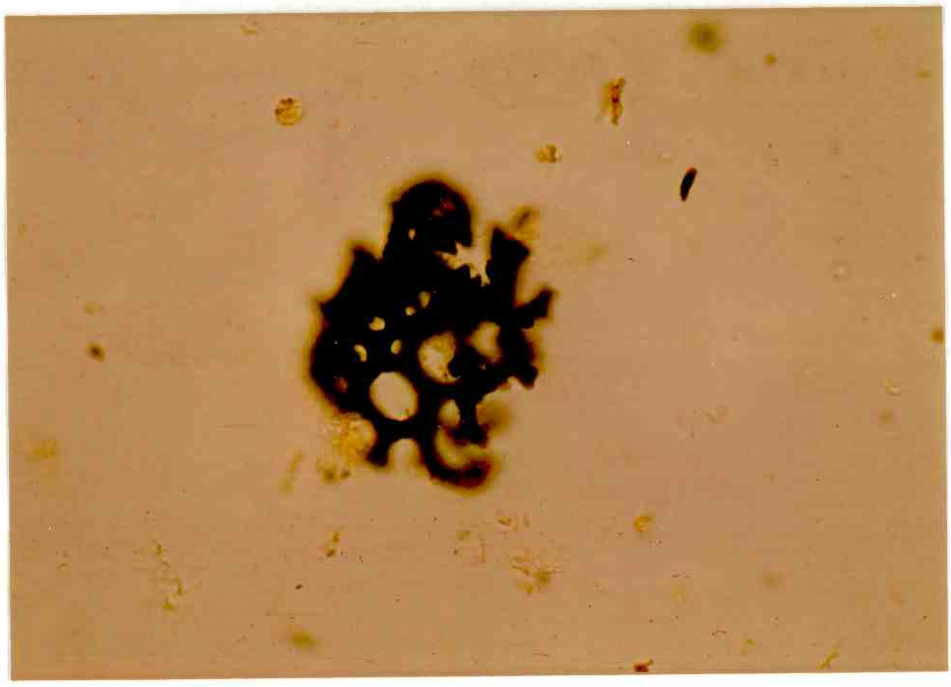
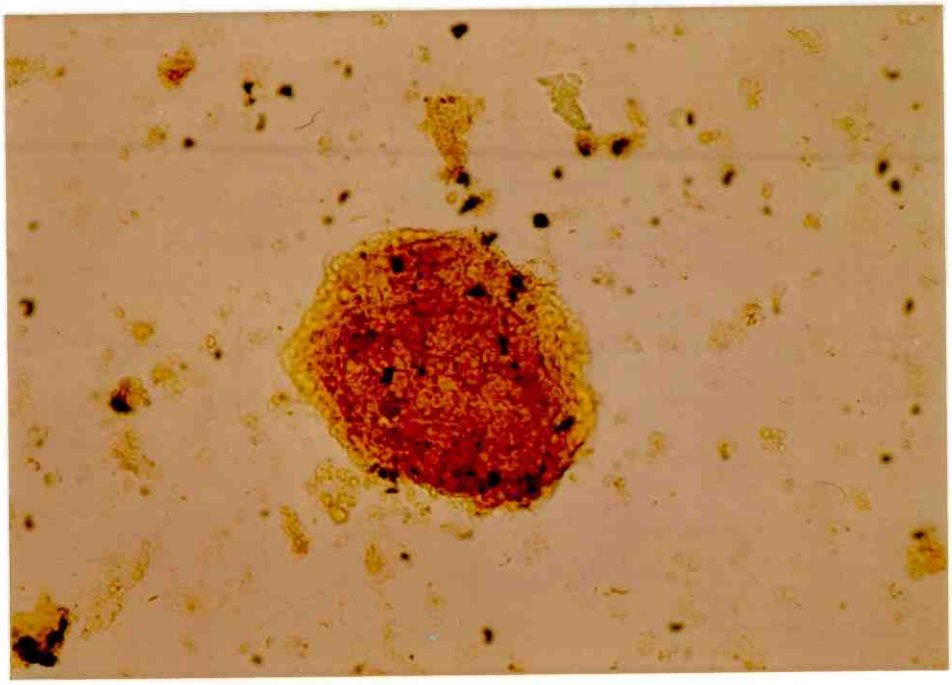


PLATE 35 : KC 74 x 103.



.PLATE 36 : KC 70 x 103.



PLATE 37 : KC 64 x 103.

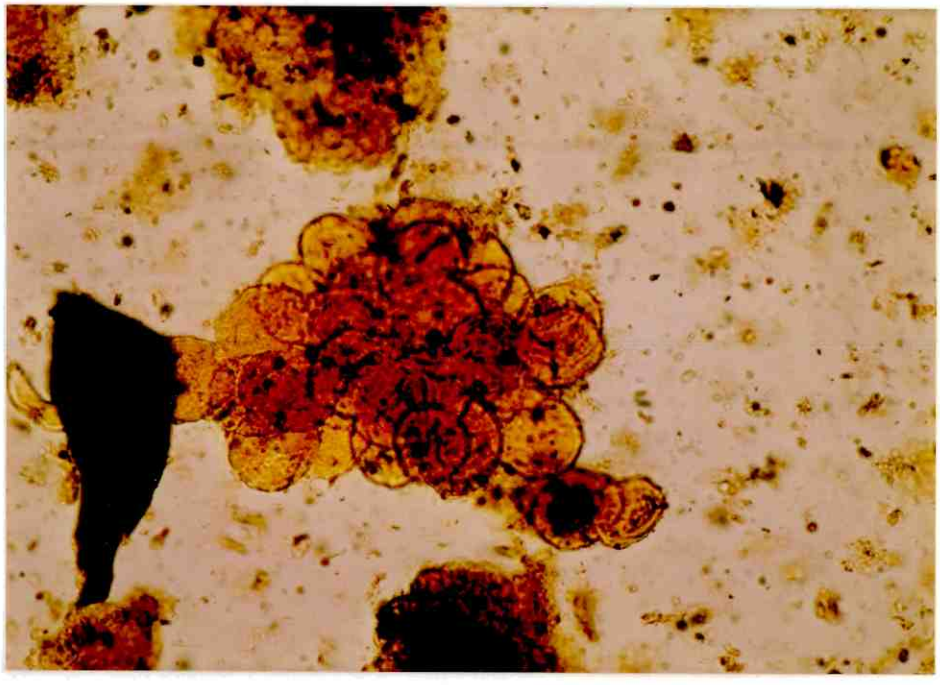


PLATE 38 : KC 64 x 103.

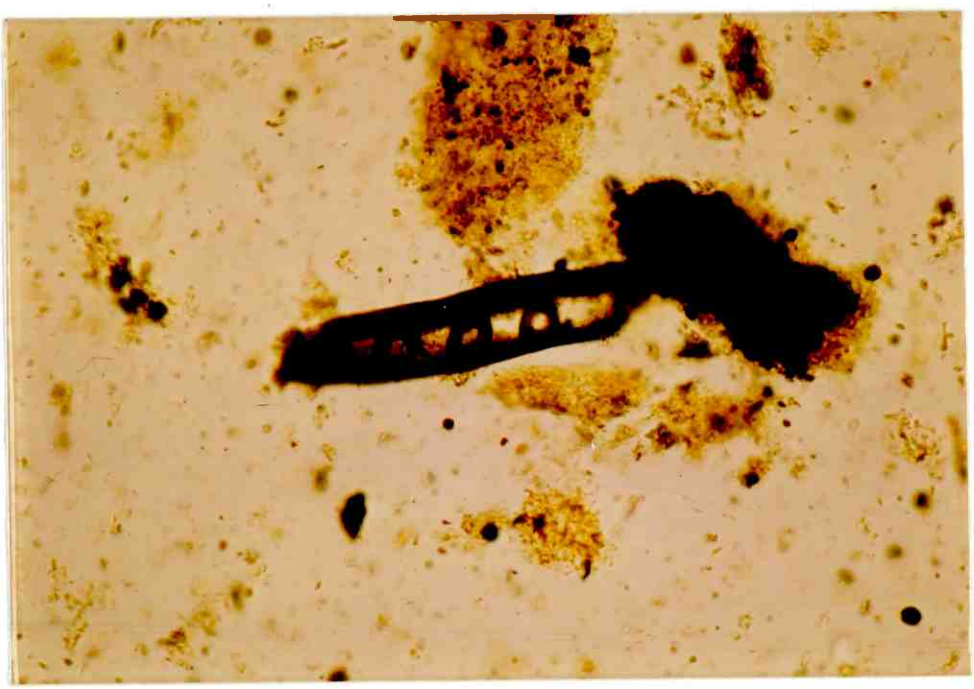


PLATE 39 : KC 58 x 103.

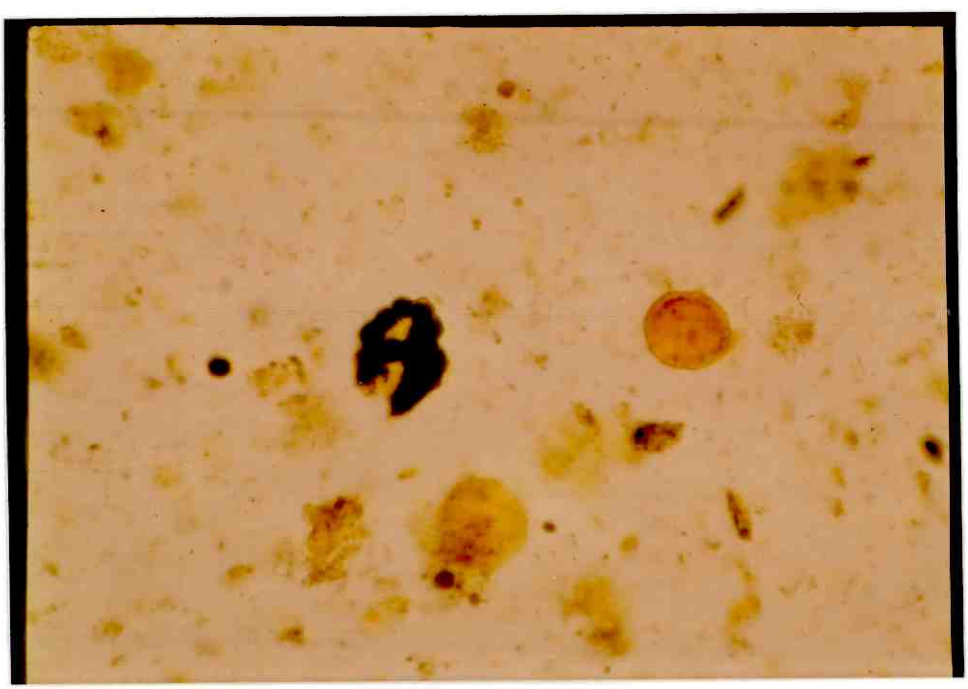


PLATE 40 : KC 36 x 165.

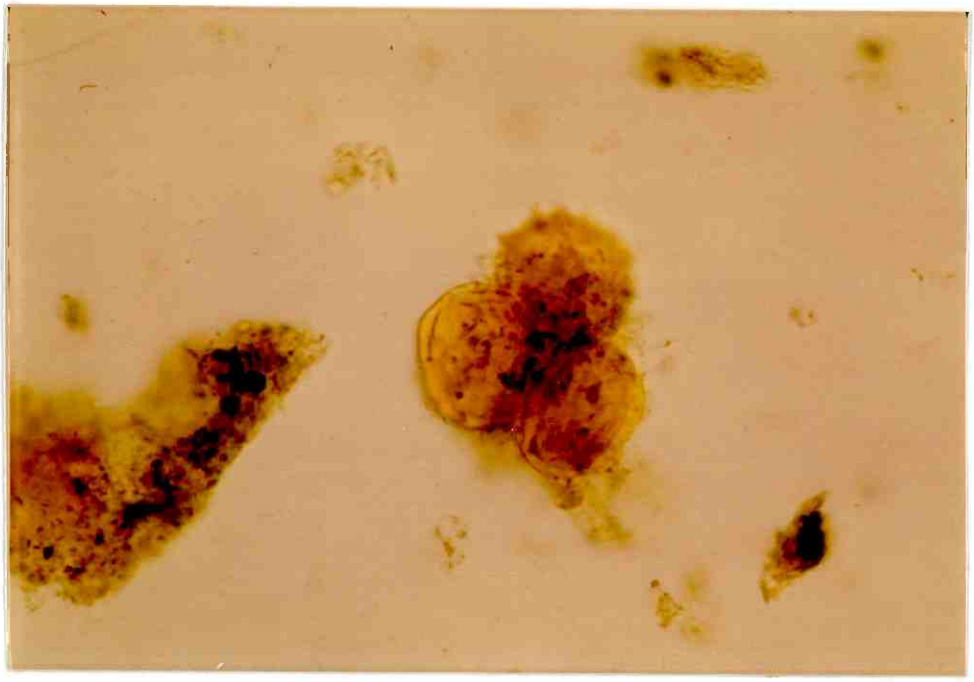


PLATE 41 : KC 36 x 103.

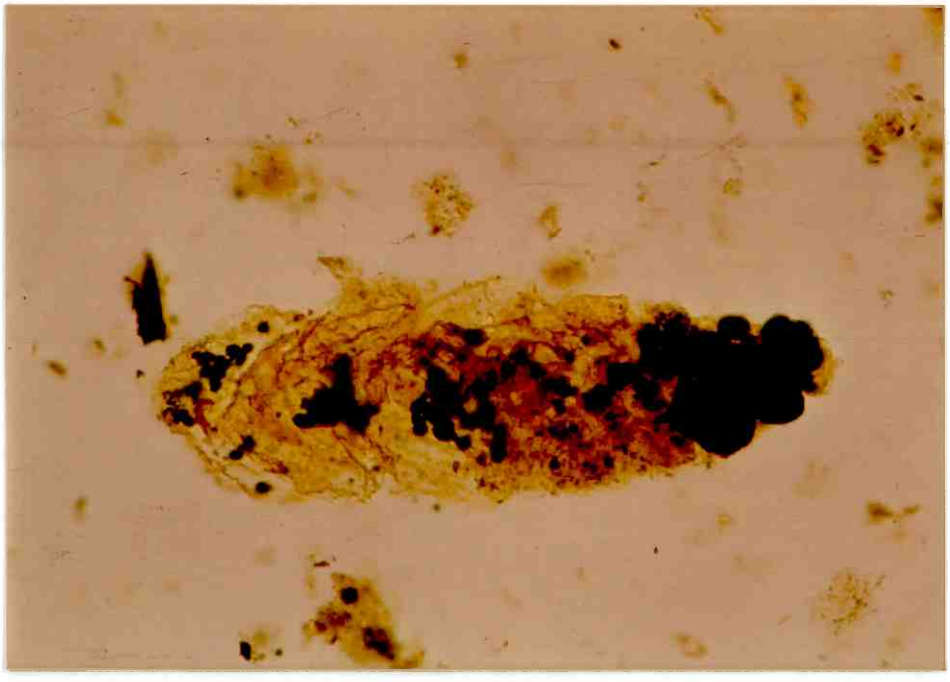


PLATE 42 : KC 36 x 103.

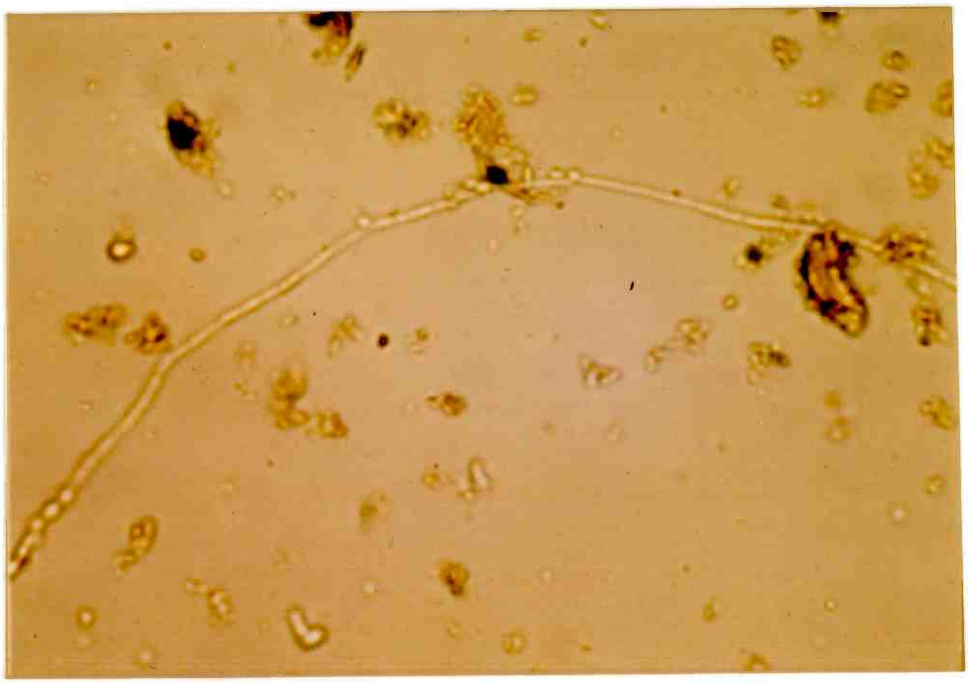


PLATE 43 : KC 7 x 165.

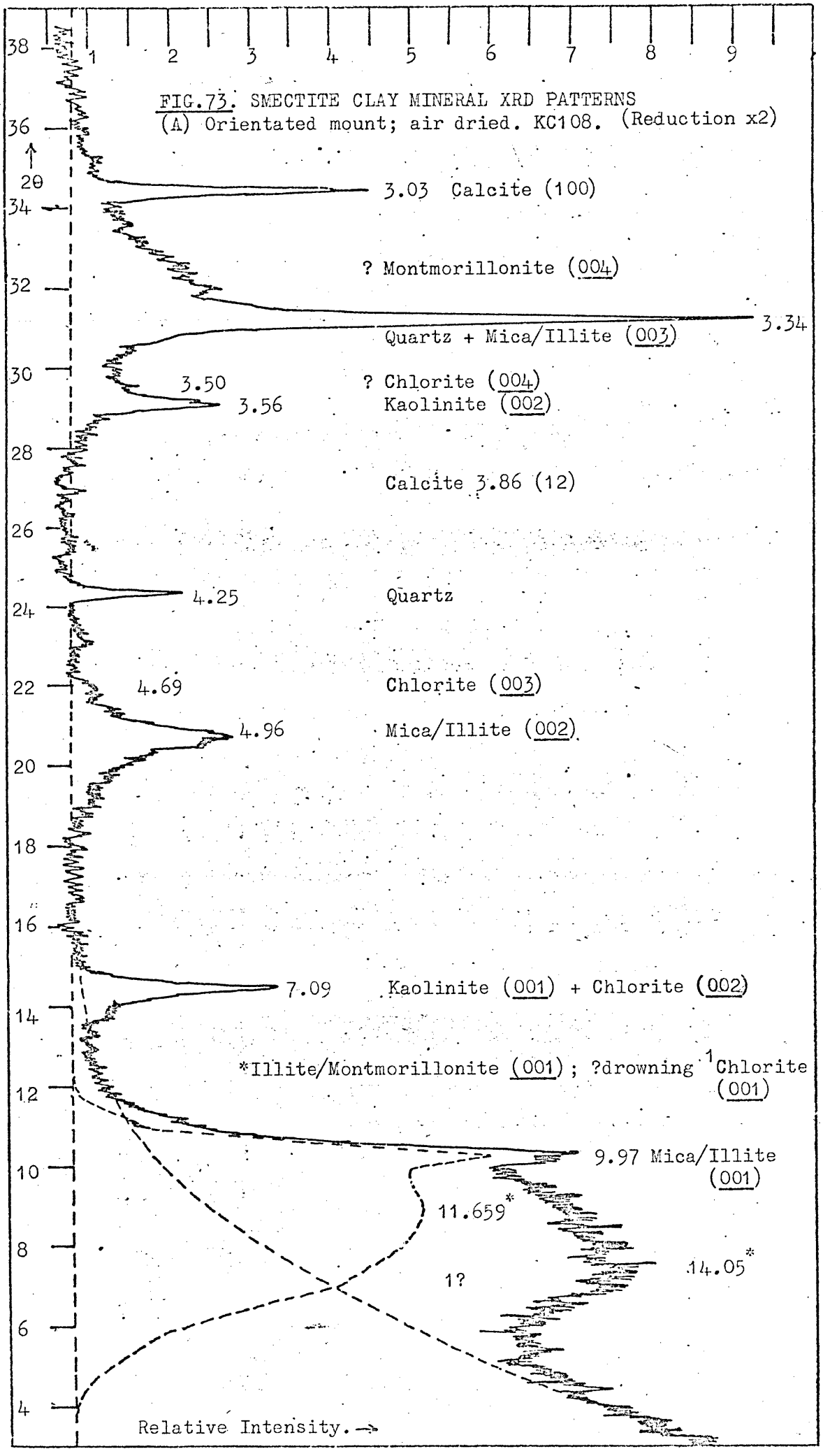


Throughout the major minerals are kaolinice, illite, quartz and calcite. Dolomite is especially accentuated at several of the cementstones although it does not occur everywhere. Chlorite, and, from the detail clay studies, mixed-layer clays also occur; KC108 is unusual in showing a very pronounced smectite (with respect to the other selected samples) (Figure 73). In a minor-trace capacity pyrite appears to be almost ubiquitous and gypsum is very common. KC86 appears unique in displaying an abundant yellow powder which via smear mounting proved to be jarosite $KFe_3(SO_4)_2(OH)_6$ (where K can be substituted by Na) (Curtis priv. comm. 1977). The occurrence of feldspars and siderite is given on Log 8.

Results for the selected detailed clay studies are summarised in Table 64 and a typical result is pictured in Figure 74. An occurrence (varying from a well defined peak through to a shoulder and sometimes exceeding the preceding calcite peak in intensity) of a peak correlating to a spacing of about 3.015Å suggests the possible (unexpected) occurrence of high magnesium calcite and the peak position by reference to Figure 75 infers about 8 mole percent of magnesium carbonate (Log 8).

The majority of the cementstones show a main 'dolomite' diffraction peak preceding 36.1° (2θ) for whole-rock studies with correction for (quartz) alignment (at 31.1°, 2θ). 36.05°, 35.95°, 36.05°, 35.95°, 36.0°, 36.0°, 35.95° and 35.90° were measured for KC5, 11, 18, 32, 39, 44, 54 and 61 respectively. The presence of ferrousions , necessary for ferroan dolomite formation, were further suggested by a random Alizarin Red S staining (Reid 1969) test upon (KC61) rock powder as a mauve colouration resulted.

Overall, the argillaceous facies of the formation conform to a 'typical' clay. However, the confirmation of mixed layer clays is encouraging with regard to enhancement of a general non-source illitic clay facies. With what little control is offered by the (poorly defined) main illite and kaolinite diffraction peaks (in whole rock studies) the ratio of the two clays appears constant throughout the section except from about KC101 and upwards when kaolinite shows a gradual decrease. At this level and in the same vertical direction a very fine sand becomes extremely conspicuous (Log 8). Taken together a change in depositional conditions is suggested and the previously postulated shallowing/


FIG.73. SMECTITE CLAY MINERAL XRD PATTERNS
(A) Orientated mount; air dried. KC108. (Reduction x2)
2θ
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
1
2
3
4
5
6
7
8
9
3.03 Calcite (100)
? Montmorillonite (004)
3.34
Quartz + Mica/Illite (003)
3.50
? Chlorite (004)
3.56
Kaolinite (002)
Calcite 3.86 (12)
4.25
Quartz
4.69
Chlorite (003)
4.96
Mica/Illite (002)
7.09
Kaolinite (001) + Chlorite (002)
*Illite/Montmorillonite (001) ; ?drowning
1
Chlorite (001)
9.97 Mica/Illite (001)
11.659*
14.05*
1?
Relative Intensity.

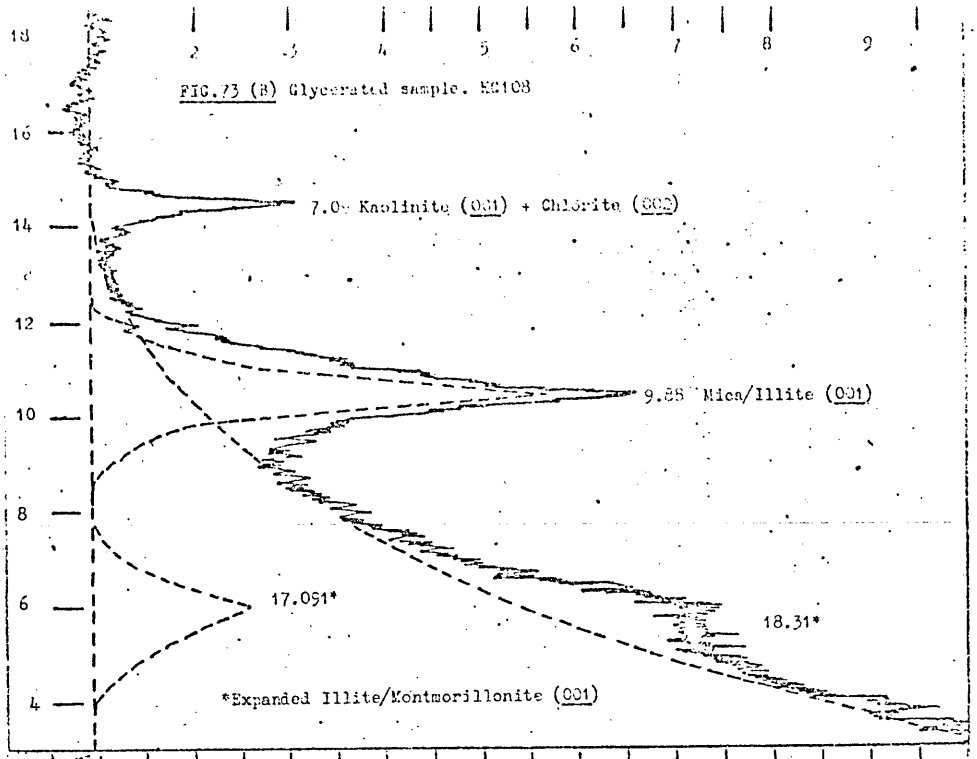


FIG.73 (B) Glycerated sample. KC108

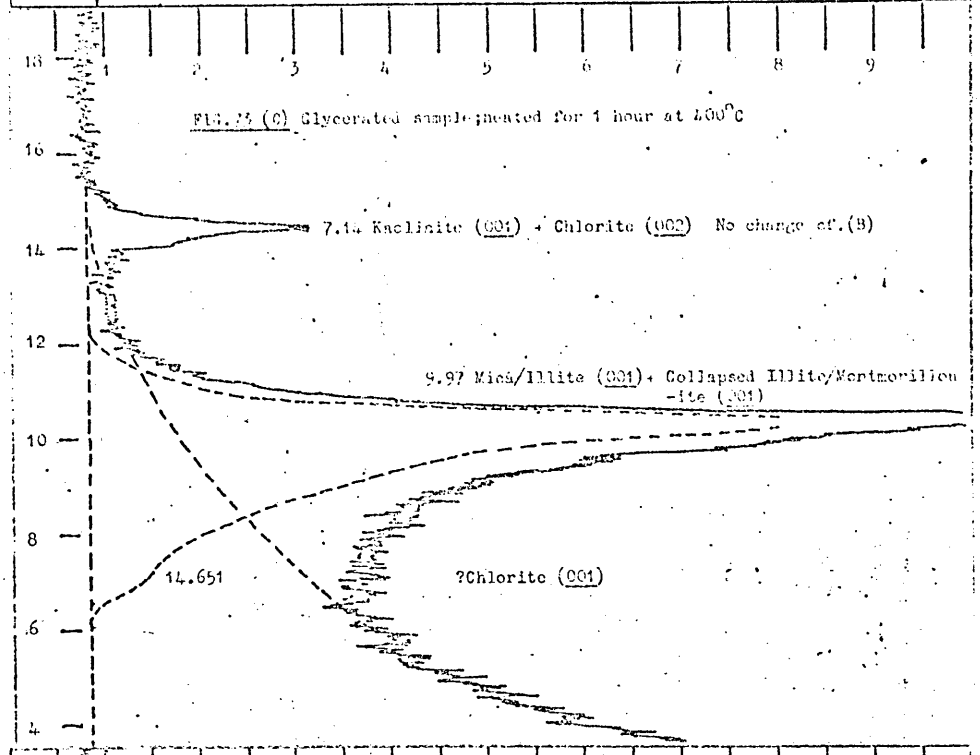


FIG.73 (C) Glycerated sample heated for 1 hour at 400°C

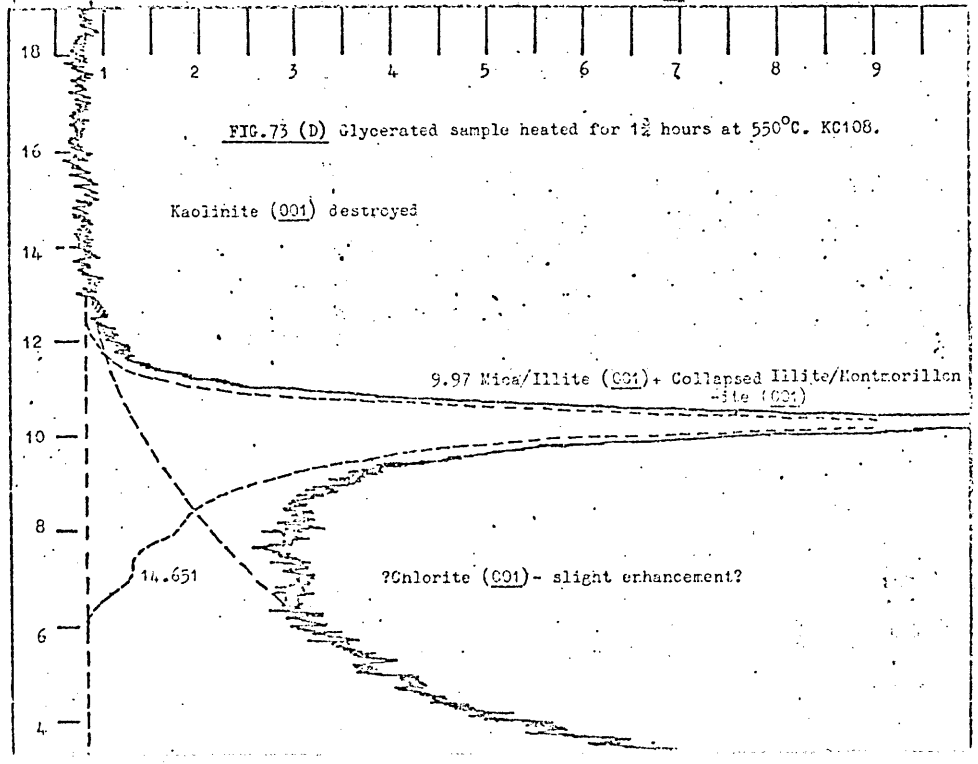


FIG.73 (D) Glycerated sample heated for 1½ hours at 550°C. KC108.

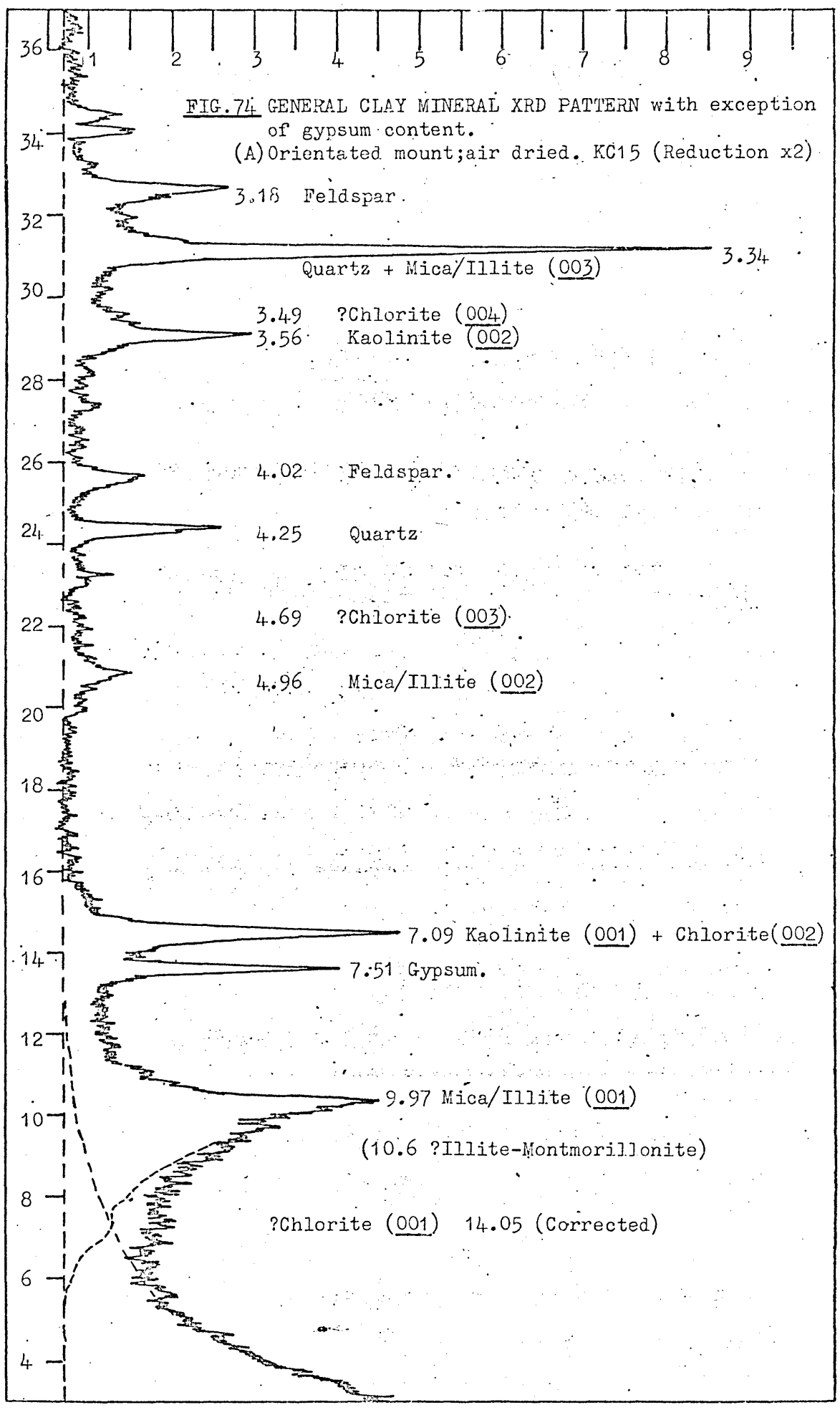


FIG.74 GENERAL CLAY MINERAL XRD PATTERN with exception of gypsum content.
(A) Orientated mount; air dried. KC15 (Reduction x2)

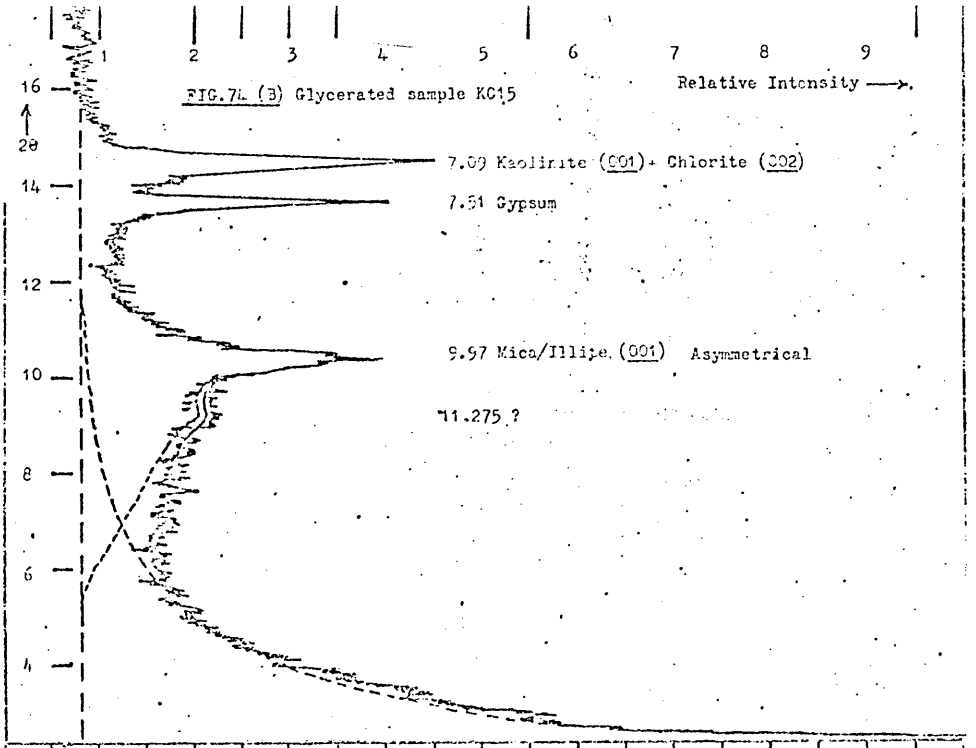


FIG.74 (B) Glycerated sample KC15

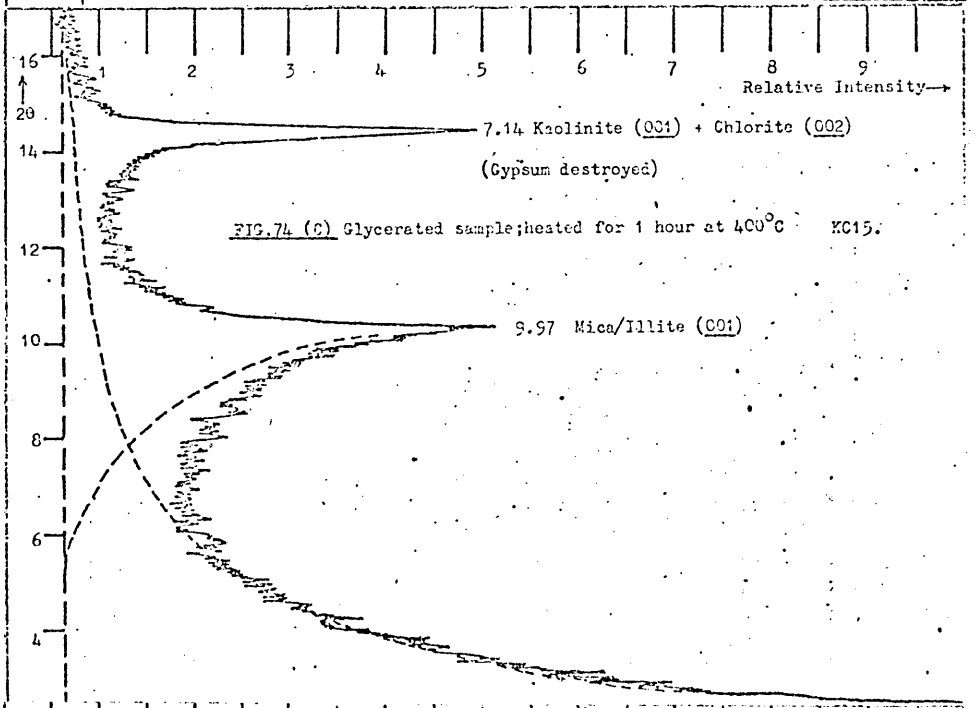


FIG.74 (C) Glycerated sample;heated for 1 hour at 400°C KC15.

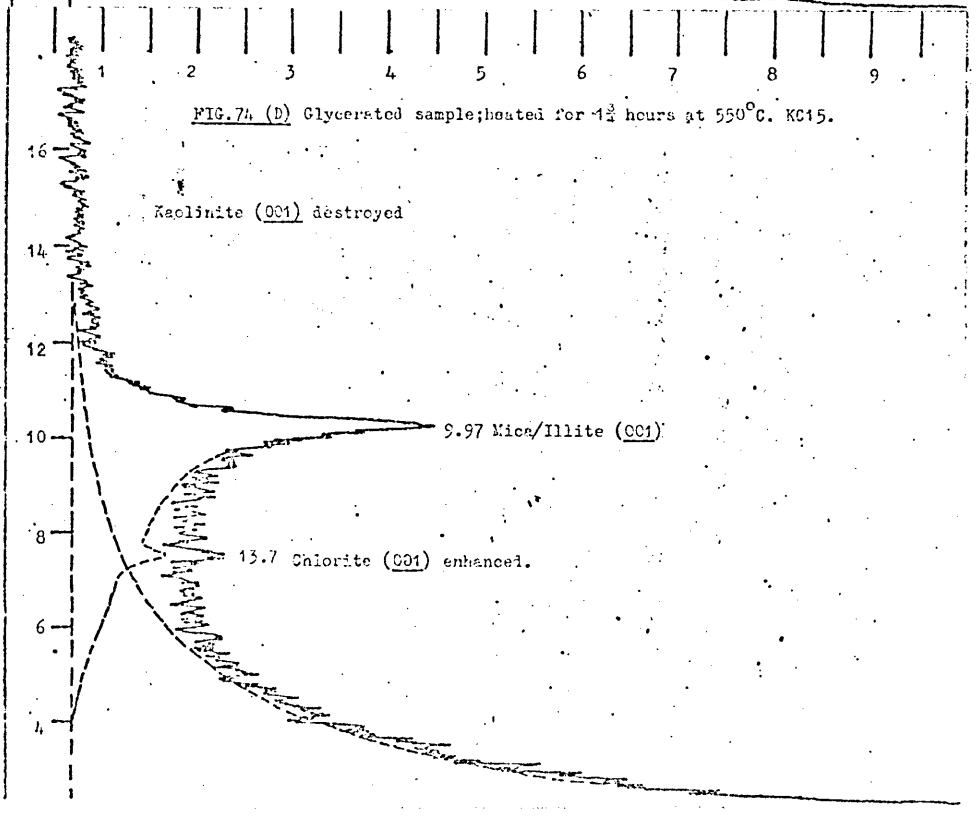


FIG.74 (D) Glycerated sample;heated for 1¾ hours at 550°C. KC15.

SAMPLE.	ILLITE.	KAOLINITE.	CHLORITE.	SMECTITE.
108	P	P	?	P
100	P	P	P	P
92	P	P	?	P
84	P	P	P	P
78	P	P	P	P
70	P	P	A	?
64	P	P	A	?
58	P	P	P	?
55A	P	P	A	?
53A	P	P	?	?
44	P	P	?	?
36	P	P	P	?
25	P	P	?	?
18	P	P	A	?
15	P	P	P	?
11	P	P	A	?
1	P	P	P	?

TABLE 64. CLAY MINERAL XRD RESULTS according to Table 38 and Figs: 73 & 74.

FIG.75 MOLE PERCENT $MgCO_3$ v. CALCITE/DOLOMITE PEAK POSITION.

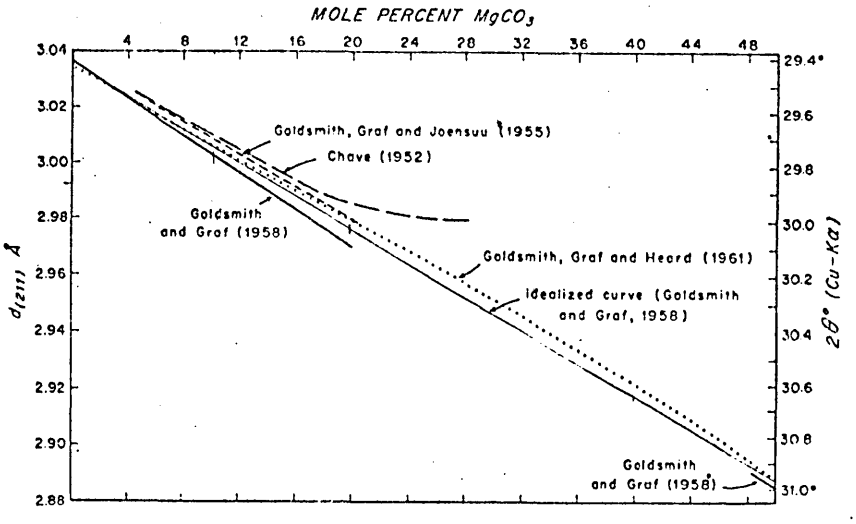


Fig. 16. Various curves relating the mole percent $MgCO_3$ in a calcite (or dolomite) with the position of the d(211) peak. The GOLDSMITH, GRAF and HEARD (1961) curve comes the closest to the idealized curve (From Milliman, 1974.)

regression is thought to occur at about 160 feet below the Massive Bed; agreeing with Blake (of 1880) and adding about 50 feet to Townson's (1975) Upper Kimmeridge Clay limit (in a downward sense). Independently, Irwin et al (Sept. 1977) have confirmed the suspicion of an iron-rich (ankerite) to iron poor (ferroan dolomite) composition for the cementstones where the limits of $(Ca_{0.548}Mg_{0.336}Fe_{0.117})CO_3$ and $(Ca_{0.554}Mg_{0.365}Fe_{0.082})CO_3$ were disclosed. *
No organic geochemical characteristics were seen to correlate with the mineralogical trends and the accummulation of organic matter appears to be independent of the sediment supply; supporting an 'in-situ' biological generation.

10 X-RAY FLUORESCENCE

In all samples examined excellent agreement is found for sulphur and chlorine whilst iron generally shows almost equally good agreement (i.e. within $\pm$3.0 of the respective recommended $K\alpha/K\beta$ ratios). However, manganese and bromine, in contrast, show an almost complete disagreement for the whole section (i.e. outside $\pm$3.0 of the respective recommended $K\alpha/K\beta$ ratios). Therefore, the ubiquitous occurrence of sulphur, chlorine and iron has not been generalised on Log 8 where only the variation in manganese and bromine is shown. Agreement within the limits for each element is taken to confirm the presence of the respective element whilst disagreement leaves the opportunity for a possible occurrence by the corresponding element (Borley priv. comm. 1976).

In summary, the universal occurrence of sulphur within the SOEs for the section is discouraging as sulphur has long been a handicap in the exploitation of the oil shales from the succession. Yet, the origin of the sulphur (and the other elements) could be a function of the extraction technique and not necessarily reflect the true nature of the SOE for all parts of the section.

11 GAMMA-RAY LOGGING

The sample counts less an averaged background are plotted stratigraphically on Log 6 where an overall higher level of activity between the Flats and Grey Ledge Stoneband (KC5 - KC39) contrasts with a lower subdued activity for the remainder of the section. Conspicuous activity is obvious for four (perhaps five) intervals: KC110 - 108, (KC76-68), KC59 - 56, KC34 - 30 and KC10 - KC 6 (approximately) and late

* By wet chemical analysis, Bellamy (1977, Journ. Sed. Petrology, v.47, n.3, pp. 973-978.) found the composition of the non-ideal Flats' dolomite to be $(Ca_{0.53}Mg_{0.40}Fe_{0.07})CO_3$; that is both calcium rich and ferroan.

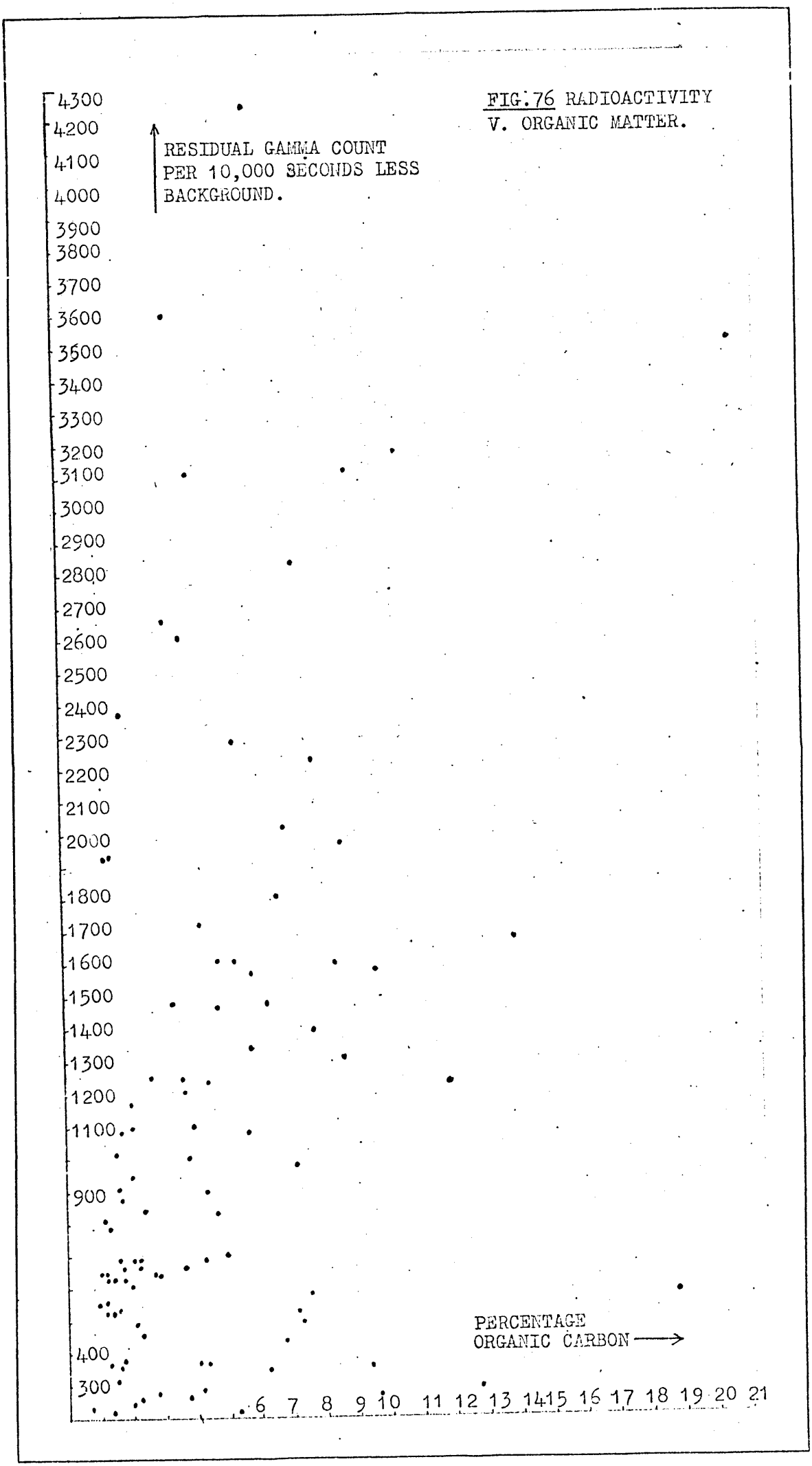


FIG. 76 RADIOACTIVITY V. ORGANIC MATTER.

efforts to determine the source/cause of activity are given under the Appendices. Now, KC110-108 follows KC107; KC76-68 follows KC66-67 and includes KC74 (and KC70); KC59-56 follows KC55B-54; KC34-30 includes KC32 and KC10-KC6 falls between KC4 and KC11. Reference to Table 59 shows that KC107, KC74, KC66, KC55B, KC54 and KC32 comprise the suite of rocks with alignite kerogen. (Relation of KC84, the only remaining alignite kerogen example to enhanced activity is not possible owing to failure to recover a sample for the KC85 horizon). Both KC4 and 11 actually fall into an intermediate algal-alginite category (error field) like KC67, but the latter is extremely close to the boundary and owing to its lithology perhaps warrants inclusion in the alginite category. Finally, KC4 and 11 rank with KC1 and 70 (White Band) as the most aliginite-rich samples of the mixed category.

Thus, the hypothesis, of relating blooms to increased nutrients which are made available with the release of radioactive elements from the mantle through the rifting of plate margins, seems applicable for the Dorsetshire Kimmeridgian section. A plot of residual activity versus organic carbon though suggests no intimate 'direct link' (Figure 76) and in absolute terms the Formation at outcrop is dead.

12 LITERATURE SEARCH

The salient points derived from the chapter on Previous Geology and Geochemistry all point to an immature status for a shallow marine 'nearshore' organic rich sediment which was deposited slowly in oxygen deficient quiet waters that were somehow shielded from the main effects of syndepositional tectonism. Geological aspects are annotated in Tables 65 and 66 and the inferences of the known organic geochemistry are summarised and developed as follows.

The vast organic richness (1.6% - 75.3% organic matter) but low solubility can be coupled with a knowledge of historic exploitation (in particular, early distillation/retorting experiments) and as a high yield of shale oil has focussed attention upon the Formation for a long time, an immature level of diagenesis can be deduced. (In principle the extraction and pyrolysis techniques of this study are not new !). In fact, the available figure for a SOE/organic carbon ratio of 0.06 does place the limit of depth of burial to an early hydrocarbon generation zone. Similarly, an average 73.6% kerogen

TABLE 65. SUMMARY OF PREVIOUS PALAEONTOLOGICAL STUDIES with application of relevant work.

OBSERVATION.	AUTHOR(S)& DATE.	DEDUCTION(S).
Poor diversity.	Brookfield,1973.	Stress conditions in a restricted basin.
Comparitive paucity of species but infinity of individuals.	Blake,1875.	
Non-ammonite fauna abundant in terms of individuals but represented by few species.	Cope,1968.	
Greater than normal occurrence of spats in oil shales.	Downie,1955.	Higher than usual mortality rate H_2S poisoning - euxinic condition
Reptiles	Hulke,1869,70,71 & 72. Mansel-Pleydell,1873.	Proximity to land.
Coprolites of large fish & reptiles.	Downie,1955	
Sizeable oysters (preferentially attached) on the underside of ammonites.	Cope,1968.	Attachment after death of cephalopod; considerable time before sediment influx killed oysters.
Infaunal suspension feeders. Eg.Lucina,Astarte,Trigonia, Protocardia & Thracia sps.	Hudson & Palframan,1969. Blake,1875	Sedimentation not fast enough to inhibit filter feeding &/or bury fauna. Surface layers not toxic.
& epifaunal suspension feeders. Eg. Serpula,Parallelodon,Ostrea, Oxytoma,?Pecten,& Modiola sps.		
Rarity of suspension feeders & reduced variety/absence of infauna(for the White Bands)	Hudson & Palframan,1969.	Soft bottom,high sedimentation rate & reduced oxygenation.
United,closed but flat-lying bivalves.	as above	Very slow winnowing from life position with almost immediate reburial.
Large numbers of benthonic & epi-benthonic organisms in the clays.	Kent,1949. Downie,1955.	Oxygen sufficient to support life Bottom waters not foul. (Class 3-4 of Schmidt,1935.)
Common oysters throughout section.	Cope,1968	Sedimentation not under true anaerobic conditions.
Rarity of deep burrowers.	Hudson & Palframan,1969	Anaerobic conditions not too far below sediment surface.
Saccocoma always as isolated plates.	Downie,1955.	Active reworking by benthos or bacterial decay during prolonged descent through deep water.
Pyrite on broken shell edges	Lloyd,1959.	Some fragmentation penecontemporaneous with sedimentation.
Coccolith impressions in bitumen.	Downie,1955	Bitumen soft when deposited.
Dinoflagellates dominant microfossil assemblage	as above.	Most important members of present day plankton; require warm & temperate waters of high nutrient content.
Number & variety of spores & pollen	as above	Prolific terrestrial flora on land source; more than 30 miles from site of deposition.
Abundant microplankton,tasmanitids & microforaminifera.	Mebradu,1975	Open sea environment.
Relatively fewer microspores & smaller number of species within families.	as above.	Offshore,far from source.
Coniferophyta dominate miospores	as above	Temperate climate over source area.
Few agglutinating foraminifera (dominated by Lagenidae.)	Lloyd,1959,62.	Marginal marine clastics.
Horizontal Rhizocorallium.	Sellwood et al,1970 Ager & Wallace,1970* (*in Hallam,1975.)	?Arthropod feeding burrow; always below the low water mark & deeper than oblique Rhizocorallium.

carbon places the rock in a pre-oil generation category whilst the average atomic H/C and O/C ratios of 1.28 and 0.1 respectively place the kerogen composition near the immature end of an (exinite) evolutionary path in a van Krevelen type diagram. (Figure 26). Specifically the identified sulphur compounds within the shale distillates (that is 'considerable' alkyl thiophens, 'some' benzothiophene and 'some' non-thiophenic sulphide with insubordinate alkyl sulphides and mercaptans) tend to suggest an immature-mature classification which is biased to immaturity by a high asphaltic SOE and asphaltene-rich distillates.

An available value for the saturates/aromatics ratio is (much) less than two and an average C/H ratio of 8.2 for the SOE confirms the long upheld 'high degree of unsaturation'; both of these characteristics contributing further to the assignment of immaturity.

Finally, the range of spore colouration from various authors has extended from green through yellow to brown and at the severest an immature-mature inference has been recorded.

With regard to the source material of the organics early opinions were divided and subsequent microscopic analyses have lead to a picture of dominant in situ biological products being diluted by some externally derived terrestrial matter. Chemically the low hydrogen and sulphur content of jet and the relatively high hydrogen and oxygen contents of the organic matter have lead to the dismissal of woody matter and resin/waxes as progenitors. Oxidation experiments upon the kerogens ($<$10% aromatics within the organic matter) have suggested an algal type kerogen.

However, the H/C and O/C atomic ratios (1.28 and 0.1) place the kerogen on a trend exhibited by exinitic material and the reported interval of an increased miospore contribution (lower Upper Kimmeridge Clay) apparently corresponds with the KC79-100 section distinguished through the pyrolysis of this study. (For the Green River Formation, Robinson et al (1965) found a mean kerogen H/C ratio of 1.6 contrasted with the 0.68-0.90 range quoted by Hunt & Jamieson (1956) for marine kerogens).

Finally, trace element studies have returned the bias in favour of predominant marine plant precursors.

Thus, overall an immature sediment where the organics are predominantly

marine algal matter with various degrees of terrestrial admixture is deduced. Additionally perhaps to the very nature of the organic matter itself, trace element work has suggested no relation between the clay minerals and the organic matter.

TABLE 66. SUMMARY OF PREVIOUS LITHOLOGICAL STUDIES with application of relevant work.

AUTHOR & DATE	OBSERVATION(S).	DEDUCTION(S).
NEAVERSON,1925:	?Upper Kimmeridgian mineralogy	Derivation from Amorican landmass
NEAVERSON,1925:	?Upper Kimmeridgian mineralogy.	Sediment supply from Amorican landmass.
LOVELY,1946:	Facies changes & thinning.	Deposition not too far frm shore.
DOWNIE,1955:	Small pyrite globules. Coccolith limestones. Lateral equivalent Hanoverian & Aquitaine evaporites. Organic rich sediments.	Anaerobic bacterial activity causes hydrotrcilite to convert to pyrite. 'Globigerina ooze' equivalents - warm waters Arid climate. No dilution by clastics - no flow of water as rivers because of arid climate over land source or an intervening sediment trap.
BITTERLI,1963:	Lack of coarse detritus. Bitumenous sequences	Mature rivers only feeding ocean; source areas of low relief. Degree & duration of anaerobic conditions important.
LLOYD,1959:	Small pyrite globules.	Organic origin penecontemporaneous with sedimentation.
COPE,1968:	Fairly uniform argillaceous section. Lack of sedimentary structures (other than parallel laminae)	Slow sedimentation.
BUSH,1972: (Verb.comm.)	Authigenic glauconite. (Californian analogues)	Slow sedimentation in a somewhat reducing marine environment.
DUNN,1972:	No abnormal mineral assemblages. Actual mineral assemblages. Pronounced pyritisation below stonebands. Change in chemistry above Basalt Band.	No extreme salinities. Slightly alkaline, negative Eh, reduzate sediment environment. Periodic acmes of anoxic conditions Major environmental change.
HALLAM,1975:	Bitumenous sequences. Minute pyrite grains.	Relative shallow water; not deep-water or lagoonal. Diagenetic formation from monosulphide has no direct bearing on bottom waters; sulphate reducing bacteria can function in a wide variety of fine grain sediments deposited in oxygenated waters.
JOHNSON,1975:	Low carbonate content. Fine grain sediments.	Steady detrital influx. Rate of deposition slow & provenance low lying.
MEBRADU,1975:	Absence of sandstones,corals limestones & thick limestones.	Open sea environment.

PART TWO: THE OXFORD CLAY FORMATION.

The results provided for a limited analysis of 14 samples are discussed and location maps are found under the Appendices.

1 Solvent extraction

The average extractability of all samples is 0.29% by weight but only half exceed "a few tenths of a percent". A crossplot of SOE v Organic carbon is illustrated in Figure 77 where the SOE/Organic carbon ratio averages at 0.07; placing the formation within the early hydrocarbon generation zone.

The trend actually mimics that of the Kimmeridgian section very closely indeed and a poorer average organic wealth is inferred.

2 Fractionation

No values are yet available for the samples in question as a fast, qualitative tlc fractionation, with recovery of the saturate fractions only, was made to permit subsequent GLC analyses. OC3, however, was conspicuous in showing no fluorescent banding (aromatics) under UV light.

3 GLC

Chromatograms for the saturate fractions are depicted in bar diagram form in Figure 78. (Where the sample number, CPI, pristane/phytane ratio and pristane/nC_{17}-alkane ratio are given in sequence from the left hand side).

Generally, a subdued branched-cyclic/naphthenic envelope (relative to the Kimmeridge Clay) is judged and the average CPI is 1.2; both features inferring a slightly higher degree of diagenesis and in fact the CPI lies at the upper limit known for functioning petroleum source rocks. (Figure 83).

Excluding OC5 and 6 (4.5 and 13.0 respectively ?) the average pristane/phytane ratio is 1.0 (0.6-1.5) whilst for all samples the pristane/$n\text{-}C_{17}$ alkane ratio varies through 0.6 - 2.0 and gives a median value of 1.2. These average values are correspondingly within the known limits for a marine environment of deposition and marine organic precursors typifying organic matter of immature rocks.

For the nC_{15}-nC_{30} alkane range a LMW bias seems apparent for OC1, 5, 6 and 11 whilst a more equal bimodal distribution is suggested in OC 5, 7 and 13. Samples OC2, 3, 4, 8, 9, 10, 12 and 14 all seem to show slight-pronounced bias over the HMW range. In fact OC1 and OC3 are

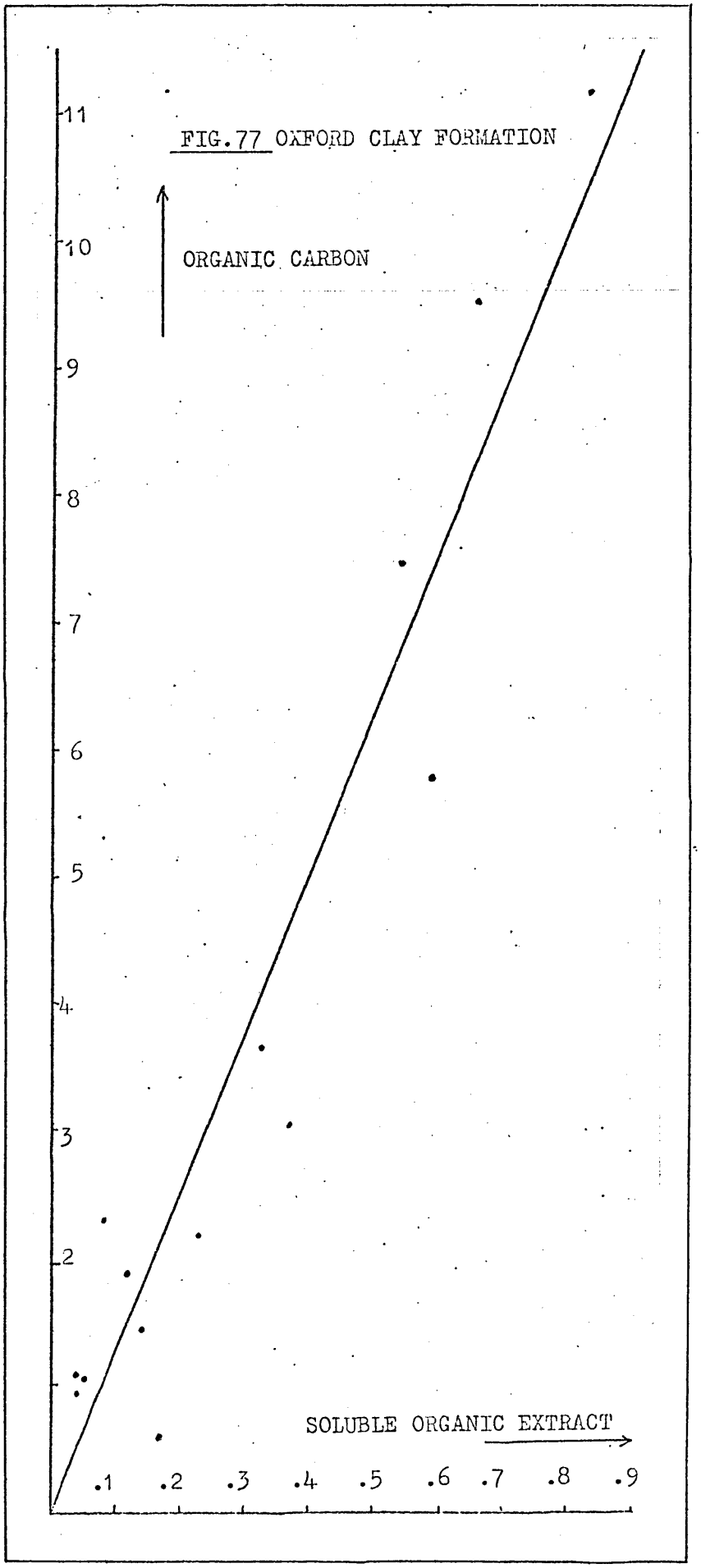

FIG.77 OXFORD CLAY FORMATION
ORGANIC CARBON
11
10
9
8
7
6
5
4
3
2
SOLUBLE ORGANIC EXTRACT
.1
.2
.3
.4
.5
.6
.7
.8
.9

FIG. 78 OXFORD CLAY GLC RESULTS. C_{15} - C_{30} n-alkanes from total saturate chromatograms expressed in bar diagram form (approximate peak areas) with sample number, CPI, pristane/phytane ratio and pristane/n-C_{17} alkane ratio reading from left to right.

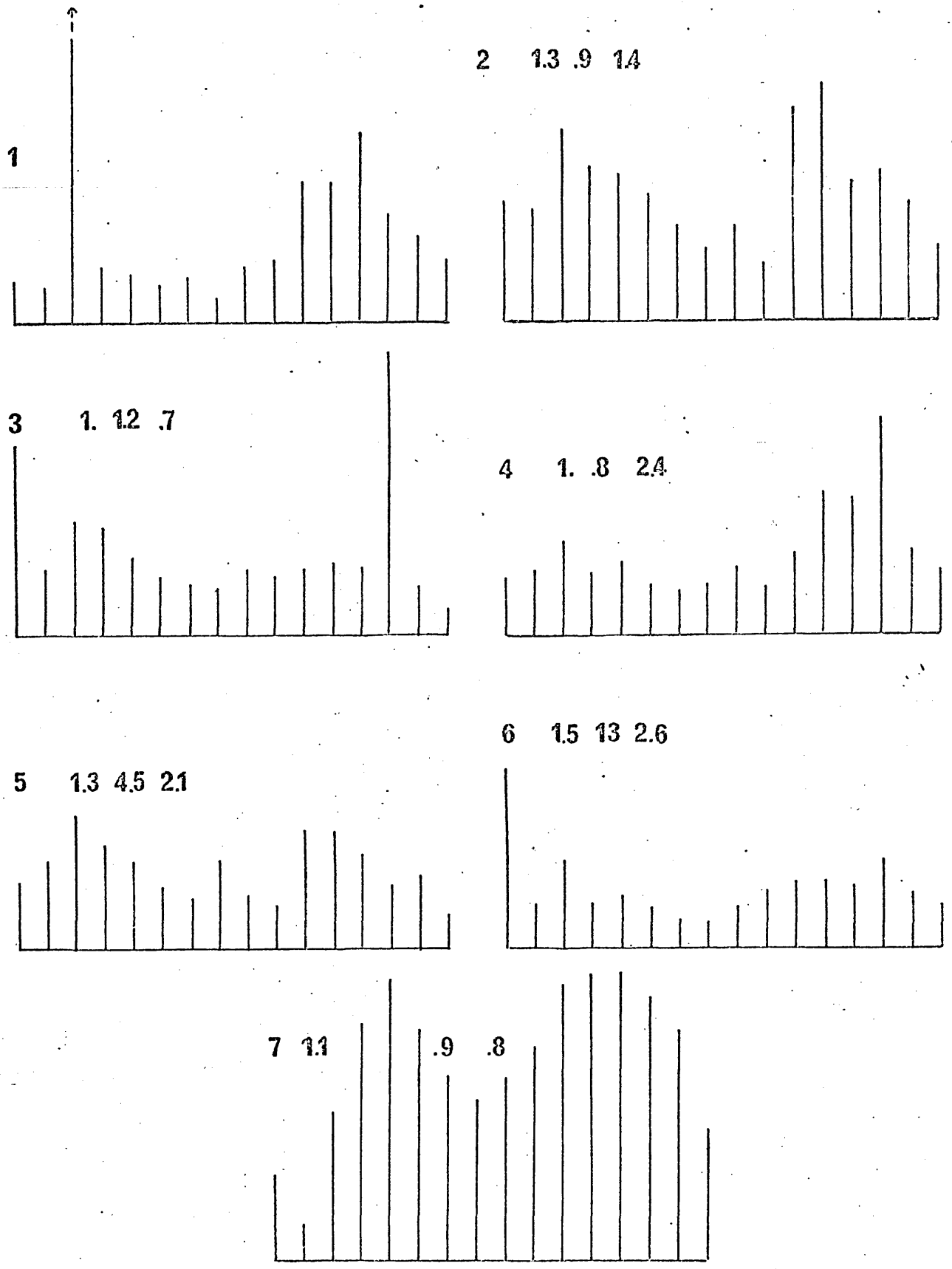
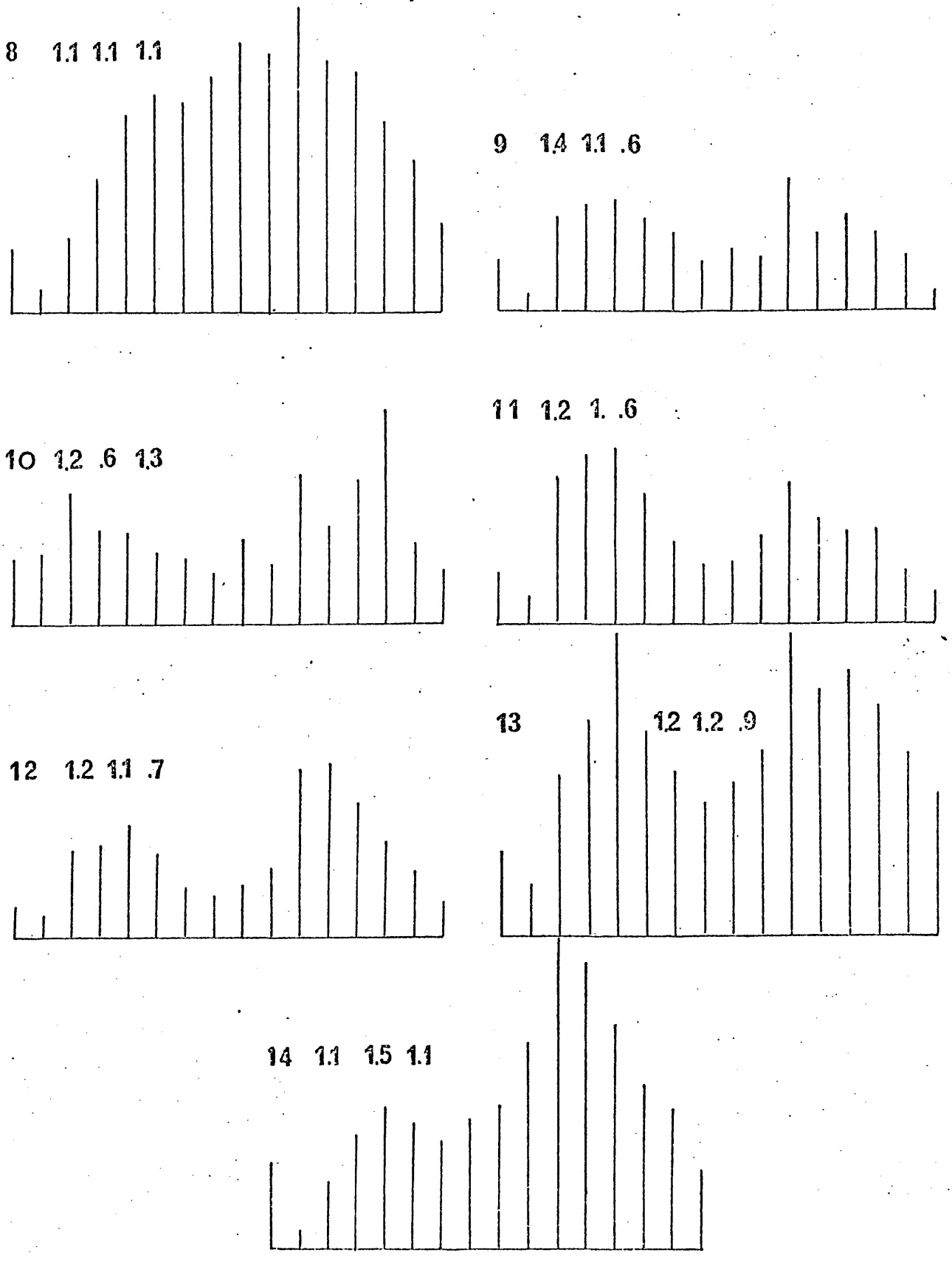


FIG. 78 cont.(2)



atypical in showing disproportionately large concentrations of the n-C_{17} and n-C_{28} alkanes respectively within their distributions. If an immature condition is assumed the general distribution suggests a more important terrestrially derived organic contribution to the total Oxfordian content (in comparison to that of the Kimmeridgian). OC 11 & 7 and 14 are illustrated in Figures 79 and 80 respectively. Strangely only a significant-very subdued branched/cyclic alkane was observed to elute before the n-C_{20} alkane and such a component is missing in OC7 and 8. However a massive and thus anomalous pre-nC_{27} alkane b/c-alkane was observed in OC1 and appears only in OC6 on a significant level; being absent in the remainder. Finally 'crowding' of b/c-alkanes in the vicinity of n$C_{27, 28, 29}$ is observed on a comparatively subdued basis in OC1-5 and OC9-11.

4 QEA

The non-calcareous-very calcareous argillites ($\pm$ jarosite) have an average organic carbon content of 3.7% (extending from 0.58%-11.17%) which exceeds the minimum source rock potential of 0.5% but indicates a lower organic content than the Kimmeridgian interval. In fact, four cases are uncomfortably close to the minimum whilst three exceed 2% (OC6, 8, 12 and 13 and OC 1, 2 and 4 respectively).

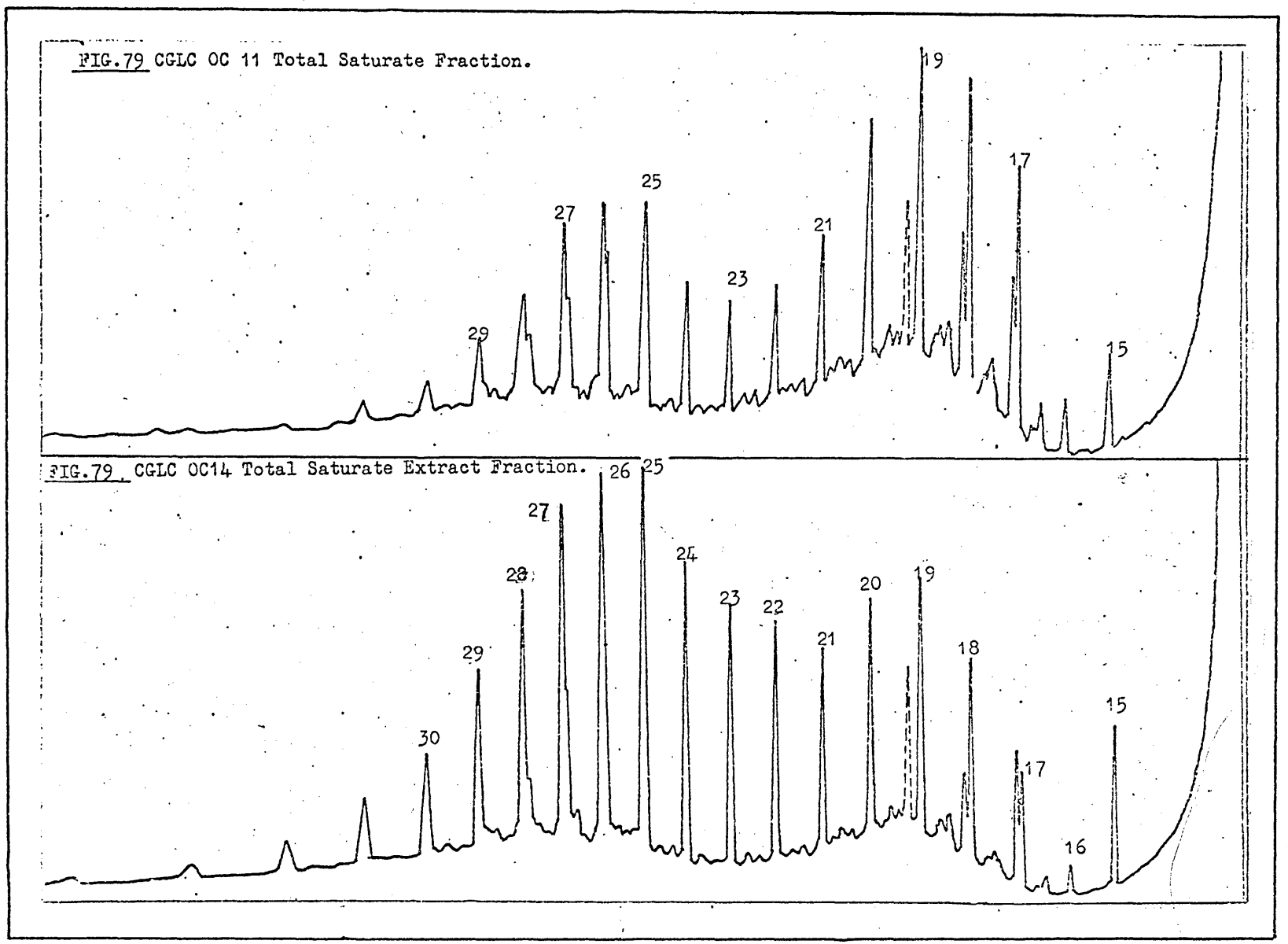
Omitting three unbelievably low values, the soluble organic carbon is still seen to vary between 38.2% and 62.7% and the presence of an unusually large non-hydrocarbon content is deduced. A C/H ratio of 7.5 is an average for the SOE (excluding OC6, 7, 8 accordingly) and a "degree of unsaturation", analogous to that in the Kimmeridgian section, is suspected.

The plot of total whole-rock carbon and total whole-rock hydrogen contents is shown in Figure 81 so that a comparison can be made with that previously noted for the Kimmeridgian; although lack of control handicaps the Oxfordian situation (?).

5 Pyrolysis

The C_R versus C_T values are illustrated in Figure 82 and the mean CR/CT ratio calculates as 0.56 where the average kerogen carbon convertibility corresponds to 44%.

Thus, the Oxford Clay is seen not to have suffered a diagenetic history which was unfavourable to hydrocarbon generation. For an immature facies, the trend would be given by organic matter of an 'intermediate'


FIG.79 CGLC OC 11 Total Saturate Fraction.
29
27
25
23
21
19
17
15
FIG.79 CGLC OC14 Total Saturate Extract Fraction.
30
29
28
27
26
25
24
23
22
21
20
19
18
17
16
15

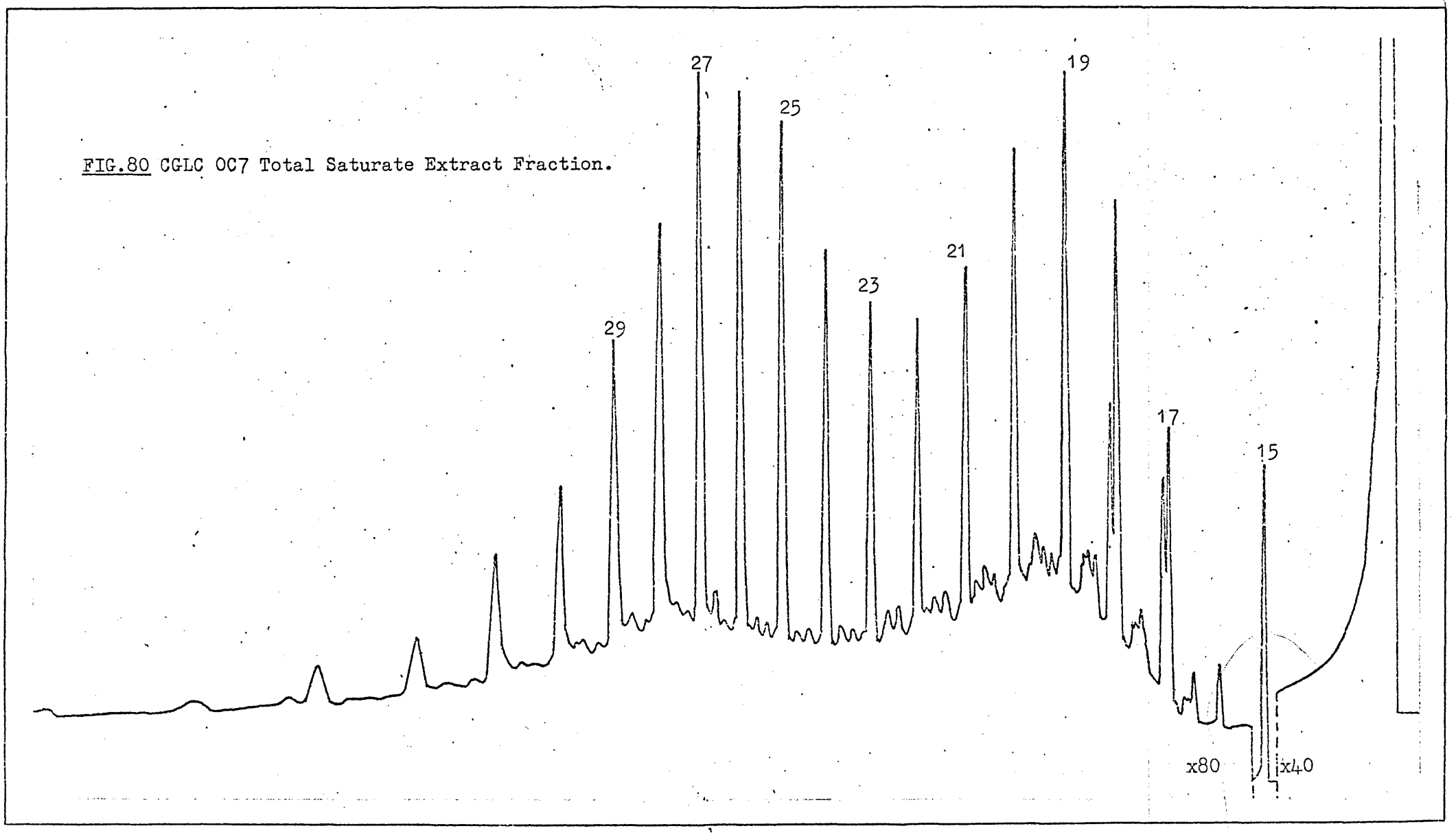


FIG.80 CGLC OC7 Total Saturate Extract Fraction.

FIG. 81 Oxford Clay.

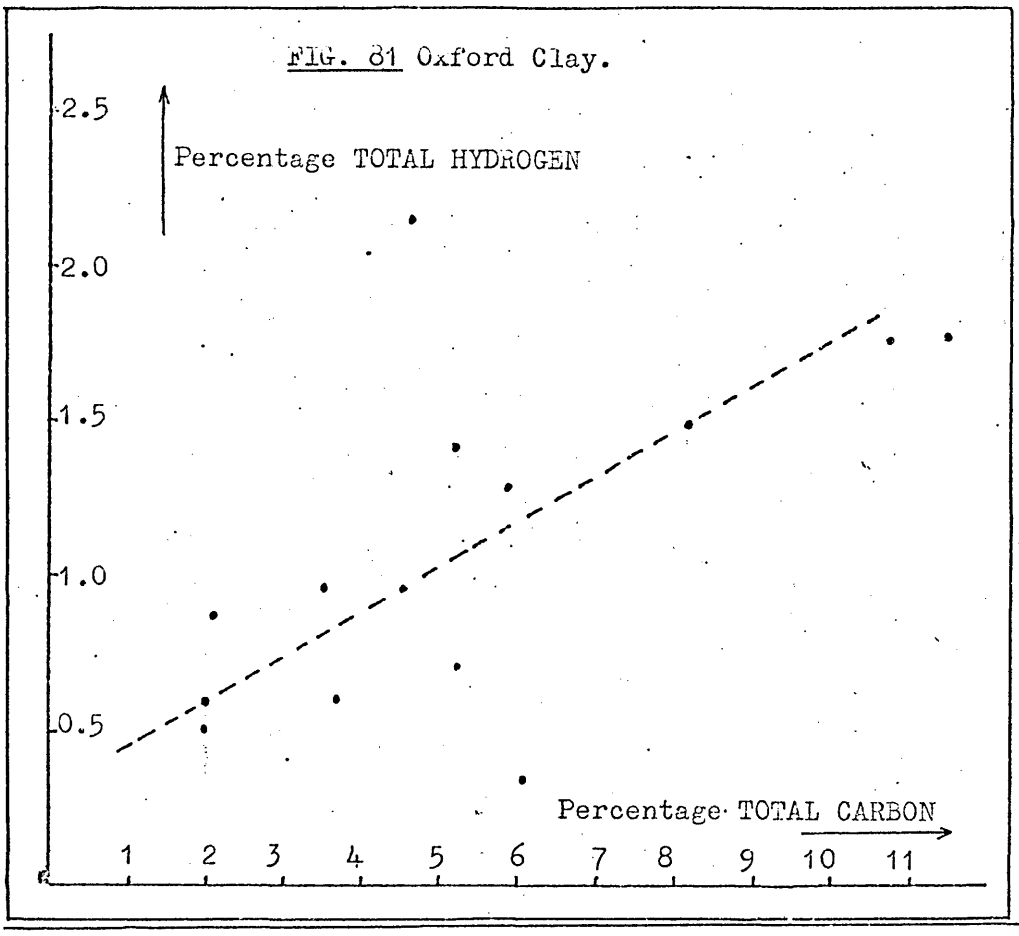
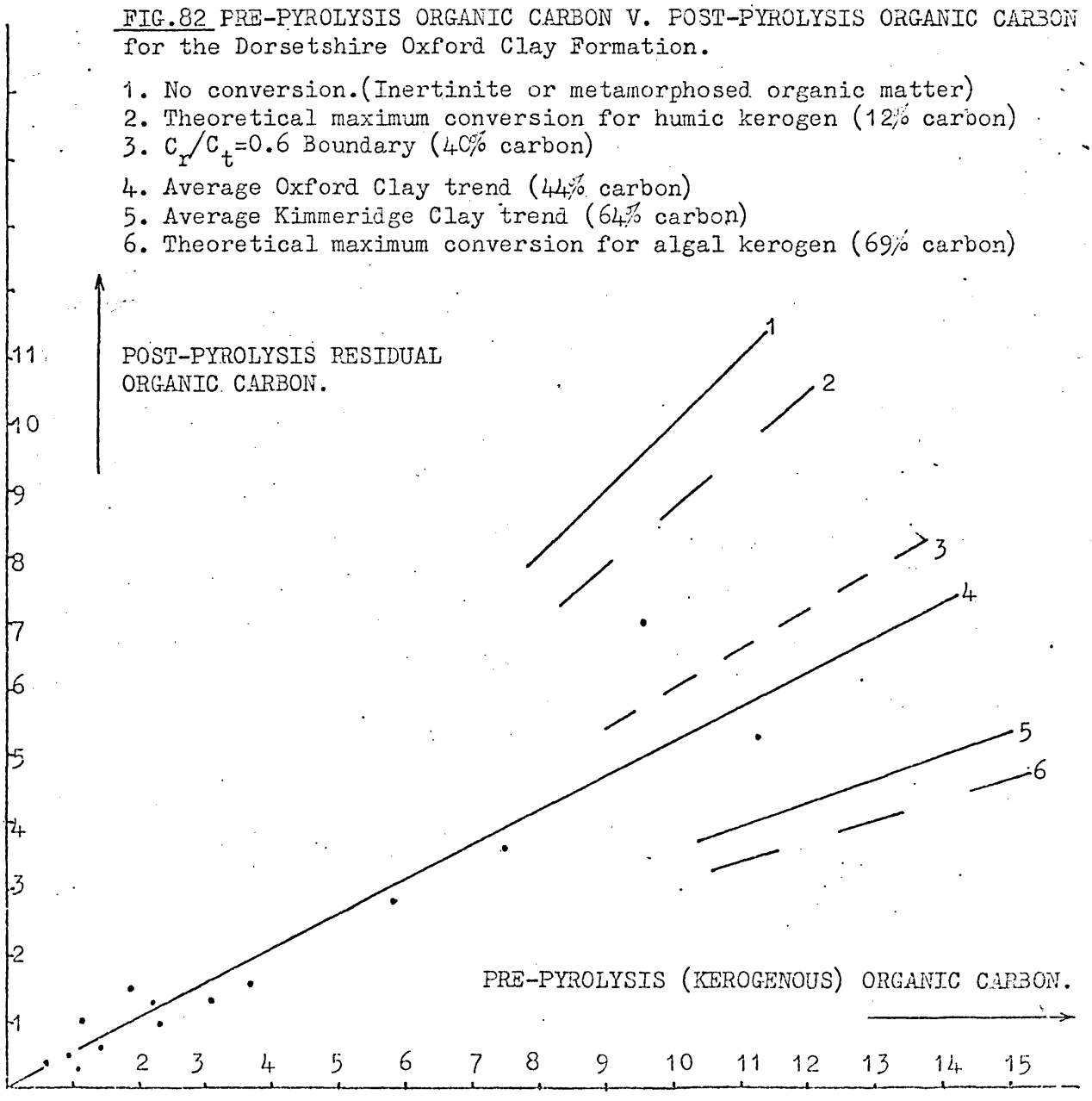


FIG.82 PRE-PYROLYSIS ORGANIC CARBON V. POST-PYROLYSIS ORGANIC CARBON for the Dorsetshire Oxford Clay Formation.

1. No conversion.(Inertinite or metamorphosed organic matter)
2. Theoretical maximum conversion for humic kerogen (12% carbon)
3. C_r/C_t=0.6 Boundary (40% carbon)
4. Average Oxford Clay trend (44% carbon)
5. Average Kimmeridge Clay trend (64% carbon)
6. Theoretical maximum conversion for algal kerogen (69% carbon)



liptinitic-algal category (as defined in this study) and this is actually within the type inferred in broad terms from the GLC n-alkane interpretation. Specifically, pyrolysis only completely contradicts the GLC in the cases of OC8 and 10.

6 Literature search

Lees and Cox (1937) recorded the figures of Barber concerning a Dorsetshire Clay specimen where 12.2 gallons per ton of oil were won by distillation and 1.75% of extract was achieved with benzene. Comparison of the distillate figure for that of a Kimmeridge oil shale (27.7 galls/ton average from the Short Joint, Rudicum, Blackstone and Main Bed in Table 49) reflects a lower organic richness for the Oxfordian; although no equivalent value for extractability was achieved here with a more polar solvent (?). Bonnet (1958) in fact concluded, from a mean 0.053% SOE for the lowest 50 feet of Formation, that the term "bitumenous" was not warranted and a fractionation was given as 9.2% para-naphthenics 20.5% aromatics, 32.7% asphalts and 37.7% residue. Accordingly the percentage of hydrocarbons and non-hydrocarbons can be deduced (c. 29.7% and 70.3%) to provide approximations of the non-hydrocarbon/hydrocarbon ratio (2.4: 1) and the saturates/aromatics ratio (0.45). The former (single) ratio is coincident with the Kimmeridgian sectional average whereas the latter is smaller by a factor of about four; although of course still below that observed for metamorphosed sediments. (The relatively large reversal of the dominance between the saturates and aromatics presumably reflects the shift in importance from marine to terrestrial precursors ?). The Dorset palynomorphs for the Callovian(-Kimmeridgian) do fall into the immature classes of Staplin's colouration scheme (Mebradu 1975).

Finally, it can be noted here that elemental kerogen compositions have indicated gas potential only ($\leq$ 6%H) for Oxfordian samples from the northern North Sea and Yorkshire outcrop (where it happens to be in a main phase (82.5%C) and early phase (79.1%C) of hydrocarbon generation respectively) (Fuller 1975) and a terrestrial phase of organic matter is therefore understood.

Owing to the non-uniformity of the Wealden Formation, the organic geochemical results are offered under the categories of the different lithologies examined. Sample location is depicted both geographically and geologically in Figures 84 and 85 (see also the Appendices) and the saturate fraction chromatograms for all samples are given together in Figure 86.

Here, prior to further discussion in the Appendices, the persistence of the pre-nC_{20} alkane, branched-cyclic component in all samples except W6, 12, 26 and 32 (where its very subdued to significant) is recorded on a large-massive scale. Additionally though 'pre-nC_{25} alkane' and 'pre-nC_{27} alkane' branched-cyclic alkanes occur in W10 and W16 and W14 respectively on a significant scale.

Also, the XRD whole rock studies reveal that nearly all the samples show quartz, kaolinite and feldspars as the main mineral phases with illite missing from W7, 8, 12, 13, 14, 16, 17, 18, 21, 31 and 32. Only W21 shows no feldspar and calcite is significant enough to be detectable in W4. Pyrite is apparent in W5, 7, 11, 15, 18, 21, 22, 27, 30 and 32.

Silty claystones

The results for ten samples from six outcrop localities are summarised in Table 67. An average SOE/organic carbon ratio is 0.15 and the fractionation provides an approximate extract composition of 30% saturates, 12% aromatics and 58% asphaltics where the saturates/aromatics and non-hydrocarbon/hydrocarbon ratios are respectively 2.5 and 1.4.

With the exception of W29, which showed no visible fluorescence, the aromatics expressed themselves with a diffuse mauve fluorescence during the tlc procedure and the limited UV/FES work (including here W5, 15 and 24) confirms the suspicion of dominant PAHS.

The mean extract ratio for C/H computes as 6.3 whilst the average CPI, pristane/phytane ratio and pristane/nC_{17}-alkane ratio are respectively 1.33, 0.7 and 0.62. From pyrolysis the mean C_R/C_T ratio is 0.64.

Now, where large conversions of kerogen are in the order of 54-83% (carbon) the corresponding GLC n-alkane distributions either support the inference of dominant immature algal matter (W5, 25, 29; Figure 87) or do not completely contradict it (W9). Very low to (apparently) zero conversion is likewise anticipated from inspection of the chromatograms for W15, 20 and 27 (Figure 88) although the GLC/pyrolysis interplay is

FIG.84 WEALDEN GEOLOGIC SECTIONS.

DUNGY HEAD (A) PLATE 19



Blue-green + Jarosite (RDW150DH4) W9.

Black boulders (RDW150DH3) W8 in dk. brown sandstone W7. (RDW150DH2) 'Oil Sand'

White (RDW150DH1) W6.

STAIR HOLE (B) PLATE 20



White.

White. (RDW151SH1) W10

White

Blue-green. (RDW151SH2) W11

Black-brown oil sand. (RDW151SH3) W12. ? conglomeratic

Blue-green.

LULWORTH COVE; WEST SIDE. (C) PLATE 21



White

Lt. blue-grey + Jarosite. (RDW152LCW2) W15

Brown.

Lt. grey

Red

Black-brown oil sand (o.p.) (RDLCW1 & 2) W13 & W14 Resp.

Beige.

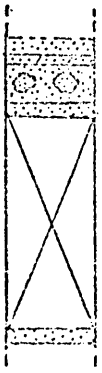
White.

Yellow

Dk. blue grey

PURBECK FM.

LULWORTH COVE; EAST SIDE. (D)



Black (RDW153LCE) W17

Dk. brown

Dk. brown oil stains (½%) in yellow white sandstone: Oil Sand.

Beige.

Black (RDW153LCE) W18.

0 FEET. A,B,D. 10

DURDLE DOOR; EAST SIDE. (E)



White.

+Jarosite

Green-grey (RDW149DDE c) W5 +Jarosite

Yellow. (RDW149DDE d) W4.

Beige + Jarosite (RDW149DDE c) W3

White. (RDW149DDE b.) W2.

+Jarosite

Pale Brown.

Lt. blue-grey – Lt. brown +Jarosite

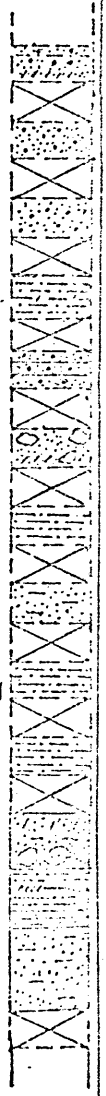
Lt blue grey (RDW149DDE a) W1.

PURBECK FM.

0 E: OMISSIONS. 50 FEET

0 E,F 10 FEET

PLATE 22 MUPE. (F)



White.

Mauve.

White. (RDW156MBc) W23.

+Jarosite

White

White W32. (RDW156M34)

Grey

Yellow

Lt green-grey

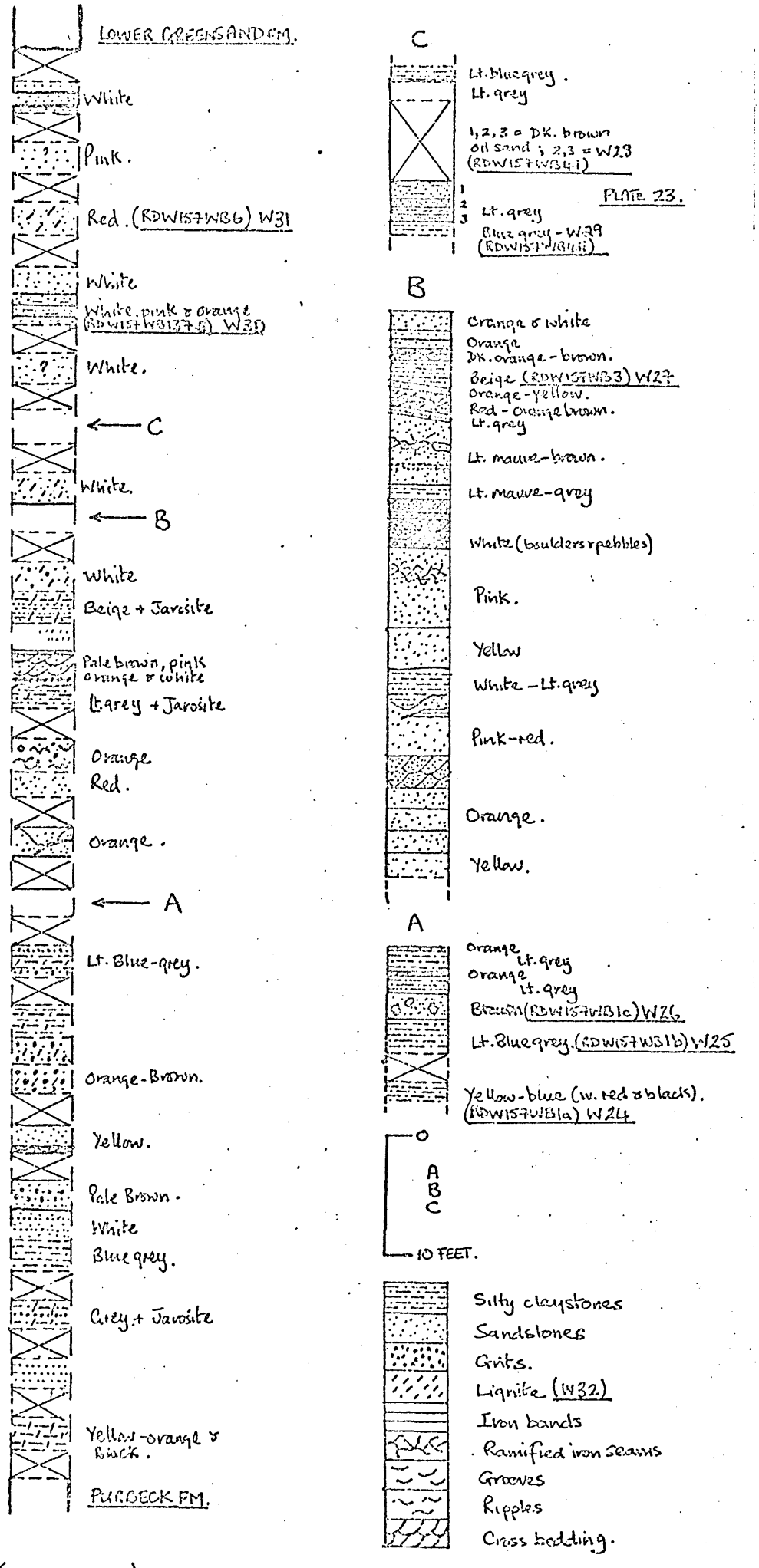
Lt. brown

Oil sand: Lt. brown-grey sand (RDW156MBc) W22. with black boulders (RDW156MBc) W21

Lt grey (walk yellow) (RDW156MBb) W20

Brown. (RDW156MBa) W19

KEY: SEE FIG. 85



(NOT TO SCALE.)

FIG.85 WEALDEN GEOLOGIC SECTION, WORBARROW BAY, DORSETSHIRE.

FIG. 86 WEALDEN FM. GLC RESULTS. C_{15} - C_{30} n-alkanes from total saturate chromatograms expressed in bar diagram form (approximate peak areas) with sample number, CPI, pristane/phytane ratio and pristane/n-C_{17} alkane ratio reading from left to right.

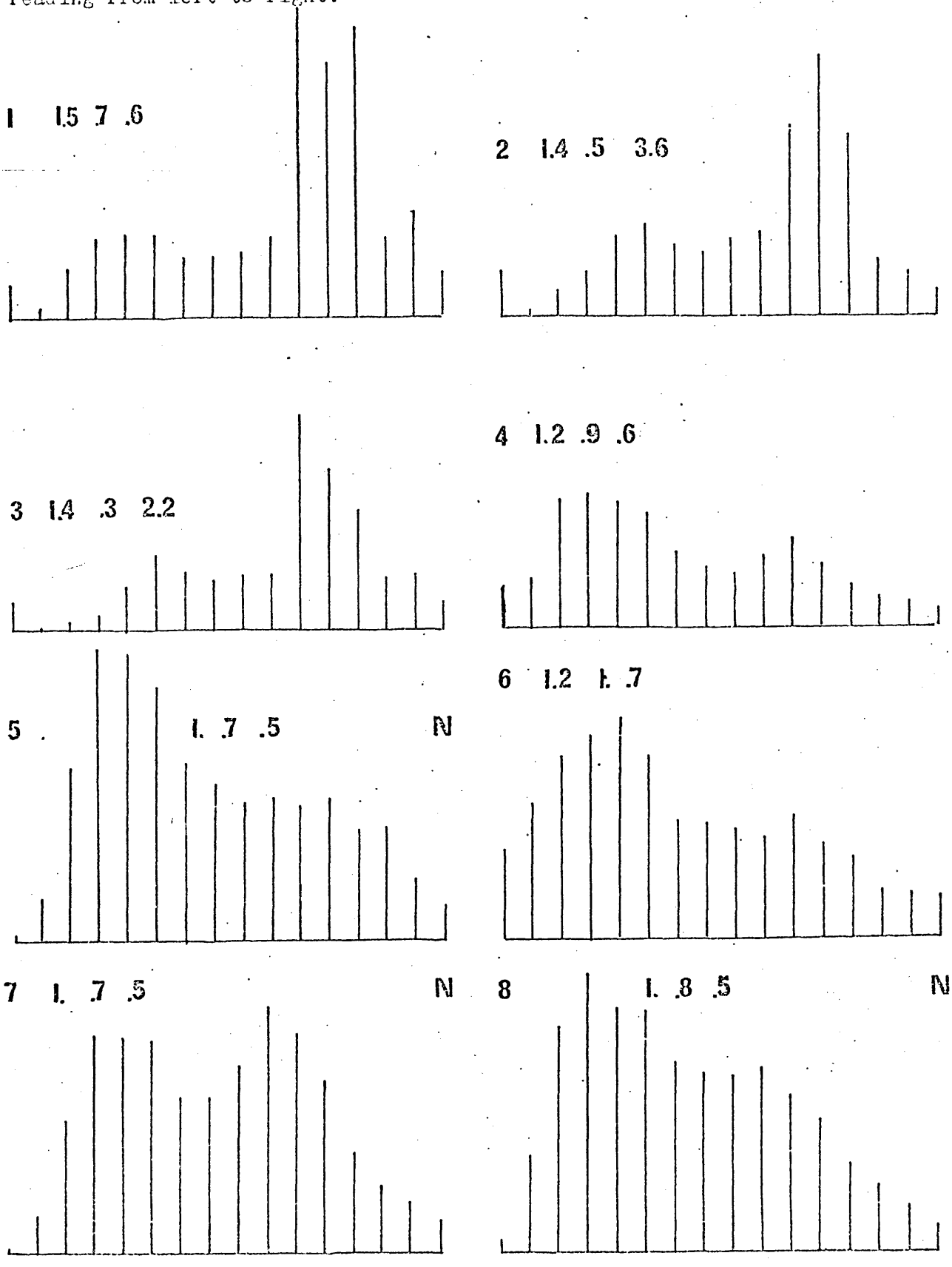


FIG. 86 cont.(2)

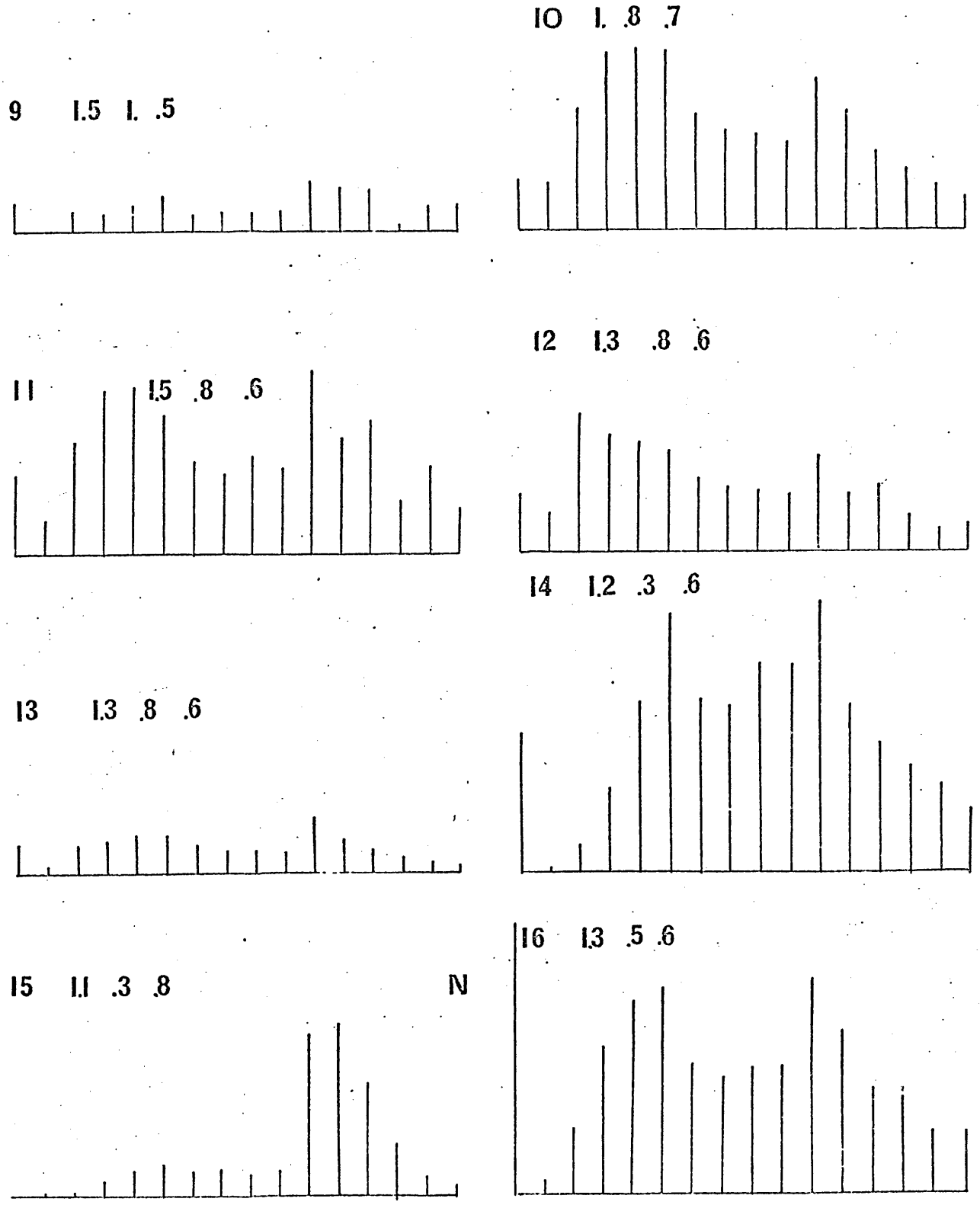


FIG. 86 cont.(3)

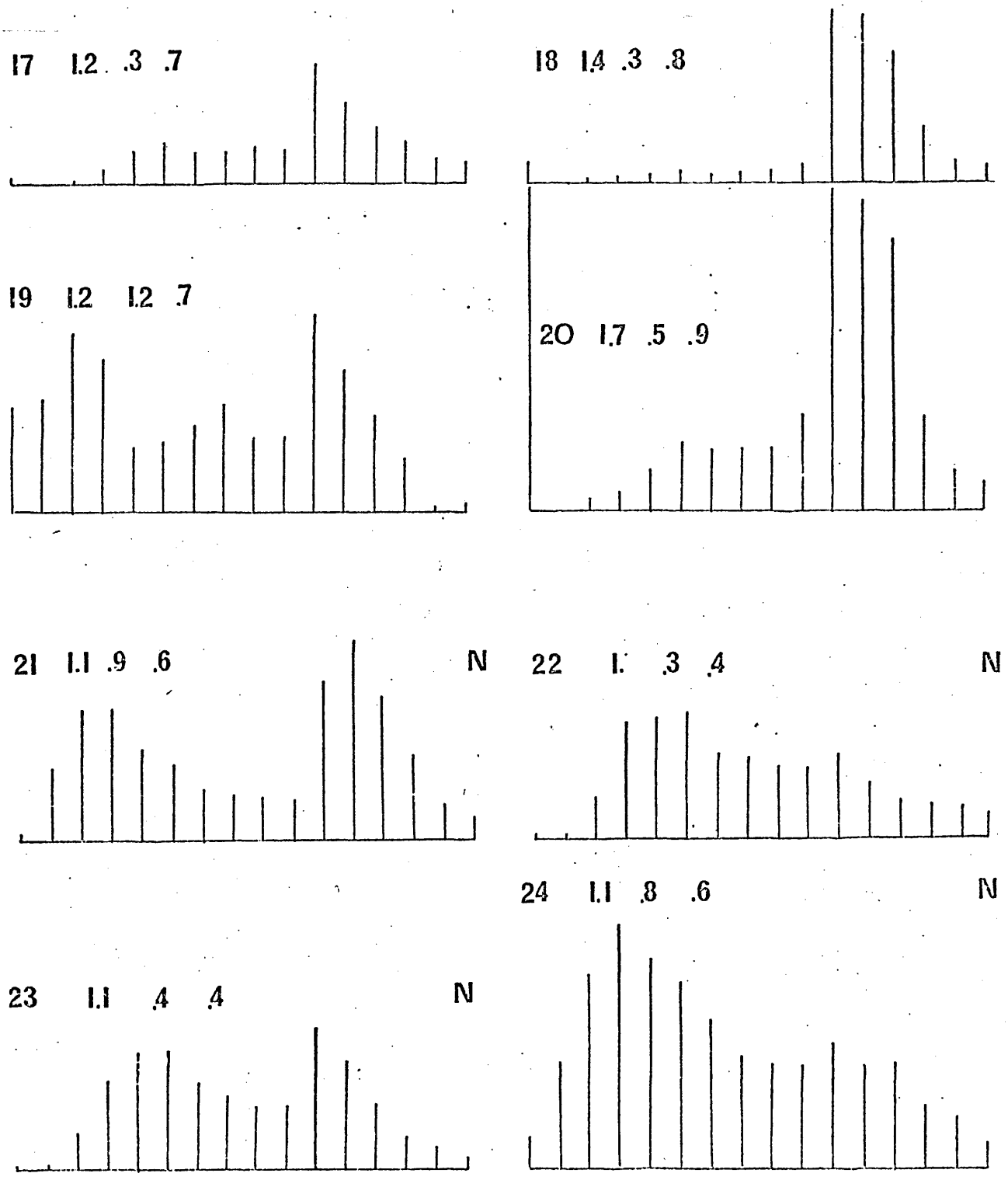

17 1.2 .3 .7
18 1.4 .3 .8
19 1.2 1.2 .7
20 1.7 .5 .9
21 1.1 .9 .6 N
22 1. .3 .4 N
23 1.1 .4 .4 N
24 1.1 .8 .6 N

FIG. 86 cont.(4)

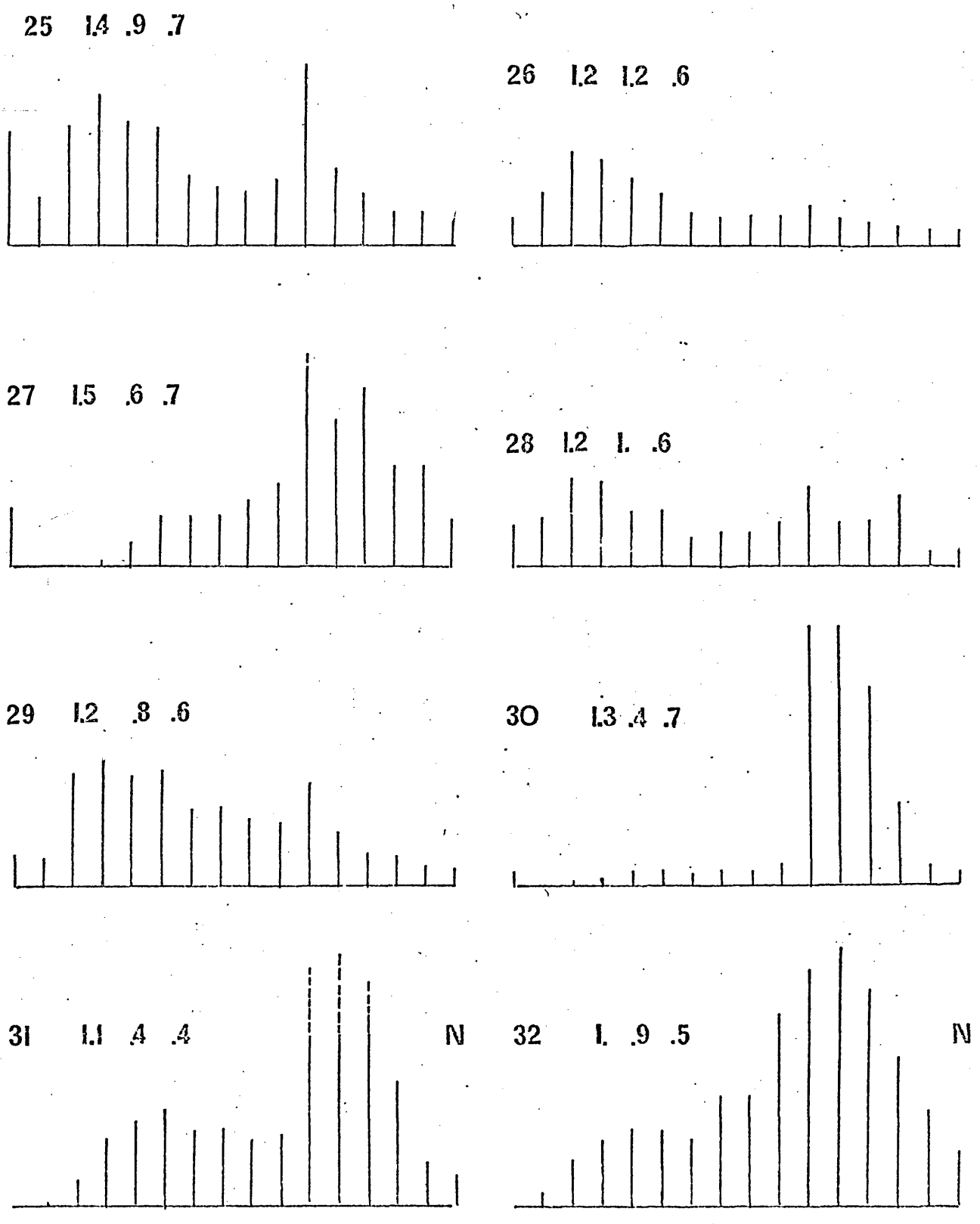

25 1.4 .9 .7
26 1.2 1.2 .6
27 1.5 .6 .7
28 1.2 1. .6
29 1.2 .8 .6
30 1.3 .4 .7
31 1.1 .4 .4 N
32 1. .9 .5 N

TABLE 67. WEALDEN SILTY CLAYSTONE RESULTS. Values are percentages by weight where * indicates an average from atleast two determinations. W32 = LIGNITE.

SAMPLE.	SOLUBLE EXTRACT.	ORGANIC CARBON.	RESIDUAL CARBON.	TOTAL WHOLE ROCK			SOLUBLE EXTRACT			SOLUBLE EXTRACT			KEROGEN CARBON.	KEROGEN C CONVERSION.	CARBONATE CARBON.
				NITROGEN	CARBON	HYDROGEN	NITROGEN	CARBON	HYDROGEN	SATURATES	AROMATICS	ASPHALTICS			
W5.	0.17	0.43*	0.16*	0.47	0.68	0.62	3.0	13.8	3.5	44.7	9.1	46.2	0.41	60.6	0.25
W1.	0.18	2.51*	1.50*	0.18	3.32*	0.64*	1.91	64.3	6.8	35.7	16.8	47.6	2.39	37.4	0.81
W9.	0.16	0.39*	0.06*	0.28	0.39*	0.74*	1.57	20.2	3.6	22.4	8.5	69.1	0.36	83.2	0.00
W11.	0.12	0.27*	0.13*	0.21	0.42*	0.95*	0.48	37.0	5.3	15.2	1.0	83.8	0.23	42.4	0.15
W15.	0.40	2.02*	1.82*	0.18	2.26*	0.76*	0.00	38.2	7.5	31.4	28.2	40.4	1.87	2.53	0.24
W20.	0.82	1.09*	0.85*	0.08	1.00*	0.48*	0.05	35.9	5.2	22.4	9.1	68.6	0.80	0.00	0.00
W29.	0.06	0.79*	0.26*	0.67*	0.44*	0.54*	0.29	20.5	4.2	45.5	0.0	54.5	0.78	66.6	0.00
W27.	0.09	6.30*	6.55*	0.48*	5.50*	0.67*	0.00	19.8	3.1	16.8	7.9	75.4	6.28	0.00	0.00
W25.	0.05	0.21*	0.09	0.11*	0.10*	0.65*	0.21	30.5	4.7	19.5	3.3	77.2	0.20	53.78	0.00
W24.	0.03	0.22*	0.18*	0.23	0.29*	0.99*	0.62	45.6	6.7	51.2	22.6	26.2	0.21	12.75	0.07
W32.	2.61	50.4*	42.9*	1.18*	41.25*	3.61*	—	57.5	5.8	9.5	7.5	83.0	48.9	12.27	0.00

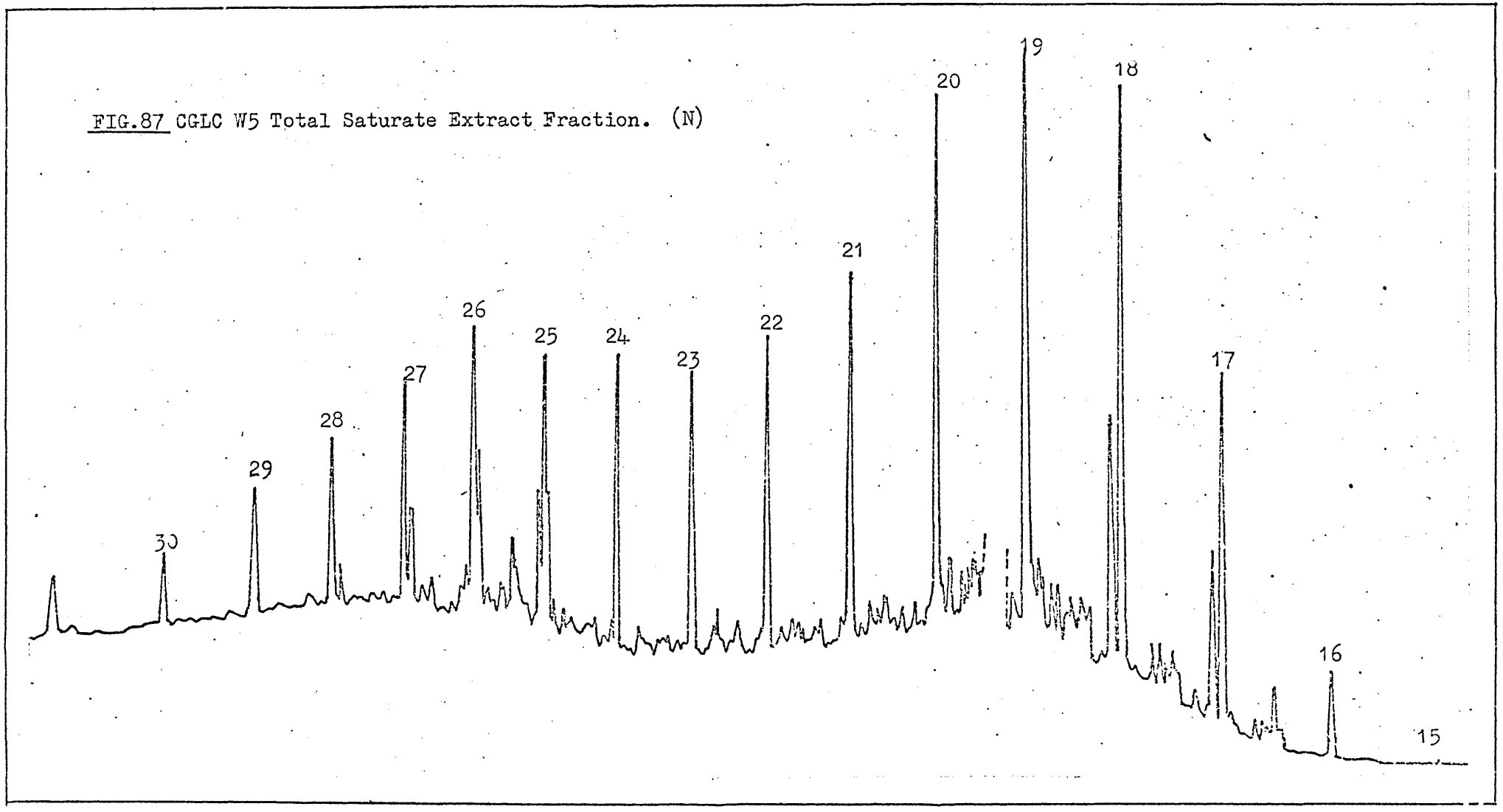
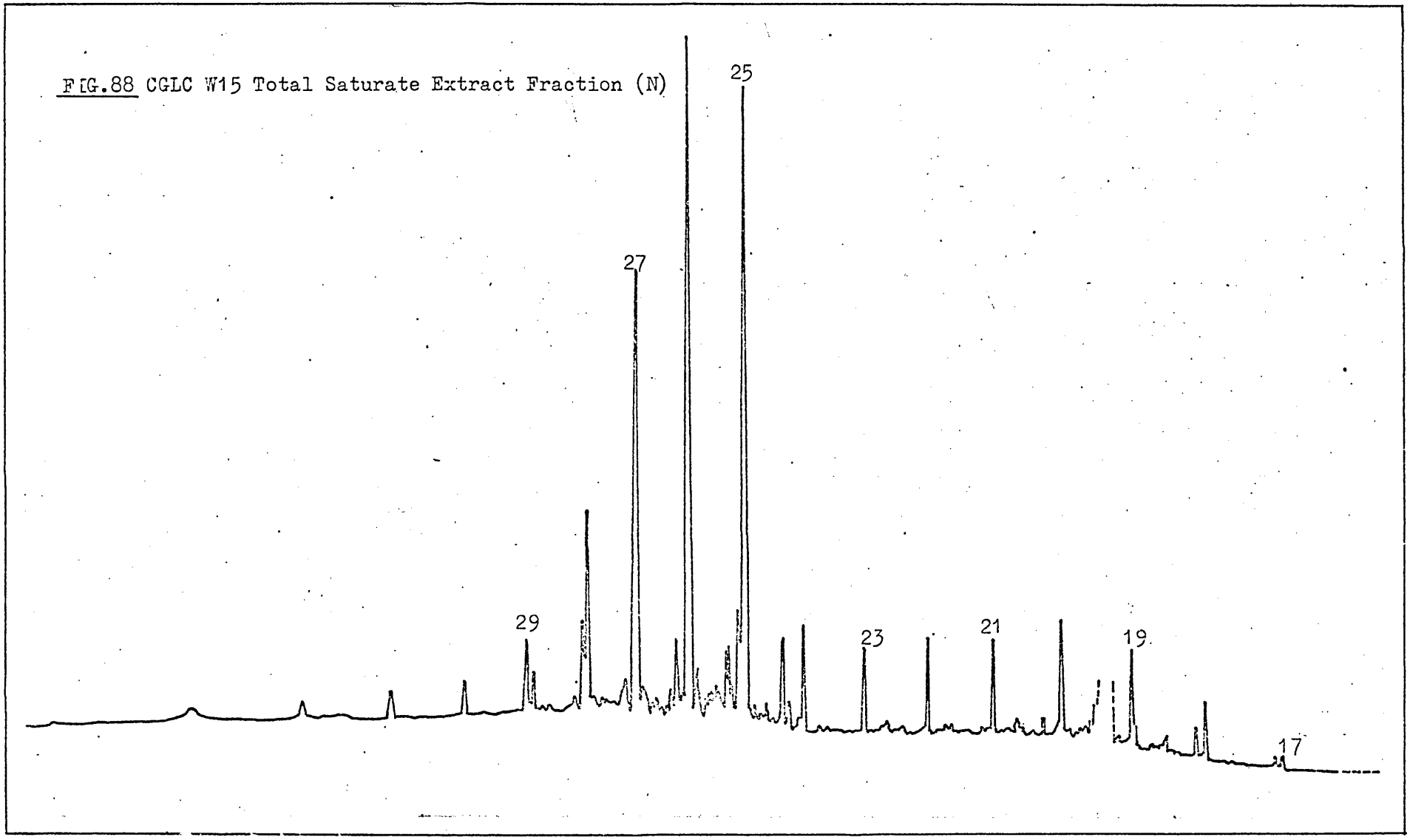


FIG.87 CGLC W5 Total Saturate Extract Fraction. (N)


FIG.88 CGLC W15 Total Saturate Extract Fraction (N)
25
27
29
23
21
19
17

anomalous for W24. A more intermediate conversion is agreed by the GLC for W11 but that of W1 does suggest a lower conversion is in order. The increased C_R/C_T ratios observed for the Kimmeridge Clay, Oxford Clay and Wealden Formations (0.4, 0.56 and 0.64) are irrespective of their stratigraphic position and do seem to confirm the increased dominance/importance of a lignitic phase which is very evident for the Wealden.

In general, the ability of the relevant organic type to correspondingly illustrate conversions in the order of their theoretical maxima predicted for their dominant type underlines an immature condition which the usual occurrence of a branched-cyclic envelope and average CPI also support.

Yet the high extractibility, high saturate extract content and low C/H extract ratio are particular anomalies. Although the branched-cyclic envelope can be missing or fairly significant it only dominates the saturate fraction of W9 (Figure 89) making the explanation for a relatively high percentage of n-alkanes in an immature facies more difficult (see Conclusion).

As the only serious source rock candidates from the Formation, the silty claystones are seen to show an average pristane/phytane ratio typical of a marine environment of deposition, whilst the mean pristance/nC_{17}-alkane ratio falls within the range observed for immature sediments where bacteria, algal mats, planktonic algae or mixed phyto/zooplankton are source materials (?).

Finally, their organic carbon content (1.4% average) and extractibility (average 0.21%) does place them within the specifications for recognised source rocks.

Conglomerates, Sandstones and Carbonaceous Sandstones

The results for eleven samples of these types of lithofacies are given in Table 68. No organic carbon determinations were entertained because of their dismissal as source rock candidates (see under the Introduction) and also as with the exception of W17 and 18, errors are enhanced for extremely low organic contents. The average extractibility for the sandstones and conglomerates is only 0.09% by weight.

Both the conglomerates and carbonaceous sands provide GLC chromatograms where the n-alkane distributions are biased over n-C_{25}, n-C_{26} and n-C_{27}; the CPI averaging at 1.33 (Figure 90). Although the pristane/phytane

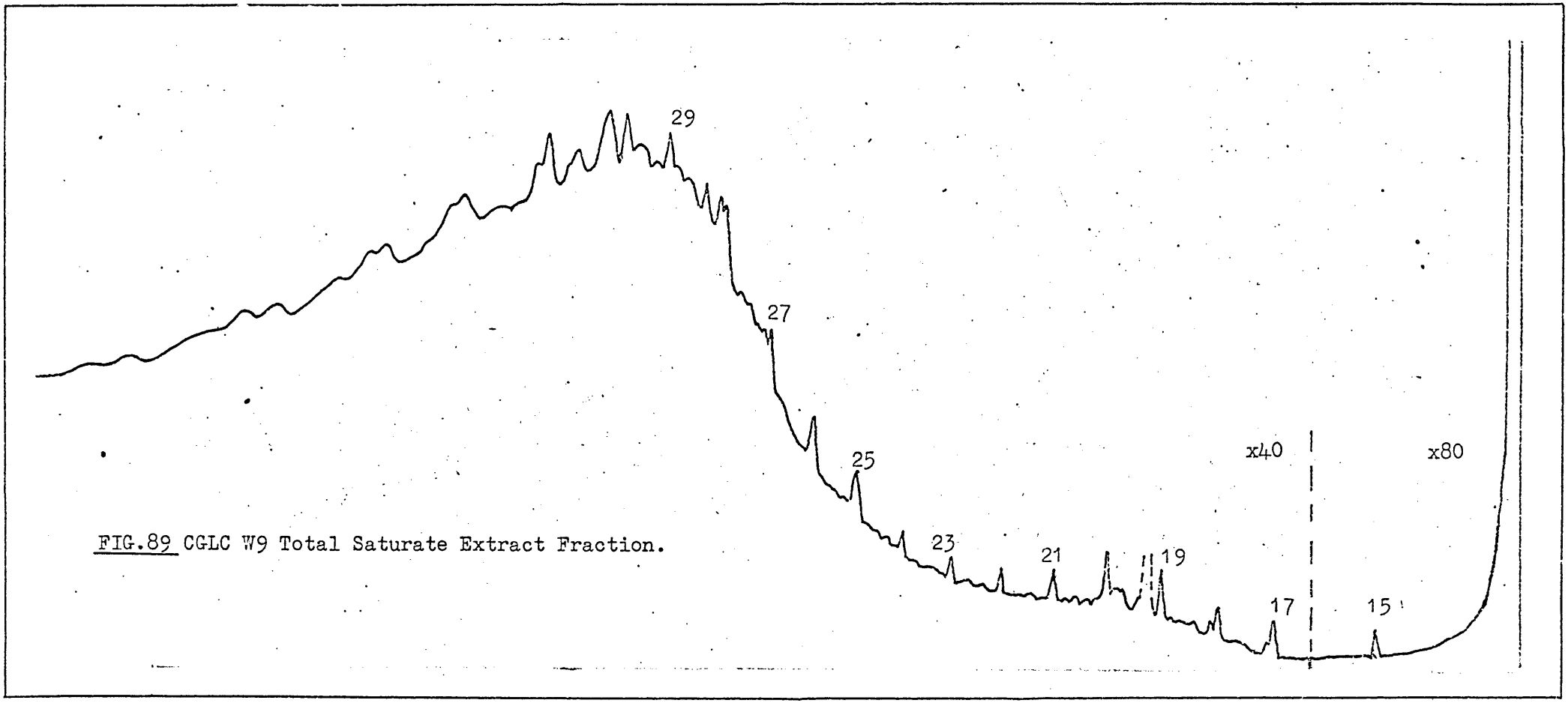
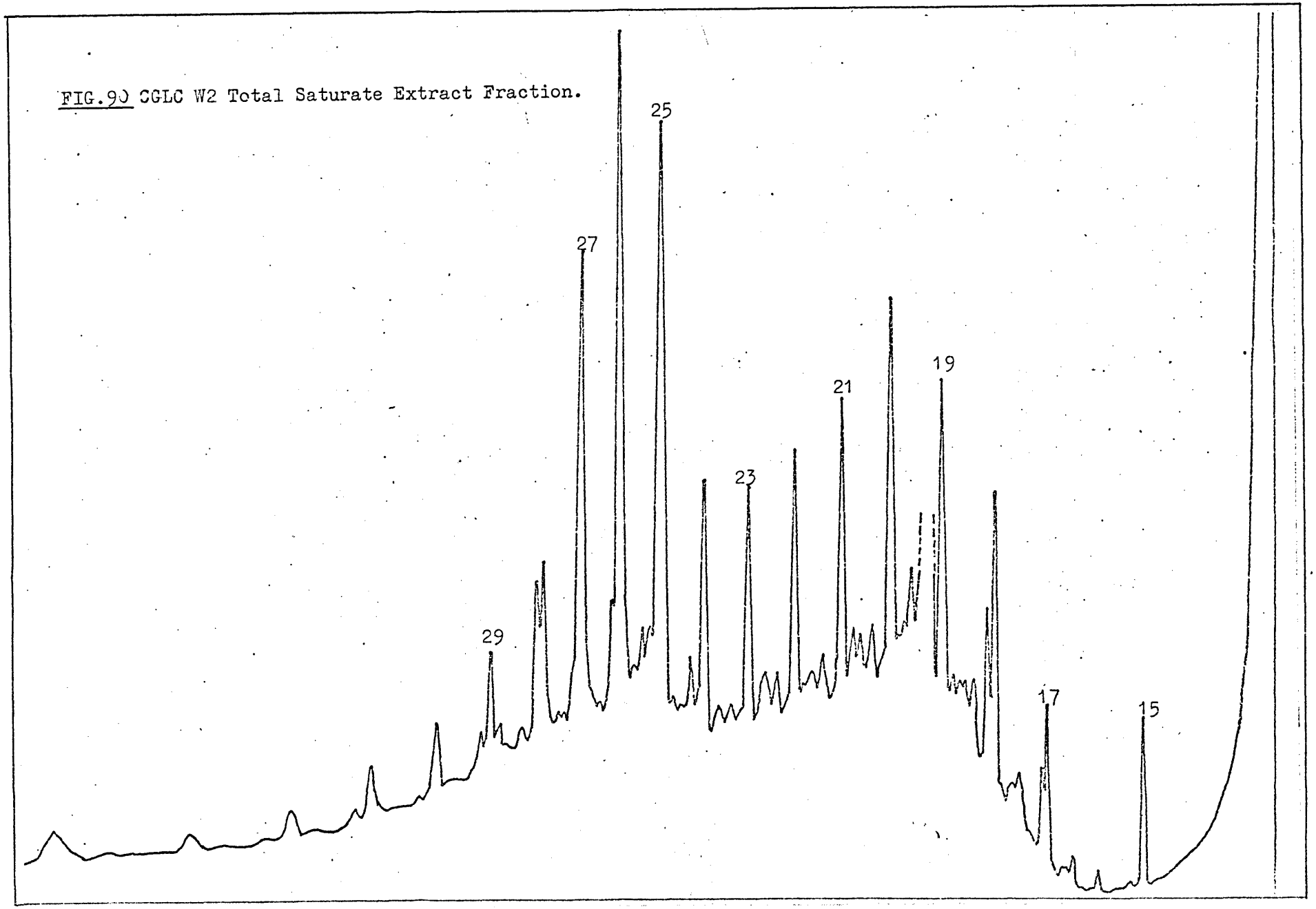


FIG.89 CGLC W9 Total Saturate Extract Fraction.

TABLE 68. WEALDEN CONGLOMERATE, SANDSTONE & CARBONACEOUS SANDSTONE RESULTS.
(Values are percentages by weight.)

SAMPLE.	SOLUBLE EXTRACT.	SOLUBLE EXTRACT.			SOLUBLE EXTRACT.			
		NITROGEN.	CARBON.	HYDROGEN.	SATURATES.	AROMATICS.	ASPHALTICS.	
W3.	0.10	1.22	31.28	4.25	48.2	5.5	46.3	Conglomerates
W2.	0.04	2.94	33.19	5.75	45.1	10.4	44.5	
W4.	0.04	1.88	50.38	8.52	34.0	11.4	54.6	Sandstones.
W6.	0.11	1.04	60.82	8.26	11.3	3.6	85.1	
W10.	0.03	3.12	26.59	6.69	25.3	7.2	67.5	
W26.	0.05	0.04	49.27	6.87	32.6	13.1	54.3	
W23.	0.06	0.28	15.73	4.04	20.1	14.3	65.6	
W31.	0.09	0.27	10.41	1.98	20.8	16.4	62.8	
W30.	0.25	0.28	9.48	3.92	37.6	0.0	62.4	
W17.	0.43	0.03	68.84	7.56	39.3	7.1	53.6	Carbonaceous sandstones.
W18.	0.17	0.87	49.96	5.60	20.7	12.7	66.6	

FIG.90 CGLC W2 Total Saturate Extract Fraction.



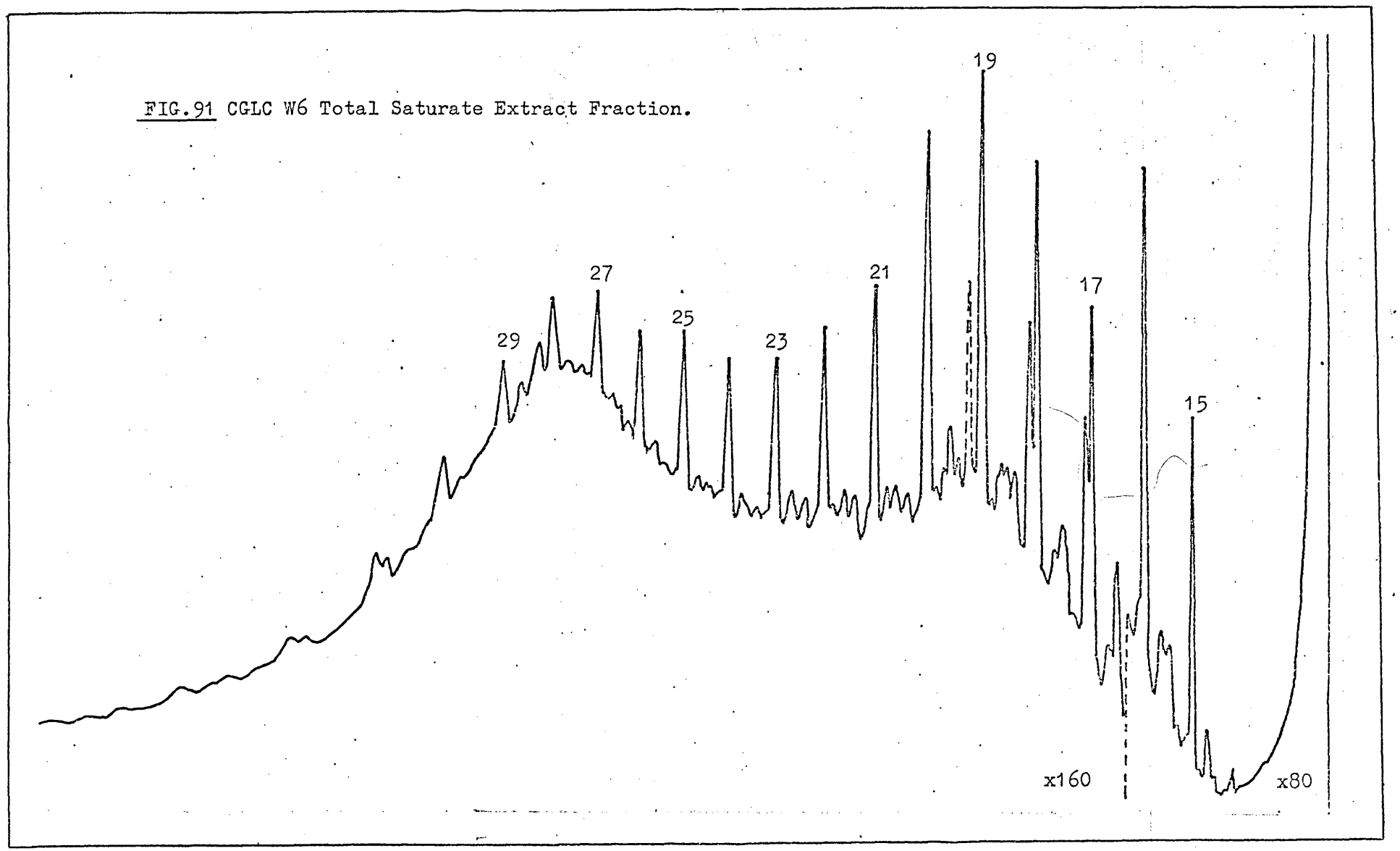


FIG.91 CGLC W6 Total Saturate Extract Fraction.

ratios are either identical or very close in both cases, the two conglomerates do provide relatively large pristane/n-C_{17} alkane ratios.

The sandstones, however, show a gradation through a LMW bias (W4, 6, 10 and 24; Figure 91) to a HMW pronouncement (nC_{25}, C_{26}, C_{27} and C_{28}) in the cases of W23, 30 and 31 for the n-alkane maxima. They exhibit average values of 1.2, 0.7 and 0.6 for their CPI, pristane/phytane ratio and pristane/n-C_{17} alkane ratio respectively.

Overall, only W(6), 18, 23 and 31 have gross extract compositions more in accord with those observed for the immature source facies of this study, but the remainder produce an average 37.4% saturates, 7.8% aromatics and 54.7% asphaltics. W30 is unique in this suite of clastics by providing no visible fluorescence for an aromatic fraction during tlc and UV/FES work employing W23 and W31 proved the dominance of PAHS in such fractions. Usually a fairly significant branched-cyclic envelope is found for the saturate fractions although it appears subdued in W18, 30 and 31.

Oil Sands

The experimental results for ten oil sand samples from six localities are annotated in Table 69.

Actually with the exception of the oil sands themselves, IR spectra proved of little use in correlating the Wealden extracts (with their lithology). W12, 16, 19, 21, 22 and 23 all gave spectra of type A whilst W7 and W8 only provided the (badly resolved) type B spectrum. W13 caused a response unworthy of grouping and W14 actually fell into a class, type C; where extracts from all of the remaining lithofacies are represented (Figure 92). In fact type C is identical with that dominating the Kimmeridgian extracts and asphalts and W14 happens to be the most asphaltic oil sand (although W16 is close by).

Of the non-conglomeratic oil sands, W12, 19 and 28 show saturate fractions with little n-alkanes but the branched-cyclic/naphthenic envelope is different to that of the silty claystone W9 (Figure 93).

The conglomeratic oil sands provide saturate fraction chromatograms which show significant envelopes and for each boulder-host pair the CPI, pristane/phytane ratio and pristane/n-C_{17} alkane ratio are each correspondingly very similar. However, all the n-alkane distributions vary between those with a LMW bias (W8; Figure 94) and a more HMW maximum (W21; Figure 95).

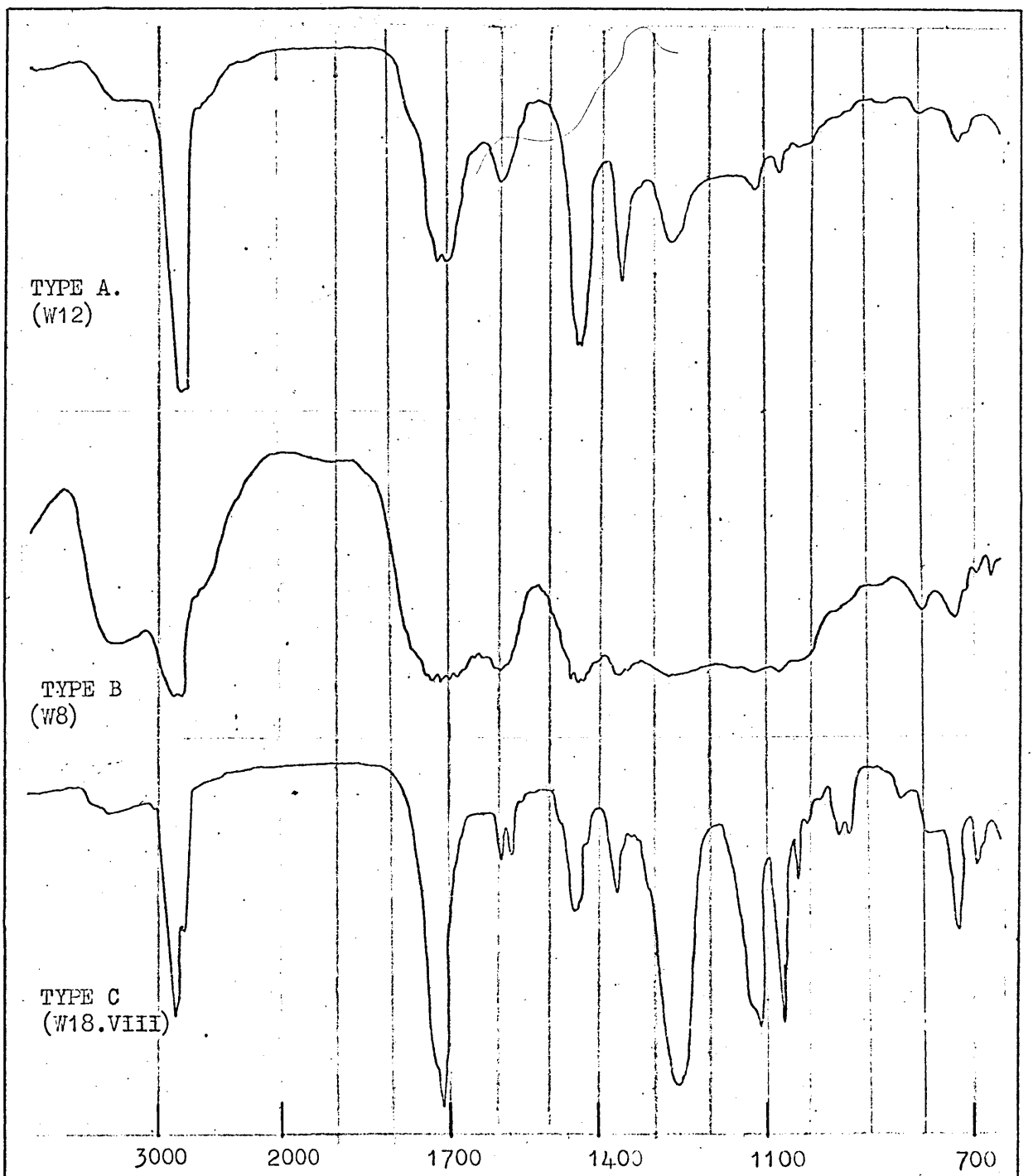


FIG.92 WEALDEN SOLUBLE EXTRACT INFRA-RED SPECTRA. (Wavenumber cm^{-1})

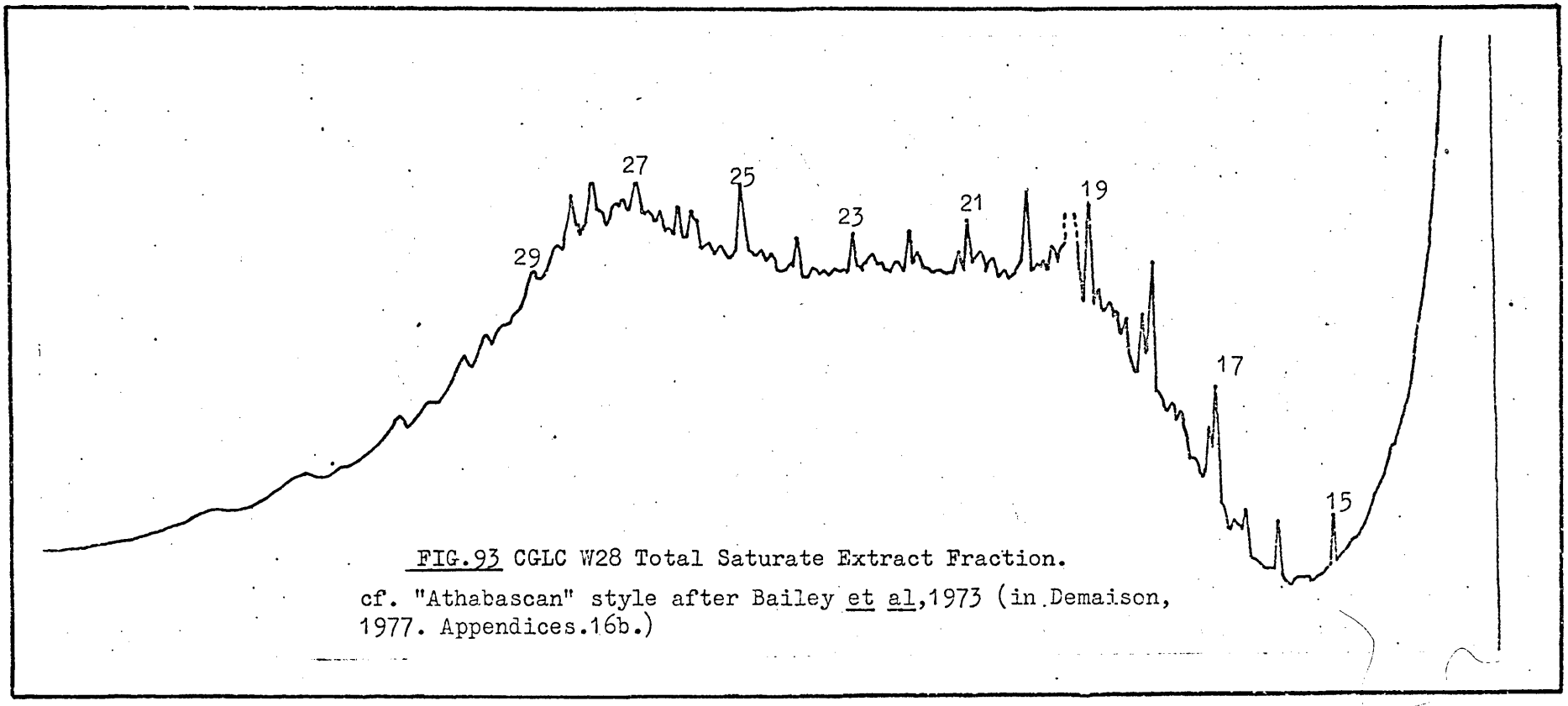


FIG.93 CGLC W28 Total Saturate Extract Fraction.

cf. "Athabascan" style after Bailey et al,1973 (in Demaison, 1977. Appendices.16b.)

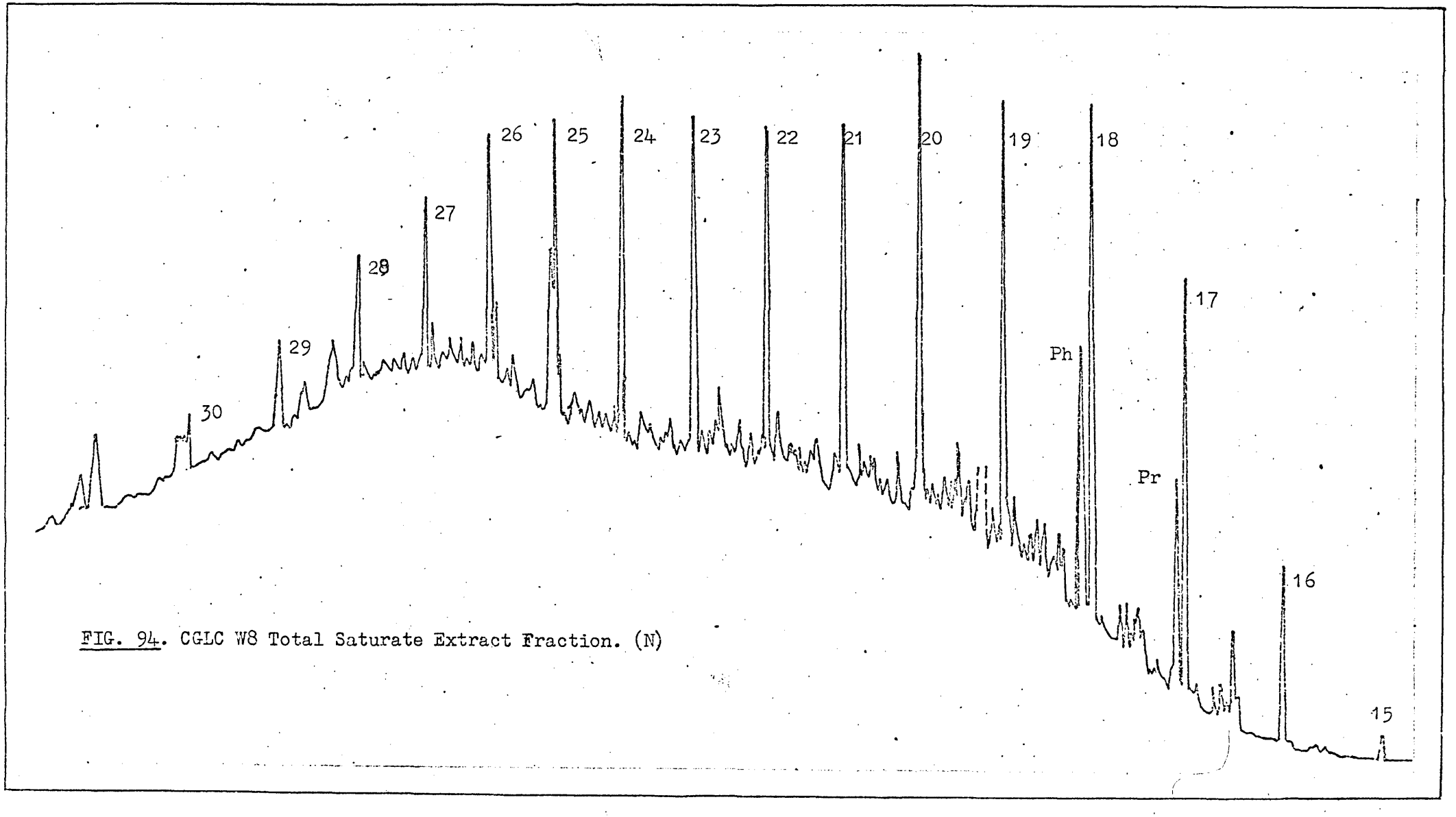


FIG. 94. CGLC W8 Total Saturate Extract Fraction. (N)

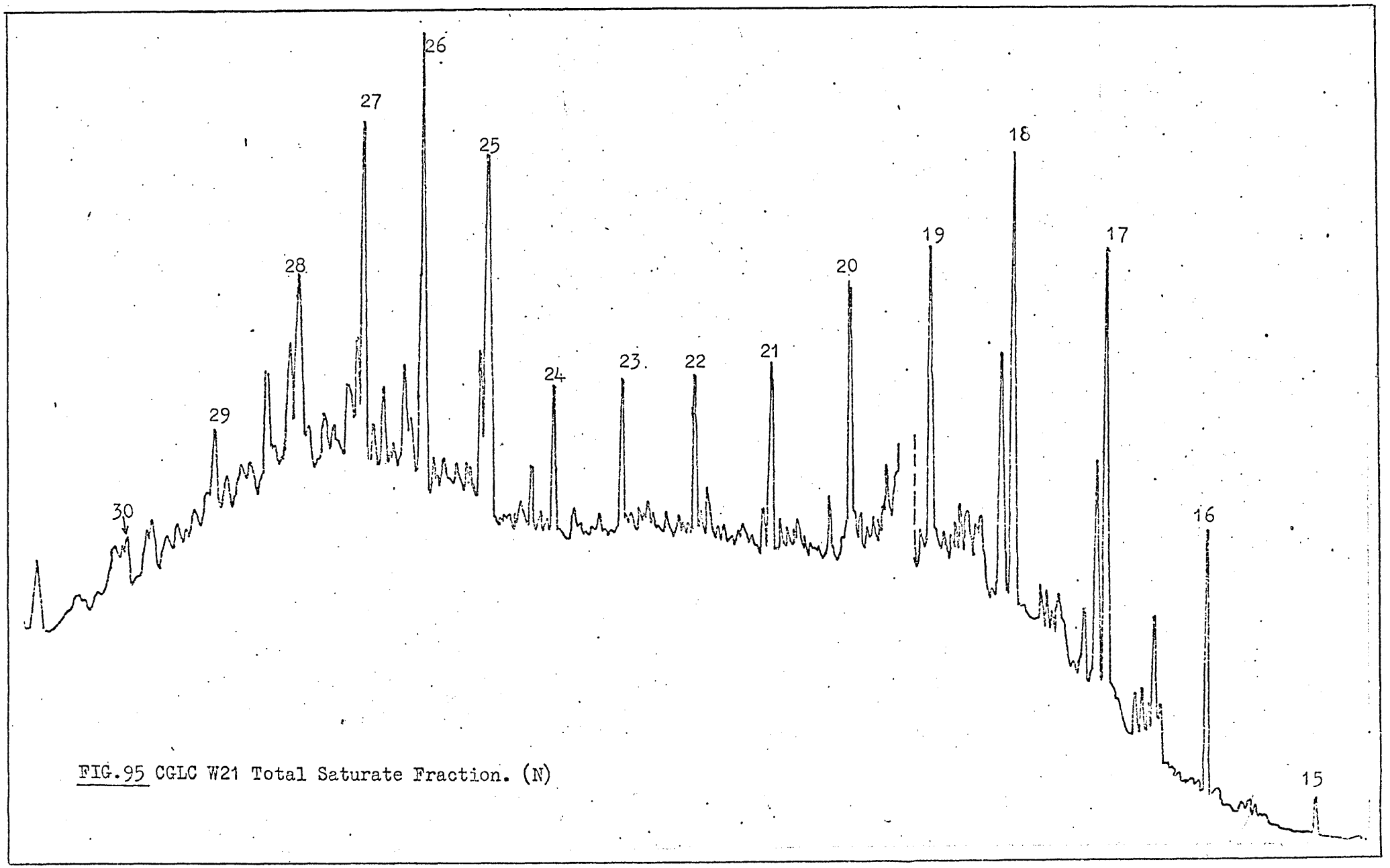


FIG.95 CGLC W21 Total Saturate Fraction. (N)

Overall, the oil sands give an average extract C/H ratio of 7.2 (excluding W13 and 14) and the percentages of carbon and hydrogen are generally very much improved with respect to those of the other Wealden lithofacies types (mean values are 80.4%C and 11.2%H excluding W13 and 14). The average CPI, pristane/phytane ratio and pristane/n-C_{17} alkane ratio are correspondingly 1.2, 0.8 and 0.6.

Petrographic analysis by Al-Gailani (Ph. D. in prep) shows that the oil sands are immature arkosic sands as they have a very low rock fragment and matrix content (no mineral cement); containing quartz as the major component but being rich in feldspar.

The grains are angular-subangular and float (only occasional point contacts) to provide a friable open framework fabric. The porosity can not be measured by laboratory technique and accordingly through impregnation estimates (13-36% ∅) indicate effective values that are much less than the total porosity. In fact blockage of the pore throats is seen as they are still choked with hydrocarbons. W21 for example is classic in showing isolated grains floating in a totally black hydrocarbon cement.

Detailed study has suggested leakage of hydrocarbons from within the boulders to the surrounding host (Speers priv.comm. 1977). The boulders (W8) and host (W7) at Dunghy Head are now seen to show almost identical grain size and the very similar extract compositions are consistent with an absence of local migration. At Mupe, the boulders (W21) are more fine grained than the host (W22) and the corresponding extract fractionations accord with the concept of preferential enrichment in 'mobile' hydrocarbons and relative depletion in 'viscous' asphalts for movement from W21 to W22. However, at Lulworth, the host (W14) is seen to be more fine grained than the boulders (W13) and the relevant fractionation is consistent with movement from W14 to W13 (on the basis of the Mupe argument; although W13 is unique amongst the oil sands in showing no aromatic fraction during the tlc procedure.

Now, owing to the disparity in grain sizes at the three localities no general tendency exists for the preferential absorption by the boulder volumes of oil introduced post-depositionally into the reservoir horizon. A diagenetic inhibition of feldspar (no dissolution and disintegration) occurs within the boulders and feldspar is concentrated with respect to the hosts. The boulders are actually carbonaceous and do sustain multiple extractions (Table 10). Accordingly Plate 22 illustrates the

currently best exemplified boulders where their conglomeratic nature can not be denied. (See Appendices 16b).

Lignite

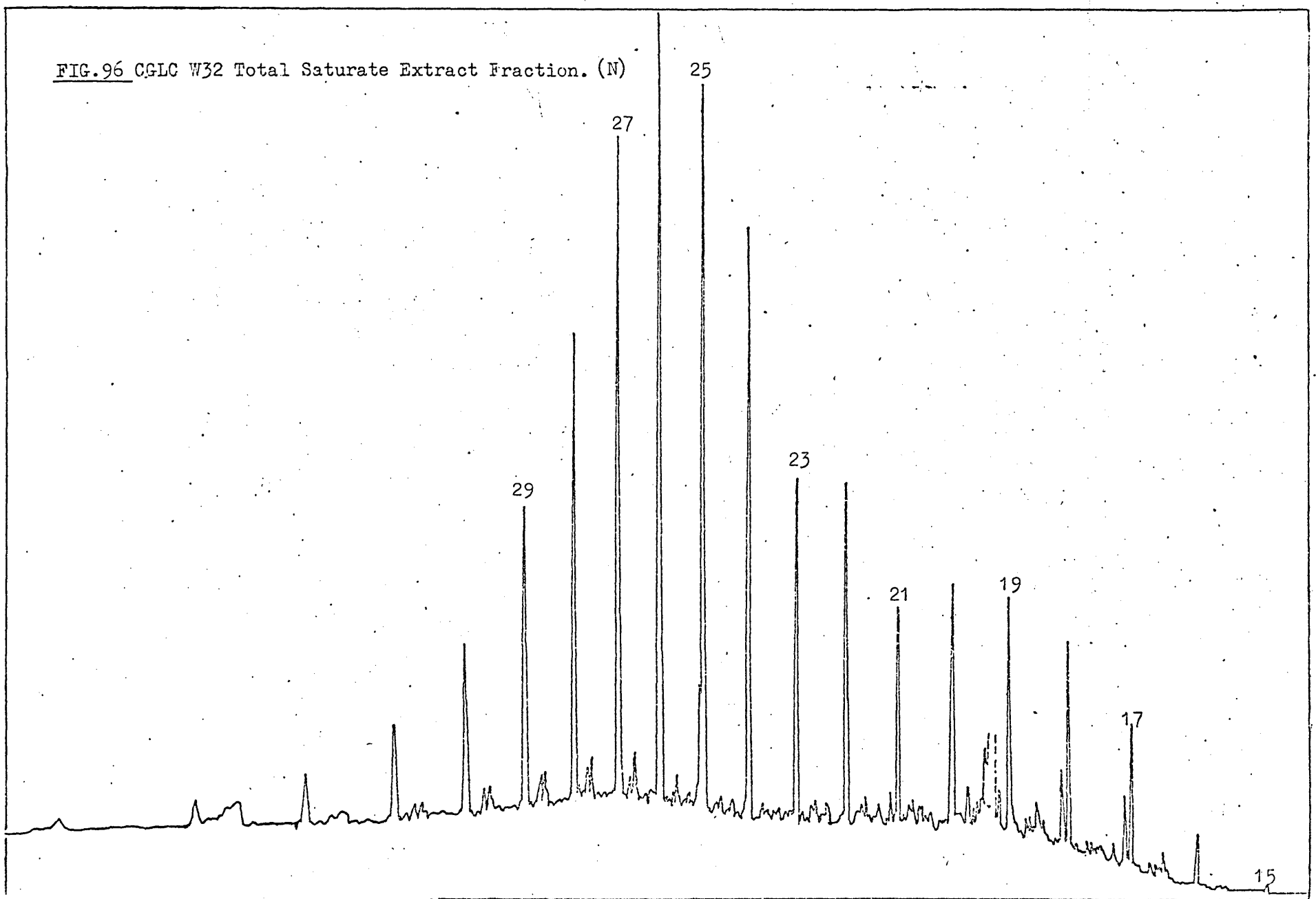
Due to the dominance of a lignitic phase in the Wealden Formation, a lignite specimen (W32) was examined (Table 67). The SOE/organic carbon ratio is 0.05 whilst the gross fractionation provides 9.5% saturates, 7.5% aromatics and 83.0% asphalts; causing the saturates/aromatics and non-hydrocarbons/hydrocarbons ratio to be respectively 1.3 and 4.9. The total saturate fraction chromatogram is depicted in Figure 96 where the CPI, pristane/phytane ratio and pristane/nC_{17}-alkane ratio are 0.96, 0.9 and 0.5. A kerogen (carbon) conversion is in the vicinity of 15% (C_R/C_T 0.85) and is close to the maximum (carbon) loss induced in immature humic kerogens (Table 58).

Overall, the characteristics are in context with those expected for an immature sediment and the 'excessive' lignite does not seem to explain the unusual geochemistry which persists throughout the Wealden facies examined here. The CPI value is anomalous though but the n-alkane distribution (maxima over C_{24}-C_{28}) accords with the general pattern (Table 30).

SAMPLE.	SOLUBLE EXTRACT.	SOLUBLE EXTRACT.			SOLUBLE EXTRACT.			
		NITROGEN.	CARBON.	HYDROGEN.	SATURATES.	AROMATICS.	ASPHALTICS.	GRAIN SIZE.
W8	0.56	0.13	77.91	10.29	28.5	14.0	57.5	0.25
W7	0.18	2.11	64.83	8.55	21.8	18.0	60.2	0.29
W12	6.48	0.13	79.04	11.86	39.6	7.2	53.2	0.19
W13	1.50	0.10	15.46	3.03	63.6	0.0	36.4	0.34
W14	0.07	0.04	31.79	4.15	14.7	3.3	82.0	0.22
W16	2.61	0.00	82.45	11.34	18.8	2.1	79.2	0.17
W21	6.81*	0.36	84.52	11.65	39.9	15.0	45.1	0.30
W22	2.63	0.05*	84.58	11.51*	61.3	21.1	17.6	0.50
W19	3.07	0.80	84.06	11.69	29.7	14.5	55.8	0.15
W28	2.31	0.00	85.40	12.79	52.6	12.3	35.1	0.26

TABLE 69. WEALDEN OIL SAND RESULTS. (Values are percentages by weight except grain size which is in millimetres from Al Gailani Ph.D. in prep.) *Denotes average values.

FIG.96 CGLC W32 Total Saturate Extract Fraction. (N)



SECTION FOUR

CONCLUSIONS FROM THIS STUDY

1 KIMMERIDGE CLAY FORMATION

For the Dorsetshire succession at outcrop the evolutionary state, type of organic matter and source rock potential can now be declared. However, the basis of any conclusions must be clarified first.

A) The postulation of an immature evolutionary state arises from several lines of evidence and is substantiated when they are taken in conjunction with one another. As mentioned in the interpretations and for this specific instance:

1 an immature nature is evident for the (shale) SOE from

a) the physical nature of the SOE

b) the elemental carbon content of the SOE

c) the elemental/atomic C/H ratio of the SOE

d) the IR spectral coincidence between the asphalt fraction and the SOE

e) the actual fractionation of the SOE when consideration of the quantity and nature embraces:

i the average relative gross fractionation values

ii the average saturates/aromatics ratio

iii the type of fluorescence exhibited during the tlc separation

2 a juvenile thermal condition is exhibited through the GLC total saturate fraction analysis by:

a) the average (C_{15}-C_{30}) CPI value

b) the branched-cyclic/naphthenic envelope

c) the occurrence of (significant) branched-alkanes

3 a thermally favourable/immature history is illustrated under laboratory pyrolysis because of

a) the amount and/or nature of the condensate

b) the average percentage of kerogen conversion

4 a low grade evolution is discernable from

a) the optical 'whole rock' microscopy

b) the lightest spore colouration and structural considerations

c) the UV/FES spectroscopic studies of the aromatic fractions

5 an immature diagenesis is suggested by 'crossplots' involving

a) the SOE v organic carbon trend or SOE/organic carbon ratio

b) the pre v post-pyrolysis organic carbon trend or C_R/C_T ratio

c) the saturates/aromatics v hydrocarbons/organic carbon

and finally,

6 an inadequate thermal career is deducible from a literature search which additionally includes a review of

a) the distillation/retorting experiments

b) the kerogen elemental carbon content

c) the kerogen atomic H/C v ^{O}/C (van-Krevelen/plot)

d) the type and classification of organic sulphur compounds

So, immaturity is applicable to the section and not in dispute but the actual degree of immaturity will remain controversial as there is yet no precise control(s) known to characterise the spectrum of petroleum diagenesis in such detail. Here it can be speculated that owing, at least, to

a) the (atypical) non hydrocarbon/hydrocarbon ratio

b) the (slightly larger than normal) extract percentage of hydrocarbons

c) the (closeness of the) CPI (to the upper limit)

d) the (diverse) saturates/aromatics v hydrocarbons/organic carbon plot

e) the SOE/organic carbon ratio (mimicing those of an early hydrocarbon generation zone)

f) the (range of reported) spore colouration

some mild thermal effects may have been experienced. On the other hand the 'enormous' kerogen conversions, that occur especially where pure alginites dominate, suggest very little previous exposure to heat. In this respect Irwin et al (1977) have deduced temperatures between 34°-66°C prevailed during the formation of the early diagenetic cementstones. Placing faith in pyrolysis however as a total kerogen measure it seems that the Kimmeridge Clay of Dorset never arrived at the liquid window (c120°F/49°C).

B) For a description and classification of organic type within the section, specific reference here for support of a final opinion can be sought from several parameters.

A gross uniformity throughout is suggested by the nature of the SOE, IR spectra, (limited) XRF extract analyses, GLC studies (pristane/phytane and pristane/nC_{17} alkane ratios with most distributions), tlc fluorescence observations reinforced by UV and FE spectroscopies and pyrolysis.

Variations in the proportions of basic parent types are reflected

by the extractibility, SOE fractionation (gross values, saturates/aromatics ratio), extract QEA (%C, H, N and C/H ratio), GLC analysis (n-alkane distributions), optical (whole rock) microscopy, visual kerogen description, pyrolysis and the literature search (additionally kerogen elemental analysis). Accordingly, from the results of this study, a scene of high 'in situ' marine biological activity is visualised where only occassional periods of reduced eutrophy and/or higher than usual continental run-off (KC114, 113, 100, 99-97, 94, 91, 83-81 (75) 61 (28) and 18) occurred with rare instances of total oligotrophy (KC (114), 103, 102, (91), 87, 57 and 39).

Terrestrial in-put into the depositional environment appears to have been variable but generally restricted between narrow limits. The relative increase in terrestrial matter for the approximate KC79-100 interval (Log 3) presumably correlates with the increased miospore count noted for a 'lower Upper Kimmeridge Clay interval' by Mebradu (1975). Declination to very low proportions or even complete cessation of allochthonous material seems to have occurred on relatively few occasions, (KC107, 84, 66, 11, 4, 1); sometimes coincident with accentuated planktonic blooming (KC74, 70, 67, 55B, 54, 32).

Overall autochthonous (marine planktonic algal) matter is concluded to be diluted by only a small allochthonous (terrestrial higher plant) contribution. Like the Green River Formation (Robinson et al 1965), the 'oil shale' kerogen here is seen to be caused by aquatic organisms exceeding land plants, pollen and spores and, similarly, although differences in source material undoubtedly occurred at different times during deposition, the vast bulk of the organic matter is remarkably uniform.

As the predominant precursors are unquestionably marine algae, the tentative suggestion by Riley (1974) that "highly bitumenous sediments are the products of the decay and degradation of wood cellulose tissue" is untenable for the Kimmeridge Clay Formation.

C) An overall "excellent" category of source rock potential is here specifically indicated for the section by

1 the extractibility and/or hydrocarbon yield

2 the average organic carbon content

3 the 'whole rock' optical microscopy

4 the pyrolysis C_R/C_T ratio

5 the literature search; notably the elemental kerogen composition

and the definite occurrence of mixed-layer clays is also encouraging in enhancing the prospects of the Formation.

Applying an average geothermal gradient of 1.4°F/100 ft (see under hydrocarbon generation in the Introduction) it can be stated that wherever lateral equivalents of the same facies type have reached an approximate minimum depth of burial of c.4,300 feet (to allow residence within the liquid window of a normally subsiding sedimentary basin) active and prolific sourcing commences (60°F ambient, 120°F liquid window limit).

It is therefore more than intriguing to observe a close similarity between the Dorsetshire section and a northern North Sea (good) source rock interval; based upon the latter containing

1 5.6% average organic carbon

2 kerogen with 7.6% hydrogen and 78% carbon

3 organic matter that gives a C_R/C_T ratio of 0.37 - 0.52

4 dominant sapropelic organics with about 20% of humic/coaly and plant material

especially since the subsurface section lies between 2600m-3200m or about 8,700 ft - 10,700 ft ! (the maximum palaeotemperature is estimated at 100°C). (Brooks and Thusu 1977).

Therefore in view of the above average oil generating property, estimated to run to tens of billions of barrels at the primary migration stage (Fuller 1975), the potential indicated here is both realistic and exciting. The origin and effect of the ubiquitous sulphur in this context requires further study.

D) Speculation here is chiefly based upon the radioactivity/kerogen type relationship, the cementstone horizons and maximum depth of burial whilst comment upon the unusual occurrence of high magnesium calcite (which is rare in ancient sediments because of its instability) is reserved until categoric substantiation of its presence is available. (Electron probe analysis)

Thus, the slightly offset/displaced correlation observed between instances of high radioactivity and pure algal kerogens suggests perhaps that the advocated relation between plate rifting and

increased planktonic activity is applicable for the Dorset Kimmeridgian. Coupled with the discussion on syndepositional tectonism, Bitterli's view that bitumenous sequences locate palaeogeographic 'turning points' is upheld here.

With regard to the cementstones, the suspicion of ferrous ions and thus a reducing environment within the sediment at an early stage of diagenesis has been independently confirmed. However, since three of the eight cementstones contain dominant terrestrial matter whilst the remainder have dominant marine algal matter, the (diagenetic) dolomitisation appears unrelated to the organic type and thus independent of the environment of deposition of the Kimmeridge Clay. Further, such horizons are typified by relatively low organic contents (with respect to their immediate backgrounds) and detrimental recrystallisation could explain this as opposed to a low fluctuation in the quantity of organic supply. In this context Irwin et al (Sept. 1977) have underlined the importance of diagenetic reactions for significant modification of organic matter where derived bicarbonate produces massive amounts of carbonate cement. Lastly, as the Rope Lake Head (KC54) and Yellow Ledge Stonebands (KC32) appear to hold 'alginite' kerogens, in the absence of dolomitisation, one may wonder whether 'white bands' would have been expressed at these horizons.

The assessment of the maximum depth equivalent of normal burial (for an ordinary subsiding basin) is critical upon the relevant geothermal gradient. In the absence of specific maximum paleotemperature data for the Wessex Basin, consideration of the world average situation (see Introduction) suggests such burial for the Kimmeridgian did not achieve 6000 ft and in fact, Degens (in Dunn, 1972) was quoted to have said that the sediments were not buried to more than 1500m (5,000 ft). If a geothermal gradient of 28°C/km can be applied (from Irwin et al 1977) the liquid window begins at a depth of 1.75km (using Pusey's limit of 120°F/49°C) which is approximately equivalent to 5,800 ft. * As the Oxford Clay is also seen to be immature and resides about 1600 ft below the Kimmeridge Clay (Figure 83), a maximum depth of burial for the Kimmeridgian outcrop is, accordingly, about 4200 ft. (The value of 28°C/km rise in temperature is

* Bellamy (1977, Journ. Sed. Petrology, V.47, n.3, pp.973-978) has noted that the Flats' megapolygons show features with affinities to fault -ing produced artificially "under elevated temperature and pressure"

approximately equivalent to 1.5°F/100 ft and close to 1.64°F/100 ft which can be derived from the D'Arcy Portsdown No. 1 if a 60°F ambient is applied; as a bottom hole temperature of 169°F at 6656 ft was recorded. See Appendices 4.) *

Finally, the shallowing upwards sequence which has long been taken to terminate Kimmeridge Clay sedimentation actually begins at 160 feet below the Massive Bed.

2 OXFORD CLAY FORMATION

Largely by analogy to the reasoning offered for the Kimmeridge Clay and specifically through the collective agreement of

1 the SOE v Organic carbon plot and the average SOE/Organic carbon ratio (between 0.05 - 0.1).

2 the gross fractionation values; in particular the non-hydrocarbons and hydrocarbons and/or their ratio

3 the saturates/aromatics ratio (<2)

4 the CPI for the n-alkanes

5 the elemental carbon content of the SOE and its C/H ratio

6 the C_R/C_T ratio (which is less than 0.6)

an immature condition can be postulated (with the reservation only of poor statistics) for the Oxford Clay of Dorsetshire. Compared with the Kimmeridge Clay it is (economically) poorer in prospects because of its reduced quantity of organics (extractibility, organic carbon content and pyrolysis/distillation) and its potential leaning towards gas (due to a greater dilution of algal matter by a terrestrial input).

Of course, merely from its lower stratigraphic position a higher degree of diagenesis was (obviously) experienced by the Oxford Clay (with respect to the Kimmeridge Clay) and this condition is perhaps reflected most in the GLC work. The increased thermal effects approximate to an additional 12.6°C (Figure 83) but the reduced pyrolysis effects are believed to reflect both the shift in dominance between the fundamental organic types and the increased temperature; not burial diagenesis alone.

Thus, at the best, the Oxford Clay came closer to the liquid window upper limit (49°C) but did not penetrate it.

3 WEALDEN FORMATION

In an overall context of immaturity, the high extractibility (per unit content of organic matter), high saturate extract content and low

* For a high (Venezuelan) geothermal gradient of 2°F/100 feet, Demaison (see Appendices 16b.) placed the top of the oil generative window at about 7,000 feet. (?)

extract C/H ratio are particular anomalies which, together with the occasional absence of aromatics, seem to have missed documentation amongst the literature reviewed here.

Specifically for the silty claystones, only certain estuarine muds of the present day are known to the student to provide hydrocarbons in the order of 50% with respect to the extract weight (Table 28). However, the n-alkane distributions are uniform and the average percentages of saturates and aromatics are the reverse to that discovered here (?).

For the non-conglomeratic oil sands, the idea of a more basinward source seems erroneous as the post-Kimmeridgian cover appears inadequate to have initiated generation before the Tertiary uplift and erosion. ** The remaining post-Kimmeridgian overburden is today only about 3,300 feet* and under world average conditions of burial a sedimentary pile at least twice the size is required (*Naylor and Mounterey 1975).

From physical, geochemical and microscopic data now furnished the conglomeratic oil sands indicate the reworking of a not too distant tar sand exposure provided the sediment source for the relatively quickly buried oil sands. At least two main phases of biodegradation (approximately Neocomian and present) have been experienced by the oil within the sands. As reservoired hydrocarbons tend to contain less aromatics than their presumed source (Brenneman and Smith 1958 in Hunt 1961) the weathering phenomena may be responsible for the accentuated reduction here (?)

Consequently, the suggestion of post-depositional invasion along the unconformity from a more deeply buried, truncated source rock facies such as the Kimmeridge Clay is discounted. For the Kimmeridgian an (c.5%) and Wealden (c.1%) hydrocarbons, a disparity in sulphur content does happen to occur. (?).

With regard to the unusual geochemistry observed for the Wealden sediments, the syn-sedimentary availability of (biodegraded) mature hydrocarbons is emphasised by the occurrence of the conglomeratic oil sands. Overall, therefore, a mixing and incorporation of previously matured organics with the synchronous organic products may provide the explanation. In particular, an unusually high (bitumen) extract ratio could mean an unusual type of organic matter rich in hydrocarbons and hydrocarbon related compounds (Palacas et al 1972).

** At the time of the first Cretaceous tectonic phase, "the lowermost dolostone (the Flats) would have been under an overburden of atleast 1,200 m." (Bellamy,1977,Journ.Sed.Petrology,v.47,n.3,pp.973-978.)

Finally, with regard to the recent radical proposal of a more continental environment of deposition, the pristane/phytane ratios are typical for sediments deposited in a marine environment and do agree more with the established view of a deltaic deposition.

GENERAL CONCLUSIONS

Ample room for improvement of the solvent extraction technique in general is apparent from the individual conclusions under Experimental Work where improved fractionation is also overdue. The application of properly handled spectroscopic studies appears more than relevant to the needs of oil exploration geochemistry.

From this study the combination of solvent type and apparatus is seen to warrant careful consideration and multiple extractions develop an interesting trend. However the advances in pyrolysis - GLC - MS techniques are ultimately observed to exceed conventional extraction and for source rock evaluation they may eventually displace the latter entirely !

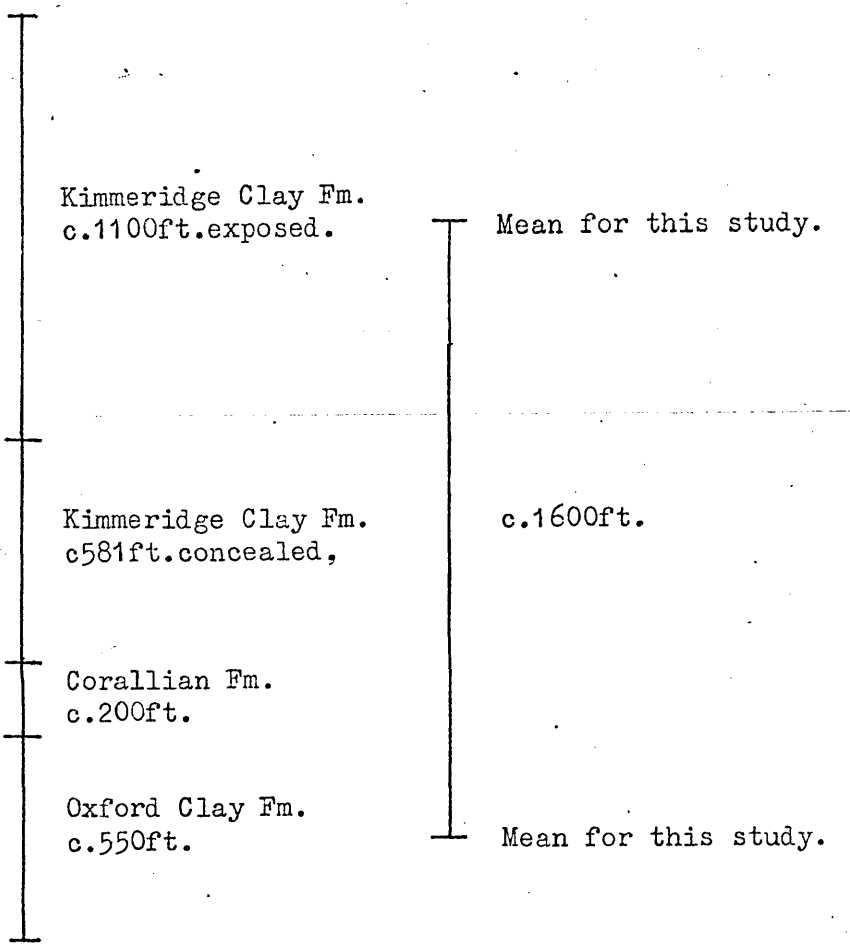
For detailed organic geochemical studies, though, routeways for the separation of extractables are depicted in Figure 97 and this is expanded under the Appendices as a guide for future work. (Albrecht & Ourisson 1971 have also depicted such a scheme).

Also, through the review afforded by this study, the reasons for organic geochemists to distingusih between the evolutionary state and type of organic matter are emphasised and the importance of future kerogen study emerges.

Since the concept of incipient metamorphism has been built to cater for changes in organic matter there is nothing more appropriate than the molecular and compositional variation of organic matter itself for classifying the stages of such diagenesis. As more data evolves to define models of contrasting organic geochemistry a better focus will be achieved. Inspection of the variation throughout the Kimmeridge Clay Section reflects the danger of drawing broad conclusions from a limited number of samples over a large rock interval. Often this is the case in the literature and here it is well demonstrated by the difficulty in interpreting the Wealden Formation.

Specifically, this presentation is centred upon the elucidation of the organic geochemistry for the Kimmeridge Clay Formation of Dorset which is adequate to meet the needs of oil exploration in the Wessex Basin.

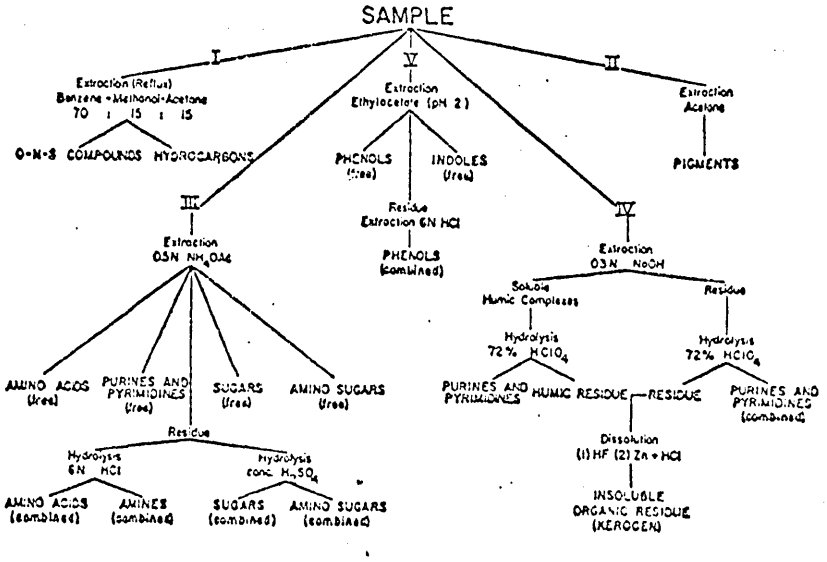
As an immature status is also jointly proved for the Oxford Clay Formation, investigation for an onshore example of a mature oil source rock facies



Using an average world geothermal gradient of 1.4°F/100ft.,1600ft.≡22.4°F or 12.6°C.rise in temperature.

FIG 83. TEMPERATURE RELATIONSHIP WITH STRATIGRAPHIC SECTION. (Compiled using Fig.41, Introduction, and Chatwin 1960,Wells & Kirkaldy 1966 and Rayner,1967)

FIG 97. FLOW DIAGRAM FOR ANALYTICAL CLASSIFICATION. (From Degens & Reuter,1962.)



is now openly directed to the sedimentary section older than the Oxfordian.

For appropriately buried lateral equivalents a difference in the potential is observed as the 'algal-rich' Kimmeridge Clay promises vast quantities of oil in contrast to the lower gas-prone yields from the 'mixed algal-humic' Oxford Clay.

The Wealden Formation remains unique in British geology because of its conglomeratic oil sands and currently confusing organic geochemical characteristics atypical of its immature condition are revealed here.

In summary, a hitherto casually designated 'source rock' has been documented on an unprecedented scale despite a limited educational budget. It now provides a broad framework upon which to build (Cooper priv. comm. 1977) and gives a standard against which new techniques may be compared. Already, on a sample-to-sample correlation basis, kerogen-pyrolysis-GLC studies and vitrinite reflectance measurements are in progress (Solli pers. comm. 1977 see Appendices 16d).

FUTURE WORK

From the introduction the reader may recall that the entire Rhaetic-Upper Greensand was sampled and in fact 350 specimens are prepared awaiting examination. Ultimately, though, in the advent of Channel drilling the importance of organic geochemistry in the Wessex Basin will undoubtedly achieve the financial recognition and support that it deserves. The Wessex Basin does, incidentally, fall within 'perspective favourables' (OEEC 1957) and the Western Channel is 'encouraging' (Wright 1973).

FINAL WORD

As for any attractive fast growing science it remains intriguing to find if the truth today will be so tomorrow.

Whatever, in a strictly chronological sense, without a source, and especially the ability today to recognise and characterise a source rock, everything else in petroleum becomes secondary and irrelevant !!

APPENDICES

1 HEALTH & SAFETY AT WORK, etc., ACT (1974)

Here it is appropriate to mention that the bulk of this work preceded (strict) enforcement of the Act within academic circles. The reader should appreciate that all stages of the sample preparation and extraction are particularly dangerous. Eglinton (1968) emphasised that the toxic aspect of solvents is serious and he advised all operations should be conducted under a fume hood. In this respect, Russell (priv. comm. 1976) has told of aromatic hydrocarbons being potential cancerogens and that alcohols can lead, for example, to liver infections. Both he and Eglinton (1968) have advocated the use of toluene as an alternative to benzene. Trichloroethylene vapour has been known to kill (Anon.). However, long term exposure to small quantities of dangerous solvent is regarded to have a far more serious effect than a short term exposure to a large quantity of such material (Russellpriv. comm. 1976). Many solvents commonly employed in source rock studies are of course inflammable as well.

Using the procedure in this presentation the amount of solvent loss for each four fold extraction, recovery and isolation can sometimes be as high as 1.25 litres per 14 litres (Gill et al unpub.). The majority of the loss can be attributed to escape through the condensers above the soxhlets and to evaporation during the final isolation. Although the extraction facilities are under constant evacuation, respirators, protective clothing and gloves and the presence of a second person within calling distance are now the rule.

2 ANNOTATED PERTINENT POINTS FOR FIGURE 98; SUMMARY OF THE BASIC COMPONENTS OF GLC

1 N, H, He, Air, CO_2 or mixtures are available in sufficient purity to warrant little more than drying and such carrier gases do not interact with the stationary phase to any significant extent. The low viscosity of gases cause no serious hinderance to the moving phase and the rapid attainment of equilibrium achieved by gases allows high flow rates to be used. Gases also allow changes in their composition to be continuously and automatically monitored but because they are compressable, probable flow variations along a column have to be allowed for in theoretical consideration.

2 This is usually connected directly to the cylinder.

3 For example, a 5Å molecular sieve activated at 200°-300°C.

4 This is usually a needle valve or oil-damped pressure regulator.

5 Incorporated when a very accurate flow rate is required.

6 Often a continuously indicating capillary device covering the range 10-1000 $cm^3\ min^{-1}$.

7 Generally thermostatically enclosed. A rotary vacuum pump oil is ideal since it has a low vapour pressure and its menicus can be clearly seen.

8 Alternatives to 5 and 6 needed if capillary columns are in use since although the flow rate is fast, actual volumes of gas moving through such columns are small.

9 For liquids, a syringe provides the most convenient and cheapest way of introducing a sample onto the column although sampling valves and sealed capsules are more accurate. Rubber or silicone serum caps may be used several times until serious leakage develops and here it is appropriate to note that occasional batches of such septa can exude high molecular weight volatiles (Eglinton *et al* 1964). The sample should be as concentrated as possible within the smallest solvent volume(fronting occurs if large samples are used) to prolong the life of the column. The injection point is heated to vaporise the sample as quickly as possible and its temperature should not be less than 50°C above the boiling point of the highest boiling component of the mixture. (Special techniques are needed for gases and solids).

10 These linearly reduce an injected sample volume to less than 1 µg with reproducibility for conveyance onto a capillary column to avoid overloading (c. 25×10^{-6} ml).

11 Columns in stainless steel (and either coiled into c.200 cm diameter helix or U-shaped) are very popular but the packing has to be taken on trust. Glass columns have lower reactivity and the packing can be checked visually but they break easily.

The lowest temperature consistent with a good separation is ideal since with increasing values the column will show enhanced 'bleeding'; that is, the stationary phase itself will be eluted. $-196^{o}C$ (liquid N) to about $500^{o}C$ are known for operating temperature extremes but most are above ambient.

In isothermal seperations the temperature must not vary by more than $2^{o}C$ and ovens with water/oil baths or refluxing liquids are needed. However, at temperatures necessary for good resolution of lower boiling components the retention of higher boiling components becomes unacceptably long and their peaks broaden (Schenk & Eisma 1962) whilst at higher temperatures necessary for rapid elution of less volatile material, the more volatile materials are incompletely resolved. Hence temperature programming is preferable for complex mixtures whose components have a wide range of boiling points. Different rates of heating can be applied efficiently by ovens with forced air circulation.

For the actual solid support, diatomaceaes earths are very popular and less expensive as compared with firebrick adsorbents. Both though are highly porous siliceous materials with large surface areas but density consideration for packed coulmns reduce the figures to 1.14 $m^{2}g^{-1}$ and 4.14 $m^{2}g^{-1}$ respectively. In fact a wide range of fused crystalline metallic or polymeric support materials is available. The usual particle size range is 30-120 mesh (BSS) and restricted 80-100 or 100-120 mesh ranges are often used to enable more even packing. The support allows the stationary phase to present a large surface area to the mobile phase.

A bewildering choice exists for liquid stationary phases but surprisingly few are necessary for separations of a very wide range. Ideally, the smaller the percentage is of a stationary phase, the more rapid are sorption equilibria established and the shorter is the separation. However tailing is often due to adsorption on the solid support and this is reduced by applying more stationary phase (and/or water if a flame ionization detector is being used). Ratios of liquid stationary phase to support are commonly 1-30:100 and many separations can be achieved before a column needs renewal.

12 Variations in column effluent are generally measured by differential cells; that is, those which give a zero signal for pure carrier gas but provide a signal for a solute in the carrier gas. Many kinds exist. For example, thermal conductivity (kathrometer), flame ionization, β-ray ionization, photo-emission, microwave emission, flame emission, flame conductivity, rapid scanning infra-red/ultra violet absorption dialectic constant, heat of sorption etc.

All however require sensitivity to a very small concentration of one component in the presence of a very large concentration of another component. They also need a very rapid response, a small dead volume and a high signal to noise ratio.

Flame ionization detectors are usually more sensitive (10^{-12}-10^{-23} moles) than others (e.g. thermal conductivity and gas density balance: 10^{-6} moles) and are applicable also to capillary columns. For such detectors, Condon et al (1960 in Stock & Price 1974) noted that the noble gases, H_2, O_2, N_2, $SiCl_4$, $SiHCl_3$, H_2S, SO_2, COS, CS_2, NH_3, NO, NO_2, N_2O, CO_2 and H_2O are not detected because of their high ionization potentials. In contrast, most organic compounds ionise relatively easily (c. 415 KJ $mole^{-1}$ / 4.3 eV) and about the only organic compound not detected is formic acid (HCOOH). The response depends upon the carbon number of the issuing components and CH_4, which is retained to a negligble degree on most stationary phases, is used to determine the "gas-hold-up" volume as no air peak is registered.

Specific detectors, such as electron capture and microwave plasma instruments, are available to respond selectively to particular types of compounds or classes of compounds. Flame photometer devices have been used to analyse for sulphur (Albrecht et al 1976) and phosphorus-containing compounds.

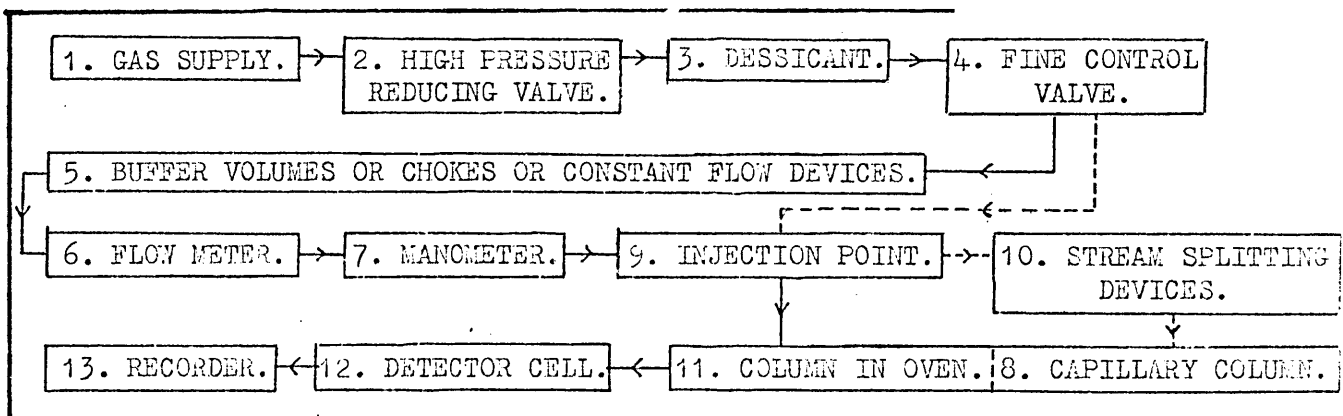


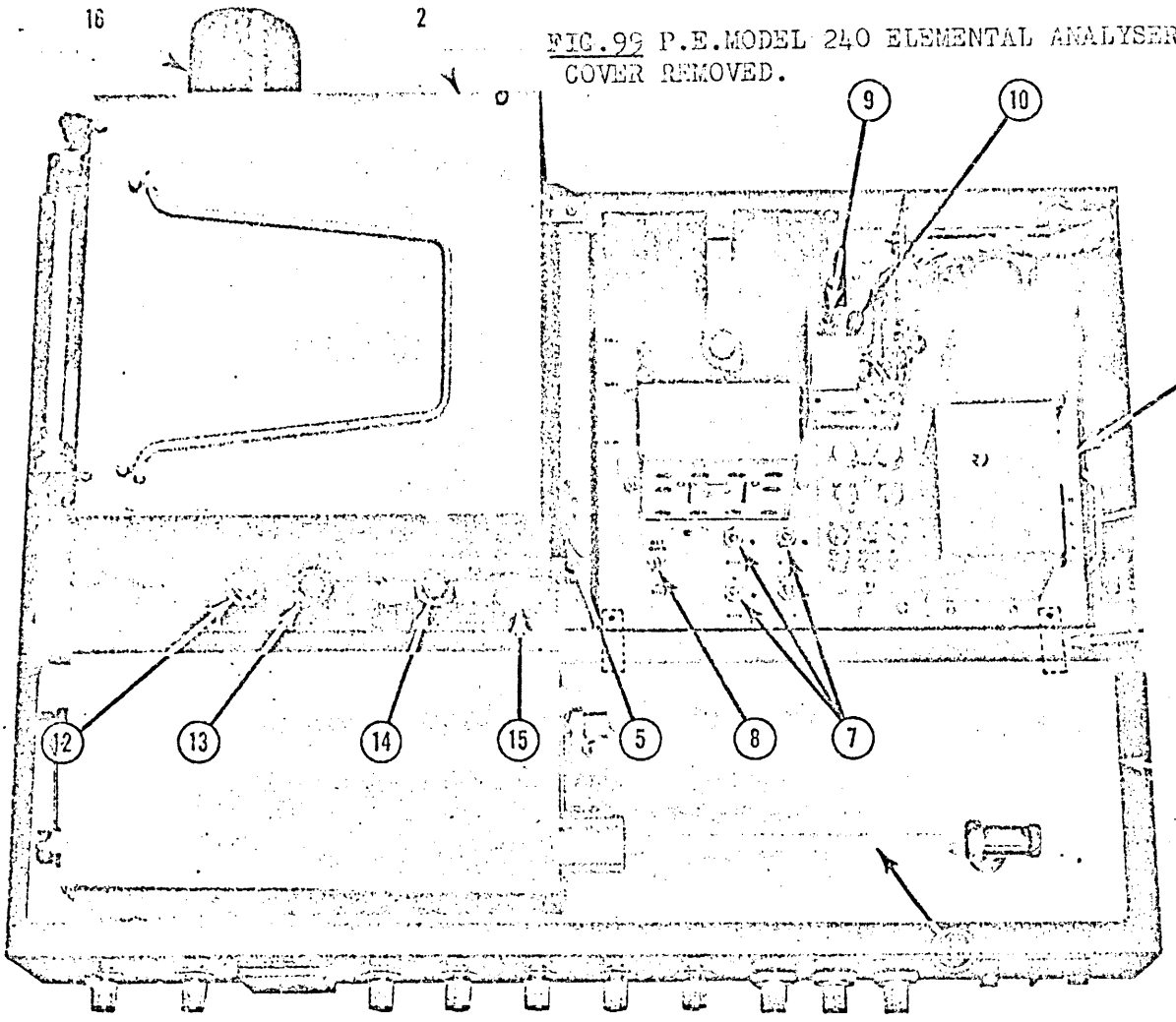
FIG. 98 SCHEMATIC DIAGRAM FOR THE BASIC COMPONENTS OF GLC. (Compiled from Stock & Rice, 1974)

3 AN EXPLANATION TO THE COMPOSITE DIAGRAM (Figs.99-101) ILLUSTRATING THE PRINCIPLES AND PROCEDURE OF THE P.E. 240 ELEMENTAL ANALYSER
(Compiled from the P.E. Manual 1972)

On placing the sample inside the sample chamber and having replaced the plug, the programme can be started. Helium flushes the system at a high flow rate for 90 seconds and then the combustion train is flushed with oxygen for 30 seconds. The system is ready for sample injection after about 135 seconds and the programme will not continue until the sample has been drawn into the combustion chamber and the programmer advised. 20 seconds after combustion has been initiated valve D closes and 30 seconds later, valve F closes (Fig.101). Combustion then occurs under static conditions in an excess of oxygen at c.940°C. Near the end of a 120 second combustion period, a high-speed high-heat furnace vaporises any condensates near the mouth of the combustion furnace(which could be produced by possible diffusion from some samples). The total products are reduced respectively to CO_2, H_2O and N_2 over copper powder at c.640°C and any residual oxygen is also removed by the reduction tube. During high heat A and D valves re-open and the products are flushed into the mixing volume. The pressure switch at the outlet operates when the mixing volume attains a pressure of 1500 mm Hg and causes D to close; dictating the so-called 'fill time'. The helium flow stops and the contents of the mixing volume are held for 90 seconds to homogenise. Whilst the gases are mixing, helium flows from valve C through the sample volume and across the detectors. Signals from each of the three detectors are recorded over 20 seconds to provide zero indications. When the mixing is complete the solenoid valves F and G open to allow the contents of the mixing volume to expand through the sample volume. During this time, valve C is closed and no flow through the detectors occurs. When the contents of the sample volume are near atmospheric pressure valves G and F close and valve C opens. H_2O, CO_2 and N_2 concentrations are then measured by displacing a sample of the gas through each detector in sequence to atmosphere with pure helium (15-20 psi). The volume of sample gas in the system is large enough so that the helium flow allows measurement for 30 seconds under steady state conditions to provide the read values.

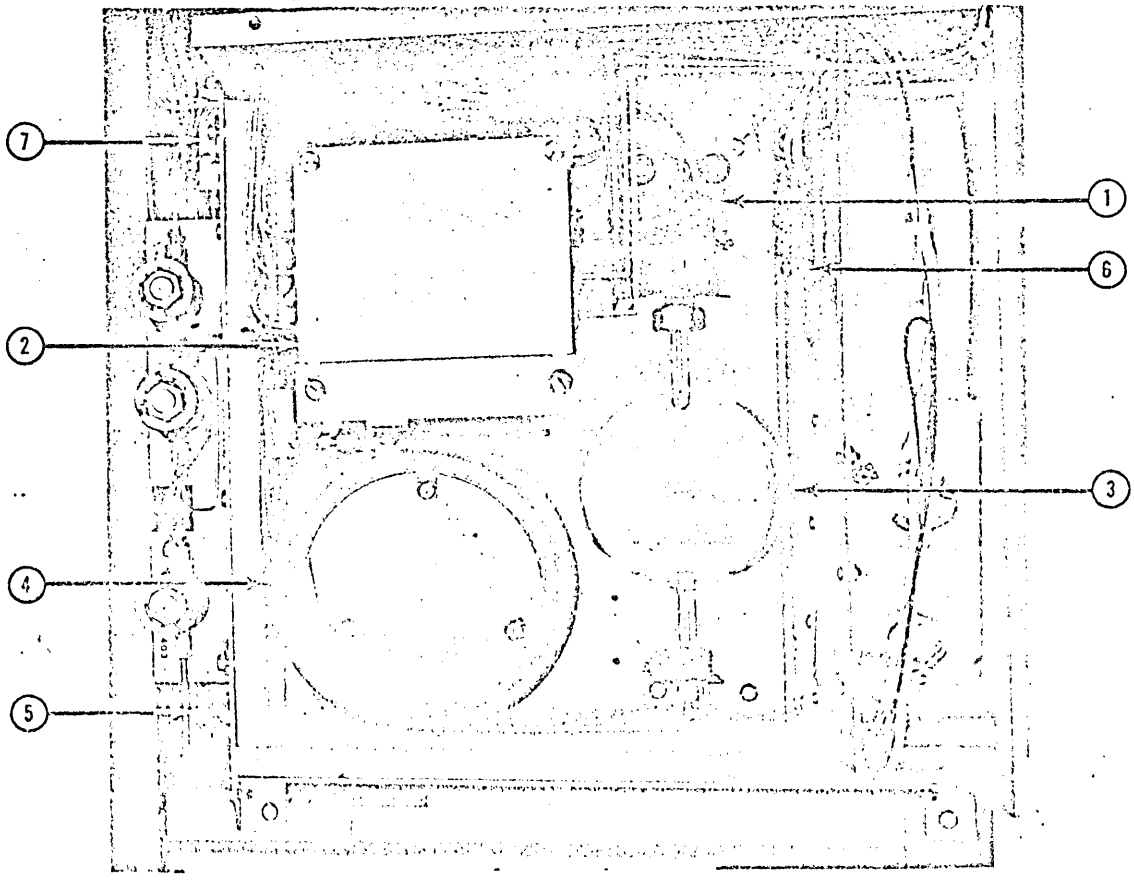
The sample gases pass through the detectors at constant rate, pressure and temperature to eliminate any variations in water vapour concentration

FIG. 99 P.E. MODEL 240 ELEMENTAL ANALYSER; COVER REMOVED.



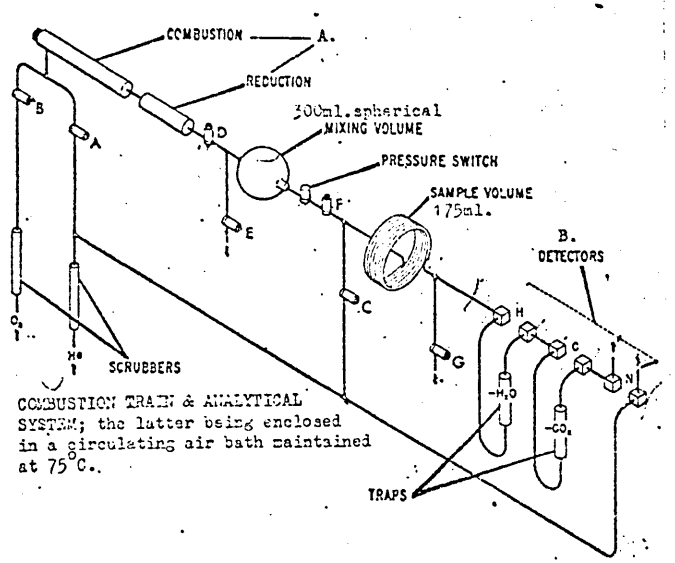
1. Combustion Train
2. Oven (Analytical System)
3. Electronics Chassis
4. Furnace Tray
5. Furnace Tray Latch
6. Locations of Metal Shipping Straps
7. Coarse Zero Controls
8. DET. OVEN Control
9. RESET Button
10. Safety Circuit Pilot Lamp
11. H,C,N Detector Output Jacks
12. Valve F
13. Valve C
14. Valve G
15. G Vent
16. Fan Motor

FIG. 100 P.E. MODEL 240 ELEMENTAL ANALYSER; ANALYTICAL SYSTEM.



1. Pressure Switch
2. Detector Assembly
3. Mixing Volume
4. Sample Volume
5. Heated Tube Assembly
6. TB401
7. Four-way Tee

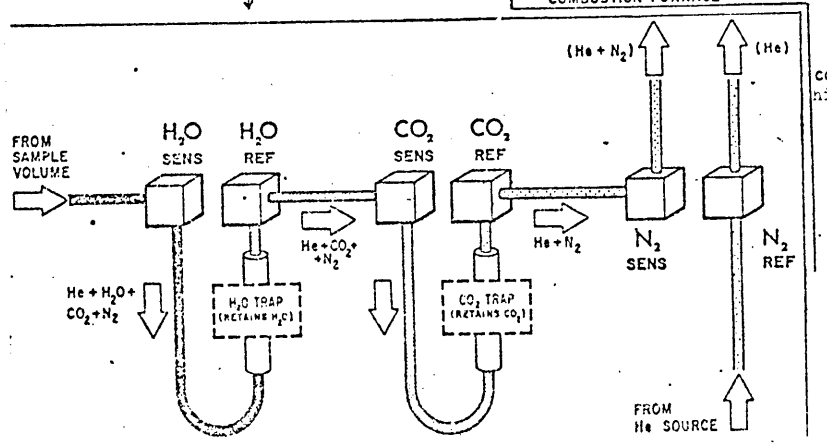
FIG.101. Composite diagram to illustrate THE PRINCIPLES & PROCEDURE OF THE P.E. MODEL 240 ELEMENTAL ANALYSER.

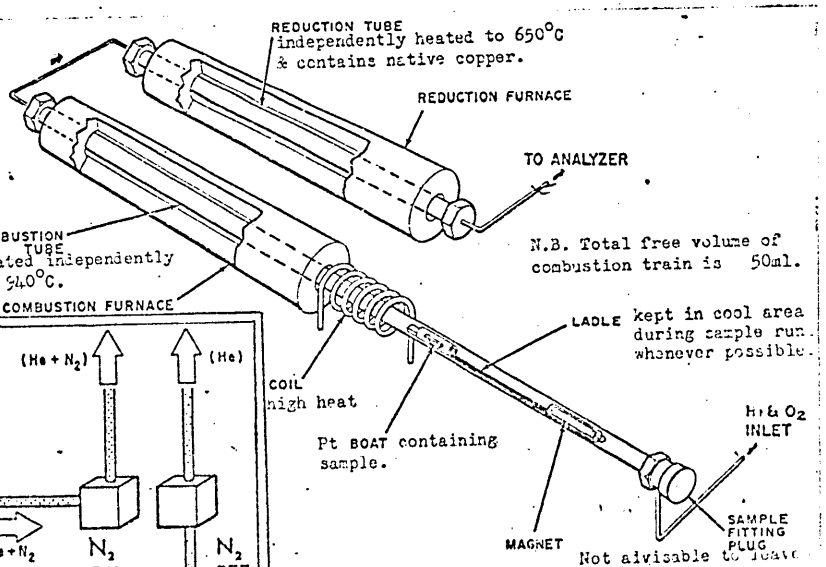


COMBUSTION TRAIN & ANALYTICAL SYSTEM; the latter being enclosed in a circulating air bath maintained at 75°C..

FIG.101 A: Combustion & Reduction Assembly→

B: Detectors; the entire system being surrounded by insulation within a large mass aluminium cavity inside an oven.





due to changes in adsorption of water on the walls of the pneumatic system.

High concentrations of air or oxygen will damage the platinum filaments if they are conducting power and thus a detector safety circuit operates to cut the power supply when the air concentration in the helium for the nitrogen sensing detector is 10% or greater (450+ mV). The filaments of each cell pair are in fact connected differentially in a bridge circuit so that any difference in the contents of the two cells will register an electrical signal.

Standard: ACETANILIDE. $C_6H_6NH.CO.CH_3$ MW= 135.17 Standard weight (measured): 2,569 micrograms.*	NITROGEN.	CARBON.	HYDROGEN.
Unweighed standard,microvolts:	——	——	——
(4th) Blank,microvolts:	15	60	94
(Recommended maximum blank values,microvolts:	100	100	200)
(Theoretical percentage by weight in standard:	10.36	71.09	6.71)
Theoretical weight in standard*micrograms:	266.15	1826.30	172.38
Zero read for standard,microvolts:	170	1130	140
Read values for standard,microvolts:	2184	37730	11776
Total values for standard,microvolts*: *Read-Zero-Blank.	1999	36540	11542
Sensitivity, microvolts/microgram:	7.51	20.01	66.96
(Recommended sensitivity range,Mv/Mg:	6.97-7.57	19.96-20.16	64.26-71.42)
KC110 SOLUBLE ORGANIC EXTRACT. Sample weight (measured): 3,851 micrograms			
Sensitivity,microvolts/micrograms:	7.51	20.01	66.96
(4th) Blank,microvolts:	15	60	94
Zero read for sample,microvolts:	167	1160	120
Read values for sample,microvolts:	441	51150	24512
Total values for sample,microvolts:* *Read-Zero-Blank	259	49930	24298
Weight in sample,micrograms: * *Total signal/Sensitivity.	34.49	2495.25	362.88
Percentage by weight in sample:	0.90	64.79	9.42

TABLE 70. P.E.ELEMENTAL ANALYSER MODEL 240: EXAMPLES FOR STANDARDISATION AND A NITROGEN -CARBON-HYDROGEN DETERMINATION.

PLATE 44 BECKMAN-R11C MICROBALANCE.



4 OIL WELLS LOCATED IN SOUTHERN ENGLAND (TABLE 71)

(Figure 102 Explained)

* denotes BHs not initially for oil but which were significant in development of drilling. Details in sequential order are Date, Name, (location), Licensee/Operator, Total depth, Bottom hole lithology, (Additional details), Prospect, Results, Conclusion.

Compiled from Adcock (1957, 1963), Armstrong(1914), Boothby (1938), British Petroleum (1962), Brunstrom (1966), Buckman (1967, 1968), Cunningham-Craig (1937), Dalton (1917), Dott (1938), Edmunds (1928), Falcon & Kent (1950, 1960), Forbes-Leslie (1916), Gardener (1963), Hepple (1966), Hewitt (1898), Holmes (1959), Kent (1959), King (1955-1977), Lees (1944), Lees & Cox (1937), Lees & Taitt (1946), Mackintosh (1938), Milner (1922, 1964), OEEC (1957), Ridd (1973), Rumsby (1946), Simpson (1939), Stacey (1977), Strahan (1920), Taitt & Kent (1939), Terris & Bullerwell (1965), Von Estorff (1950-1954) and Weeks (1947-1949).

1. 1836-1840 HAWKHURST.-/-.148 ft.? Wealden Fm. (Hastings Beds).(Pearson 1903-1904 Trans. Inst. Min. Metall. v26 p494 ?); gas issued from cavity in Hastings Beds after passing through heavy sand and oily flaky clay; two men killed by 20 ft. flame upon ignition; well burnt itself out. Filled in.

2 1874-1875 MOUNTFIELD*.(Lime Wood). Br. Ass. Adv. Sci/-.1906 ft. Up. Jurassic.(1st Subwealden Explr. Comm. BH). Surface anticline with Purbeck core nr. centre of Weald Anticlinorium. Log in Edmunds (1928); 2 ft. hard light coloured bed v. rich in petroleum in K. Clay at 602 ft; gypsum discovered smelling of petroleum. Abd; with no hope of coal at economic depth.

3 1875 NETHERFIELD.($7\frac{1}{2}$ miles E. of Heathfield). Br. Ass. Adv. Sci/Le Grand and Sutcliffe.-.-.-.See Willett (13th Quart. Rep. Subwealden Explr. Comm.); 'strange oscillations' in water level attributed to gas discharge from 'petroleum bearing strata beneath'; petroleum indications all through K. Clay; little gas caused explosion.-.

4 1884 CUCKFIELD.(Workhouse). -/Easton and Co. 450 ft. Wealden Fm (Ashdown Sands). -.Log in Edmunds (1928); 'A lot of gas bubbled up and a lot of gas met with at $195\frac{1}{2}$ ft. and 223 ft. in the Wadhurst Clay.—.

5 1893 HEATHFIELD (HOTEL) No 1*. Hotelier ?/ditto ? 249 ft. Wealden

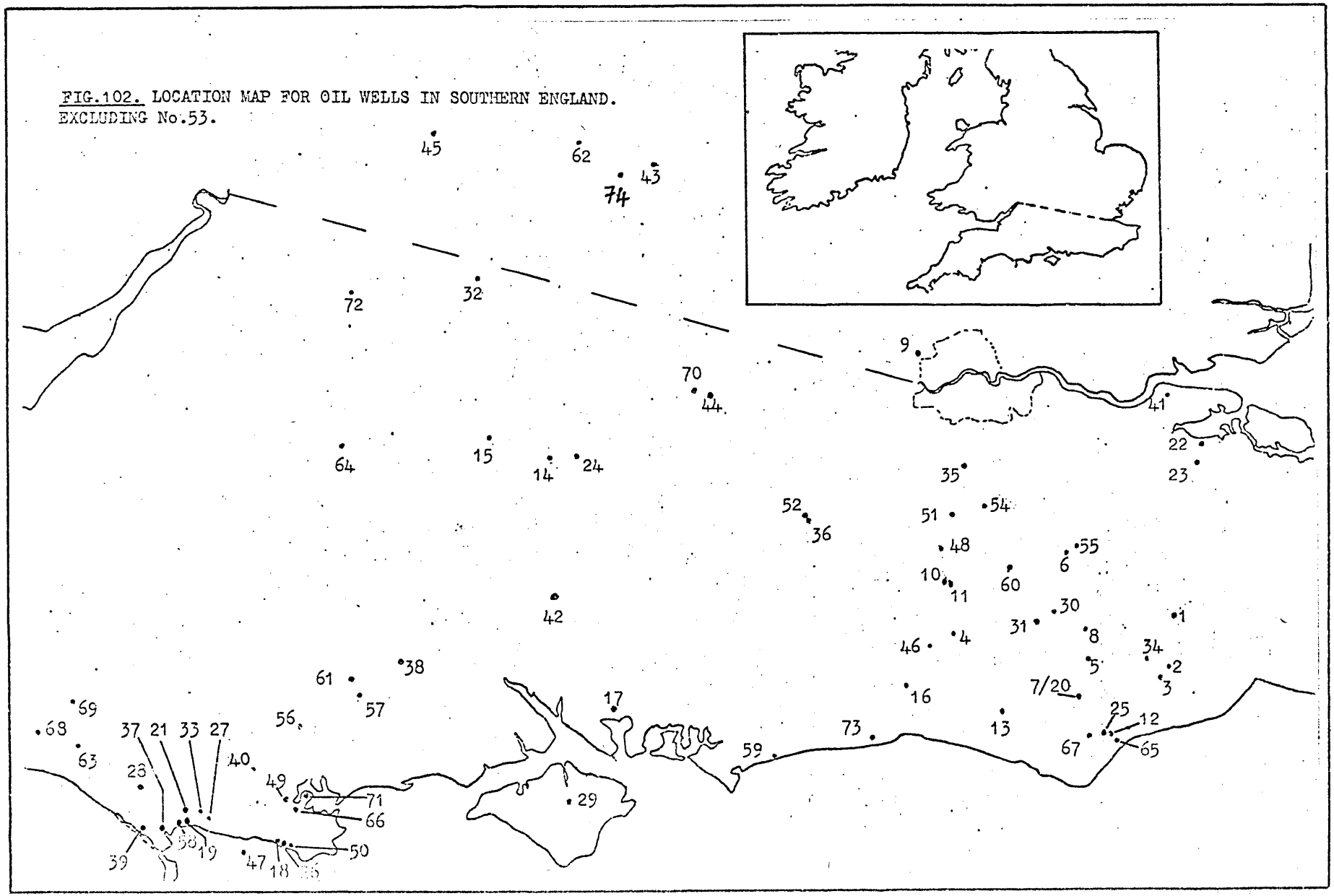


FIG.102. LOCATION MAP FOR OIL WELLS IN SOUTHERN ENGLAND. EXCLUDING No.53.

Fm. (Fairlight Clay). Surface anticline. Log in Edmunds (1928); inflammable gas first noticed at 228 ft; 6 ft. flame after ignition on noticing drilling fluid. 'boil'; 91.9% CH_4, 0.9% N_2/inert gases, 7.2% H_2 (Hewitt 1897) or 18% O_2, 5.5% higher HCs, 4.0% CO_2, 72.5% CH_4, tr. C_2H_6 (Woodhead 1898) or 1% CO, 93.16% CH_4, 2.94% C_2H_6, 2.9% N_2/inert gases (Dixon & Bone, Roy. Comm. 1902; Strahan 1920) ? ! 'Deep' artesian filled in and top cemented.

5 1896 HEATHFIELD. (Railway Station-Tunnel) No 2. London, Brighton and Southcoast Railway Co./Le Grand and Sutcliffe, 377 ft, Purbeck Fm. Surface anticline. Log in Edmunds (1928); pronounced rush of gas at 312 ft from sandy blue marl of ? Fairlight Clay; flame height dwindled from 16 ft to 3/4 ft (1922) through 6" BH (134-200 psi); 'Standard' newspaper challenge for utilisation (May 1898) lead to station lighting and heating, cooking and lighting for 80 cottages. BH sealed in 1963 with branch line closure; gasometer dismantled; cumulative production est. 20M. cu. ft. (Adcock 1963).

6 1897-1899 PENSHURST. -/-. c.2000 ft. Up. Jurassic. "The shales associated with the gypsum were often bitumenous and all the beds smelt strongly of petroleum" (Lamplugh and Kitchen 1911). —.

7 1898/1922 HELLINGLY. No. 1*. (50 yds. W. East Sussex Mental Hospital Office). -/-, 425 ft. Wealden Fm. (Ashdown Sand). (Nunn, 1898, sunk shaft to 183 ft; BH deepened to 211 ft. in 1902 and in 1921 enlarged to 7 ft. dia. with brick lining). -. Log in Edmunds (1928); soft water gave out a very strong smell of gas. BH plugged off from well on 30.11.22 which supplied 13,200 galls/day.

8 c.1902 MAYFIELD. (Station) No 1. Nat. Gas Fields of England Ltd/ ditto ? -.-.-.6 ft flame through $\frac{1}{4}$" choke via 6" BH with 200 ft water, ? 140 psi. -.

8 c.1902 MAYFIELD. No 2. Gas Fields of England Ltd/ditto ? -.-.-. Gas bearing strata penetrated but hole full of water and gas not ignited; ? c. 200 psi. from deeper 400 ft. source; ? 'gypsum saturated with petroleum". -.

5 c.1902 HEATHFIELD. (Station- Britannia Mill) 3 & 4; 5; (East side of Waldron Gill) 6. Nat. Gas Fields of England Ltd/ditto ? -.-. Surface Anticline. Gas in all but one of ? six holes; gas from ? three est. at 15M. cu. ft/day ('Times', Sept "output of deepest boring is something like 15M cu. ft/day" ?). -.

9 1912 (?/1-6/9 ?) WILLESDEN. No. 1*. White Heather Laundry Co/-.-.? Up.

Dev. (Artesian BH). -.Gas and oil in large quantities of salt water below Gault and between 1400-1800 ft. —.

7 1923 HELLINGLY*.No.2 & 3 (Park Farm; 1⅛ miles from Church). -/-.170 ft. Wealden Fm.(Tunbridge Wells Sand), in either case. (Artesian wells). -. Water flowed in No.3; Logs in Edmunds (1928). -.

10 1931 THREE BRIDGES. NMD Syndicate Ltd/ditto ? 2,000 ft.-.-.-.-.

11 c.1932 ? WORTH (FOREST). NMD Syndicate/ditto ? -.-.-.Oil show. Norman M.Dudgeon converted own company to public company; well followed by share issue to raise capital for deeper drilling in 1935.—.

11 1935.WORTH No.2. Kent and Sussex Oilfields Ltd/-. 1886 ft.—. Surface Anticline. Oil trace reported. Permission for 3rd hole on same prospect granted.

12 1936.(14/1-30/1).PEVENSEY No 4A. D'Arcy Explr. Co/ditto ? 218½ ft. Wealden Fm.(Wadhurst Clay). -.-.-.

12 1936 (2/2-3/2). PEVENSEY No 2A. D'Arcy Explr. Co/ditto ? 307 ft. Wealden Fm (Wadhurst Clay).-.-.-.

12 1936.(24/2-5/3).PEVENSEY No 1A. D'Arcy Explr. Co/ditto ? 210 ft. Wealden Fm.(Ashdown Sand). -.Sl.oil stain at 195 ft.in top of Ashdown Sands. —.

12 1936.(10/3-27/3).PEVENSEY No 8A. D'Arcy Explr. Co/ditto ? 222 ft. Wealden Fm.(Wadhurst Clay).-.-.-.

13 1936.(1/4-3/4).LEWES No 1. D'Arcy Explr. Co/ditto ? 76 ft. Gault. -.-.-.-.

13 1936.(6/4-9/4).LEWES No 2. (Swanborough Farm). D'Arcy Explr. Co/ditto ? 101 ft. Lower Chalk. -.-.-.

14 1936.(16/4-15/5). KINGSCLIFFE. D'Arcy Explr. Co/ditto ? 528 ft. Wealden Fm.(Weald Clay). -.-.-.

15 1936.(3/6-4/7) HAM. D'Arcy Explr. Co/ditto ? 528 ft. (Stratigraphic hole). -.-.-.

16 1936-1937. (20/3-15/3). HENFIELD/PYECOMBE. D'Arcy Explr. Co/ditto ? 5,105 ft. ? Up. Carb. Lst. (Lower Carb. Lst, Pringle & Stubblefield in Lees & Cox 1937).* Elongated closed dome on south flank of Weald with Weald Clay core. Log in Falcon and Kent (1960); Hastings Beds have sl. alkaline brine; oil shows in Lower Purbeck, K. Clay, Corallian and Kellaways; gas in upper Gt. Oolite Series (78.8% CH_4, 19.3% N_2, 6.9% H_2). All potential reservoirs absent as v.f.g. silty sands and non-porous lsts.hit; move to north for more littoral facies and improved ϕ and K ? *Basal beds are Rhaeto-Liassic; Amendment by Kent, 1965 in "Deep Boreholes at Portsdown (Hants) and Henfield (Sussex)", Taitt, A.H. & Kent,P.E.,1958. B.P.Co.Ltd.London.

17 1936-1937. (30/3-15/2). PORTSDOWN No 1. (1°5' 32" W; 50°51' 15" N). Chalk Pit, Paulsgrove. D'Arcy Explr. Co/ditto ?. 6656 ft. Triassic Fm. (Keuper Marl). (First well to be spudded in after Pet. Prod. Act 1934; Bottom-hole temp. 169°F). Surface Anticline; 20 miles long. Log in Falcon and Kent (1960); basal Purbeck, Corallian & Kellaways had small heavy oil shows in fractures; Ox. Clay and K. Clay had notable bitumen content; Inferior oolite gave significant water prod. despite low Ø. All reservoir facies poor; only v.f.g. silty sands and non-porous lsts. hit.

18 1936-1937. (3/12-22/8). BROADBENCH. D'Arcy Explr. Co/ditto ? 943 ft. Corallian Fm. (Os. Oolite Series). (Stopped only because drill stem broke and wedged in hole). Surface Anticline. Minor oil show in Corallian at 825 ft. Abd.

19 1937. (1/3-1/4). RINGSTEAD D'Arcy Explr. Co/ditto ? 161 ft. Corallian Fm. (Nothe Grit). -.-.-.

20 1937. (18/5-17/9). GROVE HILL (0° 10' 33" E; 50° 50' 11" N). Anglo American Oil Co. 2506 ft. ? Up. Carb. Narrow but well defined closed structure for surface anticline with Wadhurst Clay core. 102 cores taken; oil traces within top 200 ft of hole in ¼" sand bands of low Ø (Ashdown Sands & Fairlight Clay). -.

21 1937. (25/5-29/7). POXWELL/MOIGNES. (20° 22' 38" W; 50° 39' 7" N) + I, II, III, (40 ft, 62 ft, 432 ft. shallow holes 3/2-10/3). D'Arcy Explr. Co/ditto ? 1666 ft. Gt Oolite Fm. (Fuller's Earth). (Sunk in consequence of Corallian oil sand discovery). Surface Anticline with K. Clay core; elongated dome (Strahan 1898) cut by saddle from larger Sutton Poyntz anticline to west. Corallian produced salt water; see Taitt and Kent (1939) and Ridd (1973). -.

22 1937. (?/9-?). RAINHAM. Gulf Explr. Co/-. 130 ft. Chalk. -. Lost circulation in cavitous chalk. Abd.

23 1937. (?/9-?/10). BREDHURST I, II, III, IV. Gulf Explr. Co/-. 130, 135, 170 and 410 ft. -. -. Lost circulation in cavitous chalk. Abd.

24 1937-1938. (29/5-17/1). KINGSCLERE. (1° 7' 5" W; 51° 19' 12" N). D'Arcy Explr. Co/ditto ?. 5125 ft. Triassic Fm. (Keuper Marl). Prominent brachyanticline with Up. Greensand core. Log in Lees and Taitt (1946) and Falcon and Kent (1960); faint oil shows in Purbeck (1027-1566 ft); bit. shales in K. Clay, Ox. Clay and Lower Lias. -.

25 1938. (18/1-15/3). HANKLAM. (0° 18' 32" E; 50° 49' 28.5" N). D'Arcy Explr. Co/ditto ? 842 ft. K. Clay. -. Sl. oil stains at top of

Ashdown Sands and in Purbeck anhydrite. -.

6 1938.(26/5-17/9).PENSHURST.(0° 12' 20" E; 51° 10' 36.5" N). Gulf Explr. Co/ditto ? 5600 ft. Low Carb Lst. - . Cavings occurred at 5600 ft.when drill stem stationary for tests and drill pipe twisted off at 2672 ft. Hole abd. few weeks later as dry.

26 1938.KIMMERIDGE No 1(A). D'Arcy Explr. Co/ditto ? 920-943 ft. -. Surface anticline. M.C. Seamark's shallow drilling rig failed through sheer overloading (max. ideal depth 250-300 ft); one good sst oil show; suspended because of war. Abd. because hole resided within artillery range danger zone after war.

27 1938-1939,(6/4-28/3) and 1945 . CHALDON DOWN G1.(2° 16' 28" W; 50° 38' 12" N). D'Arcy Explr. Co/ditto ? -. - . (drilled to 178 ft before suspension because of war). Pitching end of Osmington-Ringstead Anticline. -. -. (See Ridd 1973).

27 1938-1939,(23/9-12/6) and 1946,(?/1-19/2). CHALDON DOWN G2.(2° 14' 13" W; 50° 37' 50.3" N). D'Arcy Explr. Co/ditto ? 1793 ft. K. Clay. (Rotary drilling to test Wealden abd. at 142 ft.due to lost circulation in fissured chalk; Duke & Ockendon Ltd.deepened hole by 962 ft before suspension because of war). -. - .(See Ridd 1973).

17 1948.(18/2-26/3).PORTSDOWN No 2.(1° 5' 29" W; 50° 51' 42.6" N). D'Arcy Explr. Co/ditto ? 2871 ft.—.Surface anticline. Despite seismics and excavations, No 2 actually structurally lower than No 1; Portland smelt (positive chlorofrom test) and Purbeck, Wealden and Low. Greensand all gave water. -.

9 1947-1948.(6/11-19/1). WILLESDEN No. 2. D'Arcy Explr. Co/ditto ? 2680 ft. Up. Dev. Lst and Shales. - . Up. Dev. Red Beds below Gault gave small gas shows; no oil found; Log in Falcon and Kent (1960). —.

28 1948 . COMPTON VALENCE. D'Arcy Explr. Co/ditto ? 164-174 ft. Inferior Oolite Fm. Surface dome; indicative of salt intrusion at depth (Terris & Bullerwell 1965). Fixed age of clays in core as Fuller's Earth not Ox. Clay and proved uplift as Cretaceous sits on K. Clay or Oxfordian in surrounding areas. (See also Falcon & Kent 1950).

29 1952-1953.(18/10-19/4). ARRETON No. 1 (1° 14' 55.2" W; 50° 40' 29" N). D'Arcy Explr. Co/ditto ? 5161 ft. Inferior Oolite Fm. Local gravity high coincident with inland culmination of Brightstone-Sandown seismic anticline; closure 300 ft. Log in Falcon and Kent (1960); no shows. Abd.

30 1954 . CROWBOROUGH WARREN No.1. BP Dev. Ltd-Gas Council/-. 4583 ft. -. -. Small non-commercial shows at several levels. -.

31 1954-1955,(3/6-21/1). ASHDOWN No.1.(0° 8' 28.5" W; 51° 3' 8" N) + I, II, III, IV (1954). D'Arcy Explr. Co/ditto ? 4990 ft. Inferior Oolite Fm. Closed pear shape dome pitching to east and exceptionally large (c.20 miles long and 4½ miles wide). Log in Falcon and Kent (1960); small gas shows in Portland and Corallian (2958 ft:20,000 cu. ft/day 1075 static psi; 92.2% CH_4, 7.6% N_2 0.2% C_2H_6 + heavier HCs); oil shows in Corallian (3721 ft) and Kellaways.

32 1954-1955.(18/11-31/1). FARRINGDON (1° 32' 1.9" W; 51° 38' 36.1" N). D'Arcy Explr. Co/ditto ? 2481 ft. Uncertain Red Beds; Dev ? -. Log in Falcon and Kent (1960). —.

33 1955.(19/1-29/3). CHALDON HERRING No 1.(2° 18' 20.4"W,50° 39' 13.3" N) + G1, G2, G3 (1954; 718, 718, 2444 ? ft). D'Arcy Explr. Co/ditto ? 1885 ft. -. Surface anticline; superficially simple but of Poxwell-type culmination; Weald Clay core. -.-.(See Ridd 1973).

30 1955.(10/7-?). CROWBOROUGH WARREN No 2.(1 mile SE of No 1). BP Dev. Ltd-Gas Council/-. 5600 ft. -. -. Non-commercial gas bearing strata penetrated. -.

31 1955.(11/7-10/11). ASHDOWN No 2.(0° 19' 18" W; 51° 2' 31.4" N). D'Arcy Explr. Co/ditto ? 5709 ft. Carb. or Dev. Red Beds dipping up to 6°. Structural high located by seismics for surface anticline and faulted dome suspected. Oil shows in sandy Lower Lias (Brunstrom 1966); formation tests gave salt water; Log in Falcon and Kent (1960). -.

34 1955.(29/8-5/11). BRIGHTLING (0° 22' 56.6" W; 50° 58' 15.8" N). D'Arcy Explr. Co/ditto? 2587 ft. Mod. dipping ? Low. Dev. Surface anticline; highest culmination in Weald where surface expression of reverse fault believed to be north margin of inlier. Gas and water in Purbeck; little oil and gas in Kellaways; Log in Falcon and Kent (1960) and cross-section in Terris and Bullerwell (1965). -.

5 1955.HEATHFIELD No 7 (?). BP Dev. Ltd-Gas Council/-. 904 ft. -. Surface anticline. Gas test on small Purbeck shows (c.660 ft) indicated max. prod. 30,000 cu. ft/day (1.6% higher HCs, 93.4% CH_4, 2.7% N_2, 2.3% C_2H_6 at 126 psi) but too many wells needed. Abd.

35 1956-1958 WARLINGHAM*. Geol.Surv/-. 4154 ft. Low Carb. Lst (Holmes 1959).-. Nat. gas and oil in Corallian below fault junction with overlying K. Clay at 2987 ft; 35,000 cu.ft/day est. —.

36 1958.(1/5-3/10). SHALFORD (0° 35' 37.5" W; 51° 12' 41" N). BP Dev.Ltd/

ditto ? 5717 ft. Silurian mudsts. dipping 40°-45° below Rhaetic. Peasemarsh surface anticline; no great amplitude; plunges west with no local closure along axis. Dry. -.

37 1958.(22/9-10/12). RADIPOLE .(2° 28' 56.8" W; 50° 37' 53.4" N). BP Dev. Ltd/ditto ? 2030 ft. Lower Lias. Surface anticline. Up. Lias ssts. showed oil trace (Brunstrom 1963). -.

38 1958.(18/10-12/12). FORDINGBRIDGE.(1° 43' 59.6" W; 50° 54' 17.7" N) BP Dev. Ltd/ditto ? 4487 ft. Triassic Fm.(Keuper Marl). Surface anticline with seismic expression over gravity anomaly. Dry. —.

39 1959.(12/1-16/2). LANGTON HERRING SOUTH. (2° 33' 24.1" W; 50° 37' 59.6" N). BP Dev. Ltd/ditto ? 2030 ft. Low Lias. Surface Anticline. -. -.

26 1959.(12/2-1/4). KIMMERIDGE NO.1(B). (2° 8' 5.1" W; 50° 36' 44.9" N) BP Dev. Ltd/ditto ? 1791-1816 ft. Base of Mid. Jurassic. Surface anticline; no westerly closure seen. First commercial Mesozoic oil discovery (in March) when second test showed 44° API gravity oil flowing at 40 ton/day (c. 200 bbls/day) through ½" choke on Oct. 19th; fully saturated with gas and coming from fracture system of impervious Cornbrash dbggery calc. 1st.at 1700 ft. Similar to Paris Basin fields found about same time,eg. Coulommes. Reservoir pressure subnormal. Closed in as producer. (See Brunstrom 1963); cumulative prod. 1959-1972 is in the order of 180,000 tons. 1976 production was 147,476 bbls.

39 1959.(3/4-28/4). LANGTON HERRING NORTH.(2° 31' 58.8" N; 50° 38" 36.5" N) BP Dev. Ltd/ditto ? 1305 ft. - . Surface anticline. Dry. -.

40 1959.(8/5-17/9). BERE REGIS. (2° 11' 32.9" W; 50° 45' 34.3" N). BP Dev. Ltd/ditto ? 5533 ft. Triassic Fm. Surface anticline with seismic expression over gravity anomaly. Dry.

41 1959.(7/7-20/8). CLIFFE-AT-HOO. (0° 28' 54.9" E; 51° 27' 32.7" N). BP Dev. Ltd/ditto ? -. -. -. -. -.

1b 1959. BROADBENCH. BP Dev. Ltd/ditto ? -. -. Surface anticline. Oil show in 1st at c. 1800 ft. -.

42 1959-1960.(17/10-10/3). WINCHESTER.(SU.503285). BP Dev. Ltd/ditto ? 4084 ft.? Top of Low Lias. Surface anticline. -. -.

26 1959-1960. KIMMERIDGE No 2.(c. 2500 ft.W of No.1). BP Dev. Ltd/ ditto ? -.-. Surface anticline a/a. Proved oil in fissured Kellaways and Oxford Clay to 130 ft above Cornbrash fissure system. Observation well.

2b 1959-1960. KIMMERIDGE No 3. BP Dev. Ltd/ditto ? 3424 ft. Up. Lias.

Bridport Sands. Surface anticline a/a. No oil below Cornbrash

1960 · KIMMERIDGE No 4. BP Dev. Ltd/ditto ? 900 ft. -. Surface anticline a/a. Dry; structural well only.

43 1960.(5/4-24/4).MARSH GIBBON.(1° 3' 27' W; 51° 54' 28.7" N) BP Dev. Ltd/ditto ? -.-.-.-.-.

44 1960.(30/4-21/5).1WYFORD.(1° 0' 38.3" W; 51° 53' 30.1" N). BP Dev. Ltd/ditto ? -.-.-.-.-.

45 1961.(25/8-11/9). STOW-ON-THE-WOLD. (1° 43' 13.1" W; 51° 54' 25.1" N) BP Dev. Ltd/ditto ? -.-.-.-.-.

46 1963.(28/5-2/9). BOLNEY.(TQ.2801-124269) Esso Pet. Co. Ltd/Kellogs Overseas Corp. 8006 ft. Frac. and steeply dipping Palaeozoics. (National 1000 rig previously in Greece; largest used to date for onshore oil search). - .Gas show at 400 ft. -.

47 1963.(?/9-?) . LULWORTH BANKS (2½ miles offshore to Lulworth Cove, 6½ miles east of Weymouth). BP Dev. Ltd/- . 2500 ft (water depth 60 ft). Bridport Sands.(First UK offshore well, c£75,000). Asymetric large EW anticline with Corallian core. Corallian gave little gas; Bridport sands oily.

48 1964.(29/9-8/12). COLLENDEAN FARM. (TQ.2480-4429) Esso Pet. Co. Ltd/ Armscot Drilling Co. 5760 ft. -.-.-. Abd.

49 1964.(18/10-11/11).WAREHAM No.1.(SY 90915-87827). BP Dev. Ltd/ditto ? 5731 ft.Triassic Fm.(Bunter Sst). Seismic anticline masked by UC Albian and younger sediments which lie in form of almost horizontal syncline (Reflections not clear as Tertiary Sands absorb energy). Closed in as potential oil producer. (Brunstrom 1966 - no details available).

50 1965.(1/4-24/4). ENCOMBE.(SY 94123-78316). BP Dev. Ltd/ditto ? 2868 ft. - .Surface anticline. -.-.

51 1965.(24/10-16/12). BLETCHINGLEY I.(TQ 36225-47727) + II, III, IV (1966; 3683 ft, 3802 ft.& 4079 ft.for prod. gas well, outpost test well and dry hole). Esso/- .6078 ft. - .(Farm-in from BP). Seismic prospect. Mod. gas producer from Jurassic at c. 3600 ft; 30 ft.well-head flare;approx. 10M.cu . ft/day for 2 years with exhaustion after 5 years estimated if produced.

49 1965. WAREHAM.No 2. BP Dev. Ltd/ditto ? 4230 ft. - . Structure still not clear if fault occurs or not. Non-economic oil well. Abd.

52 1966.(3/1-16/-) . STRAT. I (SV. 9478, 5278) Esso Pet. Co. Ltd./-.3160 ft. - . Prospect unreported. - . Abd.

53 1966.(27/1-7/2). STRAT. II (SU.6822, 6522). Esso Pet. Co. Ltd/- . 2463 ft. - .Prospect unreported. - .Abd.

54 1966.(28/10-19/11).TATSFIELD. (TQ. 4242, 5699). Esso Pet. Co. Ltd/- . 4610 ft. - .(Farm-in from BP). Seismic anticline. Dry. -.

55 1966-1967.(13/12-5/2). LEIGH. (TQ. 2170, 4751). Esso Pet. Co. Ltd/- . 2959 ft. - .(Bit stuck and rig buckled on attempt to retrieve stem). Prospect unreported. Home Counties search given up after well completed and over £2 million spent with no commercial return. Abd.

56 1968.(4/6-26/6). SHAPWICK. (ST. 9428, 0134). BP Dev. Ltd-Gas Council/- . 1623 ft. - .Strat. well. - .Abd.

57 1968.(9/7-25/7). WOODLANDS.(SU. 06590, 06272). BP Dev. Ltd-Gas Council/- . 2194 ft.—.Strat. well. -. Abd.

58 1970.(15/10-6/11). OSMINGTON No 1. (SY. 7170.8360). Superior Oil (UK) Ltd/- . 1654 ft. -.-.-. Abd.

58 1970.(14/11-25/11). OSMINGTON No 2.(SY. 7170.8390). Superior Oil (UK) Ltd/- .7176 ft. -.-.-. Abd.

59 1971.(6/3-4/5).MIDDLETON.(SU. 9739.0157). Ulster Pet. (Canada) Ltd/- . 6982 ft. -.(Penzoil (UK)-Mesa Pet. on farm-in from Ulster ?) -.Dry. Abd.

60 1971.(21/9-19/10). COWDEN. (TG. 4661.4278). BP Dev. Ltd-Gas Council-Ball & Collins (Oil & Gas) Ltd/- . 6037 ft. -.- .Dry. Abd.

61 1972.(6/3-19/4). CRANBORNE.(SU. 0355.0895). BP Dev. Ltd/-. 6996 ft. -.-.Dry. Abd.

62 1972.(27/3-12/4). STEEPLE ASTON.(SP. 4687.2572). Consolidated Oil & Gas (UK) Ltd-Teck Resources (UK) Ltd/-. 3345 ft. -.-.Dry. Abd.

63 1972.(4/7-29/9). NETTLECOMBE. Page Pet.-Berkley Pet/-. 7005 ft. -.-. Dry. Abd.

64 1972.(26/8-16/9). DEVIZES.(ST. 9602.5698). Ulster Pet. (Canada) Ltd/-. 3000 ft +. -.-. Dry. Abd.

65 1973.(8/6-25/6). WESTHAM.(TQ. 6097.0535). Ulster Pet. (Canada) Ltd-Cambrian Expl. Ltd/-. -.-.-.-.-.-.-.

66 1973.(2/12- ?). WYTCH FARM No 1.(SY. 9804.8536). BP Dev. Ltd-British Gas/-. -.-.-. Oil prod. from 2 Jurassic pay zones c. 500 bbls/day at c. 3000 ft. Development drilling proposed.

67 1973. POLEGATE. Ulster Petroleum/- . 6000 ft +. -. -. Dry. Abd.

68 1973-1974.(1/12-12/1). MARSHWOOD.(SY. 3885.9880). Cangeo--Western Warner (UK) Ltd/-. 500 ft. Broad Marshwood anticline; surface and seismic prospect. Dry. Abd.

59 1974.(21/1-15/2). SEABOROUGH (ST. 4348.0620). Page Petroleum-Berkley Pet/-. 6500 ft. -.-.Dry. Abd.

70 1974.(25/2-13/3). SONNING EYE.(SW. 742.758). Bralorne Explr. (UK) Ltd/-. 3000 ft. -.-. Dry. Abd.

29 1974.(13/3-5/6). ARRETON No 2.(SZ. 532.858). BP Dev. Ltd-British Gas/- 9000 ft. -.-.Dry. Abd.

66 1975.(6/1-20/2). WYTCH FARM No 2. BP Dev. Ltd-British Gas/-. 3746 ft. -.(Delineation well to No. 1 but not drilled sooner due to problems in obtaining permits for well sites). -.Oil prodn. -.

66 1975. WYTCH FARM No 3. BP Dev. Ltd-British Gas/-. -.-.-.Oil prodn. -.

71 1975.(21/11-29/12). ARNE G1.(3 km. NW to Wytch Farm). BP Dev. Ltd-British Gas/-. 3731ft. -.(suspended).-.Oil discovery. -.

72 1975-1976.(18/8- ?). COOLES FARM. Shell/-. 11525 ft? -.-.'Completing' ? -.

73 ?. TOXWELL. D'Arcy Explr. Co./ditto ? -.-.-.-.-.

74 1976 (14/6-28/6). BICESTER No. 1. (Oxfordshire). Shell-Consolidated Oil & Gas UK Ltd/-. "shallow". -. -. Dry. Abd.

5 SUMMARISED HISTORICAL EXPLOITATION OF THE DORSETSHIRE AND NORFOLKSHIRE OIL SHALES

Compiled from Arkell (1947), Cronshaw (1921), Dalton (1917), Downie (1955), Forbes-Leslie (1916), Institute of Petroleum (1971), Kent (1959), Lidgett (1920), MacDougall and Cawley (1951), Macleod-Mathews (1975), Manfield (1916), Mansel-Pleydell (1873), Oxy Today (1974), Pitt-Rivers (1966), Prien (1951) and Thompson et al (1923).

c. 2000 BC: (Neolithic times) Oil shale first prized for ornaments; beads taken as far as Wookey and beads/buttons continued to be made until c. 1400 BC.

c. 1400-400 BC: No evidence for continued working.

c. 400 BC: (Iron Age) Armlets exported to Glastonbury.

c. 150 AD: (Phoenician times) Circular discs, $1\frac{1}{4}$"-$2\frac{1}{8}$" dia. and $\frac{1}{4}$"-$\frac{3}{4}$" thick, turned with great accuracy; only found in neighbourhood of Kimmeridge and often in tombs. Sir C. Hoare noted that discs were "Neither British or Roman" but before. Discs were made for "mysteriously prized property" - "coal money". * Shale also possibly used as fuel for evaporating seawater at this time. *"throwouts from laths" ?

c. 200: (Roman times) Elaborate carvings in oil shale found at Dorchester.

(c. 1300: (Middle Ages) Oil shale first used in Europe - 'Ichthyol', dark sulphurous oil shale from Switzerland and Austria).

c. 1550: 6th Baron Jountjoy (died 1593) discovered some 'schists' yielded alum and started working them.

c. 1613: Sir W. Clavell built alum works and pier but due to objection by farmers he started producing glass using 'coal' as fuel. The slagheaps can still be found today. Also, he evaporated seawater.

1558-1603: Parliamentary statutes of Queen Elizabeth make reference to oil bearing shales.

(1684: First recorded attempt to make shale oil is English patent 330; for production of "oyle from a kind of stone" but embryo of shale industry really not until Selligne Process of 1838 initiated in France).

1826: Kimmeridge Clay ignited at Burning Cliff and burnt for several years.

1835: Bitumenous shale recorded in Norfolk by Rose.

1848: Bitumenous Shale Company erected works at Weymouth in January; shipped in oil shale and distilled it to produce 7½ gallons naphtha, 10 gallons lubricating oil, 1 cwt pitch, 11½ cwt residue (sold as fertiliser) and some white fine paraffin wax and grease (from one ton of shale).

1850: Young took out patent for low temperature distillation of coal and in 1851 he was distilling from the Alfreton seepage. Legal action taken against Bitumenous Shale Company and company wound up.

1854: Ferguson and Muschamp took over property of Bitumenous Shale Company and erected works at Wareham; directing attention to the production of manure from oil shale via low temperature distillation with addition of sulphuric acid and water to the residue. Despite a degree of success, the firm was forced to quit the property and "unknown reasons" stopped it continuing.

c. 1856: Whilst digging the foundations for a water-wheel, Manfield's father found the oil shale at Portisham Dairy, but as it was eight miles from the nearest railway, no real advantage was taken. Although a few tons were won the pit was drowned out.

1858: Wanostracht and Company, mainly comprised of Frenchman, constructed works to supply Paris with gas and several audits were dug. 1,149 tons of shale were exported to Australia, USA and France and a new pier was built.* Reasons for failure though "will be dangerous to refer to" (?) but the import of petroleum from the USA led to the company's downfall. (Downie recorded 149 and 170 tons respectively ?) * 1170 tons went out in 1859.

(1860: Scottish oil shale industry appears to have started about now).

? : Wareham Oil and Candle Company formed but works destroyed by fire.

? : Forbes-Leslie credited Selwyn with the first discovery of the Norfolk oil shales but later Lidgett (1920) attributed Forbes-Leslie with the first observation !

? : Bitumenous clay off Castleton, Isle of Portland, used to be dug for fuel. It was said to be 10" thick and lie at about 200 feet from the top of the outcrop.

1864: 2nd August; Vice Chancellor Stuart ruled that "the manufacture of offensively smelling and unmarketable oils from Kimmeridge shales could not be held to an anticipation of Young's patent".

1872: Alston company, which was formed to manufacture mineral oil, was liquidated (?).

1872: Messers Emmens' "Sanitary Carbon Company" tried to provide sanitary agents from the residual coke (left by destructive distillation of the shale) as a substitute for coal charcoal. The company competed with products from America but was unsuccesful for the lack of capital and wound up in 1875-1876 (?).
(The Sanitary Carbon Company and Emmens' Company have been recorded as separate entities with the former going into bankruptcy because of "internal dissentions" ?).

1873: The argillaceous tabular limestones were "brought into a marketable condition in the form of medina cement".

1877: A railway cutting east of Portisham station revealed the oil shale outcrop and the coal was mixed with clay and about 2000 tons burnt for ballast.

1879: De Grelle and Company formed the "Kimmeridge Oil and Carbon Company" at Sandford, near Wareham, to try to produce oil, gas, paraffin, manure, fertiliser, insecticide and a mildew preventative called 'Oidium'. However, it was not operating when Greene wrote in 1886.

1883: A shaft was sunk at Portisham but unlike the previous attempts remained dry, until the 'coal' was reached when 11,000 gallons of water per hour issued into the hole. The principal bed was 137 ft below the surface and the shaft reached a total depth of 189 ft; being

bored to a further 126 ft.

c. 1883-1884: Sir George Elliot interested himself in Manfield's discovery upon the completion of a branch line. Manfield Jnr, Butterfield and Elliot were asked to prove the extent of the shales and one hundred tons were sent to Scotland for retorting.

1890: Elliot sent a further cargo of shales to Scotland but it accidentally caught fire on the way.

1895: Bitumenous shale was recorded at Downham Market.

1903: Sir B. Redwood sent a quantity of shale from Ringwood. Kimmeridge and Portisham to Scotland for retorting in the presence of Sutton and Manfield Jnr. It was thought that the reduction of sulphur content was necessary to permit large scale working. An estimate of $1\frac{1}{2}$ million tons of oil shale reserves at Kimmeridge was given to the Royal Commission.

c. 1914: Churchill focussed the public's attention to the oil source potential with his remark ".... there is plenty of oil"....(for the Navy).

1916: Forbes-Leslie asserted tests in Norfolk revealed numerous seams of rich sulphur free shale occurred over almost the whole property owned by English Oilfields Ltd and an aggregate thickness of 150 ft of shale was expected to produce c. 2000 million tons of oil.

1917: Dalton reported that a minefield at West Wynch was connected to Setch by rail and an 11 ft thick seam about 70 feet below the surface, was the target. However escaping gas (70% volatiles with large quantities of incondensable gas; Bunet) stopped work in the shafts.

1917-1918: The extent and evaluation of the Kimmeridge oil shales were reassessed by the Ministry of Munitions (Dept. Dev. Min. Resources) and boreholes were sunk at Kimmeridge, Portisham and Donnington (Lincolnshire). W. T. Anderson summarised the results (Table 49).

1919-1920: English Oilfields Ltd was flourishing with the Setchy Shaft in Norfolk but by about 1925 the company conceded failure due to "the limited quantity of shale, the

thinness of the bed, the quantity of overburden all coupled with the low yield of oil per ton of shale" .... and the fact that the beds were "confused".

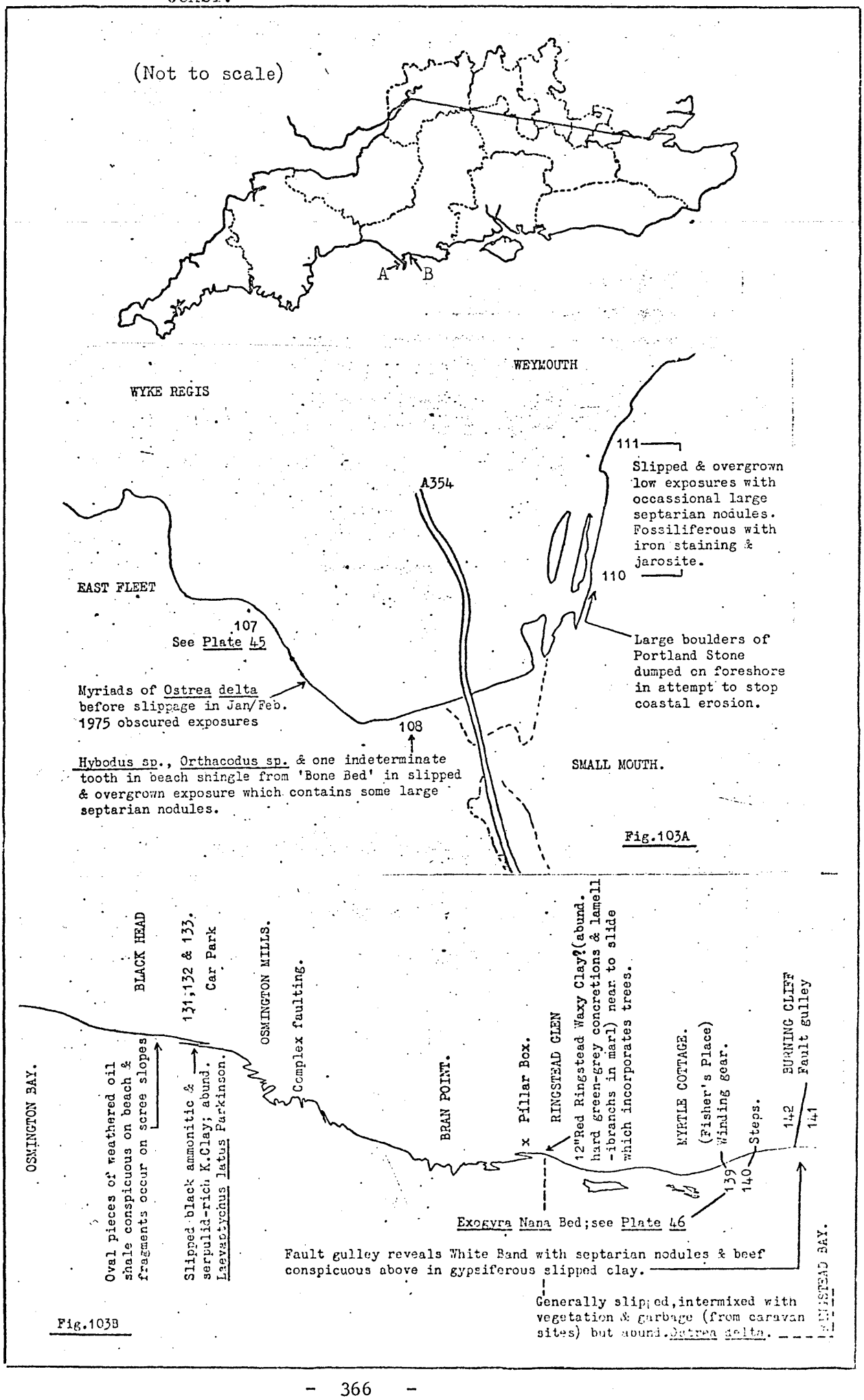
1923: Thompson et al declared that the free liquid crude was not in commercial quantities and no favourable structures exist in Norfolk anyway.

1947: The landowner of Snedmore was still receiving an annual royalty from a company for the mineral rights.

1952: A successor to English Oilfields Ltd was still operating with "ichthyol" production.

(1962/1965 (?): Scottish Oils Ltd (eventually a subsidiary of BP) finally closed down; its peak production being just prior to the War when 3½ million tons of shale yielded 265,000 tons of oil. The operations were no longer profitable).

(6) FIG.103. LOCATION MAP FOR KIMMERIDGE CLAY SAMPLES ELSEWHERE ALONG THE COAST.



6. LOCATION, DESCRIPTION & EXPERIMENTAL DATA FOR THE KIMMERIDGE CLAY FROM ELSEWHERE ALONG THE DORSETSHIRE COASTLINE.

6

SAMPLE & LOCATION NUMBERS	EXAMINED HAND SPECIMEN.	FIELD DESCRIPTION OF PARENT HORIZON.
KC 117. 107.(A).	Lt.blue-grey/pale brown limonitic claystone with white shell debris; some lamellibranch fragments.	See explanation to Plate 45. & Fig.37
KC 118. 108.(A).	Pale grey claystone with abundant ammonite & lamell. fragments.	As annotated in Fig.103; see Fig.37
KC 119. 110.(A).	Dk.grey limonitic claystone with ammonite & lamell. frags. Some jarosite.	As annotated in Fig.103; see Fig.37
KC 120. 111.(A).	Dk.grey claystone with abund. white shell frags; some large oyster frags. & Pecten sps.	As annotated in Fig.103; see Fig.37
KC 121. 131.(B)	Dk.grey claystone with abund. white shell frags; some pyritised. Abund. lamells & one ammonite impression. Some Serpulae	As annotated in Fig.103; see Fig.37
KC 122. 132.(B).	Md.grey sl.limonitic claystone with abundant lamell.frags & one ammonite impression.	As annotated in Fig.103; see Fig.37.
KC 123. 139.(B).	Lt.grey very shelly hard lime stone. Abundant Exogyra nana, some Pecten sps., possible bitumenous stains on shells & black vertebrate frags.	See explanation to Plate 46; see Fig.37
KC 124. 140.(B).	Md.grey claystone with abund. lamell.frags.	As annotated in Fig.103; see Fig.37
KC 125. 141.(B).	Md.grey claystone with lamell. & ammonite frags.	East side of fault; gypsiferous shaly clay with ammonites & c.8 feet above KC 126. Followed by clay with septarian nodules. See Fig.37
KC 126. 141.(B).	White/cream chalky limestone One lamell.impression & bitumenous staining on indeterminate shell fragment.	See Fig.37 Like KC 125, peeps through vegetated fossiliferous talus which incorporates in particular derived Portland material. c.32" thick.
KC 127. 142.(B).	White/cream chalky limestone with very fine parallel or undulating dk.brown-black laminae.	Displaced & fallen boulders in colonised clay slide
KC 128.Bran.Pt.(B).	Smooth rounded hard coherent dk.brown finely laminated 'oil shale' pebble with black plant frags on bedding planes. Fissile	Longshore drift from Black Head (?)

TABLE 72. DESCRIPTION OF KIMMERIDGE CLAY SAMPLES OUTSIDE HORBARROW BAY - CHAPMAN'S POOL.

PLATE 45 RINGSTEAD CORAL BED, EAST FLEET, WEYMOUTH.

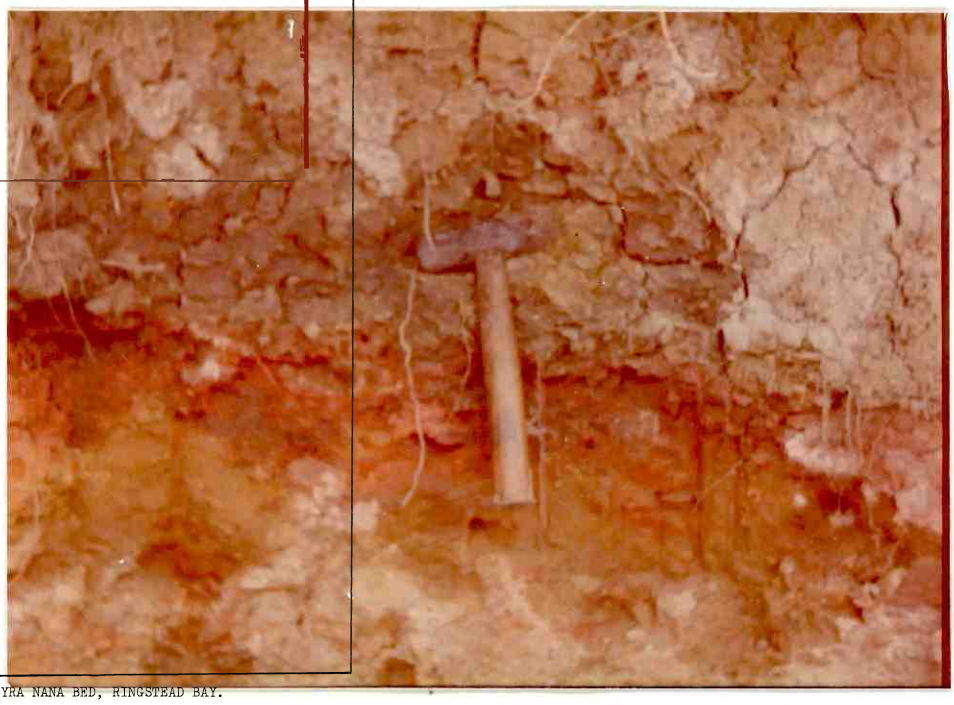


PLATE 46 EXOGYRA NANA BED, RINGSTEAD BAY.



TABLE 73.

EXPERIMENTAL DATA FOR KIMMERIDGE CLAY SAMPLES OUTSIDE HORBARROW BAY - CHAPMAN'S POOL.

B: Brown. BL: Blue. G: Grey.
C: Colourless Y: Yellow. Lt: Light.
V: Very. Vis: Viscous. Fl: Fluid.
CA: Crystalline aggregates.
Tr: Trace. P: Present.

SAMPLE.	SOLUBLE EXTRACT.	SOLUBLE ORGANIC EXTRACT.				WHOLE ROCK.			ORGANIC CARBON.	RESIDUAL ORG. CARBON.	KEROGEN CARBON	KEROGEN C CONVERSION.	CARBONATE CARBON.	SOC CARBON/HYDROGEN.	NON-HCs/HYDROCARBONS.	SATURATES/AROMATICS.	HYDROCARBONS.	HYDROCARBONS/ORG.CARBON.	ROCK POWDER COLOUR.	PYROLYSED ROCK POWDER.	PYROLYSIS CONDENSATE.
		CARBON.	HYDROGEN.	NITROGEN.	SATURATES.	AROMATICS.	ASPHALTICS.	CARBON.	HYDROGEN.	NITROGEN.											
117	0.05	50.38	6.74	3.39	14.79	11.24	73.96	0.48*	0.60*	0.27*	0.70*	0.35	0.67	50.75	0.00	7.47	2.84	1.31	0.0156	0.0223	Lt.Bl.G-B	Lt.G-B	C/Lt
118	0.23	47.18	5.68	0.47	12.22	16.57	71.17	2.87	0.69	0.00*	1.50	1.00	1.39	21.64	1.37	8.31	2.47	0.73	0.0663	0.0442	Lt.Grey	Grey	C/Lt
119	0.12	63.70	8.34	0.73	18.53	12.23	69.23	2.72*	0.84*	0.11*	2.85*	1.37	2.75	50.25	0.00	7.64	2.25	1.51	0.0369	0.0130	Dk.Grey	Black	C/Lt
120	0.05	67.63	8.43	0.60	15.28	7.23	77.47	1.47*	0.63*	0.03*	1.34*	0.74	1.31	43.34	0.13	8.02	3.44	2.11	0.0113	0.0084	Dk.Grey	Grey	C/Lt
121	0.13	73.03	9.38	0.77	13.53	5.05	81.41	5.13	0.79	0.11*	3.35	1.44	3.26	55.76	1.78	7.79	4.38	2.67	0.0242	0.0072	Dk.Grey	Dk.Grey	C/Lt
122	0.10	70.31	8.91	0.83	12.35	8.57	79.06	3.51	0.67	0.00*	2.44	0.68	2.37	71.31	1.07	7.89	3.78	1.44	0.0209	0.0086	Md.Grey	Lt.Grey	C/Lt
123	0.02	25.97	3.34	0.83	26.73	7.69	65.56	9.21*	0.11*	0.05*	0.39*	0.18	0.39	53.25	8.82	7.78	1.91	3.47	0.0069	0.0177	Lt.Grey	Lt.Y-B	C/Lt
124	0.13	41.53	6.30	0.88	30.79	15.25	53.95	2.08*	0.74*	0.00*	2.29*	1.05	2.24	53.04	0.00	6.59	1.17	2.01	0.0599	0.0262	Md.Grey	Dk.Grey	C/Lt
125	0.20	70.16	9.41	0.80	14.07	14.07	71.84	5.18	1.06	0.00*	3.81	1.14	3.67	68.94	1.37	7.46	2.55	1.00	0.0563	0.0148	Md.Grey	Grey	C/Lt
126	0.33	32.59	6.13	0.44	11.19	10.77	78.03	12.58	0.14	0.00	3.04	0.27	2.93	90.79	9.54	5.32	3.55	1.03	0.0725	0.0238	White	White	C/Lt
127	0.09	59.96	8.05	0.47	19.45	6.98	73.56	12.40	0.08	0.00	1.79	0.48	1.74	72.35	10.61	7.45	2.78	2.78	0.0238	0.0133	White	Brown	C/Lt
128	1.82	41.53	6.30	0.88	7.75	15.69	76.35	45.14*	5.44*	0.33*	43.45*	31.85	42.69	25.32	1.69	6.59	3.23	0.48	0.4303	0.0099	Brown	Black	Dk.Y/Hv

SAMPLE.	IR SPECTRAL CLASSES. EXTRACT.		SATURATES.	AROMATICS.	ASPHALTICS.	SOLUBLE EXTRACT R.T.P.	SOLUBLE EXTRACT (XRF)	QUARTZ. d= 4.23/20= 24.35°	CALCITE. d=3.03A/20=34.4°	DOLOMITE. d=2.89A/20=36.1°	MICA-ILLITE.d=9.97A/20=10.2°	KAOLINITE-CHLORITE d=7.19A/20=14.2°	PYRITE. d=2.7A/20=38.5°	GYPSUM. d=7.56A/29=13.7°	APATITE. d=2.815	SPHALERITE.	SIDERITE. d=2.7A/2.80
117	D	C2	B	A	A	V.Vis.Fl.+ CA	S,Mn?,Fe,Cl,Br?	44	17.5	3	12	9.5	6.5	?	?	?	?
118	X	C2	A1	A	B1	V.Vis.Fl.+ CA	S,Mn?,Fe,Cl,Br.	40			12	9.5		?	?	?	?
119	D	C2	A1	A	A	V.Vis.Fl.	S,Mn?,Fe,Cl,Br.	54.5	5		9.5	10		?	?	?	?
120	D	X	B	A	A	V.Vis.Fl. + CA	S,Mn?,Fe,Cl,Br?	39.5			11.	7	5	5	?	?	?
121	D	C1	B	A	A	Vis.Fl.	S,Mn?,Fe,Cl,Br?	32	24		8.5	6.5	4	4.5	?	?	?
122	D	C1	B	A	A	Vis.Fl.+ CA	S,Mn?,Fe,Cl,Br.	34.5	35		10.5	7.5	5	5	?	?	?
123	D	C1	B	A	A	V.Vis.Fl.+ CA	———	21.5	103	20	4		1		?	?	?
124	X	C1	B2	A	A	V.Vis.Fl.+ CA	S,Mn?,Fe,Cl,Br?	34.	61.5	3	13	9	7.5	5	?	?	?
125	X	C1	B	A	A	V.Vis.Fl.	S,Mn?,Fe,Cl,Br?	25.	58.5		8	7.5	4	12.5	?	?	?
126	A	C1	B	A	A	V.Vis.Fl.+ CA	S,Mn?,Fe,Cl,Br.	tr	206		2				?	?	?
127	D	C1	A	A	A	V.Vis.Fl.+ CA	S,Mn?,Fe,Cl,Br?	tr	215						?	?	?
128	X	C1	B	B2	B2	Solid +CA	[illegible] Fe,—,—	14	63	3.5	2	3.5	4	4.5	?	?	?

Values where appropriate are percentages by weight and * denotes an average result. Numerical data from XRD are relative intensities. IR spectral classes are illustrated in Figs. 66 - 69 incl.

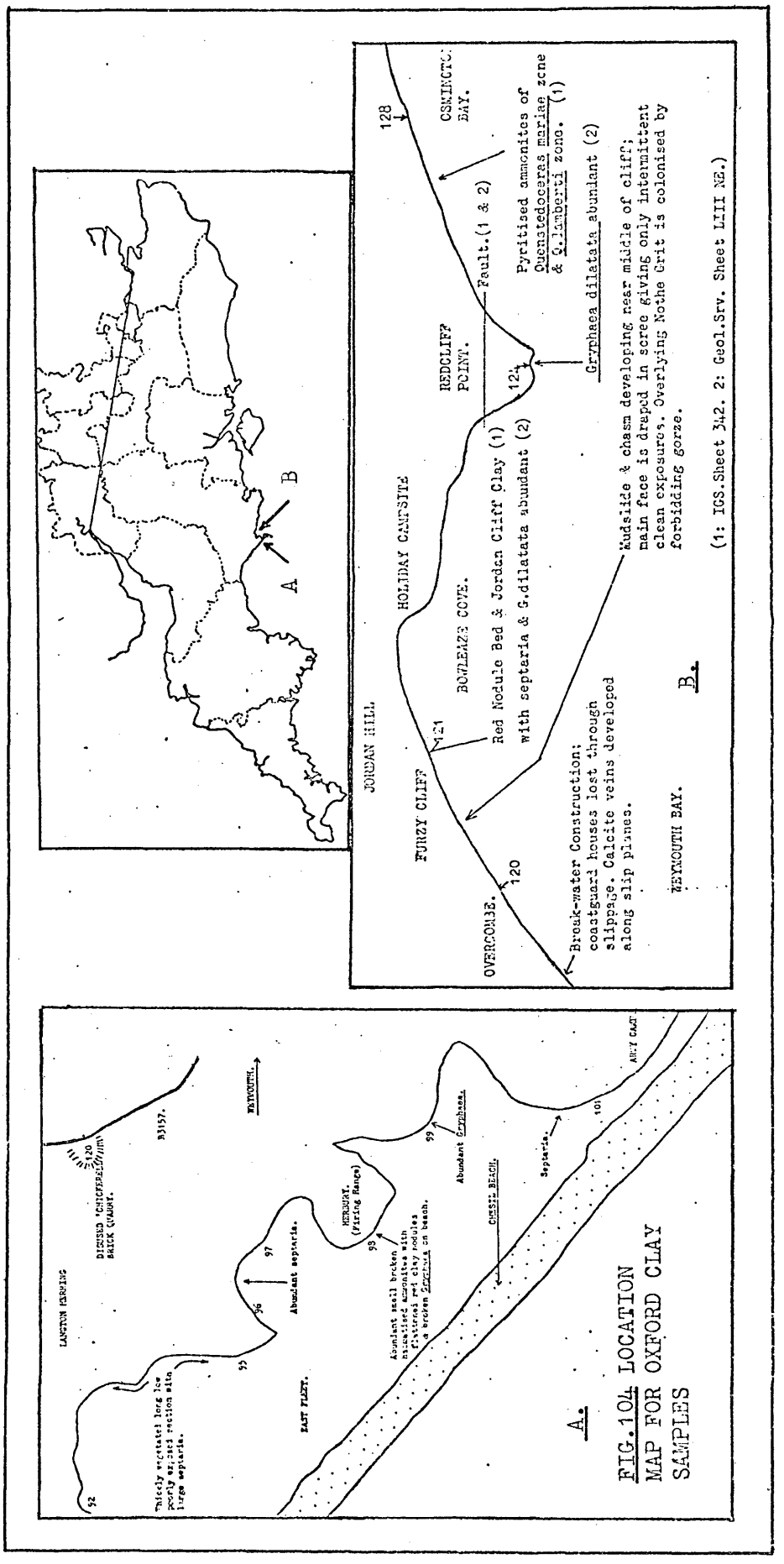


FIG.104 LOCATION MAP FOR OXFORD CLAY SAMPLES

TABLE 74. DESCRIPTION OF THE OXFORD CLAY SAMPLES.

AMMONITE ZONES.	APPROX. STRATIGRAPHIC POSITIONS POSITIONS.
Cardioceras cordatum.	OC 7,8,11, 12,13 & 14.
Quenstedtoceras mariae.	
Quenstedtoceras lamberti.	OC6**
Peltoceras athleta.	OC 2,3,4,& 5. OC 9 & 10*
Erymnoceras coronatum.	
Kosmosceras jasoni.	OC1

**Arkell,1947. *Chatwin,1969 ('Lower beds')

SAMPLE & LOCATION NUMBERS.	EXAMINED HAND SPECIMEN	FIELD DESCRIPTION OF PARENT HORIZON.
OC 12. 121.(B).	Blue tacky silty clay.	About 2½ feet below Nothe Grit (?)
OC 14. 128.(B).	Lt.grey claystone. (? Black 'speckles' & 'streaks' with limonitic halos.)	Slipped clay with red nodules & Gryphaea dilatata.
OC 13. 124.(B).	Lt.grey claystone with sparse indeterminate white shell fragments.	Slipped clay with red nodules,abund. Gryphaea (some with attached serpulae), abund. serpulae,lamellibranchs & fossil wood.
OC 11. 120.(B).	Med.grey claystone with scarce white shell fragments	Immediately below 2" 'nodular limestone' band in bioturbated,pyritic clay which contains Gryphaea,ammonites,other bivalves serpulae,vertebrae & fossil wood.
OC 8. 101.(A).	Lt.grey,sl.limonitic claystone.	Bioturbated clay which contains Gryphaea (with attached serpulae) & septarian nodules.
OC 7. 99.(A).	Blue-black clay with occass-ional cream claystone inclusions. Indeterminate ammonite & lamellibranch impressions.	Very fossiliferous clay with ?cylindrical burrow infills.
OC 6. 98.(A).	Blue-grey claystone.	Loose red flattened claystone nodules Gryphaea,'haematised' small ammonites & serpulae all abund. Also lamellibranchs crinoid ossicles & turreted gasteropods.
OC 5. 97.(A).	Rusty brown-grey shale with jarosite.Ammonite impressions on bedding planes with one ornamented,turreted gasteropod impression.	Seen to c.13 feet; above OC4. Contains septarian nodules & bivalves.
OC 4. 97.(A).	Dk.grey limonitic shale with jarosite & sl.pyritised small bivalves.Also small turreted gasteropod impression & ? ammonite whorl fragment.	Maximum c.2½ feet with septarian nodules. Above OC3
OC 3. 97.(A).	Dk.blue-grey claystone with limonitic fine ribbed bivalve impressions & small ornamented gasteropods.	Seen to c.9 feet with septarian nodules.
OC 9. 120.(A).	Blue tacky sparsely fossil. claystone.	Above OC10 & with septarian nodules.
OC 10. 120.(A).	Brown shale with abund. fine ribbed lamellibranch impress-ions & jarosite.	Weathers rusty brown.
OC 2. 96.(A).	Chocolate brown shale with abund.fine ribbed lamells.	Weathers blue-grey & white-grey; one septarian nodule. (Beneath thick bramble canopy.)
OC 1 95.(A).	Med.grey-brown sl.shaly ammonitic claystone;gypsif-erous with jarosite & limonitic bivalve impress.	Weathers lt.grey-white;seen to 5½ feet.

TABLE 75. EXPERIMENTAL DATA FOR THE OXFORD CLAY SAMPLES; values are in percentages by weight & * denotes an average figure. (Worked by H.Solli.)

SAMPLE.	SOLUBLE EXTRACT.	SOLUBLE ORGANIC EXTRACT.			WHOLE ROCK.			ORGANIC CARBON.	RESIDUAL ORG.CARBON.	KEROGEN CARBON.	KEROGEN C CONVERSION.	CARBONATE CARBON.
		CARBON.	HYDROGEN.	NITROGEN.	CARBON.	HYDROGEN.	NITROGEN.					
1.	0.59	47.65*	6.42*	0.85*	5.87	1.28	0.09	5.78*	2.83*	5.50	48.54	0.09
2.	0.83	59.77	7.39	0.81	11.46	1.77	0.20	11.17	5.27	10.67	50.63	0.29
3.	0.37*	61.32*	7.89*	0.91*	4.64*	2.15*	0.06	3.06*	1.27	2.83	55.17	1.58
4.	0.66	60.69	7.86	0.93	10.70	1.76	0.12	9.51*	6.97*	9.11	23.49	1.19
5.	0.33	57.82	6.80	0.98	5.22	1.42	0.17	3.65	1.54	3.46	55.48	1.57
6.	0.14	36.41	1.69	0.25	5.25	0.72	0.12	1.44	0.58	1.39	58.24	3.81
7.	0.23	25.19	5.08	0.79	4.51	0.96	0.18	2.19	1.26	2.13	40.90	2.32
8.	0.17	7.27	3.41	0.30	2.01	0.59	0.18	0.58	0.36*	0.57	36.58	1.43
9.	0.12	38.15	5.73	1.11	2.13	0.86	0.12	1.87	1.46	1.82	19.97	0.26
10.	0.54	62.65	7.77	0.84	8.18	1.49	0.29	7.48	3.59	7.14	49.73	0.70
11.	0.08	37.68	4.90	1.13	6.12	0.34	0.04	2.30*	0.91*	2.27	59.91	3.82
12.	0.04	61.58	8.37	0.60	1.99	0.50	0.22	0.93	0.49	0.91	45.88	1.06
13.	0.05	43.30	6.42	1.07	3.55	0.96	0.04	1.05	0.38*	1.03	63.11	2.50
14.	0.04	41.07	6.35	1.20	3.67	0.60	0.04	1.08	0.97	1.06	8.80	2.59

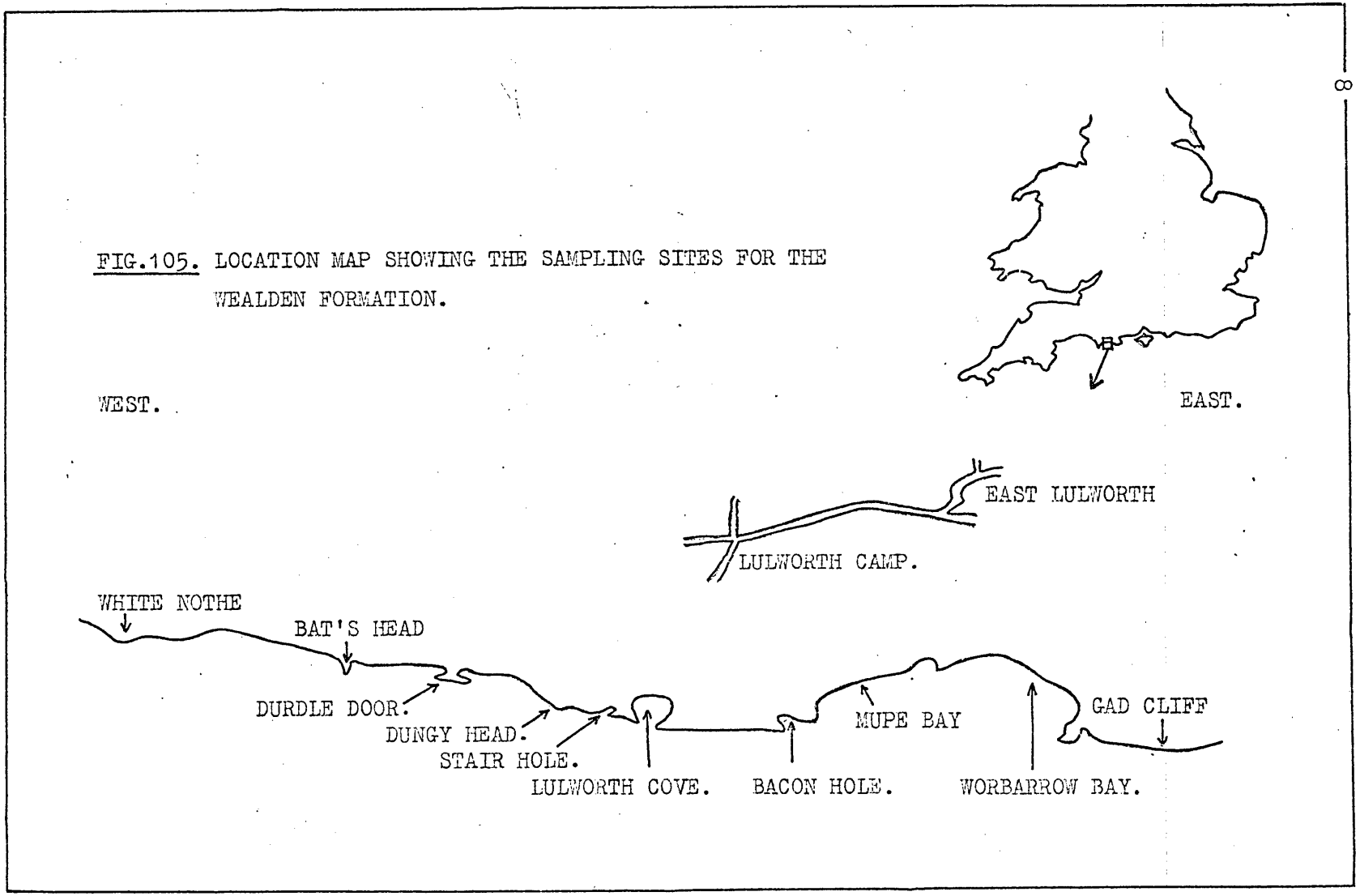


FIG.105. LOCATION MAP SHOWING THE SAMPLING SITES FOR THE WEALDEN FORMATION.

9 GLC ANOMALIES

Throughout no attempt has been made to ignore the spurious peaks which plagued the GLC analyses of the total saturate fractions.

In summary, a pre n-C_{20} b/c-alkane ranging from very subdued to massive was evident for all samples from the three suites of rock with the exception of one Kimmeridge Clay and two Oxford Clay samples. A 'massive' b/c-alkane eluting before the n-C_{23} alkane was unique in one Kimmeridge Clay sample whilst a b/c-alkane came before the n-C_{25} alkane in just two Wealden samples on a large-significant scale. Finally a significant-massive pre-nC_{27} b/c-alkane appeared in two Oxford Clay samples and one Wealden sample.

Now, Hoering (1967, in Douglas and Grantham 1973) extracted unspecified hydrocarbons from Kraft paper, laboratory wiping tissue, aluminium foil and geological sampling bags; all of which were used here (!). Specifically, the pre-nC_{20} b/c alkane is thought to be a phthalate (Hall and Solli, pers. comm.) and as phthalaic acid esters are used in the manufacture of polythene, direct or indirect (laboratory ware made by injection moulding, e.g. vials) contact with polythene could be the source of contamination (Douglas & Grantham, 1973). Here, checks with solvent, lubricating grease and the small flexible tubing used in the tlc all proved negative but a randomly chosen sample, KCl13, gave a cold (distilled azeotropic benzene-methanol) solvent washing in which the pre-nC_{20} b/c-alkane was proved by GLC (Figure 105).

In the absence of detailed work, it remains intriguing that Reed (1977) has reported some effects of weathering where, in particular, the appearance of pre-nC_{20},-nC_{21} and-nC_{22} alkanes accompanied a growth in the nC_{22} alkane for increasing degradation (?).

FIG.106 CGLC KC113 Total Cold Solvent (Azeotropic Benzene-Methanol) Washings.

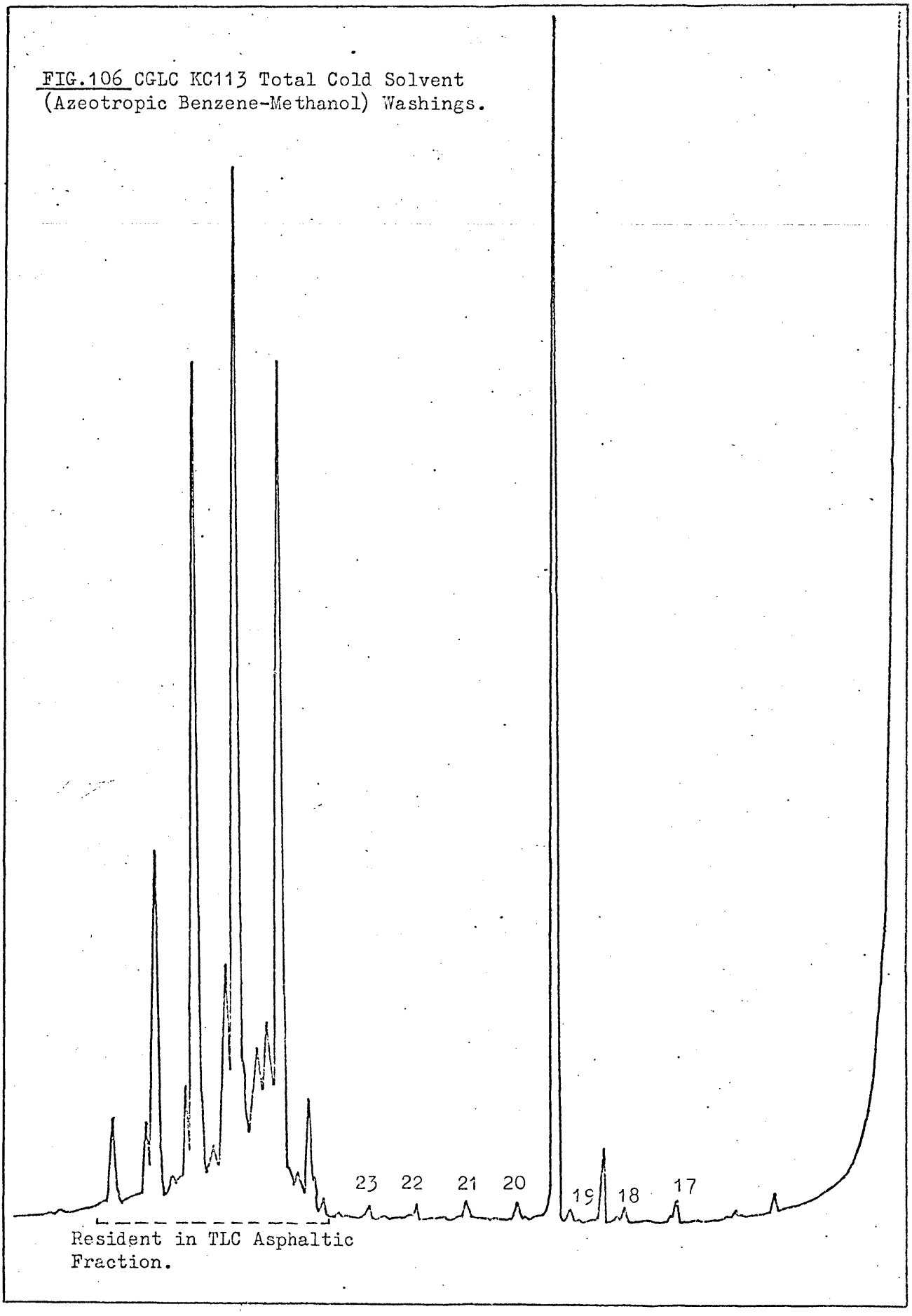
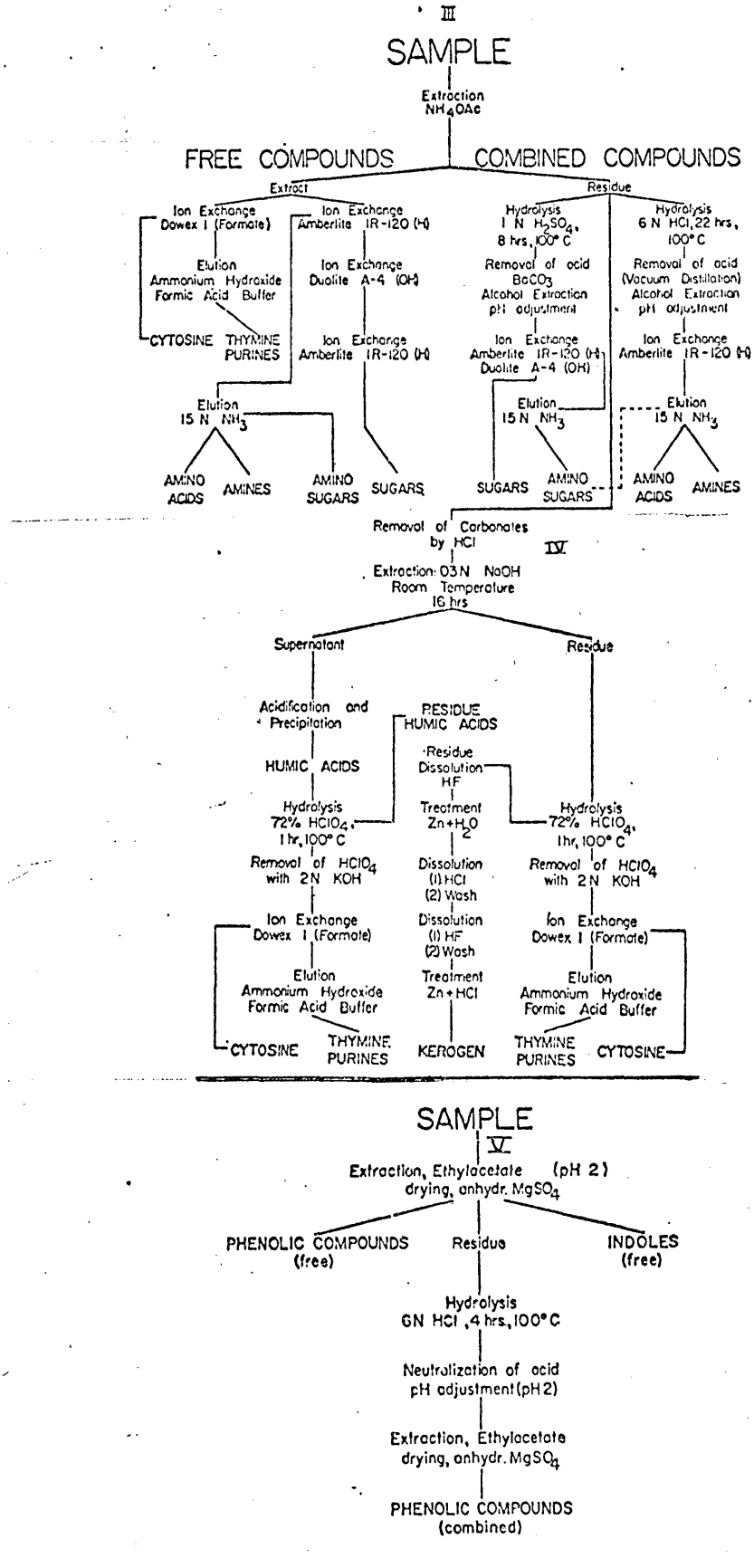


FIG. 107 EXPANDED FLOW DIAGRAMS FOR ANALYTICAL CLASSIFICATION. FROM FIG.97. (After Degens & Reuter,1962.)



11 GAMMA-RAY LOGGING

Using an unshielded intrinsic germanium detector and a 1000 channel pulse height analyser, it appears that only a very small change at best is apparent for a sample-background comparison (Bennet priv. comm. 1977).

For example, KC33 (Figure 109) appears to show only a very slight increased activity (integrated peak area) over background (Figure 108) for gamma rays of 1.46 MeV (K^{40}) and approximately 1.12, 0.97, 0.91, 0.60, 0.58 and 0.51 MeV energies. In the lower energy region, additional very small peaks seem to occur (0.86, 0.83, .79 and .77 MeV) but it should be remembered that if cosmic activity occurs it will plague this region.

Thus, the preliminary effort, upon a Kimmeridge Clay sample to determine the source(s) of (residual) activity, has focussed future detailed work upon the low energy region of the gamma ray spectrum.

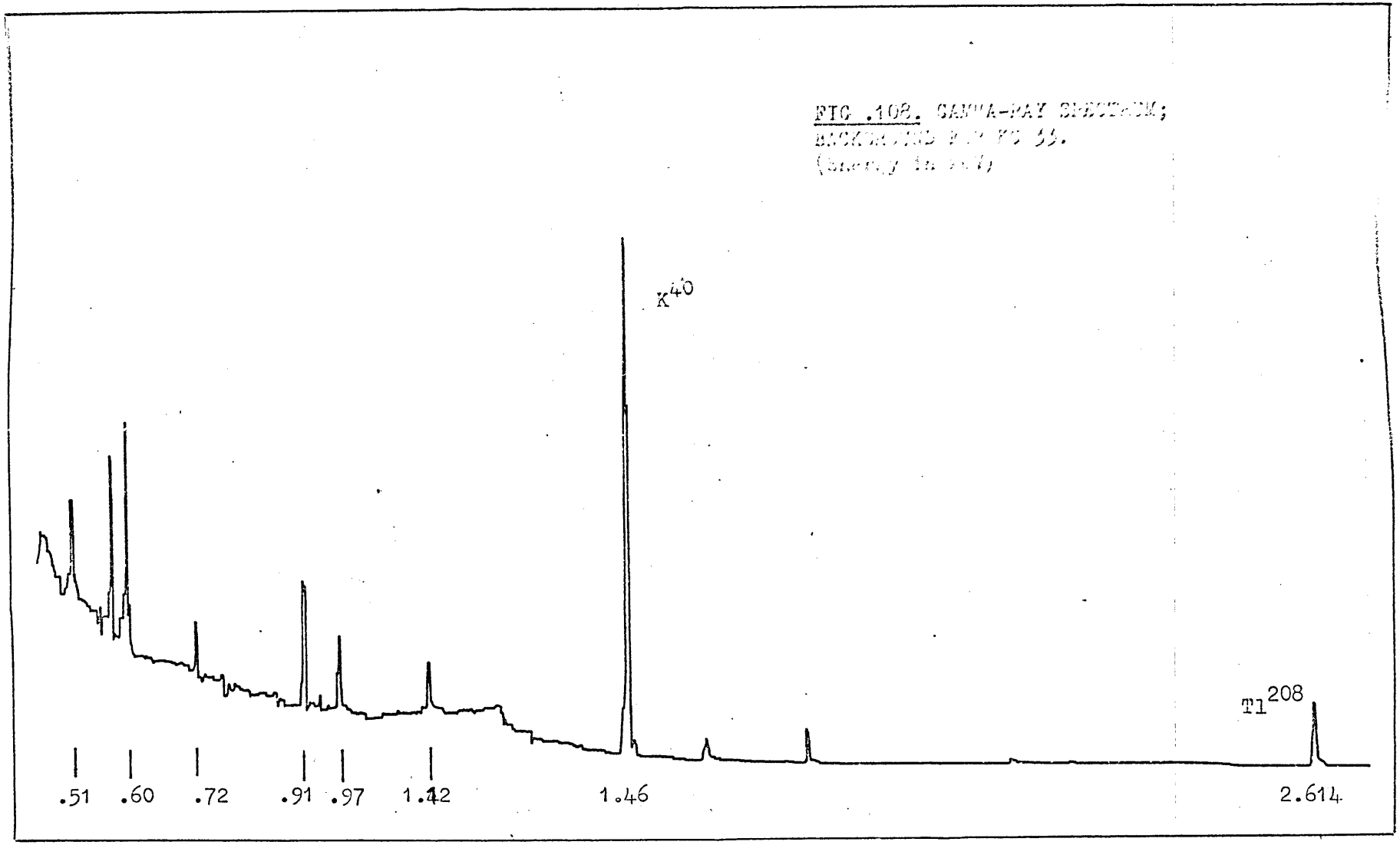


FIG .108. GAMMA-RAY SPECTRUM;
BACKGROUND FOR FIG 99.
(Energy in MeV)

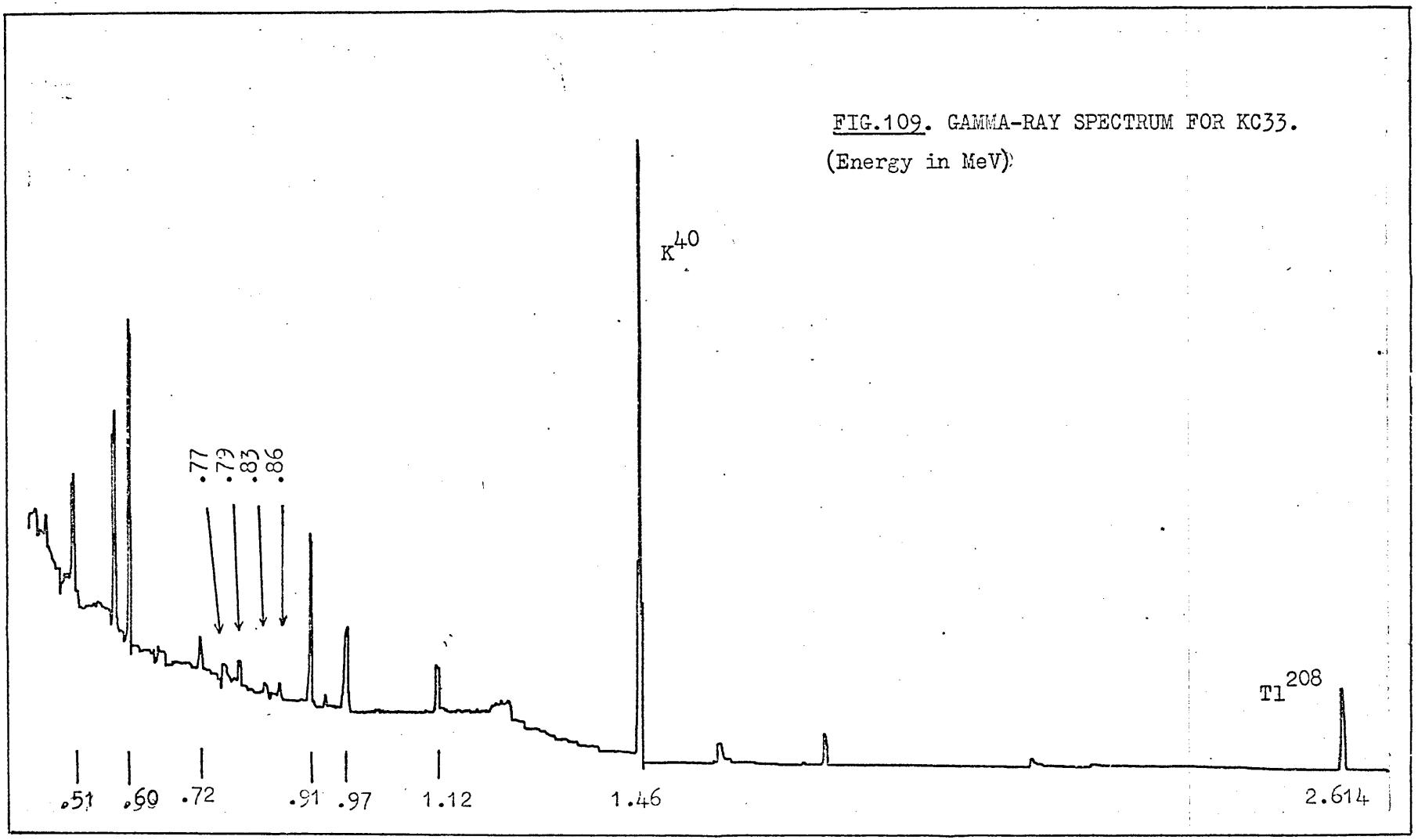


FIG.109. GAMMA-RAY SPECTRUM FOR KC33.
(Energy in MeV)

Abund.	Abundant.
Alt.	Alternate.
Ammon(s).	Ammonite(s).
Apprcach.	Approaching.
Bds.	Bands.
Bels.	Belemnites.
Bit.	Bitumenous.
Bl.	Blue.
Calc.	Calcareous.
Cemst(s).	Cementstone(s)
Conc.	Concentration.
Dk.	Dark.
Foss.	Fossils/Fossiliferous.
Forams.	Foraminiferids.
Hd.	Hard.
Ind.	Indurated.
Inart.	Inarticulate.
Irreg.	Irregular.
Jura.	Jurassic.
Lam.	Laminated.
Mudst.	Mudstone.
Nod(s).	Nodule(s).
P.	Paper.
Py.	Pyrite.
Res.	Residue.
Sh(s).	Shale(s).
Sps.	Species.
Ssts.	Sandstones.
Sub.	Subplanites.
Unfoss.	Unfossiliferous.
W.	With.

12. KEY TO LOG. 1.

Pl.11 LOOKING WEST FROM EMMIT HILL across Chapman's Pool to Hounstout (a), Egmont Bight (b), Freshwater Steps (c), the spur below Swyre (d) and Rope Lake Head(e). Pb denotes the Parallel Bands within the Portland Formation and the Massive Bed (mb) is obvious to serve as a permanent boundary between the latter and the Kimmeridge Clay Formation. In the extreme distance Arish Mell is conspicuous in the Chalk of Worbarrow Bay. Hounstout attains a height of approximately 500 feet.(See in conjunction with Fig.39)

Pl.12 LOOKING EAST FROM out at sea on the YELLOW LEDGE towards Clavell's Hard (CH) and Rope Lake Head (RLH) Through the displacements in the oil shale horizon (OS), in particular the white Short Joint Cementstone, two faults are evident in the photograph. Ct locates Pl.14 in the face of Cuddle (Cu).(Arrow indicates person serving as scale.)See Fig.39

Pl.13 DISUSED BLACKSTONE/KIMMERIDGE COAL (OIL SHALE - OS) LEVEL penetrates Clavell's Hard for about 80 feet with an approximate height of $6\frac{1}{2}$ feet and constantly drips water. Calcite veining characterises the obvious normal fault plane immediately to the east, which has been emphasised by erosion. To the west (* in Fig.38)a disused narrow gauge railway (35") traverses the Dorset Coastal Footpath and protrudes over the cliff top edge.

Pl.14 DISUSED CEMENTSTONE LEVEL, as cited in Pl.12, is according to the Geological Survey one of twelve cut in a band of marl of $2\frac{1}{2}$ feet thickness.

Pl.15 LOWEST BEDS SEEN,HORBARROW BAY form the core of the Weymouth Anticline and are infact the oldest rocks visible in the Isle of Purbeck. The Broad Bench cementstone marker (BB) is displaced by about 38 feet and WL indicates the Washing Ledge cementstone

Pl.16 FAULT OF UNKNOWN THROW,KIMMERIDGE BAY, just east of Gaulters' Gap,is well defined by the Maple Ledge cementstone and Arkell estimated the minimum throw as 22 feet. See Fig.39

Pl.17 ROTUNDA NODULE BED,HOUNSTOUT CLIFF is located at about 6 feet above the Hard Shale platform. The level here was reached by a vertical traverse up from Egmont Bight en route to the Massive Bed.

Pl.18 STEEPLY DIPPING STRATA,BRANDY BAY as seen on the north limb of the east-west trending Weymouth Anticline from below Gad Cliff (Fig.39) BB marks the Broad Bench and Clavell's Tower (CT) resides on the east corner of Kimmeridge Bay. In the foreground two white bands are conspicuous.

Pl.19 WEALDEN OIL SAND,DUNGY HEAD. A blue-green silty claystone with jarosite overlies the oil sand,which shows black sandstone boulders in a dark brown sandstone matrix but is covered by a blue-grey clay downwash. An iron-lithified white sandstone underlies the oil sand and the exposure is sited above a spring. See Fig.84

Pl.20 WEALDEN OIL SAND,STAIR HOLE. Centrally located in line with the Cove mouth a brown sticky,spongy oil rich sandstone occurs between two blue-green silty claystones and is indicated by the white pages of the field notebook. See Fig.84

Pl.21 WEALDEN OIL SAND,LULWORTH COVE, west side,gives rise to oil films on spring water. The outcrop site is currently located by a concrete sewer cover in the foreshore.See Fig84

Pl. 22 WEALDEN OIL SAND,MUPE BAY. Immediately next to the recently built stairway which leads down from the Army firing ranges,the finest exposure of the Wealden oil sands occurs Soft black oil rich sandstone boulders (maximum 'diameter' seen was 13") lie in the basal layers of a brown-grey lignitic sandstone which has light grey claystone inclusions. See Fig.84 Below a lignitic,sandy,ferruginous grey silty claystone seperates a brown sand.

Pl.23 WEALDEN OIL SAND,WORBARROW BAY. See Fig.85(C) An oil sand with grey silty claystone laminae and/or lenses, sometimes hardened by iron cementation, is generally dark brown but weathers white. It lies above a gypsiferous silty blue-grey claystone which also shows jarosite.

Pl.45 RINGSTEAD CORAL BED,EAST FLEET,WEYMOUTH. At location 107 in Fig.103(A) blue-grey/ brown Kimmeridge Clay,rich in Ostrea delta is seen to about 18" above the Ringstead Coral Bed. A red silty,sandy clay with nodular concretions and an irregular base,$3\frac{1}{2}$" - $5\frac{1}{2}$" thick, (10), lies above a serpulid rich clayey ferruginous oolite (9) which is seen to 15". (Bed numbers are assigned after Arkell,1947.) See also Fig.37

Pl.46.EXOGYRA NANA BED,RINGSTEAD BAY. At location 139 in Fig.103(B)a 3" thick slab of a blue-grey very hard shelly limestone resembling the classic Forest Marble facies was found in a slipped mass of Kimmeridge Clay. See also Fig.37

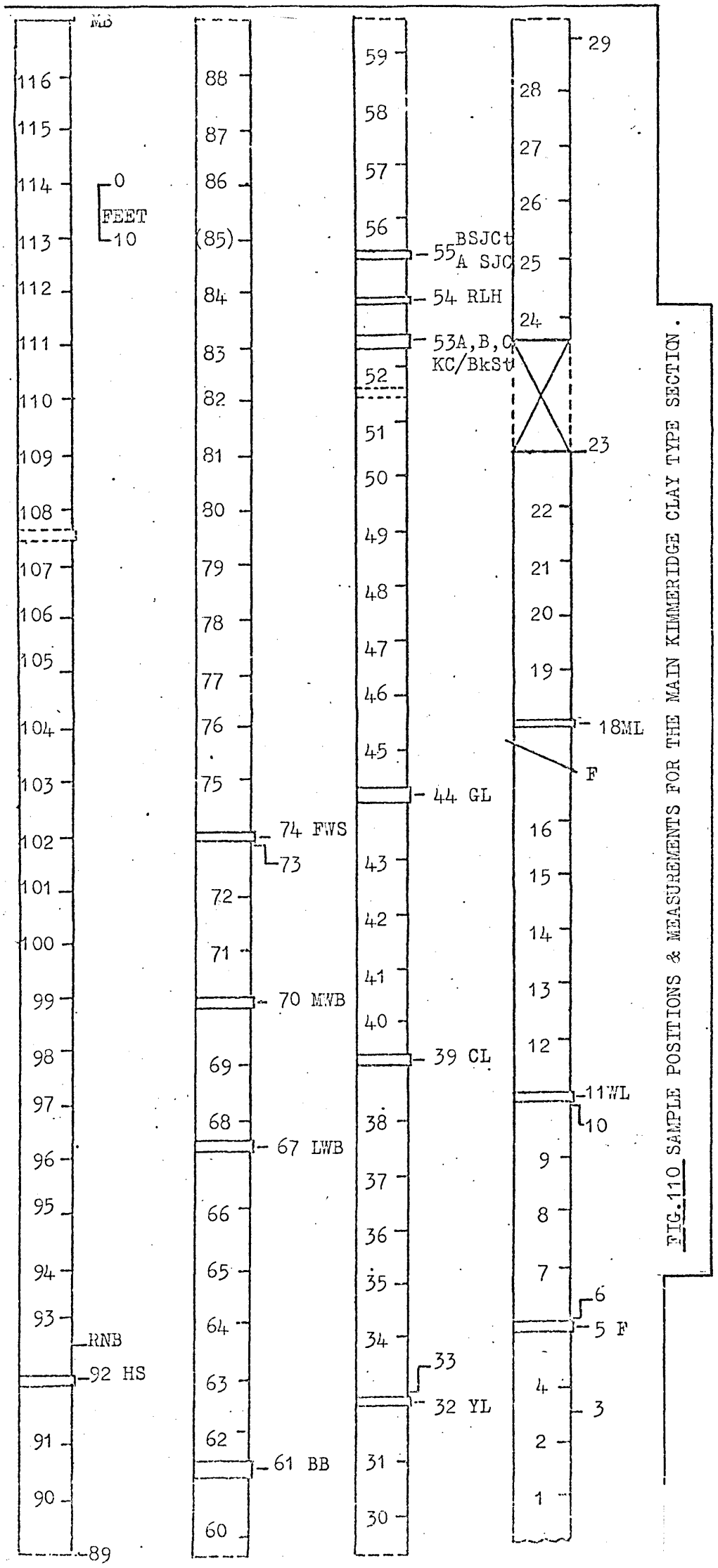


FIG.110 SAMPLE POSITIONS & MEASUREMENTS FOR THE MAIN KIMMERIDGE CLAY TYPE SECTION.

15. EXPERIMENTAL DATA FOR KIMMERIDGE CLAY BETWEEN HORBARROW BAY - CHAPMAN'S POOL.

KEY TO TABLE 76: EXPERIMENTAL DATA FOR KIMMERIDGE CLAY BETWEEN HORBARROW BAY - CHAPMAN'S POOL, Dorsetshire.

1. Sample number. (As located in Fig.110.)
2. % Soluble organic extract.(SOE)
3. %Carbon
4. %Hydrogen
5. %Nitrogen

— in the SOE.

6. %Saturates
7. %Aromatics
8. %Asphaltics

— in the SOE.

9. %Carbon
10. %Hydrogen
11. %Nitrogen

— in the Whole Rock. (WR)

12. %Organic carbon
13. %Post-pyrolysis organic carbon.
14. Gamma-ray count (per 10,000secs.less background.)
15. %Kerogen carbon (Organic carbon - soluble extract carbon.)
16. %Kerogen carbon conversion.
17. %Carbonate carbon (Total WR carbon - organic carbon.)
18. C/H ratio for the SOE. (3)/(4)
19. Non-hydrocarbons/Hydrocarbons. (8)/(6+7)
20. Saturates/Aromatics (6)/(7)
21. %Hydrocarbons in the Whole Rock. (2 x $\overline{6+7}$)
22. %Hydrocarbons/%Organic carbon (21/12)
23. Relative potential: Kerogen carbon - Post pyrolysis organic carbon. (15 - 13)

24. Quartz..d=4.25A
25. Calcite.d=3.03A
26. Dolomite. d=2.89A
27. Mica-Illite.d=9.97A
28. Kaolinite-Chlorite.d=7.19A
29. Pyrite. d=2.70A
30. Gypsum.d=7.50A

— Relative Intensities.

Percentages where appropriate are % by weight.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
116	0.02	66.22	8.94	0.80	16.0	11.5	72.5	1.32	0.28	0.06*	0.71*	0.26	229	0.70	62.86	0.61	7.41	2.64	1.39	0.0065	0.0077	0.44	35	26.5	6	5	3	1.5	2
115	0.05	60.09	8.09	0.99	26.7	9.3	64.0	2.91	0.33	0.00	1.00	0.36	54	0.97	62.89	1.91	7.43	1.78	2.86	0.0180	0.0180	0.61	27	35.5	9	4.5	3	3	0
114	0.04	59.57	6.59	1.74	12.0	9.3	78.7	5.29*	0.23*	0.10*	0.68*	0.57	18	0.66	13.64	4.61	7.67	3.69	1.29	0.0085	0.0125	0.09	14.5	91	33	3.5	0	4.5	0
113	0.07	74.54	9.47	0.86	16.3	3.7	80.0	2.06	0.54	0.00	1.61*	1.12	354	1.56	28.21	0.45	7.87	4.00	4.35	0.0139	0.0087	0.44	31	25.5	0	5	3.5	6.5	0
112	0.05	72.52	9.10	0.79	13.8	1.2	85.0	1.93	0.43	0.00	1.07	0.46	0	1.03	55.34	0.86	7.97	5.66	11.72	0.0075	0.0070	0.57	23	44	14	4	3	2	0
111	0.05	79.14	9.90	1.25	30.0	9.3	60.7	4.09	0.37	0.63*	1.42	0.48	78	1.38	65.22	2.67	7.99	1.55	3.21	0.0196	0.0138	0.90	24	41	24.5	7	4	2.5	0
110	0.07	64.79	9.42	0.90	8.9	8.4	82.7	4.07	0.51	0.11*	1.55	0.56	1012	1.51	62.91	2.52	6.86	4.77	1.05	0.0121	0.0078	0.96	28.5	48.5	6	4	2	2.5	0
109	0.08	86.74	10.45	1.73	9.3	28.4	62.3	4.29	0.44	0.07*	1.36	0.46	1927	1.29	64.34	2.93	8.30	1.65	0.32	0.0302	0.0222	0.83	21.5	59	5	3	3.5	2	3
108	0.07	71.02	8.80	0.53	8.8	7.0	84.2	2.10	0.37	0.31*	1.49	0.44	1930	1.44	69.44	0.61	8.07	5.31	1.25	0.0111	0.0074	1.00	34.5	38.5	0	4	3	5.5	0
107	0.04	53.66	6.94	0.90	16.4	7.2	76.4	2.13*	0.39*	0.17*	1.35*	0.21	214	1.33	84.21	0.78	7.73	3.27	2.28	0.0094	0.0069	1.12	28.5	40.5	2	5	1	3	0
106	0.05	51.80	6.58	3.24	30.4	0.4	69.2	3.35	0.29	0.00*	0.89*	0.42	26	0.86	51.16	2.46	7.87	2.25	80.02	0.0154	0.0173	0.44	29	62.5	4	4	3.5	2	2
105	0.08	73.64	9.05	2.16	11.1	1.6	87.3	3.32	0.66	0.46*	2.00*	0.67	240	1.94	65.46	1.32	8.14	6.86	6.85	0.0102	0.0051	1.27	26	29	0	7	4	0	2.5
104	0.12	74.42	9.15	2.52	13.3	12.1	74.6	4.84	0.62	0.43*	2.76*	0.90	272	2.67	66.29	2.08	8.13	2.94	1.09	0.0304	0.0110	1.77	17	78.5	0	5	3.5	0	0
103	0.09	60.72	7.63	1.96	12.4	10.0	77.6	3.90	0.38	0.00	1.07*	1.03	645	1.02	0.00	2.83	7.96	3.47	1.25	0.0202	0.0188	0.00	15	69	8	5.5	4.5	1	0
102	0.03	55.25	6.70	1.36	12.8	3.6	83.6	4.53	0.61	0.00	1.19*	1.10	809	1.15	4.35	3.34	8.25	5.08	3.53	0.0131	0.0110	0.05	20.5	66	4.5	6	5	2.5	3?
101	0.05	45.66	5.61	2.50	10.9	13.4	75.7	3.75	0.53	0.00	1.75*	0.62	1080	1.73	64.16	2.00	8.14	3.13	0.81	0.0121	0.0069	1.11	20	63.5	0	6	6	2	3?
100	0.09	63.87	7.86	0.64	13.0	9.0	78.0	5.83*	0.47	0.17	1.63	1.13	690	1.57	28.03	4.20	8.13	3.54	1.45	0.0198	0.0122	0.44	14	35	32	4.5	6	2	0
99	0.06	70.11	8.30	1.02	48.0	0.5	51.5	3.67	0.66	0.47*	1.56	0.96	535	1.52	36.84	2.11	8.45	1.06	98.02	0.0291	0.0187	0.56	20.5	46	4.5	6	5.5	2	4
98	0.09	25.85*	3.17*	2.48*	22.7	12.0	65.3	3.34	0.71	0.02*	1.23	0.75	525	1.21	38.02	2.11	8.65	1.89	1.89	0.0312	0.0254	0.46	25	43	4	7	7.5	2	3
97	0.15	48.54	5.69	1.69	21.8	13.8	64.4	3.13	0.75	0.02*	2.26	1.39	665	2.19	36.53	0.87	8.53	1.81	1.58	0.0534	0.0236	0.80	20.5	27.5	0	7.5	9	4.5	3.5
96	0.06	68.40	8.33	1.40	19.6	10.9	69.5	2.44	0.72	0.14	1.34	0.80	786	1.30	38.46	1.10	8.21	2.28	1.79	0.0183	0.0137	0.50	27.5	27.5	0	8.5	8	3	8
95	0.11	55.44	6.61	0.00	12.9	9.4	77.7	3.90	0.81	0.67	2.79*	1.21	640	2.73	55.68	1.11	8.39	3.48	1.36	0.0245	0.0088	1.52	25.5	37	8.5	6.5	7	4.5	0
94	0.15	41.43	5.04	0.20	12.3	7.9	79.8	3.97	0.68	0.10	1.80	1.26	627	1.74	27.59	2.17	8.22	3.95	1.56	0.0303	0.0168	0.48	24.5	34	2	7	8	19	0
93	0.06	61.44	7.50	0.74	10.5	26.3	63.2	3.54	0.70	0.31	2.00*	0.80	606	1.96	59.18	1.54	8.19	1.72	0.39	0.0221	0.0111	1.16	21	36.5	0	7	7.5	6	4
92	0.45	73.52	9.17	1.99	20.5	8.4	71.1	9.76	1.19	0.41	6.24	3.50	341	5.91	40.78	3.52	8.02	2.45	2.44	0.1302	0.0208	2.41	14.5	62.5	0	6.5	9.5	9.5	7
91	0.19	48.35	6.08	1.29	14.9	3.7	81.4	4.32	0.60	0.00	1.31	1.04	369	1.22	14.75	3.01	7.95	4.36	4.03	0.0354	0.0270	0.18	18	44	0	7	5	5	2.5
90	0.09	43.38	5.36	0,10	26.5	14.2	59.3	2.96	0.51	0.32	0.90	0.56	553	0.86	34.88	2.06	8.09	1.46	1.85	0.0366	0.0406	0.30	27.5	40	4	6	4	3	2
89A	0.08	44.87	5.49	0.13	11.2	2.8	86.0	2.62	0.51	0.00	1.37*	1.29*	0	1.33	3.01	1.25	8.17	6.12	3.95	0.0112	0.0082	0.04	27.5	8.5	0	9	8	5.5	3
89	0.30	77.34	10.56	0.01	31.7	12.0	56.3	3.57	0.60	0.46	1.75	1.12	662	1.52	26.32	1.82	7.32	1.29	2.63	0.1311	0.0749	0.40	23.5	55	0	7	8	5.5	0
88A	0.37	84.83	12.45	0.53	46.9	17.2	35.9	1.74	0.74	0.61	1.56	0.63	0	1.25	49.60	0.18	6.81	0.56	2.73	0.2371	0.1520	0.62	43	34.5	3	6	6	4	2.5
88	0.18	81.29	11.62	0.59	40.1	15.5	44.4	1.60	0.72	0.62	1.51	0.54	315	1.36	60.29	0.09	7.00	0.80	2.58	0.1002	0.0664	0.82	29.5	7	0	8.5	8	5.5	0
87	1.18	82.74	12.28	0.00	32.1	18.8	49.1	3.53	0.81	0.29	2.35*	1.42	451	1.37	0.00	1.18	6.74	0.97	1.70	0.5996	0.2552	0.00	12	31.5	0	7.5	7.5	3.5	3
86	0.18	75.94	9.25	2.50	16.1	13.2	70.7	5.65	0.92	----	4.12	1.88	283	3.98	52.80	1.53	8.20	2.42	1.22	0.0527	0.0128	2.10	20.5	42.5	0	7	9.5	5.5	5
84	0.18	72.19	8.97	0.93	10.6	3.7	85.7	1.87*	1.14	0.17*	2.25*	0.32	260	2.12	84.91	0.00	8.05	6.00	2.83	0.0257	0.0114	1.80	27.5	11	0	8.5	8.5	0	36
83	0.18	53.12	6.54	1.06	14.3	6.7	79.0	2.36	0,80	0.09	1.72	1.12	376	1.62	31.11	0.64	8.12	3.77	2.12	0.0378	0.0220	0.50	25	14	0	9.5	10	7	6
82	0.10	69.97	8.53	1.27	15.2	16.4	68.4	2.49	0.72	0.00	1.23	0.87	624	1.16	25.00	1.26	8.20	2.16	0.93	0.0316	0.0257	0.29	34.5	32.5	0	8.5	9.5	4.5	6.5

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
81	0.13	69.70	8.39	1.48	13.4	11.8	74.8	2.83	0.72	0.34	1.40	0.99	520	1.31	24.37	1.43	8.31	2.96	1.14	0.0328	0.0234	0.32	24	45	0	8	7	6	5
80	0.23	75.53	9.35	1.19	15.8	14.1	70.1	4.91	0.83	0.27	3.65	1.89	662	3.48	45.63	1.26	8.08	2.35	1.12	0.0686	0.0188	1.59	23	51	0	7	9	6.5	4
79	0.13	60.24	7.44	2.44	16.2	11.5	72.3	3.14	0.78	0.28	2.10	1.13	685	2.02	44.11	1.04	8.10	2.60	1.40	0.0361	0.0172	0.69	25.5	25.5	0	7.5	8.5	5	4
78	0.10	73.10	8.78	1.05	20.9	12.9	66.2	2.47	0.61	0.31	2.14	0.65	489	2.07	68.55	0.33	8.33	1.96	1.61	0.0338	0.0158	1.42	30.5	23.5	3	5.5	5.5	5	2
77	0.15	53.10	6.62	1.60	15.8	2.9	81.3	2.38	0.50	0.09	1.20	0.53	559	1,12	52.68	1.18	8.02	4.36	5.50	0.0279	0.0233	0.59	37	30.5	0	6	6	6	2
76	0.15	63.74	8.06	1.08	17.5	9.3	73.2	2.75	0.90	0.32	2.07	0.55	1094	1.97	72.14	0.68	7.91	2.73	1.89	0.0402	0.0194	1.42	22	5	0	10.5	8	5	0.
75	0.12	57.57	7.00	1.34	35.7	11.0	53.3	2.41	0.68	0.00	1.63	1.10	905	1.56	29.53	0.78	8.22	1.15	3.25	0.0559	0.0343	0.46	23	21	0	8.5	6.5	5	4
74	0.40	44.59	7.73	0.86	21.4	11.9	66.7	12.85	0.47	1.42	4.38	0.19	364	4.20	95.48	8.47	5.77	2.01	1.79	0.1330	0.0504	4.01	3.5	118	2	1	1	0	6
73	0.28	41.96	5.50	4.46	21.1	6.6	72.3	6.17	0.93	0.00	4.25	2.13	1718	4.13	48.50	1.92	7.63	2.61	3.21	0.0776	0.0183	2.00	21	48	0	8.5	11	6.5	4
72A	0.27	49.27*	6.64*	5.17*	40.2	5.1	54.7	5.00	0.83	0.87	3.62	1.40	0	3.49	59.85	1.38	7.42	1.21	7.85	0.1222	0.0338	2.09	14.5	46.5	0	8.5	8	5	4
72	0.85	76.67	9.58	1.40	37.2	13.1	49.7	11.06	1.40	0.07	8.61	2.89	1309	7.96	63.68	2.45	8.00	0.99	2.84	0.4278	0.0497	5.07	14	59.5	0	6	10	8.5	5.5
71A	0.76	74.36	9.85	0.92	22.8	11.1	66.1	4.24*	0.87*	0.22*	3.35*	2.90	0	2.79	0.00	0.89	7.55	1.95	2.05	0.2579	0.0770	0.00	24.5	37	0	10	9	9	3
71	0.33	73.40	9.37	1.13	15.2	11.0	73.8	7.11	0.98	0.00	4.43	2.36	1230	4.19	43.63	2.68	7.83	2.82	1.37	0.0865	0.0195	1.83	14	64	3	6.5	7.5	8	4.5
70	1.06	76.83	9.56	3.70	14.1	14.1	71.8	18.15	1.70	0.82	13.97	3.36	1670	13.16	74.46	4.18	8.04	2.55	1.00	0.2985	0.0214	9.80	8.5	117	2	4.5	7.5	5	6.5
69	0.16	59.52	7.44	0.83	10.8	14.8	74.2	5.30	0.47	0.42*	1.70*	0.72	871	1.61	54.97	3.60	8.00	2.91	0.72	0.0409	0.0241	0.89	24	52.5	28.5	6	4	4.5	0
68	0.21	55.36	7.07	1.23	14.9	11.0	74.1	6.37	0.71	0.73	3.70	1.45	1201	3.58	59.54	2.67	7.83	2.86	1.34	0.0544	0.0147	2.13	12	76	3.5	8	4.5	0	3.5
67	2.48	83.54	12.05*	0.16*	48.2	14.4	37.4	14.55	0.51	0.00*	4.05*	0.35	366	1.98	82.31	10.50	6.93	0.60	3.35	1.5512	0.3830	1.63	0	162	1	0	0	0	0
66	0.27	43.54	5.99	4.63	25.5	12.1	62.4	10.70	0.64	0.00	3.74	0.47	260	3.62	87.02	6.96	7.27	1.66	2.10	0.1015	0.0271	3.15	6	167	3	3	3	5	2
65	1.19	63.84	9.07	1.26	16.4	7.4	76.2	11.15	1.18	0.01	7.18	1.99	528	6.42	69.00	3.97	7.04	3.19	2.20	0.2838	0.0395	4.43	14	90	0	6	4.5	4.5	18
64	0.51	74.28	9.66	0.88	18.7	9.2	72.1	10.25	0.81	0.19	4.96	1.31	699	4.58	71.40	5.29	7.69	2.58	2.02	0.1423	0.0287	3.27	9	143	3	4	4	7	4
63	0.63	76.34	9.70	1.83	20.7	7.1	72.2	11.01	1.19	0.50	7.18	2.19	977	6.70	67.31	3.83	7.87	2.59	2.89	0.1753	0.0244	4.51	12.5	69	2	7.5	7.5	6	7.5
62	0.20	45.29	6.33	1.89	17.0	5.9	77.1	8.52	0.38	0.00*	1.43*	0.36	627	1.34	73.11	7.09	7.15	3.23	2.88	0.0478	0.0334	0.98	6.5	36	43.5	3.5	0	3	37
61	0.13	66.05	9.23	0.87	11.4	4.2	84.4	9.88	0.25	0.00	0.80	0.55	166	0.71	22.97	9.08	7.16	5.41	2.67	0.0203	0.0254	0.16	3.5	5	133.5	3	3.5	0	0
60	0.17	62.60	8.52	1.08	18.8	7.8	73.4	5.35	0.61	0.00	2.81	1.21	640	2.70	55.25	2.54	7.35	2.76	2.40	0.0452	0.0161	1.49	17	42	5	6	5.5	3	2
59	0.17	71.15	9.75	0.84	29.8	18.1	52.1	4.30	0.61	0.00	2.01	0.95	947	1.89	49.71	2.29	7.30	1.09	1.64	0.0814	0.0405	0.94	16.5	29	4	9	5.5	2.5	0
58	0.17	74.19	10.19	1.82	28.9	3.5	67.6	5.85	0.77	0.22	3.68	1.61	1243	3.55	54.70	2.17	7.28	2.09	8.38	0.0551	0.0150	1.94	12.5	30	3	8.5	6.5	2	2
57	0.20	62.84	8.76	0.62	19.1	1.9	79.0	5.56	0.59	0.44*	1.87*	1.68	2370	1,74	3.67	3.69	7.17	3.77	10.02	0.0419	0.0224	0.06	17	33.5	3	4.5	4.5	2	0
56	0.72	78.75	12.29	0.81	26.5	10.9	62.6	9.30	1.48	0.24*	9.00*	4.19	3118	8.43	50.31	0.30	6.41	1.68	2.42	0.2691	0.0299	4.24	29	0	0	9.5	10	5	3
55A	1.87	79.28	12.39	1.61	21.8	12.3	65.9	27.69	3.20	0.53	23.34	8.65	1126	21.86	60.42	4.35	6.40	1.93	1.78	0.6371	0.0273	13.21	19	34	0	7	7	6	2
55B	0.88	72.69	10.14	1.25	27.3	5.2	67.5	18.26	1.11	0.18*	9.59*	0.22	725	8.95	97.54	8.67	7.17	2.08	5.25	0.2856	0.0298	8.73	1.5	139	0	0	0	0	0
54	0.43	71.63	10.16	0.83	21.0	8.2	70.8	12.96	0.48	0.00	3.83	0.50	0	3.52	85.80	9.13	7.05	2.42	2.54	0.1256	0.0328	3.02	2.5	87	59.5	0	2.5	3.5	2
53A	1.10	75.99	10.12	1.23	7.6	6.9	85.5	22.17	2.53	0.83	21.87	9.45	0	21.03	55.07	0.30	7.51	5.90	1.09	0.1594	0.0073	11.58	25	11	0	11	11	5	9
53B	1.08	76.99	10.50	1.20	11.7	12.1	76.2	20.28	2.22	0.62	18.82	8.35	575	17.99	53.58	1.46	7.33	3.20	0.96	0.2573	0.0137	9.64	20	34	0	6.5	6.5	6.5	3
53C	1.17	76.33	10.57	1.17	33.9	15.4	50.7	18.49	2.03	0.67	15.55	6.17	0	14.65	57.88	2.94	7.28	1.03	2.20	0.5756	0.0370	8.48	19.5	53.5	4	6.5	6	6.5	17
52	0.23	76.50	10.56	1.61	18.6	15.4	66.0	4.97	0.89	0.13	4.36	2.13	897	4.18	49.09	0.61	7.24	1.94	1.21	0.0781	0.1018	2.05	33	14	0	9	7	4.5	3

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
51	0.88	45.12	6.65	0.97	19.4	10.4	70.2	15.94	1.57	0.82	12.71	3.50	287	12.31	71.57	3.23	6.78	2.36	1.86	0.2617	0.0206	8.81	20	65	3	5	6	6	7
50	0.76	77.29	10.29	1.22	17.0	16.8	66.2	7.82	1.17	0.56	7.26	3.13	493	6.67	53.09	0.56	7.51	1.96	1.01	0.2567	0.0354	3.54	27	7	0	11	10.5	7	4
49	0.71	75.97*	10.53*	2.00*	19.2	23.3	57.5	7.71	0.92	0.88	6.78	2.59	435	6.23	58.45	0.93	7.31	1.35	0.82	0.3016	0.0445	3.64	28	33	6	7	6	4.5	3
48	0.85	43.53	7.11	0.99	18.0	11.7	70.3	10.62	1.28	0.62	9.66	4.08	266	9.29	56.08	0.96	6.12	2.37	1.53	0.2525	0.0261	5.21	30	28	0	8	7	6	3
47	1.02	66.60	9.51	1.14	8.9	7.8	83.3	14.31	1.26	0.49	9.42	2.95	363	8.74	66.25	4.89	7.00	4.99	1.13	0.1702	0.0181	5.79	13	84.5	4	5	5	6	2.5
46	0.54	74.04	10.73	1.40	13.1	5.2	81.7	9.96	1.24	0.29	7.60	3.59	582	7.20	50.15	2.36	6.90	4.46	2.52	0.0989	0.0130	3.61	23	45	0	7	8	8	3.5
45	0.64	68.10	9.89	0.82	9.3	4.3	86.4	11.02	0.96	1.13	6.71	1.82	168	6.27	70.99	4.31	6.89	6.37	2.17	0.0868	0.0129	4.45	17.5	96	3	6.5	5.5	2.5	4
44	0.18	69.46	9.61	1.31	15.0	5.3	79.7	9.13	0.29	0.00	1.61	0.61	142	1.48	58.92	7.52	7.23	3.93	2.84	0.0365	0.0227	0.87	4	8	169	3	2.5	5	0
43	0.26	71.32	9.85	0.16	6.9	0.8	92.3	6.75	0.53	0.04	2.26	0.79	689	2.08	61.93	4.49	7.24	12.12	9.16	0.0198	0.0088	1.29	20	32.5	18	5	3	2.5	2?
42	0.23	52.22	7.16	0.43	8.7	6.1	85.2	5.68	0.59	0.28	2.49	1.13	840	2.34	51.79	3.19	7.29	5.76	1.43	0.0414	0.0166	1.21	18	24	9	6	5	2	2?
41	0.43	48.11	6.74	1.35	15.1	11.3	73.6	6.65	0.80	0.46	4.27	1.84	686	4.06	54.71	2.38	7.14	2.78	1.33	0.1136	0.0266	2.22	25.5	30.5	2.5	9	6	2.5	2.5
40	0.57	75.19	9.50	0.51	8.7	6.8	84.5	6.71	0.92	0.70	5.70	2.16	1080	5.27	59.02	1.01	7.92	5.45	1.29	0.0884	0.0155	3.11	32	23	0	7	6.5	2.5	7
39	0.20	39.57	4.90	0.00	4.8	5.6	89.6	10.56	0.26	0.01	1.20	1.02	649	1.12	9.01	9.36	8.08	8.63	0.84	0.0208	0.0173	0.10	5	3	150	2.5	0	0	0
38	0.24	74.74	9.24	1.42	10.0	4.4	85.6	3.69	0.75	0.12	2.70	1.38	1247	2.52	45.26	0.99	8.09	5.95	2.24	0.0345	0.0128	1.14	50.5	14.5	4	7.5	7	4.5	0
37	0.60	76.82	9.91	0.35	12.4	7.1	80.5	8.21	1.47	1.69	7.80	3.18	2224	7.34	56.67	0.41	7.75	4.12	1.74	0.1172	0.0150	4.15	36	6	0	9.5	11.5	6.5	4
36	0.53	68.31	8.97	0.36	15.5	9.9	74.6	5.06	1.09	0.12*	4.78	1.83	1605	4.56	59.82	0.28	7.62	2.94	1.56	0.0839	0.0176	2.73	35	7	0	9.5	10.5	5	8
35	0.47	47.33	6.22	0.62	17.7	14.1	68.2	9.57	1.33	0.10*	7.75	2.68	1393	7.53	64.39	1.82	7.61	2.14	1.25	0.1496	0.0193	4.85	25	38	0	7.5	9.5	4	4.5
34	0.32	73.72	9.64	0.06	12.5	6.9	80.6	9.59	1.48	1.03*	6.91	3.39	2013	6.53	48.06	2.68	7.65	4.16	1.82	0.1007	0.0145	3.14	39	13	0	6.5	10.5	3	5
33	0.49	72.07	9.43	0.00	8.2	8.4	83.4	9.48	1.55	0.33*	7.99	3.29	5723	7.64	56.92	1.49	7.64	5.03	0.98	0.0813	0.0102	4.35	34.5	0	0	6	6	5	3
32	0.49	74.07	9.28	0.65	6.4	10.7	82.9	16.62	0.79*	0.18*	6.03	0.17	4236	5.67	97.00	10.59	7.98	4.83	0.59	0.0840	0.0139	5.50	3	12	158	0	0	2.5	0
31	0.80	75.94	9.67	0.85	14.9	12.7	72.4	5.37*	1.12*	0.32*	5.48*	2.66	5200	4.87	45.40	0.00	7.85	2.45	1.17	0.2364	0.0431	2.21	37	4	0	10	11.5	6	3
30	0.95	78.52	9.89	0.79	22.8	17.9	59.3	14.08	1.73	0.18*	11.91	4.12	1232	11.16	63.10	2.17	7.94	1.46	1.27	0.3863	0.0324	7.04	23.5	20	0	7.5	11.5	6	7
29	0.48	75.56	9.59	0.00	14.7	13.6	71.7	4.55	1.01	0.20*	3.97	1.91	1098	3.61	47.05	0.58	7.88	2.54	1.08	0.1381	0.0348	1.70	39	0	0	9	11.5	5	3.
28	0.42	46.51	6.30	0.96	13.0	11.5	75.5	4.26	0.93	0.15*	3.80	2.30	1003	3.61	36.20	0.46	7.38	3.09	1.13	0.1025	0.0270	1.31	38	7	0	8	13	4.5	4
27	0.64	78.51	10.12	0.51	10.6	14.2	75.2	12.52	1.55	0.21*	10.50	3.91	3171	9.84	60.27	2.02	7.76	3.03	0.75	0.2083	0.0198	5.93	37.5	8.5	0	6	10.5	7.5	4
26	0.26	74.28	9.17	0.14	28.1	3.6	68.3	3.38	0.74	0.13*	3.23	1.27	2656	3.04	58.18	0.15	8.10	2.15	7.72	0.0826	0.0256	1.77	41	6	0	4.5	7.5	3.5	3
25	0.38	73.47	9.37	0.30	16.4	3.8	79.8	4.21	0.92	0.24*	3.45	1.30	3599	3.17	59.00	0.76	7.84	3.95	4.25	0.0767	0.0222	1.87	22.5	36.5	0	5	11	6	4
24	0.59	75.46	9.49	0.63	26.7	5.6	67.7	8.04	1.48	0.16*	7.30	3.62	2832	6.86	47.19	0.74	7.95	2.10	4.72	0.1906	0.0261	3.24	32.5	7	0	7	15	6	4
23	0.47	74.18	9.33	0.29	18.9	6.0	75.1	5.96	1.21	0.15*	5.36	2.10	2282	5.01	58.09	0.60	7.95	3.03	3.16	0.1166	0.0218	2.91	38	4.	0	9	12	5	3
22	0.18	64.87	8.54	1.02	37.3	11.1	51.6	3.53*	0.82*	0.22*	4.05*	1.59	3109	3.93	59.57	0.00	7.60	1.07	3.37	0.0871	0.0215	2.34	34	4.5	0	8.5	11.5	5	0
21	0.28	72.33	9.18	0.00	10.9	6.2	82.9	2.73*	0.96*	0.39*	3.73*	1.18	2606	3.53	66.54	0.00	7.88	4.88	1.76	0.0476	0.0128	2.35	34	6	2.5	8	15	5.5	0
20	0.53	75.50	9.67	0.29	14.6	6.4	79.0	7.08	1.13	0.20*	4.75	2.11	1465	4.35	51.49	2.33	7.81	3.76	2.27	0.1112	0.0234	2.24	22.5	29.5	0	6	10	5	0
19	0.77	47.95	6.64	0.37	10.5	5.6	83.9	6.31*	1.27*	0.43*	6.34*	2.29	1477	5.97	61.65	0.00	7.21	5.23	1.87	0.1237	0.0195	3.68	24	9	0.	8.5	12.5	4.5	4
18	0.23	56.54	8.08	0.95	13.2	9.1	77.7	11.21	0.49	0.00	2.03	1.30	1165	1.90	31.58	9.18	7.00	3.48	1.44	0.0513	0.0253	0.60	5	5	80	3.	4.5	4.	0
17	0.63	74.65	9.59	0.64	16.5	7.9	75.6	6.57*	1.09*	0.66*	6.69*	2.46	1806	6.22	60.45	0.00	7.78	3.10	2.08	0.1537	0.0230	3.76	23.5	17.5	2	9.5	12	3	3
16	0.55	76.71	10.21	0.11	26.8	11.5	61.7	9.06*	1.41	0.29*	8.64*	3.41	1966	8.22	58.51	0.42	7.51	1.61	2.34	0.2104	0.0244	4.81	21	18	0	8	13.5	3	3.5

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
15	0.63	80.23	10.24	0.20	19.5	18.5	62.0	10.48	1.59	0.12	9.66	3.07	1573	9.16	66.47	0.82	7.83	1.63	1.05	0.2395	0.0248	6.09	29.5	14	0	11	14.5	6	4
14	0.27	76.69	10.03	0.22	5.9	13.0	81.1	4.73*	1.05*	0.13*	5.84*	1,84	1567	5.63	67.34	0.00	7.65	4.30	0.45	0.0509	0.0087	3.79	37.5	12.5	0	8.5	13	1.5	3
13	0.58	60.34	9.31	0.76	18.2	14.1	67.7	10.33	1.40	0.04*	8.44	2.38	1597	8.09	70.58	1.89	6.48	2.10	1.28	0.1872	0.0222	5.71	21	35.5	3	8	11	4	4
12	0.19	77.86	9.94	0.60	18.0	11.2	70.8	3.73	0.74	0.26*	3.41	1.72	1475	3.26	47.27	0.32	7.83	2.43	1.60	0.0555	0.0163	1.54	41.5	10.5	5.5	7	8	8	9
11	0.29	76.28	10.16	0.85	10.5	15.4	74.1	22.97	0.62	0.03	4.68	1.17	826	4.46	73.76	18.29?	7.51	2.86	0.68	0.0751	0.0160	3.29	3	3.5	143	3.	3	4	0
10	0.37	56.07	7.64	1.20	15.8	16.3	67.9	6.12	1.25	0.57*	5.79	2.30	1338	5.58	58.80	0.33	7.34	2.12	0.96	0.1185	0.0205	3.28	28.5	6	6	12	11	6	0
9	0.45	80.32	10.34	0.58	21.4	17.8	60.8	7.55*	1.32*	0.17*	7.65*	3.15	5997	7.29	56.78	0.00	7.77	1.55	1.20	0.1761	0,0230	4.14	36	9	3	5	13.5	5	0
8	0.34	75.62	10.25	0.75	17.9	9.9	72.2	3.92*	1.09*	0.45*	5.01*	1.78	4886	4.75	62.55	0.00	7.39	2.60	1.80	0.0944	0.0188	2.97	26	0	0	11	16	4	3
7	0.30	80.46	10.63	0.75	18.0	17.9	64.1	5.26*	1.09	0.26*	5.31*	2.48	1606	5.07	51.08	0.00	7.57	1.78	1.00	0.1078	0.0203	2.59	34	4	0	9	13	3.5	4
6	1.08	78.81	10.59	1.23	19.2	14.9	65.9	22.52	2.86	0.69*	20.76	7.11	3504	19.91	64.29	1.76	7.44	1.93	1.28	0.3680	0.0177	12.80	21.5	30	0	7.5	15	12.5	5
5	0.15	54.12	8.28	1.80	19.4	13.2	67.4	13.66	0.41	0.00*	3.15	1.43	0	3.07	53.41	10.51	6.54	2.07	1.47	0.0488	0.0155	1.64	3	0	199	0	0	2.5	0
4A	0.85	77.14	10.27	0.65	23.1	16.6	60.3	7.09*	1.21	0.54*	9.62*	3.22	0	8.96	64.08	0.00	7.51	1.52	1.38	0.3370	0.0350	5.74	23.5	14	2	9.5	12	8	12
4	0.32	38.43	5.76	1.07	17.3	15.3	67.4	4.64*	1.22*	0.18*	5.26*	1.36	214	5.14	73.53	0.00	6.67	2.06	1.12	0.1044	0.0198	3.78	29	5	4	11.5	13	5	0
3A	0.60	80.12	10.42	0.33	11.1	33.4	55.5	11.30	1.71	0.28*	10.95	4.31	0	10.47	58.83	0.35	7.69	0.50	0.20	0.3995	0.0365	6.16	28.5	14	0	8.5	16	7.5	3
2A	0.50	70.02	10.05*	1.13*	18.1	17.6	64.3	8.66*	1.49	0.24*	8.75*	3.78	0	8.40	55.00	0.00	6.97	1.80	1.03	0.1786	0.0204	4.62	28	12	3	9.5	12.5	7	4
2	0.27	80.24	10.16*	1.23*	27.1	15.9	57.0	5.29	1.17	0.20	4.83	1.91	19	4.61	58.59	0.46	7.90	1.32	1.70	0.1162	0.0241	2.70	29	10	0	10	13.5	4	3
1	0.95	77.28	10.11	0.72	17.5	17.3	65.2	16.93	2.02	0.14	14.88	3.66	0	14.15	74.13	2.05	7.64	1.87	1.01	0.3307	0.0222	10.49	16.5	44	0	6	10	6.5	7

TABLE 76. EXPERIMENTAL DATA FOR KIMMERIDGE CLAY BETWEEN HORBARROW BAY - CHAPMAN'S POOL.

16. FACTA ADDITA TARDISSIME

16a. Lam and Porter have recently published an account of "the distribution of palynomorphs in the Jurassic rocks of the Brora outlier, N.E. Scotland" (Q.J.G.S. v. 134 pp. 45 - 55, 1977) where 36 samples were analysed for the Kimmeridgian section. (c. 737.5 metres.)
The microplankton was low throughout and a fluctuating marine influence, with at least one major (Middle Kimmeridgian) transgression and numerous oscillations, was deduced. An abundance of bisaccate pollen was taken to support (either the proximity of an adjacent land mass or) strong offshore currents capable of bringing pollen grains into the depositional area. A greater trilete spore abundance in the Lower and Middle Kimmeridgian was deduced to infer a widening of the marine basin and restriction of marginal swamp floras from the Wheatleyensis zone upward. Finally, recycled Carboniferous spore genera mainly in the Lower Kimmeridgian indicated erosion of Carboniferous sediments.

16b. The postulated reworking of a tar sand exposure to explain the Wealden oil conglomerates perhaps necessitates an explanation for the formation of the parent tar sand itself. In this respect the observed characteristics for "tar sands and supergiant oil fields" (Demaison, B.A.A.P.G., v. 61. n. 11. pp. 1950 - 1961, 1977) may be applicable. Common features for their formation include:-

1) stratigraphic control in combination with structure
2) marginal marine or non-marine host sediments
3) thermally immature host sediments without associated local source beds

and,

4) the geochemical composition of the accumulation

Such features result from

a) a paleodelta system (1 and 2); comprising organic rich source beds and very far reaching, interfingering, (high Ø and K, fluvial) carrier sandstones of foreland (and exceptionally intermountain) basins (3ii and I)
b) a widespread regional cap (e.g. marine shale I); restraining vertical fluid escape from the underlying paleodelta system and channelling fluid movement laterally to the edges of the basin.
c) a homocline; with an updip stratigraphic convergence and preferably low amplitude arching plunging into the basin (1)

and,

d) the degradation of the (medium gravity, fluid) oils by water-washing (loss of light hydrocarbons, especially the aromatics) and bacterial action (loss of n-alkanes) to heavy, sour tars (increased density and sulphur content; the latter being tied to the more bacteria-resistant heavy and complex cyclic compounds). These two phenomena are ubiquitous wherever a crude is in contact with oxygen and bacteria-carrying meteoric water at temperatures less than 200°F ("tar mat" invades the accumulation from the oil - water contact downwards) and the situation is most favourable in "Foreland basins (cf. rift basins) (1 and 3).

In summary, it is the chance of undegraded oil, still remaining in the reservoir down dip to the tar sand, which can provoke exploration of such unconventional prospects.

16c. Using a pyrolysis - GLC - MS technique based upon Larter (Ph.D. In prep. Univ. Newcastle 1978), Solli has finger-printed twenty-one kerogen concentrates/macerates of this study. Pyrograms of hand-picked coal macerals have allowed a framework to be built around algal (type I), exinite (type II) and vitrinite (type III); in which natural kerogens can be classified and between which "hybrids" can be placed.

Table 77 designates the basic kerogen types (according to the van Krevelen diagram, Figure 26) which the Kimmeridge Clay samples most closely resemble through their pyrograms. For comparison, the kerogen types discerned through this study by analogy to weight loss at 900°C is added. The disagreement is disturbing and currently puzzling and perhaps one conceivable explanation is the lack of programmed heating to a reduced temperature (600°C) for a weight loss determination (?).

Figure III is a typical algal/kerogen type I pyrogram where pronounced alkene - alkane homologies provide a 'clean' picture; the aromatic background is subdued. Figure 114 shows a typical vitrinite/kerogen type III pyrogram where pronounced aromatics cause clustering about the alkene - alkane homologies. Figure 112 is the intermediate exinite/type II.

Comparison of Figure 112 and Figure 113 illustrates the feasibility of utilising (extracted) whole rock samples instead of (extracted) kerogen isolates and hence offers the chance to dispense with the laborious maceration procedure.

16d. It is interesting to appreciate that chemical bond energy requirements suggest the extreme (highly aliphatic) "algal type" kerogen should not be upheld as the ideal petroleum source material on a kerogen degradation

Sample	Pyrogram Type	Weight Loss Analogue Type
KC 1 SHALE	III	Algal - Alginite
KC 5 CMTST	III	Algal
KC 11 CMTST	III	Algal - Alginite
KC 15 SHALE	II	Algal - Alginite
KC 25 SHALE	II	Algal - Alginite
KC 32 CMTST	III	Alginite
KC 36 SHALE	III	Algal
KC 44 CMTST	I	Algal - Alginite
KC 53A OIL SHALE	III	Algal
KC 55A OIL SHALE	III	Algal - Alginite
KC 55B WHITE BAND	III	Alginite
KC 58 SHALE	III	Algal
KC 61 CMTST	III	Leiptinitic
KC 67 WHITE BAND	III - II	Algal - Alginite
KC 70 WHITE BAND	II	Algal - Alginite
KC 74 WHITE BAND	II	Alginite
KC 78 SHALE	II	Algal - Alginite
KC 84 SHALE	II	Alginite
KC 92 OIL SHALE	I	Leiptinitic - Algal
KC 108 SHALE	I	Algal - Alginite
KC 116 SHALE	I	Algal - Alginite

TABLE 77. SUMMARY OF PYROLYSIS - GLC - MS KEROGEN ANALYSES contrasted with types as deduced from percentage carbon conversion analogy to weight loss.

It can be noted here that a kerogen,whose H/C & O/C ratios indicated a leiptinitic structure,was suggested to be a highly aliphatic alginite by pyrolysis-hydrogenation-chromatography!? McKirdy,Kantsler,McHugh & Tardif. In prep. Peat.Written Comm. 1978.

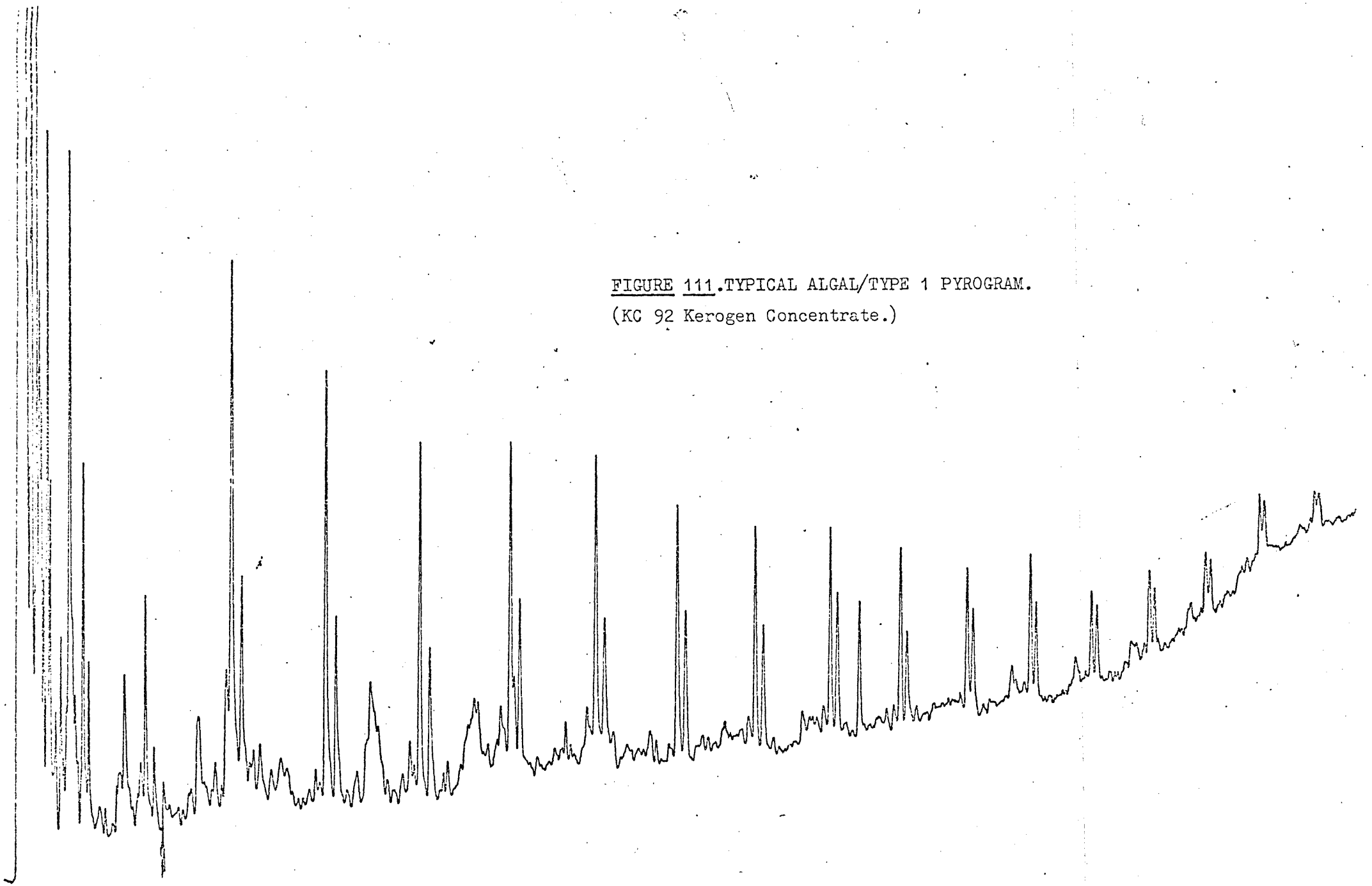


FIGURE 111.TYPICAL ALGAL/TYPE 1 PYROGRAM.
(KC 92 Kerogen Concentrate.)

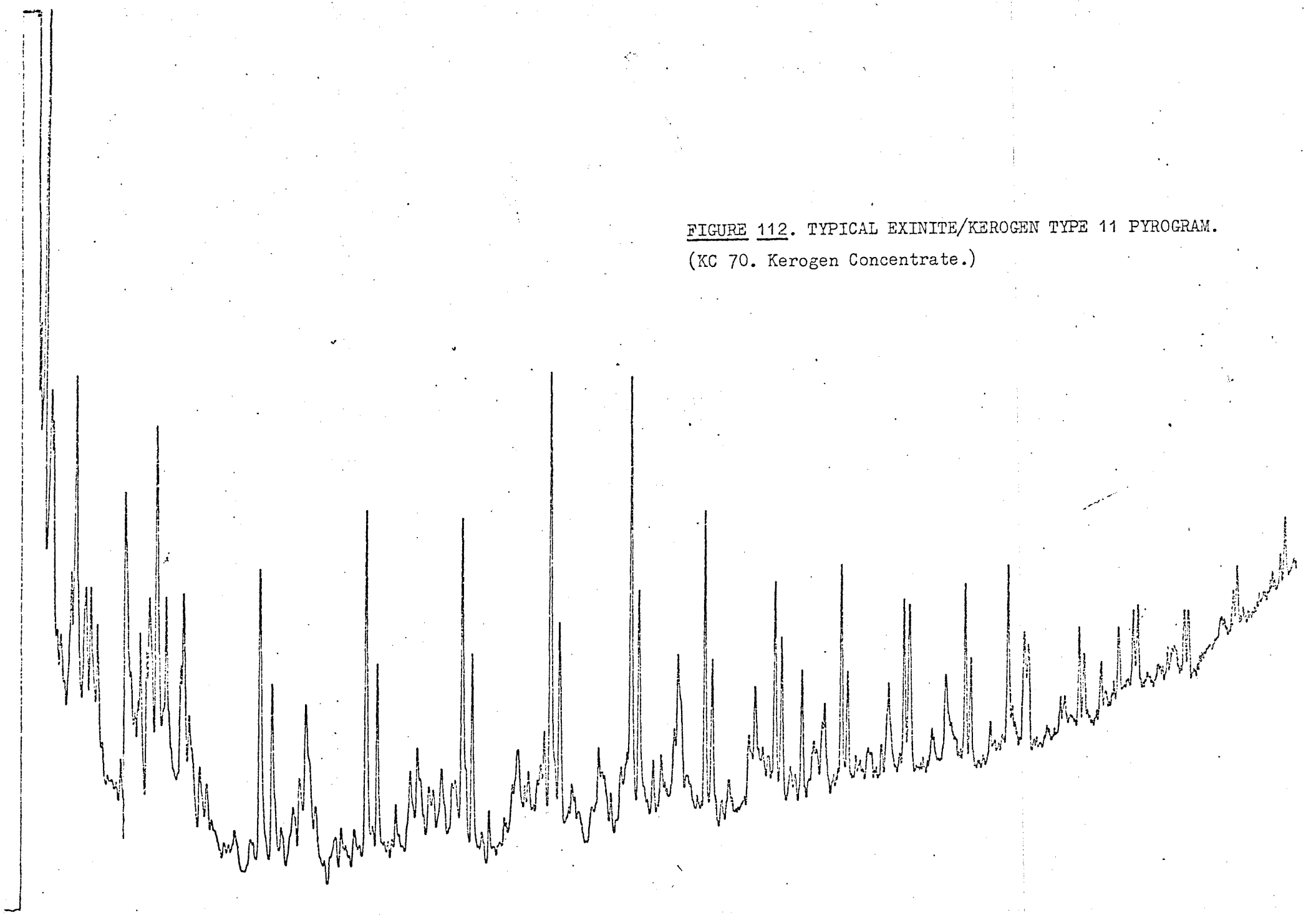
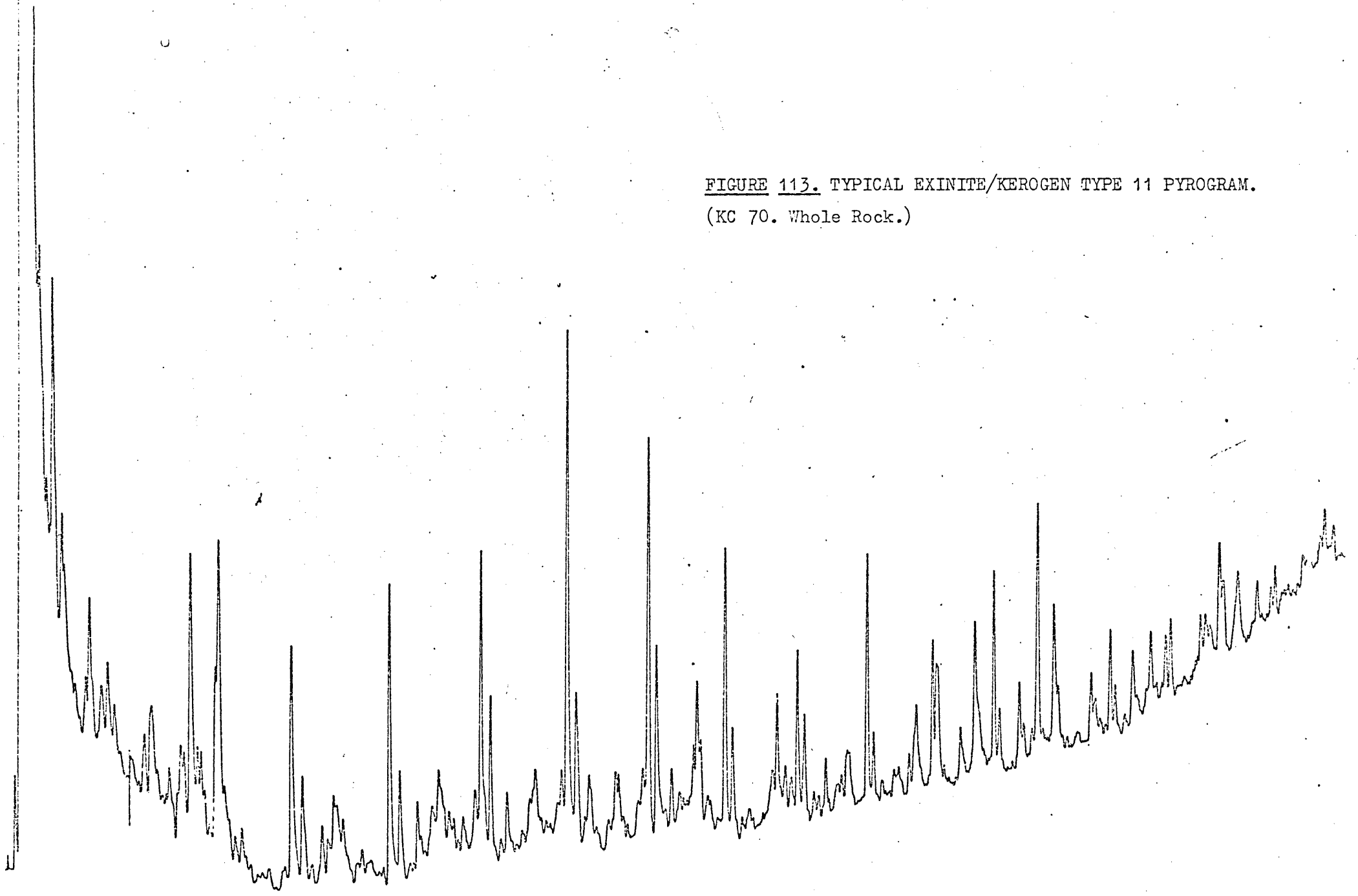


FIGURE 112. TYPICAL EXINITE/KEROGEN TYPE 11 PYROGRAM.
(KC 70. Kerogen Concentrate.)

FIGURE 113. TYPICAL EXINITE/KEROGEN TYPE 11 PYROGRAM.
(KC 70. Whole Rock.)



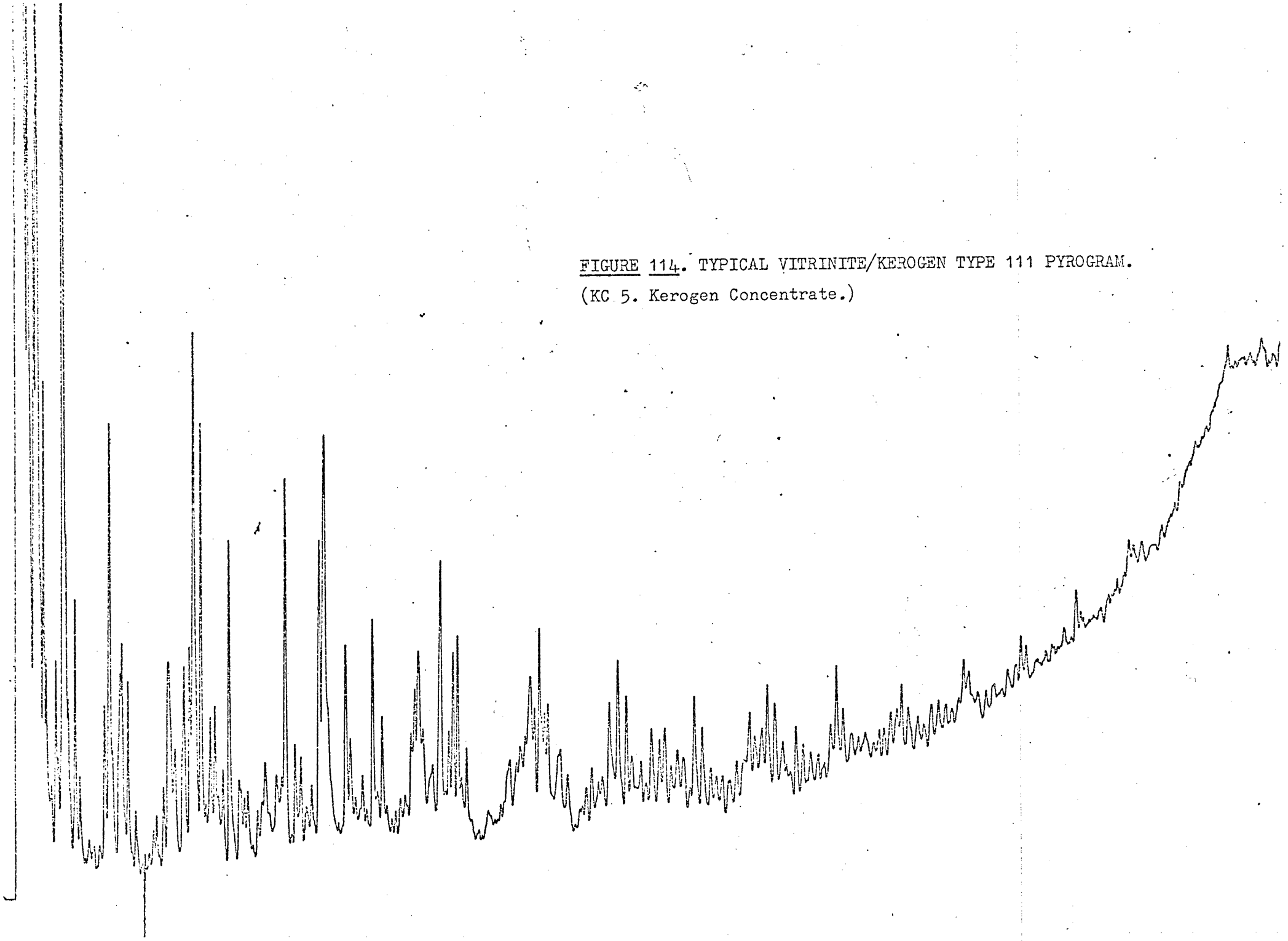


FIGURE 114. TYPICAL VITRINITE/KEROGEN TYPE 111 PYROGRAM.
(KC 5. Kerogen Concentrate.)

mechanism alone. Larter (Ph.D. In prep. Univ. Newcastle 1978) can show that induced "pure algal" kerogen degradations are mimicked by the cracking of polythene where relatively high energies* are required. This is predictable from the lack of appropriate residual structured possibilities for stabilisation of the fragmented molecules. (Charged species can not be neutralised owing to the lack of aromatics). Converseley vitrinitic kerogens contain (abundant) aromatics to assist natural hydrocarbon evolution/cracking and generate at reduced temperatures/ lower energy. (Independently this point has been illustrated by work on coal macerals where vitrinite gives the most soluble extract, relative to exinite and algal matter at the same level of carbonisation. Allen Ph.D. 1975 Unpub. Univ. Newcastle.) However, the total aliphatic content is low in vitrinites.

Consequently it seems from practical aspects that exinite type kerogens should perhaps be regarded as the most desired oil-generating candidates; especially for "immature - mature" (low energy)* situations, since their total hydrocarbon generating capacity will exceed those of the other kerogen types in a quality versus quantity compromise (?). Algal kerogens can of course remain attractive however through their possible association with primary lipid accumulation but deltas appear more frequent in time and space than unprecedent algal blooms!

In conclusion to the controversy invoked under 16c. and as mentioned in the text, future work must provide more information upon kerogen at a molecular level. (Davies and Solli. Priv. Discussion.)

ALPHABETICAL LIST OF REFERENCES

KEY:

BAAPG:	Bulletin of the American Association of Petroleum
Geochim:	Geochimica et Cosmochimica Acta
HMSO:	Her Majesty's Stationery Office
IGS:	Institute of Geological Sciences
JIPT:	Journal of the Institute of Petroleum Technology
PGA:	Proceedings of the Geologists' Association
QJGS:	Quarterly Journal of the Geological Society of London

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ERRATA

FIGURE 1: ANNOTATED FLOW DIAGRAM TO ILLUSTRATE POSSIBLE DERIVATIONS, DISTRIBUTIONS AND CONVERSIONS OF ORGANIC MATTER WITHIN SEDIMENTARY ENVIRONMENTS AND SEDIMENTS [UNDER NORMAL CONDITIONS OF BURIAL] R.A. DAVIES 1978

TERRESTRIAL ENVIRONMENT

AQUATIC ENVIRONMENT

ATMOSPHERIC CARBON DIOXIDE[1]

LIVING PLANTS[1,2] ANIMALS[1,2]

RESPIRATION[1] ASSIMILATION[1]

SOIL WATER

[0.7x10^18 GMS.] DISSOLVED [C & CO_2 IN OCEANS][16]

SURFACE LAYERS[1] —ASSIMILATION→ PHYTOPLANKTON[1,2]

ONLY c2% OF POPULATION REACHES SEA FLOOR IN THE SHALLOWS; c0.02% IN THE OPEN SEA[3]

ZOOPLANKTON & FISH[1,2]

SEEPAGE

SOIL RESPIRATION[1] EROSION RE-DEPOSITION

INITIAL DEAD ORGANIC MATTER[1,2] — EROSION → ALLOCHTHONOUS ORGANIC MATTER

AFFECTED BY MICRO-ORGANISMS [FUNGI & BACTERIA][3] IN-FAUNA/FLORA & WEATHERING, POSSIBLE EARLY CATALYTIC TRANSFORMATION[38]

TRANSPORTED & OR RECYCLED INTO DEPOSITIONAL ENVIRONMENT[3]; ACCOUNTS FOR MORE OF TOTAL ORGANICS IF SEDIMENTATION IS FAST[22]

BIOGENIC METHANE

AUTOCHTHONOUS ORGANIC MATTER — BIOLOGICAL PRODUCTS WITHIN DEPOSITIONAL ENVIRONMENT[3]; ACCOUNTS FOR MORE OF TOTAL ORGANICS IF SEDIMENTATION IS SLOW[22]

REDUCTION[1] BICARBONATES & CARBONATES → CARBON DIOXIDE[1] (c70% C LOST AS CARBONATES)

VARYING CONTRIBUTIONS FROM EITHER [DICTATED BY DISTANCE FROM LAND &/OR BASIN CONFIGURATION[24]] CONTROLS TYPE, AMOUNT & DISTRIBUTION[3] OF

INITIAL DEAD ORGANIC MATTER[1,2]

WHICH IS COMPRISED OF FOUR BASIC TYPES OF BIOPOLYMERS[16]:

	LIPIDS	PROTEINS	CARBOHYDRATES	LIGNIN-HUMICS	
				3,6,12,16,19	
SPRUCE WOOD	4%	1%	66%	29%	
OAK LEAVES	4%	5%	44%	32%	
SCOTS PINE NEEDLES	24%	7%	41%	15%	16
LYCOPODIUM SPORES	50%	8%	42%	—	
DIATOMS	8%	29%	63%	—	
PHYTOPLANKTON	11%	15%	66%	—	
COPEPODS	8%	65%	22%	—	11
HIGHER INVERTEBRATES	10%	70%	20%	—	9
% CARBON	80	53	44	63	
% HYDROGEN	10	7	6	5	
% SULPHUR	—	2	—	0.1	16
% NITROGEN	—	16	—	0.3	
% OXYGEN	10	22	50	31	
ORDER OF ABUNDANCE IN RECENT MARINE SEDIMENTS:	C>L≫SC	L>SC>C	L≈ 2x SC or C	C≫L≫SC	32

[C= CLAY, L= LIMESTONE, SC= SHELLY CARBONATE]

MOST SIMILAR COMPOUNDS TO NATURALLY OCCURING HYDROCARBONS[27]

LIPIDS BROAD TERM INCLUDES OIL-SOLUBLE/WATER-INSOLUBLE FATS [USUALLY ESTERS OF FATTY ACIDS WITH GLYCOL- OR SIMPLE OR MIXED GLYCERIDES[26]], WAXES [ESTERS OF ALCOHOLS OF STEROL-SERIES, HIGH M.W. EVEN NUMBERED ALIPHATIC ALCOHOLS C-16 —C-36, PRIMARY KETONIC ALCOHOLS[34],ETC], FATTY ACIDS, STEROLS, PIGMENTS, TERPENOIDS, ETC[16]

PROTEINS ESSENTIALLY POLYPEPTIDES OF THE TYPE: $-C-N-C-C-N-C-C-N-$ (H, O, R) WITH FATS & CARBOHYDRATES IS VERY COMPLEX SINCE, FOR EXAMPLE, WITHOUT CONSIDERING OPTICAL ACTIVITY, A DECAPEPTIDE INWHICH ALL 10 CONSTITUENT AMINO ACIDS ARE DIFFERENT HAS 10! OR 3628800 ISOMERS ONE OF THE THREE MAIN CLASSES OF FOODS

CARBOHYDRATES NAMED AS SUCH FROM 'HYDRATE DE CARBON' AS THEY USUALLY CONTAIN HYDROGEN & OXYGEN IN THE SAME PROPORTION AS WATER— GENERAL FORMULA IS $C_x[H_2O]_y$ — BUT EXCEPTIONS DO OCCUR [EG. KHAMNOHEXOSE $C_7H_{14}O_6$ IS A CARBOHYDRATE; CH_2O IS FORMALDEHYDE; ETC] ALL CARBOHYDRATES ARE POLYHYDROXY ALDEHYDES OR KETONES OR SUBSTANCES WHICH YEILD THESE ON HYDROLYSIS

LIGNIN-HUMICS LIGNIN OCCURS WITH CELLULOSE IN WOODY PLANTS & IS SOMEWHAT SIMILAR TO CARBOHYDRATES IN COMPOSITION. HUMIC SUBSTANCES ARE PRODUCED BY THE ANOXIC DECAY OF WOODY MATERIAL & ARE ISOLATED FROM SEDIMENTS BY ALKALINE SOLUTIONS[28]

WATER EXCHANGE[1] SHALLOW / DEEP

DESTRUCTION, REWORKING & CONTRIBUTION OF ORGANICS BY EPI/INFAUNA, MICRO ORGANISMS[4,5,6,12,13,16,] & INORGANIC REACTION-HYDROLYSIS[21] TO LEAVE <1% OF ORIGINAL ORGANICS DEPOSITED IN SEDIMENTARY BASIN[15]

RECENT SEDIMENT HAS AN AVERAGE 2.5% BY WEIGHT OF ORGANIC MATTER[9]

SEDIMENT

BIOMONOMERS[16]

SUGARS, AMINO ACIDS, FATTY ACIDS, PHENOLS[16] [MARINE SAPROPEL: 52%C 6%H 30%O 11%N][9]

→SEEPAGE

GEOPOLYMERS[6,16]

VIA CONDENSATION, POLYMERISATION[9,12,13,14,16], AROMATISATION & CYCLISATION[17]

—1 METRE; c25°C[16,30]—

DIAGENESIS[6,16]

REDUCTION, DECARBOXYLATION, DEAMINATION, CYCLISATION & DEMETHYLATION[16]; EH CONTROLLED[5] & POSSIBLY MINERAL CATALYSED

BITUMEN[6] | KEROGEN[6] | PROTOPETROLEUM[6,16] | METHANE[6]

95-99% OF ALL ORGANIC MATTER IN SEDIMENTS IS KEROGENOUS[7,8,18]

MAX. c0.3% IN SEDIMENTS[25]

→ "DISSEMINATED ORGANIC MATTER"[2]

AS DISSEMINATED PARTICLES, ISOLATED CARBONISED FOSSILS, THIN DEPOSITS ALONG OR INCLINED TO THE BEDDING, IN INTERLAYER POSITIONS WITHIN CLAYS, IN PORE FLUIDS &/OR AS ADSORBED COATINGS/PORE LININGS ON MINERAL GRAINS[23]. 1,200 x 10^{18} GMS. OF CARBON ESTIMATED IN SEDIMENTARY ROCKS[16]. ANCIENT ORGANICS ARE 73%C, 9%H, 14%O & 3%N; SEDS. HAVE 1.5% ORGANIC MATTER[9] [AVERAGES BY WT]

—1000 METRES; c50°C[16]—

INTER-RELATED TIME, TEMPERATURE & PRESSURE GENERATION[6,15,16]

NATURAL COMBUSTION, SEEPAGE &/OR EXPLOITATION

LIQUID WINDOW THIN IN AREAS OF HIGH GEOTHERMAL GRADIENT & THICK IN AREAS OF LOW GEOTHERMAL GRADIENT[8]

RELATIVE CONCENTRATION OF H.M.W. AROMATICS[29]

?COMPLEX FIRST ORDER REACTIONS[6,15] RELATIVE CONCENTRATION OF L.M.W. ALIPHATICS[29] THERMAL CRACKING[16]

NATURAL COMBUSTION, MIGRATION &/OR EXPLOITATION

'ASPHALTS'[1] AND/OR COALS[1] — 15x10^{18} GMS. OF C[16] — AND/OR[10] PETROLEUMS[1] [GEOMONOMERS][16]

80%C 10%H 4%S 1%N 2%O[16]

82%C 13%H 2%S 1%N 2%O[16]. 201 x 10^{18} GMS OF C[16]; ABOUT 0.003 — 0.03% OF ORIGINALLY INCORPORATED ORGANIC MATTER[20] (?)

QUALITY & QUANTITY CONTROLLED BY AMOUNT, TYPE & THERMAL MATURITY OF ORGANICS[5,6]

—6,000 METRES; c175°C[16]—

METAMORPHIC/THERMAL DESTRUCTION [REDUCTION][31]

CH_4 METHANE + GRAPHITE, C

THERMALLY INDESTRUCTIBLE BUT ATTACKED BY O & S[5,6] — RESIDUAL[11]

INCREASING BURIAL UNDER NORMAL GEOTHERMAL GRADIENT

COMPILED FROM: 1 BOLIN 1970 2 BAKER 1972 3 MADANI 1977 4 BORDOVSKY 1965a & DEGENS 1967; BOTH IN DUNN 1972 5 MILNER Et al 1977 6 DOW 1977 7 ABELSON 1967 8 PUSEY 9 HOBSON Verb.Comm. 1972 10 GILL Verb.Comm. 1977 11 KARKANIS 1975 12 CORDELL 1972 13 McIVER 1967 14 EGLINTON & CALVIN 1967 15 CONNAN 1974; TISSOT Et al 1974 16 HUNT 1976 17 SOLLI Pers.Comm. 1977 18 DEGENS & REUTER 1962 19 PHILIPPI 1968 20 STOUT 1936; TRASK & PATNODE 1942. ALL IN ERDMAN 1962. 21 ABELSON 1956 22 ALBRECHT Et al 1976 23 CORDELL V. PHILLIPI 1974 24 WAKSMAN 1931 IN BLOXAM 1972 25 TRASK & WU IN PHILIPPI 1968 26 FIESER & FIESER 1956 27 MEINSCHEIN 1959 28 PALACAS Et al 1972 29 HAJI-VASSILIOU & KERR 1973 30 LATSKAYA & ZHABREV 1965 IN DUNN 1972 31 NERUCHEV 1965 IN DUNN 1972 32 DEGENS Priv.Comm. IN ? 33 CATE 1960

ORGANIC MATTER

BITUMENS
SOLUBLE IN CS_2[7]

LIQUID

ALL CRUDES & SEEPS[7]

TYPICAL CRUDE:
82-87% CARBON 12-15% HYDROGEN 0.1-5.5% SULPHUR 0.1-1.5% NITROGEN 0.1-4.5% OXYGEN[2]
30% PARAFFINS 49% NAPHTHENES 15% AROMATICS 6% ASPHALTICS[4]
3% GASOLINE C_4-C_{10} 10% KEROSENE $C_{11}-C_{12}$ 15% GAS OIL $C_{13}-C_{20}$ 20% LUBRICATING OIL $C_{21}-C_{40}$ 24% RESIDIUM $>C_{40}$?

FRACTION	B.P °F	C. NO.	CHIEF COMPONENTS[6]
GAS	≤ 40	1-5	N & S-ALKANES
GASOLINE	40-180	6-10	ARENES ALKANES CYCLO-ALKANES
KEROSENE	180-230	11-12	" " "
DIESEL FUEL	230-405	13-25	" " "
LUBRICANTS	405-515	26-38	ALKANES

A MIXTURE OF HYDROCARBONS CONTAINING SMALL QUANTITIES OF O, S & N-BEARING COMPOUNDS AND TRACES OF METALLIC CONSTITUENTS[3]

MINERAL WAXES

OZOCERITE[7]/OZOKERITE/CERESINE[1]/CERESIN: (KEROS-WAX; OZEIN-TO SMELL)[1] FIRST FOUND AT SLANC, RUSSIA IN 1883[1] BUT OCCURS AS IRREGULAR VEINS[9] IN WASATCH GROUP OF UTAH[7] YELLOW-JET BLACK[7,8] BUT USUALLY DARK BROWN[1] MODERATELY HARD[7] LOW IN HETERO-ATOMS WITH LARGE PERCENTAGE PARA-NAPHTHENIC HYDROCARBONS[7] ESSENTIALLY C-22 — C-29 ALKANE DERIVATIVE[1] MANY VARIETIES (EG: BAIKERITE, CELESTIALITE, HELENITE, MELDARITE & PIETRICIKITE)[8] - VARIABLE M.P. BLEACHED BY HEATING WITH 20-30% CONC. SULPHURIC ACID AT 120°-200°C[8], WHITE VARIETY USED FOR CANDLES[1] CONSIDERED A METAMORPHIC OR POLYMERISED PRODUCT OF PETRO-LEUM[7]/DEHYDRATION PRODUCT OF PARAFFIN-BASE CRUDE[1]? (SYNONYMS: ADER WAX/EARTH WAX/FOSSIL WAX/MINERAL WAX/NATIVE PARAFFIN[8])

MONTAN WAX[7]/

SCHEERERITE[7]: FOUND IN BROWN COAL AT UZNACH, SWITZERLAND; WHITISH, MONOCLINIC[9] ?POLYMER OF MARSH GAS[9]

HATCHETITTITE[7]/HATCHETTINE/ADIPOCIRE/ADIPOCERITE/MINERAL TALLOW/MOUNTAIN TALLOW/NAPHTHINE[8]: SOFT YELLOW-WHITE PARAFFIN WAX M.P. 55°-65°C IN NATURAL STATE; 75°C WHEN PURE. ?$C_{38}H_{78}$ OCCURS AS VEIN-LIKE MASSES IN IRONSTONE NODULES ASSOCIATED WITH COAL BEARING STRATA OR IN LIMESTONE CAVITIES[8] S.G. = 0.94[9]

SOLID
DIFFICULT FUSIBILTY[7]

ASPHALTITES

BROWN BLACK SOLIDS; EXTREMELY HARD[7] MICROBIALLY ALTERED, WEATHERED OR METAMORPHOSED ASPHALT[8]

GILSONITE/UNITALITE[1]/UNITAHITE[9]: NAMED AFTER S.H. GILSON WHO OWNED FIRST FOUND DEPOSIT IN UNITA MOUNTAIN RANGE OF UTAH & COLORADO[1] BLACK SHINY WITH BROWN STREAK & CONCHOIDAL FRACTURE[8] ASPHALTENES ARE CHIEF CONSTITUENTS[2]

GRAHAMITE: NAMED AFTER J.A & J.C GRAHAM WHO OWNED MINE IN WHICH IT WAS FIRST FOUND KNOWN IN WEST VIRGINIA OKLAHOMA CUBA & MEXICO[1] BLACK VARIABLE LUSTRE WITH BLACK STREAK, HIGH SPECIFIC GRAVITY & HIGH FIXED CARBON[8] OCCURS IN SUBSURFACE LENSES & DIAGONAL FAULTS; NOT ASSOCIATED WITH OIL SHALES[7,1,15][9]

GLANCE PITCH/MANJAK[1]: FOUND IN BARBADOS, CUBA, MEXICO, ARGENTINA, RUSSIA, ETC, SIMILAR TO GILSONITE BUT HIGHER SP. GRAVITY & FIXED CARBON AND FUSES BETWEEN 230° 250°F[8] ASPHALTENES ARE CHIEF CONSTITUENTS[2] RICH IN HETERO-ATOMS & MOST PROBABLY HIGHLY AROMATIC; CONSIDERED TO BE A RESIDUE OF PETROLEUM BY EVAPORATION[7]

SOLID
FUSIBLE[7]

ASPHALTS

80-85% CARBON 8.5-11% HYDROGEN 2-8% SULPHUR 0-2% NITROGEN[2]

TABBYTE: FOUND IN SERIES OF VEINS IN TABBY CANYON MINE, UTAH. NEAR SOLID[7]

LIQUID GILSONITE

ARGULITE

BERMUDEZ PITCH

PYROBITUMENS
INFUSIBLE & ESSENTIALLY INSOLUBLE (<2%) IN CS_2

ASPHALTIC BITUMENS / ASPHALTOIDS[7]

HARDER THAN ASPHALTITES; DECOMPOSE BEFORE MELTING[1] LOW OXYGEN CONTENT[7]

WURTZILITE: NAMED AFTER H. WURTZ. FOUND IN VEINS IN UNITA REGION. ELASTIC[1] BLACK MASSIVE SECTILE; CLOSELY RELATED TO GILSONITE[8]

ELATERITE/MINERAL RUBBER/ELASTIC BITUMEN/LIVERITE/MINERAL CAOUTCHOUC[8]: FIRST FOUND IN DERBYSHIRE LEAD MINE; ELASTIC[1] SOFT BROWN; BECOMES HARD & BRITTLE ON EXPOSURE TO AIR[8]

ALBERTITE/ALBERT COAL/ASPHALTIC COAL[8]: FOUND IN 1-16 FT. THICK VERTICAL FISSURES IN ALBERT SHALE OF ALBERT MINES, HILLSBORO, NEW BRUNSWICK[9] DARK BROWN - BLACK, BRILLIANT LUSTRE, CONCHOIDAL FRACTURE[8] HARDNESS 1-2 S.G. = 1.1[9] HAS LOWER OXYGEN CONTENT THAN BITUMENOUS COAL & HIGHER H/C RATIO THAN ANTHRACITE[7]

IMPSONITE: FOUND IN THE IMPSON VALLEY OKLAHOMA[1] DULL BLACK HACKLY FRACTURE WITH HIGH FIXED CARBON[8] S.G. = 1.175 ?SOLUBLE IN CS_2 TO <35%[9]

INGRAHAMITE: BROWN-BLACK WITH LOWER OXYGEN CONTENT THAN BITUMENOUS COAL & HIGHER H/C RATIO THAN ANTHRACITE[7]

ANTHRAXOLITE[7]: COAL-LIKE, LUSTROUS, HARDNESS = 3-4, S.G. NEARLY 2; SAME TERM USED TO DESCRIBE BITUMENOUS & ANTHRACITIC MATTER OCCURRING AS ENCLOSURES IN IGNEOUS ROCKS[9]

NON-ASPHALTIC BITUMENS[7]

HIGH OXYGEN CONTENT[7]

PEAT: UNCONSOLIDATED SEMI-CARBONISED PLANT REMAINS OF A WATER-SATURATED ENVIRONMENT SUCH AS A BOG OR FEN & OF PERSISTENTLY HIGH MOISTURE CONTENT (AT LEAST 75%) CARBON & OXYGEN CONTENTS ARE ABOUT 60% & 30% RESPECTIVELY. STRUCTURED VEGETAL MATTER OBVIOUS. BURNS FREELY WHEN DRY[8]

LIGNITE: BROWN-BLACK, CONSOLIDATED. CALORIFIC VALUE <8300 BTU/lb, ON MOIST MINERAL FREE BASIS. INTERMEDIATE BETWEEN PEAT & SUB BITUMENOUS COAL[8]

COAL: READILY COMBUSTIBLE WITH >50% BY WEIGHT & >70% BY VOLUME OF CARBONACEOUS MATERIAL; HAS INHERENT MOISTURE; FORMED BY THE COMPACTION & INDURATION OF VARIOUSLY ALTERED PLANT REMAINS[8]

DISPERSED ORGANIC MATTER: (SEE TEXT)

KEROGEN: SEE TEXT & TABLE 37

COMPILED UPON ROGERS Et al, 1974 WITH ADDITIONS AFTER 1 HOBSON, Verb. Comm. 1972 2. LEVORSEN, 1954 3 COLUMBO, Miscell? 4 GEHMAN, Miscell? 5 HUNT, 1976 6 BUSH, Verb. Comm. 1973 7 YEN & SPRANG, 1977 8. AGI GLOSSARY 9 RICE, 1947

FIGURE 2 CLASSIFICATION OF ORGANIC MATTER PERTINENT TO PETROLEUM GEOLOGY

R. A. DAVIES 1978

CHROMATOGRAPHY

THE NUMBER OF POSSIBLE SOLVENTS AND SUBSTRATES IS NOW "STAGGERING" & OFTEN THE MOST SUITABLE COMBIN-ATION IS BASED UPON "TRIAL & ERROR"

ADSORPTION CHROMATOGRAPHY: SOLID STATIONARY PHASE

AS A SEPERATIVE METHOD GENERALLY BETTER FOR SUBSTANCES OF DIFFERENT CHEMICAL TYPES

GAS-SOLID CHROMATOGRAPHY

GASEOUS MOBILE PHASE.

IN 1946 CLAESSON PUBLISHED ONE OF FIRST IMPORTANT ACCOUNTS & PHILLIPS IN 1952 SIMPLIFIED THE APPARATUS; SHOWING IT WAS CAPABLE OF HIGH ACCURACY. MAIN USE IS FOR SEPERATION OF PERMANENT GASES & LOW BOILING MOLECULES SINCE PROLONGED HEATING CAN ALTER THE ACTIVE SITES OF THE SOLID BY LOSS OF CHEMI-SORBED SPECIES OR SINTERING — MOLECULAR MASS LIMIT IS c150 REPRODUCIBILITY FROM BATCH TO BATCH OF ADSORBENT IS DIFFICULT; OTHER DISADVANTAGES INCLUDE TAILING & THE GENERATION OF ARTEFACTS SINCE ACTIVE SOLIDS ARE EFFECTIVE CATALYSTS ADSORBENTS INCLUDE SILICA GEL, ALUMINA, MOLECULAR SIEVES, POROUS POLYMERS ETC.

LIQUID-SOLID CHROMATOGRAPHY

LIQUID MOBILE PHASE

COLUMN/ADSORPTION CHROMATOGRAPHY

THE FIRST SUCH SEPERATIONS WERE ACHEIVED BY THE RUSSIAN BOTANIST TSWETT IN 1903, WHEN CHLOROPHYLL WAS ISOLATED FROM PLANT PIGMENTS USING A CALCIUM CARBONATE ADSORBENT & PETROLEUM ETHER ELUANT, BUT c 25 YEARS ELAPSED BEFORE KUHN Et al REDISCOVERED TECHNIQUE. UP TO 1931 THE METHOD WAS RESTRICTED TO SUBSTANCES SOLUBLE IN FAT SOLVENTS SMALL DIFFERENCES IN THE ADSORPTION FORCES BETWEEN THE VARIOUS COMPONENTS OF THE MIXTURE STATIONARY PHASE & MOBILE PHASE ARE EXPLOITED. SEE TEXT

THIN LAYER CHROMATOGRAPHY

IZMAILOV & STRAIKER, 1938, APPEAR TO BE THE FIRST IN SUGGESTING AN INERT RIGID SUPPORT TO HOLD ADSORBENTS AS THIN LAYERS. MEINHARD & HALL FOLLOWED WITH AN 'OPEN COLUMN' IN 1941 & IN 1951, KIRCHNER Et al SEP-ERATED TERPENES ON 'CHROMOSTRIP'. STAHL IN THE LATE 1950'S DEVELOPED A CONVENIENT WAY OF MAKING PLATES & HE SHOWED THE WIDE APPLICATION OF TLC. NOW EXTREMELY POPULAR. SEE TEXT

ION EXCHANGE CHROMATOGRAPHY

SYNTHETIC RESINS WERE INVENTED IN 1935 & GENERALLY THE ELECTROSTATIC FORCES OF THE COMPONENTS TO BE SEPERATED ARE EXPLOITED UPON THESE. HOWEVER VAN DER WAAL FORCES ALSO OPERATE SINCE NON-IONIC SUBSTANCES CAN SOMETIMES BE SEPERATED [EG. 'SALTING OUT']

GEL [FILTRATION/PERMEATION] CHROMATOGRAPHY

NAMED BY DETERMANN, 1964 [WITH MODIFICATIONS BY PORATH & FLODIN 1954 AND MOORE 1964 RESPECTIVELY]. MARTIN & SYNGE PEFORMED A SEPERATION OF UNCHARGED PARTICLES THROUGH GELS DURING ELECTRO-OSMOSIS IN 1954 AND PORATH & FLODIN INTRODUCED ITS SYSTEMATIC USE IN 1959. THE SOLUTES ARE GENERALLY SEPERATED ACCORDING TO MOLECULAR SIZE AS SMALL MOL-ECULES CAN PENETRATE THE GEL PORES WHILST LARGE MOLECULES PASS BY IN THE MOBILE PHASE. THE PROCESS CAN HOWEVER BE VIEWED AS ONE OF PARTITION SINCE THE MOBILE PHASE SATURATES THE GEL PORES TO MAKE THE MOBILE & STATIONARY PHASES APPEAR THE SAME.

[AFFINITY CHROMATOGRAPHY]

PARTITION CHROMATOGRAPHY: LIQUID STATIONARY PHASE

AS A SEPERATIVE METHOD GENERALLY BETTER FOR SUBSTANCES OF CLOSELY RELATED CHEMICAL TYPES

LIQUID-LIQUID CHROMATOGRAPHY

LIQUID MOBILE PHASE

COLUMN/PARTITION CHROMATOGRAPHY

PIONEERED BY MARTIN & SYNGE IN c1941 WHEN THE STATIONARY PHASE WAS SUPPORTED ON A POROUS MATERIAL PACKING AND THE DIFFERENCES IN SOLUBI-LITIES OF THE COMPONENTS OF A MIXTURE IN THE STATIONARY LIQUID PHASE & MOBILE LIQUID PHASE WERE EXPLOITED. SINCE IT IS DIFFICULT TO COVER ALL OF THE SURFACES OF A SOLID'S PARTICLES ENTIRELY WITH LIQUID SOME ADSORP-TION EFFECTS MUST OCCUR

PAPER CHROMATOGRAPHY

USED BY MARTIN Et al IN 1944 AND No1 WHATMAN FILTER PAPER NOW MOST WIDE-LY USED. ORGANIC SUBSTANCES & INORGANIC IONS CAN BE SEPERATED. ADSORPTION EFFECTS OCCUR BECAUSE OF THE CELLULOSE FIBRES [SEE TEXT]

[ELECTROCHROMATOGRAPHY]

HIGH EFFICIENT/PERFORMANCE/PRESSURE LIQUID CHROMATOGRAPHY

MOST SIGNIFICANT SINCE c1966 AND OF INCREASING USE. 50-100 ATMOSPHERES TYPICAL INITIAL PRESSURE FOR THE MOBILE PHASE. VERY FAST, VERY EFFICIENT & MORE EASILY REPRODUCIBLE. COMPLIMENTARY TO GLC AS THERMALLY UNSTABLE COMPOUNDS CAN BE RESOLVED. SOLID-LIQUID & LIQUID-LIQUID SYSTEMS BOTH POSSIBLE

SUPERCRITICAL PHASE CHROMATOGRAPHY

SIE & RIJNDERS 1969, PROMINENT IN THIS FIELD OF STUDY WHERE HIGH PRESSURE GASES OR SUPERCRITICAL LIQUIDS USED.

GAS-LIQUID CHROMATOGRAPHY

GASEOUS MOBILE PHASE

GAS-LIQUID CHROMATOGRAPHY

PREDICTED IN 1941 BY MARTIN & SYNGE. BUT FIRST ACCOUNT BY MARTIN & JAMES IN 1952. SEE TEXT

CAPILLARY GAS-LIQUID CHROMATOGRAPHY

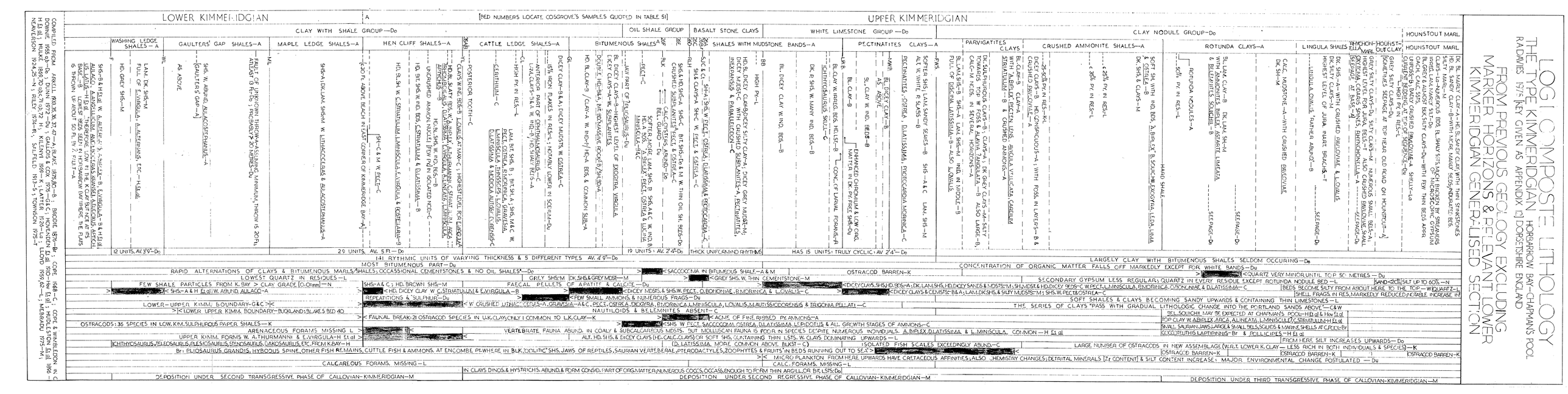
GOLAY INTRODUCED COATED CAPILLARY COLUMNS IN 1957. TODAY EFFICIEN-CIES IN THE ORDER OF ⩾500,000 THEORETICAL PLATES CAN BE USED FOR RAPID AND/OR DIFFICULT ANALYSES SEE TEXT

PYROLYSIS CHROMATOGRAPHY

INVOLATILE MATERIALS SUCH AS POLYMERS ARE THERMALLY DECOMPOSED IN A PRE-COLUMN UNIT [FILAMENT TYPES, CURIE POINT DEVICES, OR MICRO-REACTORS] & THE PRODUCTS ARE IMMEDIATELY SWEPT ONTO COLUMN TO REDUCE SECONDARY REACTIONS [SEE TEXT]

FIGURE 6 A GENERAL CLASSIFICATION OF CHROMATOGRAPHIC METHODS WITH ANNOTATED DETAILS. R.A.DAVIES. 1978

COMPILED FROM STEIN & MOORE 1951; KELLER 1961; DONE Et al 1972 AND STOCK & RICE 1974


LOGI COMPOSITE LITHOLOGY
THE TYPE KIMMERIDGIAN
RADAVIES 1975 (KEY GIVEN AS APPENDIX 1) DORSETSHIRE ENGLAND
HORDARROW BAY-CHAPMAN'S POOL
FROM PREVIOUS GEOLOGY EXCLUDING MARKER HORIZONS & RELEVANT LOWER KIMMERIDGIAN GENERALISED SECTION
LOWER KIMMERIDGIAN
UPPER KIMMERIDGIAN
[RED NUMBERS LOCATE COSGROVE'S SAMPLES QUOTED IN TABLE 5]
CLAY WITH SHALE GROUP—Do
OIL SHALE GROUP
BASALT STONE CLAYS
WHITE LIMESTONE GROUP—Do
CLAY NODULE GROUP—Do
HOUNSTOUT MARL
WASHING LEDGE SHALES—A
GAULTERS' GAP SHALES—A
MAPLE LEDGE SHALES—A
HEN CLIFF SHALES—A
CATTLE LEDGE SHALES—A
BITUMENOUS SHALES—A
PECTINATITES CLAYS—A
PARVIGATITES CLAYS
CRUSHED AMMONITE SHALES—A
ROTUNDA CLAYS—A
LINGULA SHALES
BRYMOTHONIA-HOUNSTOUT MARL OUT CLAY
HOUNSTOUT MARL
12 UNITS, AV 3'9"—Do
29 UNITS, AV. 5 FT—Do
141 RYTHMIC UNITS OF VARYING THICKNESS & 5 DIFFERENT TYPES AV. 4'9"—Do
19 UNITS : AV. 2'4"—Do
THICK UNIFORM IND RHYTHMS
HAS 15 UNITS: TRULY CYCLIC : AV 2'4"—Do
MOST BITUMENOUS PART—Du
LARGELY CLAY WITH BITUMENOUS SHALES SELDOM OCCURING—De
RAPID ALTERNATIONS OF CLAYS & BITUMENOUS MARLS/SHALES; OCCASSIONAL CEMENTSTONES & NO OIL SHALES"—Do
CONCENTRATION OF ORGANIC MATTER FALLS OFF MARKEDLY EXCEPT FOR WHITE BANDS—Du
LOWEST QUARTZ IN RESIDUES—L
SECONDARY GYPSUM LESS REGULAR; QUARTZ IN EVERY RESIDUE EXCEPT ROTUNDA NODULE BED —L
FEW SHALE PARTICLES FROM K. BAY > CLAY GRADE (0.01mm)—N
BEDS BECOME SILTY FROM ABOUT HERE TO THE TOP—W QUARTZ—L
LOWER—UPPER KIMM. BOUNDARY—G&C
SOFT SHALES & CLAYS BECOMING SANDY UPWARDS & CONTAINING THIN LIMESTONES—L
THE SERIES OF CLAYS "PASS WITH GRADUAL LITHOLOGIC CHANGE INTO THE PORTLAND SANDS ABOVE"—C&W
LOWER UPPER KIMM. BOUNDARY—BUCKLAND & BLAKE'S BED 40
NAUTILOIDS & BELEMNITES ABSENT—C
OSTRACODS: 36 SPECIES IN LOW. KIM. SULPHUROUS PAPER SHALES—K
ARENACEOUS FORAMS MISSING L
VERTEBRATE FAUNA ABUND. IN COALY & SUBCALCAREOUS MDSTS. BUT MOLLUSCAN FAUNA IS POOR IN SPECIES DESPITE NUMEROUS INDIVIDUALS. A. BIPLEX, D. LATISSIMA & L. MINISCULA. COMMON—H Et al
UPPER KIMM. FORMS W. A. THURMANNI & E. VIRGULA—H Et al
ALT. HD. SHS. & DICEY CLAYS (HD. CALC. CLAYS) OR SOFT SHS. CONTAINING THIN LSTS. W. CLAYS DOMINATING UPWARDS—L
ICHTHYOSAURUS, TELEOSAURUS, PLESIOSAURUS, STENOSAURUS, DAKOSAURUS, ETC. FROM K.BAY—H
(D. LATISSIMA MORE COMMON ABOVE BLKST—C)
ISOLATED FISH SCALES EXCEEDINGLY ABUND—C
LARGE NUMBER OF OSTRACODS IN NEW ASSEMBLAGE (W.R.T. LOWER K. CLAY— LESS RICH IN BOTH INDIVIDUALS & SPECIES)—K
Br: PLIOSAURUS GRANDIS, HYBODUS SPINE, OTHER FISH REMAINS, CUTTLE FISH & AMMONS. AT ENCOMBE PIWHERE IN BLK. OOLITIC" SHS. JAWS OF REPTILES, SAURIAN VERTEBRAE, PTERODACTYLES, ZOOPHYTES & FRUITS" IN BEDS RUNNING OUT TO SEA">
OSTRACOD BARREN—K
OSTRACOD BARREN—K
OSTRACOD BARREN—K
MICRO PLANKTON FROM HERE UPWARDS HAVE CRETACEOUS AFFINITIES, ALSO CHEMISTRY CHANGES; DETRITAL MINERALS [Zr CONTENT] & SILT CONTENT INCREASE: MAJOR ENVIRONMENTAL CHANGE POSTULATED —Du
CALC. FORAMS, MISSING—L
CALCAREOUS FORAMS, MISSING—L
IN CLAYS DINOS & HYSTRICHS ABUND. & FORM CONSID. PART OF ORG. MATTER; NUMEROUS COCCS, OCCASS. ENOUGH TO FORM THIN ARGILLOR BIT. LSTS—Do
DEPOSITION UNDER SECOND TRANSGRESSIVE PHASE OF CALLOVIAN-KIMMERIDGIAN—M
DEPOSITION UNDER SECOND REGRESSIVE PHASE OF CALLOVIAN-KIMMERIDGIAN—M
DEPOSITION UNDER THIRD TRANSGRESSIVE PHASE OF CALLOVIAN-KIMMERIDGIAN—M
COMPILED FROM: ARKELL 1933-36, 37, 47—A; BLAKE 1875, 80—B; BRODIE 1878—Br; COPE 1968—C; COPE & WIMBLEDON IN C DOWNIE 1956, 58—Do; DUNN 1972—Du; GALLOIS & COX 1976—G & C; HOWARTH 1955—How Et al; HUDLESTON 1861—H Et al; HULKE 1866, 70, 84, 78, 72—H; KILENYI 1969—K; LATTER 1956—L; LLOYD 1959, 62—L; MERRAU 1975—M; NEAVERSON 1934, 35—N; RILEY 1974—R; SAUFLEY 1913—S; WIMBLEDON 1975—W

LOG 2 MARKER HORIZONS

THE TYPE KIMMERIDGIAN HORBARROW BAY - CHAPMANS POOL DORSET SHIRE ENGLAND

R A DAVIES 1978

INCLUDING RELEVANT GENERALISED LOWER KIMMERIDGIAN SECTION

MASSIVE BED: CALCAREOUS SANDSTONE—Ds

CALCAREOUS SANDSTONE—Ds

CALCAREOUS SILTSTONE—Ds

SEEPAGE—Ds; [HARD BAND WEATHERING WHITISH & PROUD—Ds]

SEEPAGE—Ds

SEEPAGE—Ds

SEEPAGE—Ds

(UNDIFFERENTIATED) CLAY

BITUMINOUS SHALE

OIL SHALE

BITUMINOUS MARL

SILTY BED/SILTSTONE

COCCOLITH LIMESTONE

DOLOMITIC LIMESTONE

VERY SHELLY MUDSTONE

PALE GREY, VERY CALCAREOUS MUDSTONE

N.B. THE COLUMN IS FROM DOWNIE, 1955

0

10 FEET

20

COMPILED FROM:
ARKELL, 1947, Etc.
BLAKE, 1875
COPE, 1967
DAVIES, 1976
DOWNIE, 1955
DUNN, 1972
GALLOIS & COX, 1976
HUDLESTON, Et al, 1896
KILENYI, 1969
MEIRIDAU, 1975
NEAVERSON, 1926
RILEY, 1976
SALFELD, 1913
WILSON, 1969

SEEPAGE—Ds

SEEPAGE—Ds

SEEPAGE—Ds

LOG 3 ORGANIC GEOCHEMISTRY I

THE TYPE KIMMERIDGIAN

HORBARROW BAY - CHAPMAN'S POOL
DORSETSHIRE ENGLAND

R A DAVIES 1978

SOLUBLE ORGANIC EXTRACT
% BY WEIGHT
0 0.2 0.5 1.0 1.5 2.0

% KEROGEN CARBON CONVERSION
DOMINANT KEROGEN TYPE
KERITNITE 3 HUMIC 5 9.5
LIPTINITE 10 14.5 20 30 32
ALGAL 40 48 50 55 60 70 80 83
ALGINITE 90

SOE RATIOS
NON-HYDROCARBONS / HYDROCARBONS
SATURATES / AROMATICS
2 4 6 8 10

80.02?

98.02?

HS
FW
J
MW
LW
J
J
J
J

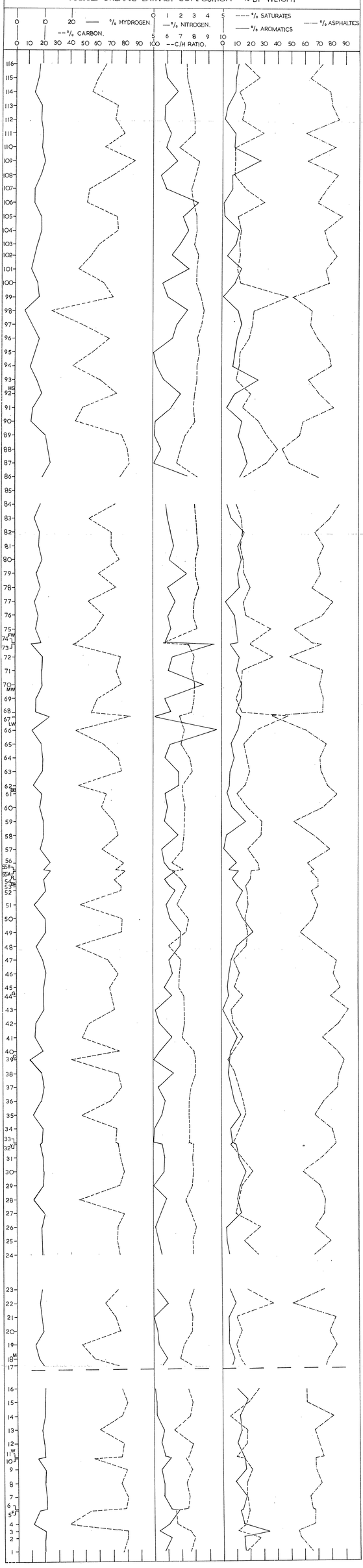
LOG 4 ORGANIC GEOCHEMISTRY II

THE TYPE KIMMERIDGIAN

HORBARROW BAY–CHAPMAN'S POOL
DORSETSHIRE ENGLAND

R A DAVIES 1978

SOLUBLE ORGANIC EXTRACT COMPOSITION °/₀ BY WEIGHT



LOG 5 ORGANIC GEOCHEMISTRY II

THE TYPE KIMMERIDGIAN

HORBARROW BAY - CHAPMAN'S POOL
DORSETSHIRE ENGLAND

R A DAVIES 1978

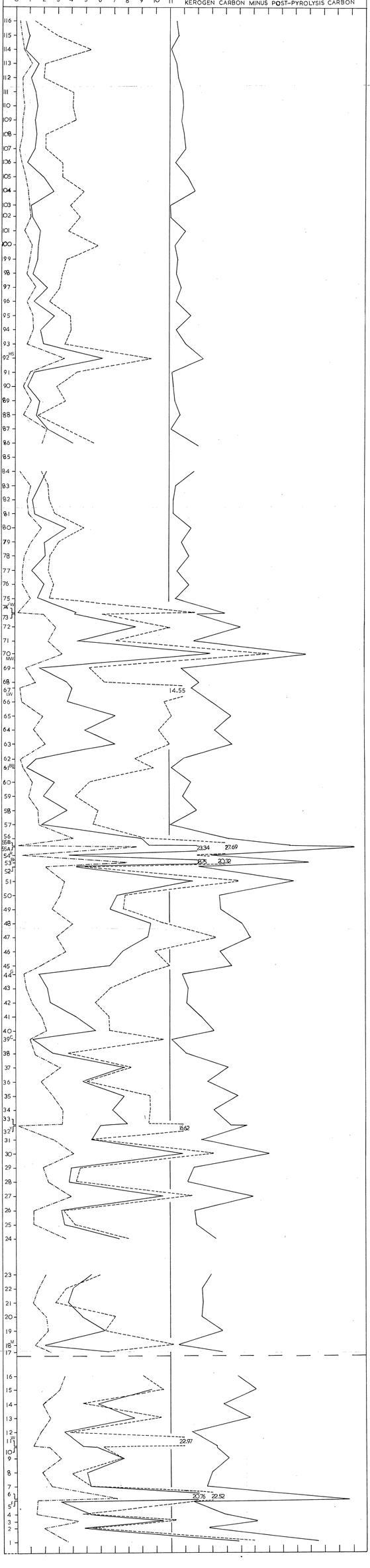
WHOLE ROCK % BY WEIGHT
—— ORGANIC CARBON
---- TOTAL CARBON
-·-·- POST-PYROLYSIS ORGANIC CARBON

0 1 2 3 4 5 6 7 8 9 10 11

RELATIVE POTENTIAL

1 2 3 4 5 6 7 8 9 10 11 12 13 14

KEROGEN CARBON MINUS POST-PYROLYSIS CARBON



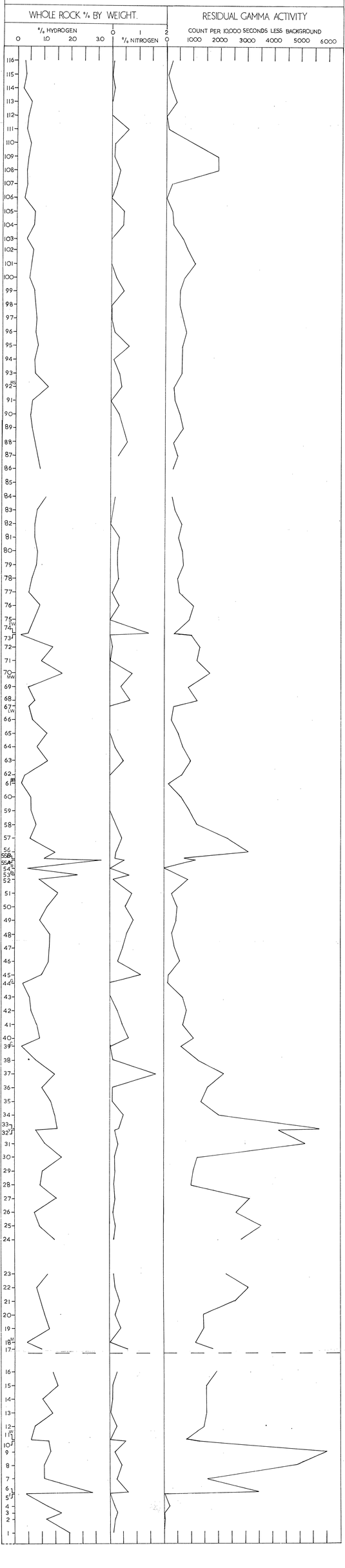
LOG 6

GEOCHEMISTRY & RADIOACTIVITY

THE TYPE KIMMERIDGIAN

HORBARROW BAY–CHAPMAN'S POOL
DORSETSHIRE ENGLAND

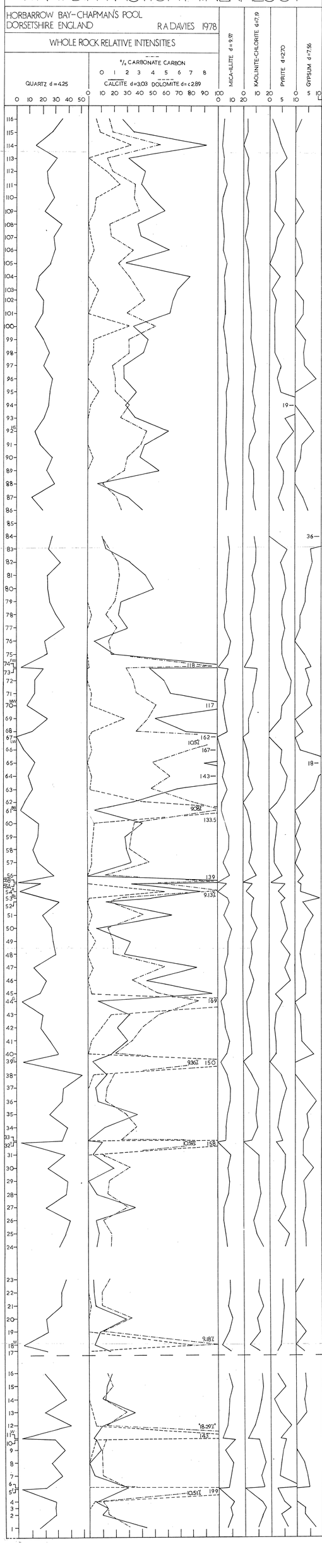
R A DAVIES 1978


WHOLE ROCK % BY WEIGHT.
% HYDROGEN
0
1.0
2.0
3.0
% NITROGEN
0
1
2
RESIDUAL GAMMA ACTIVITY
COUNT PER 10,000 SECONDS LESS BACKGROUND
1000
2000
3000
4000
5000
6000
HS
LW
MW
LW
BB
BB
BB

LOG 7 THE TYPE KIMMERIDGIAN
X-RAY DIFFRACTION MINERALOGY

HORBARROW BAY – CHAPMAN'S POOL
DORSETSHIRE ENGLAND
R.A. DAVIES 1978

WHOLE ROCK RELATIVE INTENSITIES



LOG 8 COMPOSITE DESCRIPTION

THE TYPE KIMMERIDGIAN

HORBARROW BAY–CHAPMANS POOL
DORSETSHIRE ENGLAND

R A DAVIES 1978

'LITHOLOGY', PYROLYSIS PRODUCTS, EXTRACTABLES & CLASSIFICATIONS.

KEY E ECHINOID SPINE F FORAMINIFERID BU BURROW B BELEMNITE V VERTEBRATE G GASTEROPOD
S T TOURMALINE Z ZIRCON A APATITE 48 PYROLYSIS E EXTRACTION O OPTICAL MICROSCOPY

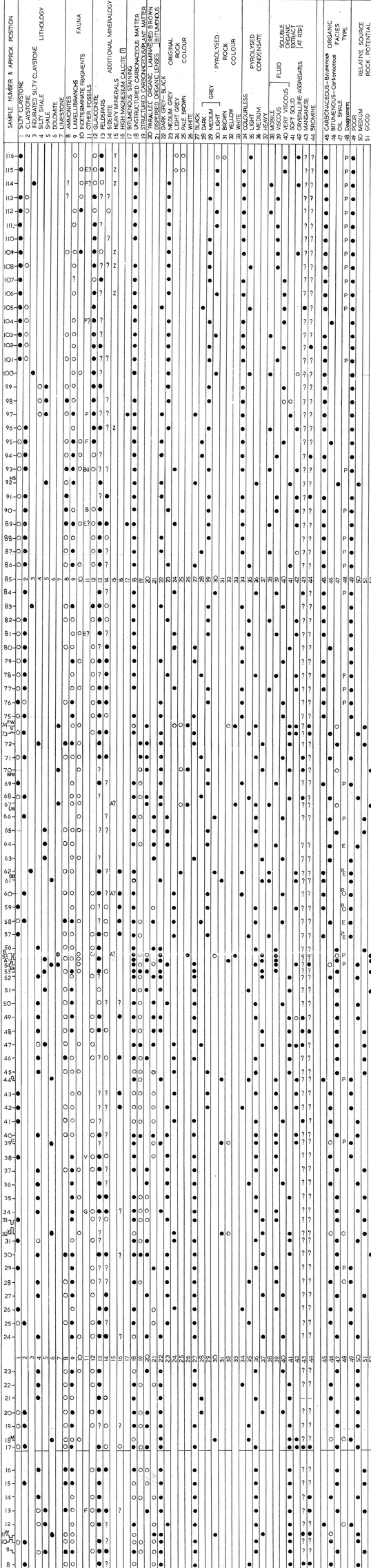
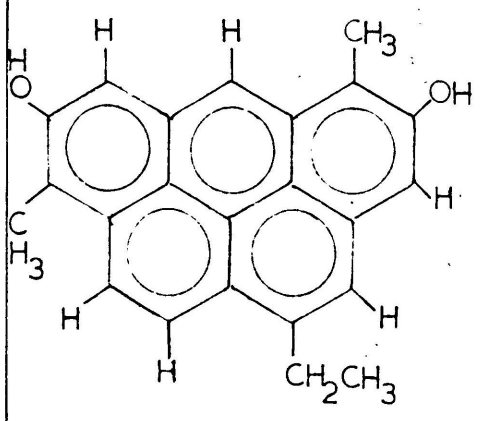


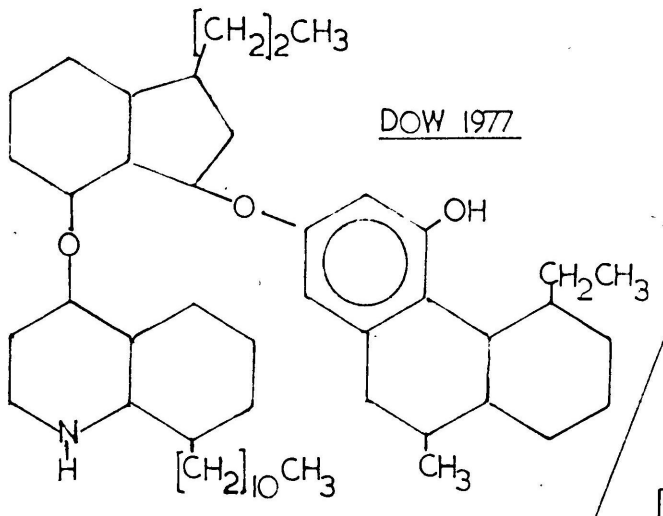
TABLE 37 KEROGEN CLASSIFICATION FOR OIL EXPLORATION

R A DAVIES 1978

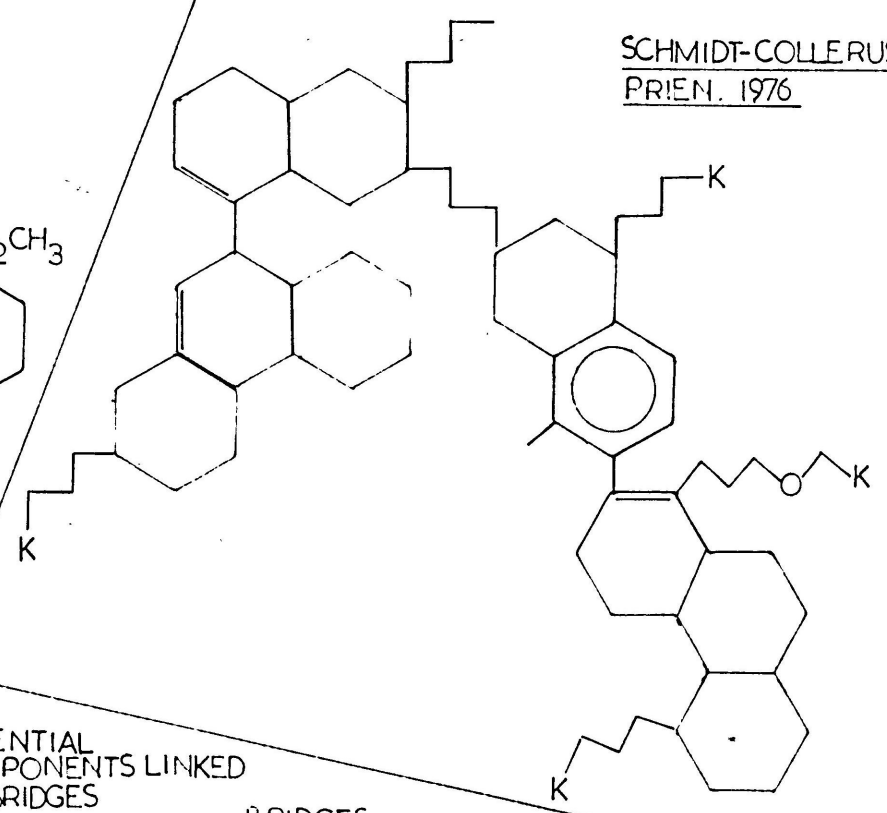
ALGAL[4]/OIL SHALE-LIKE[1,11,3,4,18]/SAPROPELIC[1,6]/LIPID-RICH TYPE[1,11]/OIL-TYPE[8] KEROGEN



LA PLANTE 1974



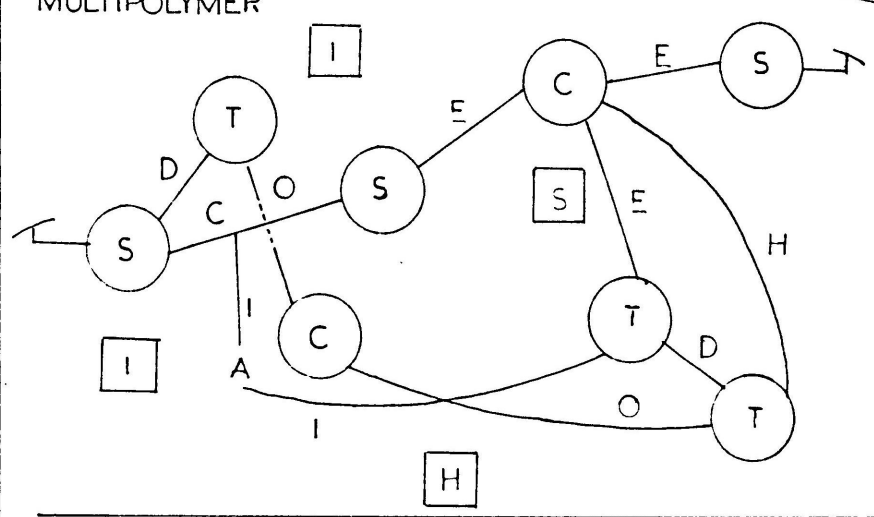
DOW 1977



SCHMIDT-COLLERUS & PRIEN. 1976

YEN 1976

MULTIPOLYMER



= ESSENTIAL COMPONENTS LINKED BY BRIDGES

= ENTRAPPED BITUMENS

BRIDGES

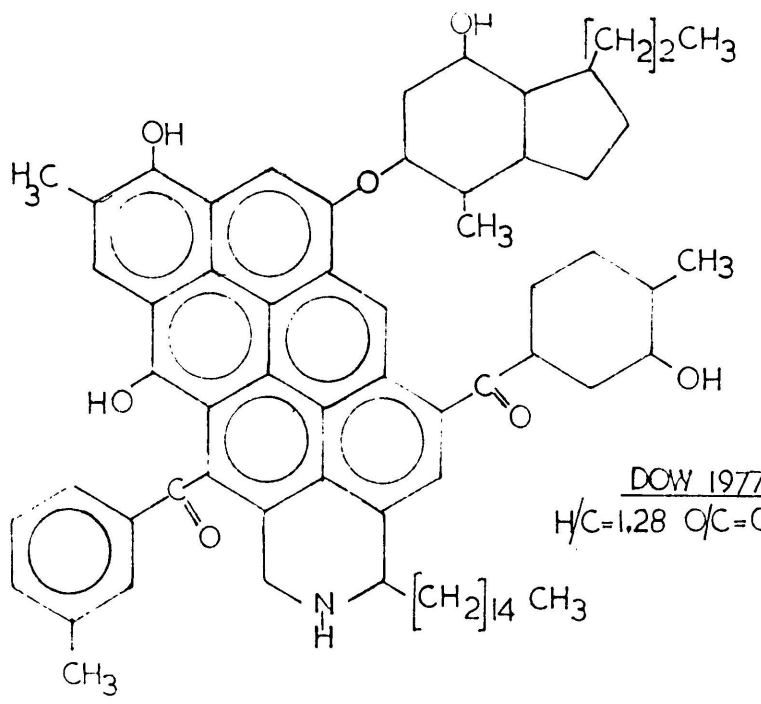
I	ISOPRENOIDS	D DISULPHIDE
S	STEROIDS	O ETHER
T	TERPENOIDS	E ESTER
C	CAROTENOIDS	I ISOPRENOIDS
		H HETEROCYCLIC
		A ALKADIENE

79.4%C, 9.8%H – 20
80%C 8%H 10%O 2%N – 3
H = 6-10% – 8 ; >7% – 3
H/C = 1.5 – 20 ; 1.6 – 15
RELATIVELY LOW O/C – 4,7 MORE H & LESS O THAN HUMIC TYPE[23]

SOURCED BY PLANKTON & HIGH LIPID RESIDUES OF SPORES & POLLEN[8]; PREFERENTIAL IN MARINE[3,6,11] & LACUSTRINE[3] DEPOSITS. ALGINITES[7] NOT COMMON IN PURE FORM. PREDOMINANTLY ALIPHATIC[17] – H.M.W. MOLECULES[8]; LONG CHAIN PARAFFINS[8]; FATTY ACID TYPE[1] & ALIPHATIC[4,7] STRUCTURES. LOW AROMATIC CONTENT[19,20] – FEWER CONDENSED RINGS[8]. WEIGHT LOSS AT 950°C = 70–85%[23]; 66%[4]/AT 500°C = 70%[24] OIL-GENERATING[7,8]: LARGE QUANTITIES OF BOTH OIL & GAS[4], MORE OIL & LESS GAS[5]; MOST OIL FROM THIS KEROGEN[1] ALGINITES GIVE RICH GASOLINE/KEROSENE FRACTION[26]; SPORINITE TYPE GIVES HIGH WAX CRUDE[26]

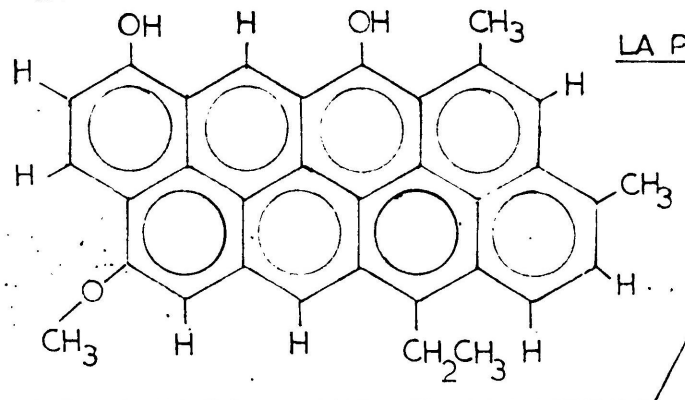
LEIPTINITE[23]/EXINITE KEROGEN

INTERMEDIATE[7] BETWEEN ALGAL & HUMIC TYPES AS EXINITE GROUP OF MACERALS CONTAINS ALGINITE, CUTINITE[12,22] [GENERALLY STRUCTURED[4] OUTER LAYER OF 'HYDROXY-FATTY ACID' WAX OF LAND PLANT CUTICLES[27]] SPOROPOLLENIN[12,22] [GENERALLY STRUCTURED[4]; A BIOPOLYMER OF UNSATURATED WAX ESTERS, CROSS-LINKED BY OXYGEN FUNCTIONS & C-C BONDS, WHICH IS THOUGHT TO BE THE MAIN CONSTITUENT OF SPORINITE[27]] AND RESINITE[12,22] [Eg AMBER; AN EXUDATE FROM PLANTS OR A POSSIBLE DERIVATIVE FROM THE MICROBIAL, SUBAQUEOUS ATTACK UPON WOOD DEBRIS WHERE CYCLO-ALKYL STRUCTURES ARE CROSS LINKED BY OXYGEN FUNCTIONAL GROUPS][27] ALKYL CHAIN & RING STRUCTURES; BENZOID NUCLEI RARE(?)[27] WEIGHT LOSS AT 500°C ≃ 34.4%[24] AT 950°C = c.40%[23,4]

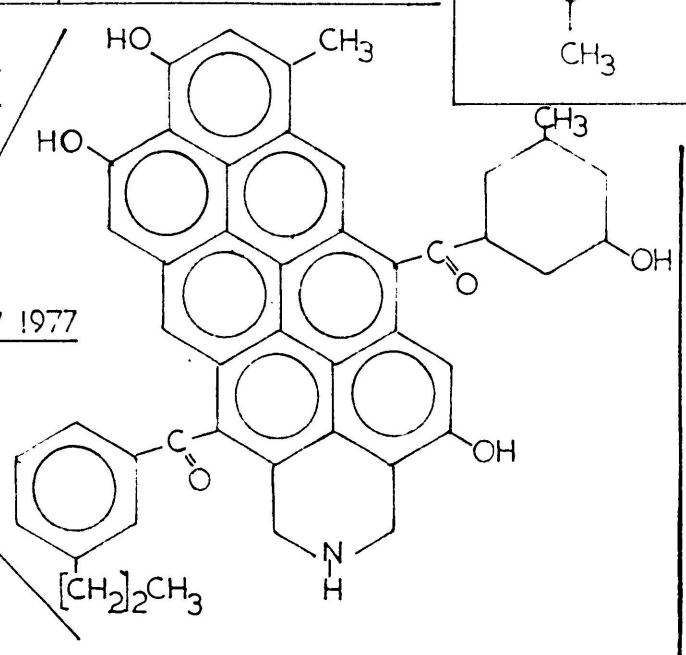


DOW 1977
H/C = 1.28 O/C = 0.1

HUMIC[1,4]/COAL-LIKE[1,8,11]/CARBOHYDRATE-LIGNIN RICH[1,2]/VITRINITIC[4,7] KEROGEN



LA PLANTE 1974



DOW 1977

75-90%C 5%H 3-15%O – 23
80%C 5%H 13%O 2%N – 3
H/C = 0.84 – 4 ; 0.68-0.90 – 16; RELATIVELY LOW[7]
O/C = 0.13 – 4 ; RELATIVELY HIGH[7]
H: DEFFICIENT[4]; < 6%[3]; 3-5%[8]
'LESS' N[11] (?)

GAS GENERATING[3,4]: LITTLE OIL POTENTIAL[21]; VERY LITTLE PETROLEUM HYDROCARBONS[10]; SMALL QUANTITIES OF LIQUID PETROLEUM MAY BE FORMED BUT NOT EXPELLED[9]; MORE GAS THAN OIL[5]; MOSTLY METHANE[8]; LIMITED DRY GAS[4]; WOODY KEROGEN GAS PRONE[14] & PREDOMINANT GASEOUS PRODUCTS[26]

DERIVED FROM LIGNIN[2,4,11], CARBOHYDRATES[11], HUMIC ACID[11] MATERIAL[7]/RESIDUES[8] & NITROGENOUS RESIDUES[8] OF HIGHER[7], CONTINENTAL & MARINE PLANTS[8]. PREFERENTIAL IN NONMARINE[6,7], NEAR SHORE BRACKISH MARINE[11] OR PARALIC[7] SEDIMENTS WITH TERRIGENOUS ORGANIC DETRITUS[3]. PREDOMINANTLY AROMATIC – L.M.W MOLECULES[3,8], MAINLY NAPHTHENIC RINGS LINKED BY HETERO-ATOMS [O, S & N PRESENT[8]], SHORT ALKYL CHAIN BRIDGES & CYCLO-ALKYL GROUPS WITH OXYGEN AS PHENOL, ETHER OR ESTER-TYPE CROSS LINKS[20,27] FEW SMALL [METHYL][23] OR LONG HYDROCARBON SIDE CHAINS[3,4,8] ie. A HIGHLY CONDENSED, NUCLEAR KEROGEN[26]
WEIGHT LOSS AT 950°C = c.16%[4,23]

[VITRINITE – FORMED BY THE HUMIFICATION OF WOODY TISSUE (LIGNIN & CELLULOSE OF CELL WALLS OF HIGHER LAND PLANTS[4,27]) IN WET, ANOXIC CONDITIONS[22] – COMMON IN PURE FORM[4]. STRUCTURED (TELLINITE) & UNSTRUCTURED (COLLINITE)[22] FORMS KNOWN]

INERT[25]/GRAPHITIC[8] KEROGEN

CHARCOAL-LIKE[27]; SOURCES INCLUDE ABIOGENIC OXIDATION OF WOODY TISSUE[23] [FOREST OR PEAT FIRES[4]], DEGRADATIVE PROCESSES IN PROLONGED SOIL FORMATION[27] & RECYCLED KEROGENS[4] VERY LOW IN HYDROGEN[4]; < 3%H[8]. LOW EXTRACTIBILITY SUGGESTS "MIGRATION INTO FUSINITE" (< 10%)[12] > 90%C[23] WEIGHT LOSS AT 950°C: O%[8,25] – LITTLE[23]. CONDENSED POLYAROMATIC RING STRUCTURES[4] WITH VERY LITTLE ALIPHATIC OR FUNCTIONAL GROUP CONTENT[27] STRUCTURED & UNSTRUCTURED VARIETIES CLASSIFIED AS FUSINITE, SEMIFUSINITE, SCLEROTINITE OR MICRINITE[22,25] LITTLE CHANGE DURING MATURATION[27] – NO CHANGES DURING DIAGENSIS[22] LOW CONVERTIBILITY[4]. LITTLE OR NO CAPACITY TO GENERATE[4]. AT BEST GIVES LARGE VOLUMES OF CO_2 & SMALL VOLUMES OF CH_4.[4] STRICTLY LIMITED[14]

COMPILED FROM: 1 CORDELL 1972 2 BREGER 1960 [HOBSON Verb Comm 1972] 3 LA PLANTE 1974 4 DOW 1977 5 HUNT 1977 6 PUSEY 1973 7 TISSOT Et al 1974 8 HUNT 1976 9 TEICHMULLER 1974 IN DOW 1977 10 ISHIWATARI Et al 1976, 1977 11 McIVER 1967 12 POWELL Et al 1976 13 CORREIA 1970 IN MADANI 1977 14 COMMERCIAL CONCERN. 15 ROBINSON Et al 1965 16 HUNT & JAMEISON 1956 17 BAKER 1972 18 ROBERTSON 1911 19 SCHMIDT-COLLERUS & PRIEN 1976 20 YEN 1976 21 BREGER 1959 IN LONG Et al 1962 22 MURCHISON & JONES 1962 23 GIVEN 1962 24 VANDENBROUCKE Et al 1976 25 SHIBAOKA Et al 1973 26 LARTER Et al 1977 27 ALLAN Et al 1977