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BULLETIN 291

ORGANIC GEOCHEMISTRY OF THE UPPER CRETACEOUS-TERTIARY DELTA COMPLEXES OF THE BEAUFORT-MACKENZIE SEDIMENTARY BASINS, NORTHWEST TERRITORIES

L.R. Snowdon



Energy, Mines and Resources Canada Énergie, Mines et Ressources Canada

1981

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Canadian Government Publishing Centre Supply and Services Canada Hull, Québec, Canada K1A 0S9

and from

Geological Survey of Canada 601 Booth Street Ottawa, Canada K1A 0E8

3

A deposit copy of this publication is also available for reference in public libraries across Canada

Cat. N	lo. M42-291E		Canada:	\$4.00
ISBN	0-660-10167-X	Other	countries:	\$4.80

Price subject to change without notice

Scientific Editor E.R.W. Neale

Critical Readers F. Young A. Foscolos

Editor Val Donnelly

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Artwork Cartography Section, ISPG

Original manuscript submitted: 1977 - 04 - 20 Approved for publication: 1977 - 07 - 08

PREFACE

This is the first major report prepared under the auspices of the Geological Survey in which the organic geochemistry of the sediments of the Beaufort-Mackenzie Basin has been described. Oil and natural gas estimates depend to a large extent on understanding the physical and chemical characteristics of each basin. Estimates can only be refined if these factors are more thoroughly understood. The Beaufort-Mackenzie Basin has been the site of significant exploration since the mid-1960s and the first hydrocarbon discovery was made in 1969. Although the Beaufort Sea is one of the most logistically difficult areas in Canada, offshore exploration drilling programs are currently under way.

under way. This study is restricted to data derived from Upper Cretaceous and Tertiary rocks but the results have implications for rocks of other ages and in other depositional basins. The main emphasis of the interpretation is on geological and geochemical interrelationships but the results are also discussed in terms of potential petroleum source rocks and theoretical geochemical models. One conclusion of the study is that existing concepts of petroleum generation must be modified to include an early stage of condensate generation. It is also concluded that organic facies do not necessarily correspond to sedimentary facies, which suggests that point bar or stream bed sands have just as much potential as reservoirs as the more highly favoured delta front sands of this region.

Ottawa, December 1978

D.J. McLaren Director General Geological Survey of Canada

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Abstract

The organic fraction of a set of borehole drill cuttings and core samples representing fluviodeltaic, delta front and prodelta marine environments of deposition from the Upper Cretaceous - Tertiary of the Beaufort-Mackenzie Basin in northern Canada has been subjected to organic carbon analysis; extraction with benzene/methanol; open-column chromatographic fractionation into saturates, aromatics and resins; gas chromatographic analysis of the saturate fraction including quantification of the n-alkanes and isoprenoids; and kerogen isolation. The kerogen was examined microscopically under transmitted light and the organic fragments quantitatively classified as herbaceous, coaly or sapropelic. Elemental analyses were carried out on the kerogen and H/C and C/N ratios calculated.

An attempt was made to observe trends in the chemical parameters as a function of the increasing marine influence. The only positive correlation observed was that the organic carbon content of fluviodeltaic sediments was statistically higher than that of either delta front or prodelta samples. None of the other parameters measured displayed depositional environment dependency. Within the three subenvironments of the delta complexes which were examined, there was a single organic facies dominated by herbaceous and coaly organic debris. The elemental hydrogen-carbon ratio data fall into a very narrow range (0.70 - 0.90) and are consistent with the optical observations. Pristane/phytane ratios increased to about 7.0 with increasing maturity but were independent of both organic matter type and depositional environment.

A few of the samples examined were classified as good or excellent potential petroleum source rocks on the basis of extractable hydrocarbon yield. The low level of thermal maturity (vitrinite reflectance about 0.45-0.60) and high concentrations of some tricyclic diterpanes (probably of the sandaracopimarane structure) suggest that the good source rock quality may be related to a high resinite content in the sediment, which has yielded the reservoired natural gas and condensate of the Upper Cretaceous-Tertiary section at very low levels of thermal alteration.

Implications of this study are: (1) The classical petroleum generation sequence of heavy oil, oil, condensate and gas with increasing thermal alteration must be modified to include an early stage of condensate generation. (2) Organic facies do not necessarily correspond with sedimentary facies or depositional subenvironments and, therefore, the delta plain sandstone reservoirs of this basin are as likely to be juxtaposed with a source rock as are the delta front sands.

Résumé

La fraction organique d'un groupe d'échantillons provenant de déblais de forages et de carottes de sondage, qui contiennent des sédiments fluvio-deltaïques, de front de delta et pro-deltaiques formés pendant le Crétacé supérieur et le Tertiaire dans le bassin de Beaufort et du Mackenzie, dans le nord du Canada, a fait l'objet d'une analyse du carbone organique; d'une extraction au benzène et méthanol; d'un fractionnement en produits saturés, produits aromatiques, et résines, sur colonne chromatographique ouverte; d'une analyse chromatographique en phase gazeuse de la fraction saturée, avec dosage des n-alcanes et des isoprénoïdes; et d'un dernier traitement, la séparation du kérogène. On a examiné le kérogène au microscope, sous lumière réfractée, et on a rangé les fragments organiques dans trois catégories: fragments herbacés, charbonneux et sapropéliques. On a fait l'analyse élémentaire du kérogène, et calculé les rapports H/C et C/N.

On s'est efforcé d'établir une corrélation entre les paramètres chimiques et l'augmentation des influences marines. La seule tendance que l'on ait pu reconnaître avec certitude était que la teneur des sédiments fluvio-deltaïques en carbone organique était statistiquement plus élevée que celle des échantillons de front de delta ou pro-deltaïques. Aucun des autres paramètres mesurés n'a révélé une dépendance du milieu de sédimentation. Dans les trois types d'environnement que comportaient les complexes deltaïques examinés, on a observé un seul faciès organique particulièrement riche en débris organiques herbacés et charbonneux. Le rapport hydrogène-carbone, obtenu par l'analyse élémentaire, ne couvrait qu'un intervalle très étroit (0.70 -0.90), et concordait avec les résultats des observations faites au microscope. Le rapport pristane/phytane s'est élevé jusqu'à environ 7.0, en fonction de l'acroissement de maturité, mais il ne dépendait ni du type de matière organique ni du milieu de sédimentation.

D'après leur concentration en hydrocarbures extractibles, on a jugé que quelques-uns des échantillons examinés pouvaient constituer de bonnes ou excellentes roches-mères du pétrole. Le faible niveau de maturité thermique (réflectance de la vitrinite située entre 0.45 et 0.60), et la concentration élevée de certains diterpanes tricycliques (probablement de même structure que le sandaracopimarane) semblent indiquer que la capacité des échantillons à constituer une bonne roche-mère est peut-être liée à la forte teneur en résinite du sédiment, où, dans la section d'âge crétacé supérieur et tertiaire, se sont accumulés le gaz naturel et le condensat dans des conditions d'altération thermique très faible.

Cette étude nous permet de constater (1) qu'il faut modifier les concepts courants relatifs à l'évolution du pétrole, d'après lesquels apparaissent successivement les huiles lourdes, les huiles, les condensats et les produits gazeux, à mesure qu'augmente l'altération thermique, et inclure une étape précoce de formation du condensat, et (2) que les faciès organiques ne correspondent pas nécessairement à des faciès sédimentaires ou à certaines catégories de milieux de sédimentation et que, par conséquent, les grès-réservoirs de la plaine deltaïque dans ce bassin peuvent aussi bien que les sables de front de delta avoisiner une roche-mère.

INTRODUCTION

Organic geochemical research over the past few years has centred on the chemical characterization of organic compounds and bulk properties of the organic material found in sediments and in crude oils (see Eglinton and Murphy, 1969). A second theme has been characterizing the influence of thermal alteration or maturation on various organic parameters: Breger (1960), Philippi (1965, 1969), Landes (1966), Louis (1966), Smith (1966), Abelson (1967), Connan (1968), Henderson et al. (1968), Califet et al. (1967), Staplin (1969), Baker and Claypool (1970), Evans (1971), Rhead (1971), Tissot et al. (1971, 1974), Wehmiller (1971), Eglinton (1972), Shibaoka et al. (1973) and Snowdon and Roy (1975).

Relatively few researchers, however, have approached the study of sedimentary organic material from the standpoint of the geology of the encompassing sediments. The present project was undertaken so that several organic geochemical parameters of sediments from three subenvironments of a series of delta complexes could be examined as a function of the changing geological processes. That is, the various organic parameters were determined for fluviodeltaic (continental) to prodelta (marine) facies in order to assess the effect of increasing marine influence on the character of the preserved organic matter. It was felt that this exercise would be useful in at least three different ways:

- by assisting in development and understanding of how organic geochemical parameters interrelate with geological processes;
- (2) by enhancing the usefulness of chemical data that are being interpreted in terms of metamorphic effects, migration history, biodegradation and source and depositional parameters by clarifying, in part at least, the sequence of organic alteration in a geological system; and
- (3) by providing insight into the relative petroleum source potential of the different facies and the probable petroleum source potential of this particular volume of sediments.

By systematically examining all the recognizable facies of an ancient delta complex, one may elucidate these three aspects. In the first case, an examination of the organic extract yield, hydrocarbon content of the extract and distribution of terrestrial kerogen will yield some insight into how effectively marine processes rework and alter the terrestrial organic matter transported into the system by the river. Little or no data have been published to indicate the extent of the marine influence on sedimentary organic material deposited in delta front and prodelta environments.

In the second case, differentiation of marine from terrestrial deposits using organic geochemistry has been attempted (Connan, 1968) without the benefit of empirically derived relationships from nearshore, transitional environments. Thus, the interpretation of geochemical data from marginal depositional facies must be considered as tentative only, because the rate of appearance of marine character dominance adjacent to the paleoshoreline is essentially unknown. It is therefore important to establish an empirical reference from a well defined transitional depocentre. The distribution of saturated hydrocarbons and the atomic hydrogen to carbon ratio as well as the change in kerogen type in samples from the various delta complex subenvironments should indicate how accurately the organic parameters reflect the changing depositional environment. This will enable one to examine other aspects of organic geochemistry with one less variable.

The third aspect of the relationship of facies correlation with organic parameters, petroleum source potential evaluation, is undoubtedy the most pragmatic objective of this project. The relative yields of hydrocarbons from sediments of the various subenvironments of deposition should indicate whether or not the petroleum potential from marine-dominated facies and hence marine-dominated deltas is particularly greater than that of terrestrially dominated deltas. The relative importance of juxtaposed marine shale sources and delta front sandy reservoirs may be evaluated on the basis of a relative source potential of the different facies. Specifically, the implications of the occurrence of oil in strata of relatively low maturity in the Mackenzie Delta (Gunther, 1976a, b) will be elucidated by the determination of the quantity and nature of the solvent-extractable organic material in the various facies of the Upper Cretaceous-Tertiary delta complexes. The usefulness of organic geochemical data for predicting oil/gas trends with respect to facies trends within the Beaufort-Mackenzie Basin also can be evaluated.

The author is indebted to the Geological Survey of Canada for granting educational leave for two years and financially supporting this research.

Thanks are extended to D.R. Baker, the author's thesis advisor, and to the thesis committee at Rice University: J.L. Wilson, J.B. Anderson and P.A. Harcombe.

The author would also like to thank many people on the staff at the Institute of Sedimentary and Petroleum Geology in Calgary, where most of the research was carried out. T.G. Powell followed the daily progress of the research and offered many helpful suggestions. P.R. Gunther spent many hours instructing the author in both kerogen smear slide preparation and microscope techniques, including organic type identification, vitrinite reflectance measurement and UV excitation fluorescence microscopy. D.W. Myhr and F.G. Young provided the geological base and depositional subenvironment interpretation for many wells in the study area. The technical support of the drafting, typing and editing personnel at the Institute are also gratefully acknowledged.

F.G. Young and A.E. Foscolos of the Institute critically read the first draft of the thesis and offered many helpful suggestions. E. Peake of the University of Calgary kindly ran the gas chromatogram mass spectra of the tricyclic diterpanes.

Previous research

The examination of organic geochemical parameters as a function of depositional environment has been restricted mainly to three general areas: (1) the organic analysis of modern sediments from a variety of geological settings; (2) the correlation of crude oil physiochemical parameters and the stratigraphy of the reservoir sediments; and (3) the study of ancient sediments.

Included in the first area of research are many projects on cores recovered during the Deep Sea Drilling Project. These samples represent a wide range of depositional environments, including pelagic sediments (Simoneit and Burlingame, 1972); turbidites and contourites (Simoneit and Burlingame, 1973); evaporite deposits (McIver, 1973); trenches, rises and island arc systems (Claypool et al., 1973); abyssal hills and underlying marine sediments deposited on a basalt (Simoneit et al., 1973); and deep ocean basins and continental rises (Simoneit and Burlingame, 1971). Whereas information on depositional environment and organic analyses is available for a substantial number of samples, a concerted effort to correlate the parameters has not been made. Other recent sediment data have been analyzed by Palacas et al. (1972), who related various organic parameters to different depositional facies of an estuarine bay. Estuarine muds and relatively clean quartz sands representing relatively low and high energy conditions, respectively, were found to contain significantly different normal paraffin distributions. The low odd-to-even predominance in carbon chain length of the n-alkanes of the sand sample was interpreted as indicating an increased input from marine organisms.

Sackett (1964) and Parker et al. (1972) observed a stable carbon isotope trend from more depleted in ¹³C to less depleted in ¹³C as more marine-synthesized organic matter was incorporated into the sediment. Their results were complicated by factors including the possibility of (1) nonbiological oxidation of carbon in the marine environment and (2) marine plant utilization of terrestrial inorganic carbon especially at a river mouth. Temperature also was found to be an isotopic fractionation factor but the magnitude of this effect was less than that of the different source materials.

The study of geochemical parameter variation as a function of depositional environment in ancient sediments has been restricted essentially to research by Powell and others, and work on the Green River Shale of Utah by several authors.

Hunt et al. (1954) discussed four lithology types from the Green River Formation which are correlative with characteristic organic chemical properties. The Wasatch Formation is predominantly continental and fluviatile and is characterized chemically by the presence of ozocerite (wax). The Green River Formation was deposited in stratified saline lake with strongly reducing bottom conditions and oxidizing fresh to brackish surface water. The organic component of these sediments consists of albertite, ingramite and gilsonite. The Uinta Formation is made up essentially of red and green shales with included channel sands and veins of wurtzilite (insoluble asphaltic pyrobitumen). The changing organic matter type reflects the increasing salinity of the lake water. The observed sequence was (1) predominantly paraffins (ozocerite), (2) predominantly condensed aromatics (albertite), (3) aromatic and nitrogen compounds (gilsonite), and (4) naphthenes with sulphur and nitrogen compounds (wurtzilite).

In a series of papers on the Green River Formation, Robinson and Cook (1971, 1973, 1975) and Anders and Robinson (1973) examined the changes in organic chemical properties with increasing depth of burial. Similar conclusions were drawn from each study, namely that thermal maturation altered some of the measured parameters but that a number of the variations observed must be due to other factors. The 'other factors' suggested were ecological differences, biological alterations and source material variations. No attempt was made to associate the chemical differences observed with geological processes other than thermal alteration.

A study of Reed and Henderson (1972) also indicated that thermal diagenesis could not account for the variability observed in crude oils in the Green River Formation but this study also stopped short of examining the processes which may have caused these differences in character.

Powell and McKirdy (1973b) observed characteristic organic distributions in several cores from Australia. Both eometamorphism and depositional environment significantly influenced the organic content of the sediments. The n-alkane distribution of the marine organic matter, which lacked the large concentrations of heavy $(C_{27}-C_{31})$ waxes, was found to be quite different from the terrestrially derived organic matter (largely higher plants), which frequently had a strong odd carbon chain length preference. Thermal alteration of terrestrial organic material resulted

in a shift of n-alkanes to shorter chain molecules and a loss of the odd carbon predominance until the land-derived n-alkane distribution was essentially indistinguishable from that of marine-derived organic matter.

Powell et al. (1976) correlated different n-alkane distributions and pristane/phytane ratios with different coal maceral contents of sediments from a cyclothemic sequence in northern England. The coal macerals contain quite different extract fractions, with vitrinite yielding large total extracts relative to exinite. On the other hand, exinite tends to have a higher proportion of hydrocarbons in the extract fraction. High saturate/aromatic ratios were related to land plant input into the sediment.

Geological setting

The Beaufort-Mackenzie Basin underlies the northern Yukon Territory, and the present-day Mackenzie Delta and Tuktoyaktuk Peninsula of the Northwest Territories as well as adjacent offshore shelf regions of the Beaufort Sea (Fig. 1). Mesozoic and Cenozoic sediments are up to 9144 m thick (McCrossan and Porter, 1973) and the Upper Cretaceous - Tertiary deltaic sediments up to 4572 m thick. Thick portions of these molassic cycles occur in the Richards Island depocentre or subbasin (Young et al., 1976, Figs. 13, 16). To obtain samples with the maximum thermal maturation range possible, several wells from this region (see Fig. 1, Table 1) were selected for analysis.

According to Young et al. (1976), the Upper Cretaceous-Tertiary sediments of this area were deposited as three major deltaic pulses with one underlying and two intervening mudstone-shale sections representing transgressive marine tongues. The lithostratigraphy essentially reflects the balance between more or less continual subsidence and discontinuous sediment supply that resulted from periodic uplifts southwest of the Richards Island depocentre. These periodic uplifts were felt to be in response to right-lateral wrench movements along the Kaltag-Rapid Fault Array (ibid., Fig. 26).

Lerand (1973) arrived at similar lithostratigraphic packages for the Richards Island Basin. Young et al. (1976) have drawn cross-sections indicating both normal and reverse faulting in association with the major wrench they have attributed to tectonic movements.

Stratigraphy and selection of samples

The geology of the Beaufort-Mackenzie Basin has been studied extensively by C.J. Yorath, F.G. Young and D.W. Myhr of the Geological Survey of Canada (Young, 1971, 1973, 1975; Myhr, 1975; Yorath, 1973; Yorath and Norris, 1975). A synthesis published by Young et al. (1976) and personal discussions with D.W. Myhr concerning as yet unpublished work were the basis for delineation of the different subenvironments (fluviodeltaic, delta front, prodelta) within the delta complexes of the Upper Cretaceous-Tertiary section in the Beaufort-Mackenzie Basin.

The data that the above workers have used include electromechanical logs from essentially all the boreholes in the delta region, and lithostratigraphy based on borehole cuttings, core samples and extensive palynological data generated by Geological Survey of Canada and various oil company personnel. Extensive outcrop studies also contributed to the development of paleogeographic models. Myhr and Barefoot (1976) have also used geochemical data to make stratigraphic correlations.

The most recently published depositional models for this area (Young et al., 1976) were evolved by plotting all the available data on cross-sectional and fence diagrams. Correlation of the data between boreholes frequently was difficult because of apparently rapid lateral facies changes



Figure 1. Index map of Beaufort-Mackenzie Basin showing the location of boreholes sampled in this study (see Fig. 2 for line of Section A - A').

and also because of the structural complications imposed by the wrench and normal growth fault systems which have been and are active in this area. Thus the depositional model has not been finalized and modifications probably will be required as additional data become available. Figure 2, an example of a cross-section published by Young et al. (ibid., Fig. 15), serves to demonstrate that lithosomes of the Beaufort-Mackenzie Basin frequently occur in only one or two boreholes. The difficulty of stratigraphic correlation, however, has not precluded the identification of individual lithotopes within the wells that were studied.

Nine lithofacies corresponding to different depositional subenvironments were recognized by Young et al. (ibid.) in the Upper Cretaceous-Tertiary molassic sequence of the Beaufort-Mackenzie Basin. They were defined on the basis of lithology, sedimentary structures, fossils and lithosome geometry based on field observations, well cuttings, core samples, and gamma ray and spontaneous potential logs (Fig. 3) from the exploration boreholes. The nine lithogenetic units and their respective facies associations are as follows:

Braided stream complex (conglomerate-sandstone and coarse sandstone)

Meandering stream complex (mixed lithologies)

Delta plain (sandstone, mudstone, coal)

- Paludal deltaic (siltstone-carbonaceous, mudstonemarlstone)
- Mixed delta front delta plain (coarsening-upward sequences, coal, sandstone)
- Prodelta delta front (coarsening-upward sequences, sandstone)

Beach bar (massive laminated sandstone)

Tidal flat (sandstone, mudstone)

Marine or offshore (mudstone, shale, sandstone)

For this study, the Upper Cretaceous-Tertiary stratigraphic sections of a number of wells were divided into three subenvironments of deposition (D.W. Myhr, pers. com., 1976; Young et al., 1976; Yorath et al., 1975) and sampled on the basis of sample availability over as wide a burial depth range as possible for each depositional facies. In most cases the samples were taken from the centre of thick, cleanly defined lithosomes to overcome as much as possible the problem of defining 'contacts' in a transitional sequence. The three environments classified were fluviodeltaic, delta front and prodelta. The first and third represent the geological extremes of a delta complex and it was felt that the organic geochemical parameters from these two sets of samples would show maximum divergence of character. Since delta front subenvironment represents an intermediate stage between the fluvial plain and prodelta deposits, it was anticipated that the geochemical results of this transitional setting would fall between the extremes of the other two.

The fluviodeltaic subenvironment includes the braided and meandering stream complexes, delta plain and paludal deltaic lithofacies of Young et al. (1976). The lithological character of the fluviodeltaic environment ranges from the sandstone-dominated fluvial deposites to the mudstone-coal lithofacies of the paludal environment. Sharp basal contacts of sandstone and conglomerate units, thin coal seams and small-scale fining-upward sequences, as observed both in the field and on resistivity and spontaneous potential logs of boreholes, characterize the fluvial delta plain environment. Paludal deposits frequently contain similar structures but tend to vary principally from siltstone to mudstone. In both fluvial and paludal-delta plain lithofacies, a blocky character in the electric logs results from abrupt changes in the lithology.

The delta front subenvironment of this study corresponds to the prodelta - delta front of Young et al. (ibid.). Sand and silt lithologies and predominant large-scale coarsening-upward cycles truncated by finer grained swamp or transgressive marine sediments characterize this depositional environment. No bedded coals are present.

The third subenvironment sampled in this study consists of the marine transgressive units within the delta complexes and has been referred to as the prodelta facies. It corresponds to the marine-offshore lithofacies as opposed to the prodelta-delta front of Young et al. (ibid.). The lithology of the prodelta subenvironment is predominantly one of siltstone to mudstone, although sandstone lenses do occur.

The beach bar and tidal flat littoral facies of Young et al. (ibid.) have been recognized only in surface sections and have not yet been characterized in the subsurface. These environments may be included in the mixed delta front delta plain lithofacies. Because of the difficulty in distinguishing these environments in the subsurface, no samples were taken from sections identified as mixed lithofacies.

Samples were obtained from six boreholes (see Table 1; Fig. 1) from depths ranging from 796 to 14,000 feet (242.6-4267.2 m). Ten conventional core samples were obtained from the Ellice O-14 well and 36 samples of drill cuttings were obtained from the other five wells.

The samples of cuttings were composites over the intervals indicated in Table 1, and the core samples from the Ellice O-14 well were broken from the core at the depth noted. Brief descriptions of the predominant lithologies of the samples also are noted in Table 1. The broad range of lithology types in individual samples is due to both the nature of the sediments of this basin (Young, 1975) and the fact that the cuttings samples were interval composites. Although some of the samples analyzed in this study were predominantly medium- to fine-grained sandstone with a mudstone or siltstone matrix (Table 1), 'clean' sandstones were not sampled because of the lack of organic matter and the increased probability of epigenetic hydrocarbons.

Well name and location	Sampled Interval feet (metres)	Lithology	Depositional Facies
Shell Kugpik 0-13 (68°52'50"N) (135°18'15"W)	2340-2430 (713.2-740.7) 6380-6440 (1944.6-1962.9)	shale, sandstone, coal shale	delta front prodelta
IOE E11ice 0-14 (69°03'56"N) (135°48'16"W)	796 (242.6) (core) 1809 (551.4) (core) 6306 (1922.1) (core) 6821 (2079.0) (core) 7888 (2404.3) (core) 7919 (2413.7) (core) 8008 (2440.8) (core) 8867 (2702.7) (core) 9486 (2891.3) (core) 9514 (2899.9) (core)	mudstone mudstone, sandstone shale shale, sandstone mudstone, sandstone mudstone, clay ironstone siltstone, sandstone siltstone, sandstone mudstone, sandstone shale, sandstone	fluviodeltaic fluviodeltaic prodelta delta front delta front delta front delta front delta front delta front delta front delta front
Shell Kumak J-06 (69°15'36"N) (135°00'58"W)	5250-5430(1600.2-1655.1)6120-6180(1865.4-1883.6)7740-7800(2359.2-2377.4)8580-8640(2615.2-2633.5)9720-9900(2962.7-3017.5)10620-10650(3237.0-3246.1)	shale, siltstone, coal shale, sandstone siltstone, coal mudstone mudstone, shale shale, siltstone	delta front fluviodeltaic fluviodeltaic prodelta prodelta prodelta
Shell Kumak C-58 (69°17'16"N) (135°13'53"W)	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	siltstone, shale siltstone shale mudstone siltstone, coal siltstone, shale sandstone, siltstone shale, siltstone mudstone mudstone mudstone, siltstone shale	prodelta fluviodeltaic prodelta delta front fluviodeltaic delta front prodelta fluviodeltaic fluviodeltaic delta front prodelta
<pre>IOE Taglu D-43 (formerly F-43) (69°22'17"N) (134°56'47"W)</pre>	3710-3720(1130.8-1133.9)3950-3970(1204.0-1210.1)6820-6850(2078.7-2087.9)8580-8660(2615.2-2639.6)890-8910(2709.7-2715.8)9910-9950(3020.6-3032.8)10460-10520(3188.2-3206.5)13400-13430(4084.3-4093.5)13910-13960(4239.8-4255.0)13970-14000(4258.1-4267.2)	sandstone, coal sandstone, siltstone sandstone, siltstone sandstone, mudstone mudstone mudstone, sandstone mudstone, shale mudstone, sandstone mudstone, sandstone	fluviodeltaic delta front prodelta delta front prodelta delta front prodelta prodelta fluviodeltaic fluviodeltaic
IMP Netserk B-44 (69°33'03"N) (135°55'58"W)	1080-1200(329.2-365.8)2910(887.0)5370-5430(1636.8-1655.1)9690-9720(2953.5-2962.7)10560-1059011400-11430(3474.7-3483.9)	mudstone mudstone mudstone shale siltstone shale, siltstone	fluviodeltaic prodelta prodelta delta front delta front prodelta





Figure 3. Representative spontaneous potential log response of upper Paleogene fluviodeltaic lithofacies (after Young et al., 1976, Fig. 19).

Petrographic analyses of the sandstones and whole rock X-ray diffraction data (ibid., Tables 2, 3) indicate that quartz, chert and lithic fragments with up to 25 per cent clay minerals (illite and chlorite) are the dominant rockforming materials in the Upper Cretaceous - Tertiary of this basin. Analyses of borehole samples (A.E. Foscolos, unpublished data) confirm that the above data are also representative of the subsurface material. Other minor constituents such as coal, dolomite, siderite, pyrite, feldspar, montmorillonite and gypsum vary in amounts.

ANALYTICAL METHODS

Organic carbon determination

The organic (or acid insoluble) carbon determinations were made using a LECO induction combustion furnace and LECO WR12 analyzer. Powdered rock samples of 250 mg were weighed into ceramic combustion crucibles and treated with 6N hydrochloric acid at about 80°C in a sand bath to remove mineral (carbonate) carbon. The powder was initially wet with distilled water and a few drops of 6N acid were added before the sample was heated to prevent scattering of the powdered sample during the evolution of carbon dioxide from the more highly reactive carbonate minerals. The samples were heated and the water and acid allowed to evaporate until there was no remaining supernatant liquid. Six normal HCI was added and evaporated repeatedly with heating until no further carbon dioxide evolution was apparent. The samples were washed several times with distilled water to remove traces of residual acid and soluble salts and then dried in the sand bath.

Smaller samples of 100 mg were used for some of the samples containing very high percentages of organic carbon in order to accommodate the range limitations of the analyzer.

Solvent extraction

All solvents for extraction, handling and fractionation of samples were reagent grade and distilled through an all-glass Vigreux-Hempel type fractionating column and then stored in glass until use. The techniques for extraction and fractionation have been modified after those of Powell and McKirdy (1973b) and were essentially those used by Foscolos et al. (1976).

Powdered rock samples were extracted with an all-glass soxhlet extractor and an azeotropic mixture of benzenemethanol (about 60/40) as the solvent. All samples were extracted for 48 hours. The solvent was removed by rotary evaporation under aspirator pump vacuum. Water extracted from the rock during the soxhlet extraction was removed by adding dry benzene and by rotary evaporation of a benzene-water azeotrope. The crude extract was dissolved in chloroform to separate the organic materials from any coextracted inorganic salts that were soluble in the wet benzene-methanol solvent. This solution was treated with an excess of colloidal copper to remove elemental sulphur (Blumer, 1957) and filtered. A 13 mm diameter glass fiber filter was used with a vacuum to preclude the loss of extract on the filter medium. The clarified solution was evaporated and dried under a stream of nitrogen and weighed as the total extract weight.

Extract fractionation

The asphaltene fraction of the total extract was isolated by precipitation out of a chloroform solution with about 30 volumes of pentane. A minimum of chloroform was used. The suspension was filtered and washed with pentane. The asphaltene fraction was washed through the filter paper using chloroform. Both fractions were evaporated to dryness under a nitrogen stream and weighed. The deasphalted fraction was loaded onto an activated alumina column (Alcoa F-20 activated at 400°C under vacuum for 16 hours) with a support to sample weight ratio of 100 to 1. The column was successively eluted with 3, 5 and 4 mL of pentane, benzene and methanol, respectively, per gram of alumina. The eluent fractions of saturates, aromatics and resins were evaporated to dryness under a nitrogen stream.

The 'saturate' fraction was found to contain aromatic compounds when tested by thin layer chromatography on plates made of 5 per cent silver nitrate in silica gel and developed with n-heptane (Powell, 1969). The plates were visualized under ultraviolet light after being sprayed with a dilute solution of 2', 7' -dichlorofluoriscein. To remove these, the 'saturate' fraction was rechromatographed on alumina, which had been activated at 400°C under vacuum for 16 hours or more. The silver nitrate TLC also indicated small amounts of elemental sulphur in the saturate and aromatic fractions. This was removed by an additional treatment of the saturate and aromatic fractions with colloidal copper. The originally calculated total extract yields were reduced accordingly.

Gas chromatography of saturate fraction

A gas chromatographic analysis of the saturate fraction was carried out to quantify the distribution of the n-alkanes and chain isoprenoid compounds. Two columns were used with known standards to identify the n-alkanes and isoprenoids. An OV-101 support coated open capillary (SCOT) column commercially prepared by Perkin-Elmer was used for qualitative purposes only because nC_{17} /pristane and nC_{18} /phytane separations were incomplete.

Quantitative analyses were carried out on a salt eutectic column, which completely resolved pristane and phytane from the adjacent n-alkanes. The sodium-, potassium-, lithium-nitrate eutectic, 18.2, 54.5 and 27.3 per cent by weight, respectively (Hanneman et al., 1960), was purchased from Analabs, dissolved in water and added to 100/120 mesh Chromosorb (Johns-Manville) support material which previously had been wetted using acetone or methanol and water. About 30 per cent loading was used. The salt/support suspension was evaporated to near dryness on a rotary evaporator and the coated support then fired overnight in a muffle furnace at 400°C. It was found that carrier gas flows of 20 mL per minute required 60 to 80 pounds per square inch of pressure for an 18-foot (5.49 m) column resulting in septum and other leaks at the head of the column. Essentially similar separation of peaks was achieved on 60/80 mesh support also loaded about 30 per cent by weight. The 11-foot (3.35 m), 1/8-inch (3.18 mm) outside diameter stainless steel column required very small head pressures to achieve a flow of 30 mL per minute at 80°C. Peak skewing was corrected by stabilizing the column at 340°C for several hours.

Quantification of the n-alkanes and isoprenoids was attained by coinjection of authentic pristane and docosane (nC_{22}) in concentrations of exactly 1 per cent each of the weight of the total saturate fraction. By using the pristane/phytane and nC_{22}/nC_{21} ratios determined from an integrated chromatogram run prior to addition of the standards, the integrator response to 1 per cent of the two standards then could be calculated. This response factor, which is a function of sample size, was used to calculate the quantity of n-alkanes and isoprenoids as a percentage of the weight of the saturate fraction.

This technique of quantitatively determining n-alkane and isoprenoid concentrations in the saturate fraction has at least two definite advantages over the molecular sieving technique described by Fabre et al. (1969). It is considerably faster because both n-alkanes and isoprenoids are analyzed at the same time and no additional preparation of the saturate fraction is required. Also, this technique eliminates steps in which losses due to volatilization and partial solubilization could occur. These losses would tend to shift the mode of the distribution to higher or lower carbon numbers.

A 10 per cent solution of the saturate fraction in benzene was made and about 0.3 to 0.5 μ L injected onto the column of a Hewlett Packard 5710A gas chromatograph. The injection port was heated to 300°C but the septum and septum retainer nut were cooled with a water jacket to prevent septum decomposition and bleed. The column was temperature programmed to hold an initial temperature of 80°C for four minutes and then to heat at a rate of 8°C per minute up to a final temperature of 340°C, which was held for four minutes. The hydrogen flame ionization detector was held at 350°C. The helium carrier gas flow was set at about 30 mL per minute at 80°C but decreased noticeably as the temperature increased. Hydrogen and air flow rates were about 30 mL and 200 mL per minute, respectively.

Kerogen isolation

An acid digestion technique was used to isolate kerogen, the solvent insoluble organic matter in sediments and sedimentary rocks. Correia and Peniguel (1975) used a threestep acid digestion followed by density separation in a heavy liquid to remove residual mineral matter. Smith (1961) described an essentially similar technique with repeated acid treatment and no heavy liquid separation of the acid insoluble minerals. This system has the advantage of reducing the possibility of inadvertent fractionation and thus was adapted for use in this project.

The samples were ground in a disc mill to particles of about 2 mm to maintain as much as possible the integrity and identity of the organic components. The ground sample was treated twice with hot (about 80°C) 6N hydrochloric acid and then repeatedly washed with distilled water, centrifuged and decanted until the supernatant was neutral. Four 48 per cent hydrofluoric acid/hydrochloric acid (4:1) treatments were made at room temperature for 24 hours each, after which the sample was again washed with distilled water until neutral. The organic concentrate was then treated with hot concentrated hydrochloric acid to remove fluorides and fluosilicates, washed until neutral and freeze dried. An aliquot of this kerogen was mounted on a microscope slide for optical (transmission) analysis. The residue was pulverized with a mortar and pestle and X-ray diffractions were run on a powder to check that no hydroxylated, hydrate or carbonate minerals were present to preclude the possibility of interference with the quantitative determination of the elemental carbon and hydrogen in the organic matter.

Kerogen microscopy

Transmitted light microscopy of the kerogen smear slides was done on a Leitz Ortholux microscope with a tungsten light source and blue filter. The objective lenses were 16 and 25 power and the oculars 10 power.

Reflected light and fluorescence microscopy were done on a Leitz Ortholux MPV2 microscope. The UV excitation radiation source was a high-pressure mercury vapour lamp and visible light with wavelengths longer than 400 nm was filtered prior to incidence on the slide. Reflected ultraviolet and visible radiation was filtered by a 400 nm cutoff UV filter so that only autofluorescent radiation was visible.

Vitrinite reflectance data were unavailable in the literature for samples from one of the wells in this study and thus polished pellets of the unpulverized kerogen sample isolated as above were made using the ASTM procedure D 2797-72. Fifty maximum reflectance values were measured for each sample on a third Leitz microscope and the modal reflectance used as the value for that sample.

Reflectance values were reported as per cent of the vertically incident light, which was vertically reflected. This reflected light was quantified by using a photometer attached to the microscope, which was calibrated with a polished sodium glass standard.

Elemental analysis

Carbon, hydrogen, nitrogen and ash determinations were made in triplicate for all kerogen samples. The dried samples were weighed on a Cahn microbalance and analyzed on a Perkin-Elmer model 240 elemental analyzer. Purified organic reagents were used to calibrate the instrument. Ash content was determined by reweighing the tared platinum combustion boat after the elemental analysis was complete. Oxygen, sulphur and other possible elemental constituents of the kerogen such as phosphorous or halides were not determined.

DATA

Organic carbon

The average value of duplicate organic carbon analyses (Table 2) was used as a normalization parameter for the extraction data. That is, the weight of extract per gram of organic carbon (Table 2) is a useful parameter for relating the yield quality of the organic matter in various sedimentary samples. The absolute total organic carbon content has been used to define potential source rocks and to describe absolute petroleum yield potentials for a sediment (Ronov, 1958; Schraver and Zarella, 1963). As Correia and Peniguel (1975) pointed out, this is probably not a particularly useful exercise because of the considerable variability in both the amount and character of the quite different types of organic matter that make up the total organic fraction. Coaly samples containing 1 per cent total organic carbon might be expected to be quite different from algal samples with a similar total carbon content. The total organic carbon content used in conjunction with the vield factor could be a useful quantitative indicator of petroleum source potential.

The organic carbon data errors due to sample contamination by drill cuttings or borehole wall cavings are probably greater than the actual analytical error, which is about 2 per cent of the carbon value or less (see duplicate analysis results in Table 2).

Extract and hydrocarbon yield

The total solvent extract (Table 2) was fractionated into four parts--asphaltenes, saturates, aromatics and resins as described above. The results are listed in Table 3. The asphaltenes were precipitated to facilitate handling of the sample in subsequent steps. The saturates were separated from the aromatics for gas chromatography, but these two groups were treated together as hydrocarbons. The resins and asphaltenes together comprise a non-hydrocarbon or heteroatomic fraction. Because petroleum consists chiefly of hydrocarbons, they can be used to evaluate the relative richness of a petroleum source (Albrecht and Ourisson, 1969; Tissot et al., 1971; Powell, 1975). The percentage of hydrocarbons in an extract also has been observed to increase with increasing maturity of the organic matter. Because of the trend toward an increasing proportion of hydrocarbons in the extract with increasing maturity, the extract fraction distribution can be used to identify possible contamination and/or staining in a sample. The most probable extractable organic contaminants in drill cuttings are diesel fuel and lubricating oil and greases, all of which contain essentially no resins or asphaltenes. Thus the proportion of hydrocarbons in the extract of a contaminated

Table 3. Extract fractions: per cent asphaltenes, saturates, aromatics and resins in the total extract; per cent and yield of hydrocarbons

(a	3/8w) TIIX		24.1	47.6	0 610	341.2	0 17	18.3	10.3	19.9	1.91	19.3	17.4	25.5	0.01	30 4	37.3	27.0	41.2	117.6	33.4	· · · · · · · · · · · · · · · · · · ·	12.6	34.8	10.4	13.7	6.76	2000	C. 2C	T40.8	46.6	30.1	33.2	51.1	59.6		7.7	13.3	32.5	112.4?	61.4	92.6	88.0	47.1	33.0	55.8		25.8	12.8	16.5	20.3	17.2	20.8
квои	ЧТРКОСА	Z	35.6	57.2	1 10	C. 40	1 12	28.5	33 3	29.2	26.9	24.2	27.9	40.5		0 07	39.7	45.6	53.1	64.1	0.02		37.4	0.05	1 78	41.6	47.1	10.01	7.70	1.4.1	46.1	30.9	36.2	53.6	54.5		22.2	29.6	37.7	62.3	52.8	60.8	56.8	50.3	36.3	51.3		42.1	23.0	42.0	26.4	32.4	29.9
SI	RESIN		19.9	20.3		14.9	70 7	1.02	17 6	16.1	15.64	14.5	0.41	18.7		0 06	18.7	18.5	23.0	14.9	16.0		1 72	0000	7 07	7 88	1 81	1.01	1.71	0.21	17.8	13.3	13.4	17.6	19.9		37.0	23.5	22.8	17.5	19.7	17.5	16.1	18.3	15.0	16.6		32.4	36.8	27.7	20.0	19.2	17.8
SOI	ТАМОЯА		21.2	33.7		7.97	P. P	15 7	1.01	18.4	15.0	15.8	18.9	20.4	+ • 01	10 0	24.3	2.95	20.5	5.10	03 0		17.9	5 00	17 5	15.4	5.00	0 01	0. LT	8.12	18.8	16.5	17.2	19.1	24.3		13.1	11.2	18.1	22.6	19.7	18.2	19.2	18.1	17.8	21.9		17.5	11.0	27.1	15.9	22.1	19.4
SET	AAUTAS		14.4	23.5	C F	6.10	1.01	0.60	14.3	10.7	11 7	8.6	0.0	20.1		6 06	15.5	16.3	32.5	42.6	27.7		13.4	38.6	16.7	26.2	26.8		1.20	40.4	21.2	14.5	19.0	34.5	30.2		9.1	18.4	19.7	39.6	33.1	42.6	37.6	32.3	18.5	29.4		24.6	12.0	14.9	10.5	10.3	10.6
SENES	TJAH92A		44.5	22.5		0.0	0.00	515	1 07	54.7	57 5	61.1	57.3	40.8	0.01	31 0	41.6	35.9	23.9	21.0	32.7		34.5	0.10	25.4	0.55	8.75	C 00	1.07	LJ.J	36.1	55.8	50.4	28.8	25.6		40.4	46.9	39.5	20.2	27.5	21.7	27.1	33.9	48.7	32.1		25.5	40.2	30.3	53.6	48.4	52.3
			(713.2)	1944.6)	10 0101	(242.6)	(+-TCC)	17.225T	10.6102	2413.7)	2440 8)	2702.7)	2891.3)	2899.9)	10.000	16 00 1	1865.4)	2359.2)	2615.2)	2962.7)	2727 0)	10.000	(984.5)	1030 4)	1322 8)	1350 3)	136 6)		(T.7677	2429.3)	2639.6)	3014.5)	3041.9)	3105.9)	3398.5)		1130.8)	1204.0)	2078.7)	2615.2)	2709.7)	3020.6)	3188.2)	4084.3)	4239.8)	4258.1)		(329.2)	(887.0)	1636.8)	2953.5)	3218.7)	3474.7)
tres) E	ат) тээ] эт) тээ]	ţ	2340	6380 (101	96/	600T	1 1689	7888 (7919 (SUOR /	8867 (9486	9514 (5050 1	6120 (1740 (8580 (9720 (106201	2	1230	3410 6	1 0727	0277	0102	1 OTO	1 0701	0161	8660 (9890 (9980 (10190 (11150 (3710 (3950 (6820 (8580 (8890 () 0166	10460 (13400 (13910 (13970 (1080	2910	5370 () 0696	10560 (11400 (
			13			-T4										90-	20						-58														0-43											-44					
l		1	0		0	Ó										_	·			_			0							_						_	_					_			_			B		_			_
EXTRACT YIELD (mg/g)	67.6 83.3	410.9	86.3 80.2	64.2	57.9	68.1	59.7	1.6/	7.70	6.70	1 22	1.0/	6.02	2.20	2 201	L 03.0	1.00	1 07	1.04	30.6	0.00	7 15		1.00	1 101	110 0	0.011	0.16	4.66	109.4		34.7	44.9	86.2	180.4	116.3	152.3 I	154.9	93.7	91.0	108.8		61.2	55.8	39.2	62.5	53.2	69.66 B					_
AVERAGE EXTRACT YIELD (mg/g)	6.576 67.6 1.610 83.3	.378 410.9	2.156 86.3 1.020 80.2 0	1.314 64.2	1.222 57.9	1.140 68.1 0	1.102 59.7	T-6/ 7+++T	1.208 02.2 1.020	6.70 DCD.T		1.01 2.542 2.5 A 216 A 22 A 2	12 676 50 2		2 COL 0/T-T		1.CO 0C2.1	1 07 010 1	800 58 0	3 00	0.00	7 LS 7LS 7L		3 001 707 1	1 101 101 101 1		2 10 7 707 2	0.17 + 460.0	7.26 9T0.1	1.354 109.4		10.060 34.7	1.426 44.9	1.494 86.2	.830 180.4	.916 116.3	.804 152.3 I I	.900	.922 93.7	5.098 91.0	4.792 108.8		2.534 61.2	1.352 55.8	1.162 39.2	1.524 62.5	.970 53.2	1.594 69.6 B					_
CARBON AVERAGE EXTRACT YIELD (mg/g)	6.600 6.576 67.6 1.608 1.610 83.3	.384 .378 410.9	2.164 2.156 86.3 0- 1.028 1.020 80.2 0	1.332 1.314 64.2	1.232 1.222 57.9	1.160 1.140 68.1 0	1.112 1.102 59.7	T-6/ 7++-T QC+-T	T.200	T-044 T-020 02.20							0C7.T 0C7.T	1 236 1 212 1 1 22	877 807 58 0	207 202 207 207 207 207 207 207 207 207							2 10 707 6 00.7 5 00.7 5		1.620 1.616 4.24	1.364 1.354 109.4		10.056 10.060 34.7	1.396 1.426 44.9	1.484 1.494 86.2	.816 .830 180.4	.916 .916 116.3	.792 .804 152.3 1	.888. 900	.928 .922 93.7	5.108 5.098 91.0	4.808 4.792 108.8		2.568 2.534 61.2	1.460 1.352 55.8	1.152 1.162 39.2	1.536 1.524 62.5	.976 .970 53.2	1.588 1.594 69.6 B					
ZORGANIC CARBON AVERAGE EXTRACT YIELD (mg/g)	6.552 6.600 6.576 67.6 1.612 1.608 1.610 83.3	.372 .384 .378 410.9	2.148 2.164 2.156 86.3 0- 1.012 1.028 1.020 80.2 0-	1.296 1.332 1.314 64.2	1.212 1.232 1.222 57.9	1.120 1.160 1.140 68.1 0	1.092 1.112 1.102 59.7	1.6/ 7.447 dCt-1 dCt-1 d7t-1	T.200	6.70 0CO'T 5500 DTO'T		2.400 5.240 5.342 79.400 7.4000 7.40000 7.4000 7.4000 7.4000 7.4000 7.4000 7.40000 7.4000 7.4000 7.4000 7.4000 7.40000 7.40000 7.4000 7.4000 7.40000				L C.201 UD2.L 242.L 027.L 027.L	0C7'T 0C7'T 0C7'T 007'T	1 188 1 736 1 710 1 188 1	012 T-200 T-		0.00 200 700 1 770 T 770	17 29/ 12 21/ 17 21/ 12 21/ 12 21/					2 10 707 C 000 C 000 C		1.620 1.620 1.616 9.5.4	I.344 I.364 I.354 I09.4		10.064 10.056 10.060 34.7	1.456 1.396 1.426 44.9	1.504 1.484 1.494 86.2	.844 .816 .830 180.4	.916 .916 .916 .116.3	.816 .792 .804 152.3 III	.912 .888 .900 154.9	.916 .928 .922 93.7	5.088 5.108 5.098 91.0	4.776 4.808 4.792 108.8		2.500 2.568 2.534 61.2	1.244 1.460 1.352 55.8	1.172 1.152 1.162 39.2	1.512 1.536 1.524 62.5	.964 .976 .970 53.2	1.600 1.588 1.594 69.6 B					
SAMPLE EXTRACT YIELD eet (metres) %ORGANIC CARBON AVERAGE (mg/g)	2340 (713.2) 6.552 6.600 6.576 67.6 6380 (1944.6) 1.612 1.608 1.610 83.3	796 (242.6) .372 .384 .378 410.9	1809 (551.4) 2.148 2.164 2.156 86.3 6306 (1922.1) 1.012 1.028 1.020 80.2 0	6821 (2079.0) 1.296 1.332 1.314 64.2	7888 (2404.3) 1.212 1.232 1.222 57.9	7919 (2413.7) 1.120 1.160 1.140 68.1 0	8008 (2440.8) 1.092 1.112 1.102 59.7	1.6/ Z1471 0C51 0C51 0C51 (7.7012)	9480 (2091.3) 1.208 1.268 1.268 0.22 0.46 (2091.3) 1.228 1.208 0.22	6720 0001 HAND TINT (2022) 7746		1200 (1965 م) 1200 م)		8580 (2615.2) 11.110 11.112 11.22		7/20 (2902.1) 1.220 1.292 1.292 1.200 1.20.7 1.0200 (7502.0) 1.220 1.200 (7502.0)		3230 (08/ 5) 1 188 1 236 1 210 / VOI			1,1,20 (1,1,2,1,2) 1,0,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1								4.26 919.1 0.29.1 T.620 1.620 0.001	11150 (3398.5) 1.344 1.364 1.354 109.4		3710 (1130.8) 10.064 10.056 10.060 34.7	3950 (1204.0) 1.456 1.396 1.426 44.9	6820 (2078.7) 1.504 1.484 1.494 86.2	8580 (2615.2) .844 .816 .830 180.4	8890 (2709.7) .916 .916 .916 .16.3	9910 (3020.6) .816 .792 .804 152.3 II	10460 (3188.2) .912 .888 .900 154.9	13400 (4084.3) .916 .928 .922 93.7	13910 (4239.8) 5.088 5.108 5.098 91.0	13970 (4258.1) 4.776 4.808 4.792 108.8		1080 (329.2) 2.500 2.568 2.534 61.2	2910 (887.0) 1.244 1.460 1.352 55.8	5370 (1636.8) 1.172 1.152 1.162 39.2	9690 (2953.5) 1.512 1.536 1.524 62.5	10560 (3218.7) .964 .976 .970 53.2	11400 (3474.7) 1.600 1.588 1.594 69.6 H B					

Table 2. Per cent organic carbon and total extract yield as mg/g organic carbon

sample would be anomalously high relative to the nonhydrocarbon yield. Oil-stained or reservoir rocks yield extract results similar to those of contaminated samples but are frequently distinguishable by the content of n-alkanes and general distribution of the saturate fraction (see discussion on saturate fraction gas chromatography below).

Because all the laboratory solvents are distilled before use and the samples are handled only in glass, the errors due to laboratory contamination are insignificant to the interpretation of the data. Occasional blanks run on the solvents and alumina confirm that there is essentially no contamination of the samples in the laboratory. Extraction of pure alumina as a blank resulted in the recovery of less than 0.1 mg of material. Since samples are often contaminated at the drill site it is an important and routine procedure to check for possible errors and to discard or refrain from interpreting data that may be artifactitious.

N-alkane and isoprenoid distributions

The gas chromatography of the saturate fraction is a useful tool for characterizing sedimentary organic matter from other materials. Bray (1961), Bray and Evans (1965), Martin et al. (1963), Clark and Blumer (1967) and Powell and McKirdy (1973b) have discussed the interpretation of n-alkane distributions in terms of thermal maturity and source character of sediment. The odd-even carbon number predominance (Scalan, 1970) has been interpreted as an indicator of both the level of maturity and nature of the source and relatively immature, terrestrially derived organic matter shows the strongest odd predominance. Also, the modal shift from heavier to lighter compounds was associated with thermal degradation as well as source character. A review by Meinschein (1969) emphasized the biological precursor aspects of saturated hydrocarbons including n-alkanes, terpene derivatives and isoprenoid compounds.

Specific parameters such as the pristane/phytane ratio (Brooks et al., 1969; Powell and McKirdy, 1973a) and wax content (Hedberg, 1968) have been interpreted in terms of the relative importance of terrestrial plant input to a sediment. In the former case, the oxidation of phytol to phytanic acid and subsequent decarboxylation results in a high pristane concentration. On the other hand, if the initial oxidation step were precluded by deposition in a reducing environment, the reduction of phytol would lead to a relatively high concentration of phytane. These proposed alteration mechanisms have been somewhat substantiated by subsequent work of Brooks and Maxwell (1975) and Ikan et al. (1975). The interpretation of pristane/phytane ratios apparently is complicated, however, by the relatively low concentrations of both pristane and phytane at very low levels of thermal maturity. This is due to the lack of analytical precision of very small amounts of these compounds. In these cases, the pristane/phytane ratio cannot be used to interpret the oxidation of the depositional environment.

Terrestrially derived organics frequently contain high concentrations of wax (Brooks and Smith, 1967, 1969; Hedberg, 1968; Leythaeuser and Welte, 1969; Powell and McKirdy, 1973a), which is associated with leaf, pollen and spore cuticles of higher land plants. Crude oils associated with terrestrial sources, however, contain hexane or heptane as the predominant normal alkane (Martin et al., 1963) as well as substantial amounts of long chain alkanes. Combaz (1970) has observed the evolution of significant quantities of C_{14} to C_{17} alkanes from sporopollenin during experimental thermal degradation. Thus, a very wide range of alkanes has been observed and predicted in various quantities for terrestrially dominated sediments.

The n-alkane and acyclic isoprenoid concentrations in the saturate fractions of the Beaufort-Mackenzie samples are listed in Table 4. Both individual carbon number values and totals are given. Quantitative errors due to coincidence of unresolved peaks and integrator interpretation of the baseline were minimized but not eliminated by injecting samples of about the same volume onto the chromatograph. The shape of the unresolved hump consisting of many isomers of branched and cyclic saturates also influenced the integrated areas somewhat because a precise baseline could not be determined. Data from replicate chromatograms (see Table 4) indicate that the uncertainty of the percentages quoted is about 0.20 per cent for individual alkane compounds and about 2.0 per cent for the totals. Estimates of peak areas on the basis of peak height were made for some of the long-chain n-alkanes for which no integrator output was available because of unresolved shoulders or because the peak area was less than the threshold value. These estimates are noted using an approximation symbol (~) in Table 4.

Unidentified but relatively large peaks were observed in some of the chromatograms at retention positions of about nC_{20} on an OV-101 column and a retention about equivalent to pristane on a salt eutectic column. Thin-layer chromatography confirmed that these were not aromatic compounds and gas chromatography mass spectrometry indicated that they were tricyclic diterpanes (see discussion below). As no standards of these compounds were available, quantification was not attempted.

Kerogen analysis

Kerogen smear slides have been used to characterize dispersed organic matter into various classes such as herbaceous, coaly and sapropelic (Staplin, 1969; Burgess, 1974; Correia and Peniquel, 1975; Gunther, 1976a, b). Amorphous or unstructured debris is believed to derive from marine organisms such as algae and phytoplankton and to be deposited in nonoxidizing environments. The atomic hydrogen to carbon ratio is higher than that of terrestrially derived and/or oxidized organic matter. McIver (1967) and Tissot et al. (1974) have observed atomic H/C ratios ranging from below 0.5 to above 1.5. The lowest hydrogen content is related to fusain type material, whereas the hydrogen-rich organic matter probably is derived from algal debris. The empirical relationship between the occurrence of hydrogen-rich, sapropelic material and oil as opposed to the hydrogen-poor coaly/herbaceous gas correlation (Staplin, 1969) also has been demonstrated experimentally (Tissot et al., 1974).

Many of the above workers also have observed the yellow to brown to black colour changes of the organic matter, which results from thermal alteration. Various numerical scales have been used to describe the level of alteration from completely unaltered through mature or partially altered to degraded or metamorphosed. The "principal zone of oil formation" (Vassoevich et al., 1969, 1974) has been correlated with intermediate alteration (yellow to brown spores and pollen).

The organic matter types recognized in this study were:

- amorphous or sapropelic material, consisting of unstructured and most often diaphanous organic debris;
- herbaceous material, consisting of membranous, vascular and cuticlar fragments, spores, pollen and the unidentified structured fragments that are at least partly translucent;
- (3) woody material, consisting of elongate fibrous material ranging in colour from pale yellow to brown, but excluding modern wood, a drilling additive, which appears colourless; and
- (4) coaly material, consisting of black, opaque, usually angular particles.

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Carbon No.	0-13 2340 (713.2 m)	0-13 6380 (1944.6 m)	0-14 1809 (551.4 m)	0-14 6306 (1922.1 m)	Carbon No.	0-14 8008 (2440.8 m)	0-14 8867 (2702.7 m)	0-14 9486 (2891.3 m)	0-14 9514 (2899.9 m)
13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33	.06 .16 .15 .19 .19 .19 .23 .24 .38 .20 .37 .25 .44 .07 .47 .47 .03 .16 .01 .05	.05 .66 .99 1.12 1.10 .89 .83 .76 .71 .79 .69 .68 .64 .54 .36 .23 .31 .12 .20	.05 .25 .38 .39 .26 1.80 3.90 3.35 2.41 1.60 1.06 .81 .51 .54 .29 .37 .13 .15	.12 .26 .37 .24 .54 1.04 .64 .34 .23 .09 .12 .09 .10 ~.03 .13	13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33	.19 .36 .45 .51 1.39 3.36 3.21 2.20 1.82 1.43 1.34 .85 .76 .32 .23 .08 .19	.13 .21 .46 .53 .53 1.46 2.76 1.67 .97 .56 .41 .47 .52 .48 .36 .41	.12 .44 .89 .87 2.48 5.22 3.90 1.75 1.02 .66 .65 .55 .54 .31 .36 .14 .12	.20 .59 .97 .98 .82 1.37 2.49 1.90 1.13 .64 .44 .48 .35 .37 .25 .33 .10 .18
TOTAL	4.03	11.68	18.25	4.73	TOTAL	18.70	11.90	20.85	13.60
OEP (27)* WAX**	10.99 2.67	1.00 4.56	1.38 7.78	1.66 1.13	OEP (27) WAX	1.30 9.22	1.07 4.18	1.24 6.10	1.26 4.27
ISO C16 ISO C18 PRISTANE PHYTANE		.23 .57 2.65 1.16	.07 .21 .14 .19	.16 .33 2.87 1.00	ISO C16 ISO C18 PRISTANE PHYTANE	0.0 .16 .78 .21	.10 .40 2.64 .43	.42 1.00 6.79 .91	.12 .35 1.47 .40
TOTAL	-	4.61	.61	4.36	TOTAL	1.15	3.58	9.12	2.33
PRIS/PHYT	-	2.29	.76	2.87	PRIS/PHYT	3.62	6.11	7.46	3.66
				Poplicato		T 06 5250	1 06 6120	1.06.77/0	1.06.9590
Carbon No.	0-14 6821 (2079.0 m)	0-14 7888 (2404.3 m)	0-14 7919 (2413.7 m)	0-14 7919 (2413.7 m)	Carbon No.	(1600.2 m)	(1865.4 m)	(2359.2 m)	(2615.2 m)
13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33	.10 .27 .51 .59 .57 1.56 2.89 1.87 1.04 .77 .46 .65 .37 .60 .26 .73 .09 .25	.20 .35 .56 .60 .61 1.94 4.18 3.58 2.57 2.19 1.90 1.87 1.43 1.41 .80 1.01 .30 .42	.15 .18 .32 .35 .42 2.13 4.39 3.31 2.33 2.04 1.88 2.20 1.65 1.71 1.05 1.31 .48 .71	.09 .14 .28 .30 .30 1.94 .44? 3.18 2.24 1.93 1.91 2.17 1.69 1.62 1.03 1.36 .51 .70	13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33	.47 2.48 2.07 1.50 .67 .22 .23 .11 .10 .13 .26 .12 .31 .21 .41 .10 .34 ~.04 .17	.82 1.74 .89 .44 .53 .19 .26 .24 .45 .27 .53 .20 .48 ~.08 .22	.40 1.58 1.33 1.73 .23? 1.28 .44 .26 .42 .40 .65 .40 .65 .40 .64 .30 .59 .19 .50	.59 2.69 2.39 1.94 1.24 .76 .63 .50 .45 .42 .43 .27 .36 .21 .28 .11 .25
TOTAL	13.58	25.92	26.61	21.84?	TOTAL	9.94	7.32	11.34	13.54
OEP (27) WAX	1.97 5.22	1.28 13.90	1.27 15.36	1.22 15.16	OEP (27) WAX	2.49 2.09	3.25 2.47	2.41 3.67	1.82 2.33
ISO C16 ISO C18 PRISTANE PHYTANE	.06 .19 .96 .33	.15 .28 1.77 .36	.12 .43 1.34 .32	.17 .39 1.37 .33	ISO C16 ISO C18 PRISTANE PHYTANE	.81 1.05 .50 .26	0.0 0.0 .83 .46	-	.83 .46 1.08 .36
	1 50	2 56	2 20	2.26	TOTAL	2.62	1.29	-	2.73
TOTAL	1.53	2.50	2.20	2.20	PRIS/PHYT	1.95	1.82	_	2.99

Table 4. Normal and isoprenoid alkane and wax concentrations as weight per cent of saturate fraction; odd-even predominance and pristane/phytane ratio

*OEP(n) = $\begin{pmatrix} C_{n-2} + 6C_n + C_{n+2} \\ 3C_{n-1} + 3C_{n+1} \end{pmatrix} - 1^{(n-1)}$

*WAX is defined as n-alkanes with 22 or more carbon atoms.

Carbon No.	D-43 3950 (1204.0 m)	D-43 6820 (2078.7 m)	D-43 8580 (2615.2 m)	D-43 8890 (2709.7 m)	Carbon No.	C-58 (2429
13 14 15 16 17 18 19 20 21 22 23 24 22 23 24 25 26 27 28 29 30 31 32	.14 .26 .53 .97 1.50 1.77 2.13 1.76 1.37 .65 .27 .23 .09	.17 .63 .43 .39 .35 .28 .28 .24 .28 .31 .35 .17 .27 .11 .37 .15 .70 .12 .47	.52 .91 1.55 1.76 1.82 1.69 1.51 1.25 1.12 .83 .59 .51 .36 .30 .20 .21	.19 .35 .64 .69 .67 .63 .60 .47 .48 .40 .25 .22 .19 .15 .10 .15 .09 .06	13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32	
33	11 66	6 09	15 15	6 31	33 	
OEP (27) WAX	2.61	3.00 3.02	1.14	1.09	OEP (27) WAX	
ISO C16 ISO C18 PRISTANE PHYTANE	.02 .22 .88 1.47	.17 .17 .36 .38	.40 .40 1.72 .70	.19 .25 .92 .61	ISO C16 ISO C18 PRISTANE PHYTANE	1.3 .6 .8 .2
TOTAL	2.59	1.08	3.22	1.98	TOTAL	3.2
PRIS/PHYT	.59	.95	2.48	1.51	PRIS/PHYT	3.0
Carbon No.	C-58 3410 (1039.4 m)	C-58 4340 (1322.8 m)	C-58 4430 (1350.3 m)	C-58 7520 (2292.1 m)	Carbon No.	C-58 (3105
13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33	.07 .10 .12 .07 .04 .06 .05 .05 .08 .11 .06 .10 .05 .10 .02 .11 .05 .07	.06 .04 .12 .09 .08 .12 .19 .13 .18 .27 .15 .25 .43 .41 .11 .49 .13 .19	.31 .22 .10 .07 .08 .08 .08 .08 .13 .20 .10 .15 .30 .21 .08 .33 .16 .23	1.13 3.86 3.38 2.68 .62 .43 .33 .21 .12 .11 .17 .09 .17 .08 .15	13 14 15 16 17 18 19 20 21 21 22 23 24 25 26 27 28 29 30 31 32 33	.1 2.9 3.3 2.7 1.3 .5 .3 .2 .1 .1 .1 .1 .0 .0
TOTAL	1.29	3.44	3.05	13.55	TOTAL	12.3
WAX	0.75	2.61	1.15	0.77	OEP (27) WAX	0.6
ISO C ₁₆ ISO C ₁₈ PRISTANE PHYTANE	.01 .05 .05 .07	.07 .12 .18 .17	.04 .14 .13 .11	1.20 2.70 .82 .31	ISO C16 ISO C18 PRISTANE PHYTANE	1.3 1.1 1.1 .2
TOTAL	.18	.53	.42	5.02	TOTAL	3.9
PRIS/PHYT	.61	1.07	1.15	2.61	PRIS/PHYT	2.0

Carbon No.	C-58 7970 (2429.3 m)	C-58 8660 (2639.6 m)	C-58 9890 (3014.5 m)	C-58 9980 (3041.9 m)
13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33		.12 .69 1.25 .31 .35 .28 .16 .10 .10 .13 .07 .13	.73 2.03 2.31 1.32 .64 .22 .26 .21 .22 .25 .15 .23 .12 .18 ~.06 .09	1.25 2.41 2.56 1.51 .66 .42 .23 .15 .15 .13
TOTAL		3.69	9.22	9.47
OEP (27) WAX		0.43	1.87 1.30	0.28
ISO C ₁₆ ISO C ₁₈ PRISTANE PHYTANE	1.39 .69 .89 .29	.04 .17 .29 .16	.24 .54 .91 .32	.51 .64 .90 .33
TOTAL	3.27	.66	2.00	2.38
PRIS/PHYT	3.05	1.83	2.84	2.74
Carbon No.	C-58 10 190 (3105.9 m)	C-58 11 150 (3398.5 m)	D-43 3710 (1130.8 m)	Replicate D-43 3710 (1130.8 m)
13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33	.12 2.90 3.38 2.73 1.30 .53 .37 .21 .14 .14 .16 .07 .12 .07	.20 1.81 2.63 2.57 1.51 .76 .47 .34 .24 .24 .24 .25 .16 .25 .15 .19 .10 .17	.13 .23 .41 .68 .89 1.10 1.31 .93 .77 1.02 .50 .86 .25 1.06 .34 1.64 .18 .82 .07 .32	.11 .20 .20 .36 .59 .77 .95 1.13 .81 .53 .88 .43 .74 .22 .92 .30 1.42 .15 .71 .06 .27
TOTAL	12.30	12.02	13.74	11.75
OEP (27) WAX	0.63	1.52 1.51	3.72 7.83	3.72 6.63
ISO C16 ISO C18 PRISTANE PHYTANE	1.30 1.13 1.14 .43	.73 .63 1.27 .43	.11 .24 .47 1.14	.10 .21 .29 1.00
TOTAL	3.99	3.06	1.96	1.59
PRIS/PHYT	2.66	2.95	.41	.29

Carbon No.	Replicate J-06 8580 (2615.2 m)	J-06 9720 (2962.7 m)	J-06 10 620 (3237.0 m)	C-58 3230 (984.5 m)	Carbon No.	D-43 13970 (4258.1 m)	B-44 1080 (329.2 m)	B-44 2910 (887.0 m)	B-44 5370 (1636.8 m)
13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33	.58 2.70 2.37 1.98 1.27 .78 .65 .54 .46 .44 .41 .25 .34 .21 .27 .13 .27	.75 3.48 2.96 2.03 1.14 .60 .38 .26 .15 .13 .13	.90 3.27 2.52 1.77 1.12 .65 .54 .43 .41 .40 .41 .24 .33 .17 .19 ~.07 .13	.09 .26 .27 .39 .38 .43 .42 .63 .37 .62 .34 .93 .35 .78 .22 .40	13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33	.09 .31 .40 .54 .57 .52 .66 .66 .55 .57 .45 .31 .38 .21 .22	.10 .15 .17 .23 .14 .17 .16 .16 .25 .34 .17 .41 .13 .74 .08 .52 ~.02 .23	.05 .10 .18 .16 .25 .26 .32 .26 .62 .27 .48 .22 .72 .26 1.19 .13 .53 ~.03 .17	.20 .32 .46 .37 .43 .50 .39 .41 .61 .28 .53 .21 .74 .25 .75 .10 .45 ~.05 .11
TOTAL	13.65	12.00	13.56	7.15	TOTAL	6.44	4.17	6.21	7.17
OEP (27) WAX	1.69 2.32	0.26	1.70	2.54	OEP (27) WAX	2.14	6.48 2.89	3.06 4.88	3.10 4.49
ISO C16 ISO C18 PRISTANE PHYTANE	.76 .44 1.07 .36	.84 .37 .68 .28	1.05 .41 1.05 .34	0.0 .10 .25 .47	ISO C16 ISO C18 PRISTANE PHYTANE	.08 .14 .69 .53	.03 .06 .20 .16	0.0 .09 .25 .17	0.0 .07 .23 .22
TOTAL	2.63	2.18	2.85	.82	TOTAL	1.44	.46	.51	.52
PRIS/PHYT	2.99	2.38	3.14		PRIS/PHYT	1.30	1.22	1.50	1.05
Carbon No.	D-43 9910 (3020.6 m)	D-43 10 460 (3188.2 m)	D-43 13400 (4084.3 m)	D-43 13 910 (4239.8 m)	Carbon No.	B-44 9690 (2953.5 m)	B-44 10 560 (3218.7 m)	B-44 11 400 (3474.7 m)	
13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33	.31 .62 .93 1.21 1.44 1.54 1.51 1.19 1.01 .70 .51 .45 .31 .23 .13 .15	.37 1.13 1.60 1.63 1.66 1.56 1.42 1.06 .98 .64 .47 .41 .27 .18 .10 .12	.30 .56 .98 1.27 1.51 1.44 1.24 .92 .70 .41 .26 .25 .15 .18 .12 .18 .05 .10	.17 .32 .39 .57 1.59 .62 .92 .72 .70 .63 .60 .49 .45 .33 .34 .19 .34	13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33	.12 .23 .30 .38 .34 .45 .51 .47 .53 .75 .51 .94 .53 .85 .37 1.11 .21 .62	.31 .37 .54 .48 .60 .66 .52 .62 .71 .52 .80 .53 .77 .41 1.02 .23 .63	.07 .13 .25 ? .15 .47 .58 .50 .59 .70 .50 .69 .44 .54 .27 .62 .15 .27	
TOTAL	12.24	13.59	10.63	9.39	TOTAL	9.22	10.18	6.92	
OEP (27) WAX	1.09 3.49	1.11 3.17	1.43 2.40	1.35 3.37	OEP (27) WAX	1.98 6.42	1.72 6.24	1.61 4.77	
ISO C16 ISO C18 PRISTANE PHYTANE	.21 .28 1.01 1.05	.14 .38 1.16 1.12	.11 .31 1.36 1.20	.14 .14? .64 .29	ISO C16 ISO C18 PRISTANE PHYTANE	.11 .32 1.73 .54	.44 .50 2.94 .64	-	
TOTAL	2.55	2.80	2.97	1.20	TOTAL	2.70	4.52	-	
PRIS/PHYT	.97	1.03	1.14	2.23	PRIS/PHYT	3.20	4.53		

The concentration of woody fragments was quite low, less than 3 or 4 counts per slide, and therefore was not treated as a separate analytical category but rather added to the herbaceous total.

The term 'coaly' is used here to describe black, opaque fragments and includes charcoal, true coal and blackened woody or herbaceous material. All of these types of organic debris contain low amounts of hydrogen relative to other types of detrital organic matter. Coal, on the other hand, refers to a collection of herbaceous macerals individually recognizable under reflected light or in thin sections.

The point count distribution of herbaceous, coaly and sapropelic material is presented in Table 5. About 700 to 1000 points were counted for each sample, the larger being counted when the mineral content of the slide was higher. Results from duplicate slides indicate that there may be as much as a 10 per cent variation in the quantity of any one group. This error may be due to misidentification of organic matter type, sample inhomogeneity and/or statistical distribution.

Carbon, hydrogen and nitrogen elemental analysis data are reported in Table 6. The triplicate analyses indicate that absolute error due to weighing, inhomogeneity of the sample, and instrument error, including incomplete combustion, is no more than 1 per cent. The atomic H/C ratio variation from the above analytical error (up to 0.090) is substantial relative to the total range observed in this set of samples, but insignificant relative to the range reported for kerogens in general (Tissot et al., 1974). The wide variation in ash content reported is due to spillage of the powder during depressurization of the instrument sample chamber. The highest value is assumed to be the most reliable, but ash-free normalization of the carbon content of high-ash samples indicates that substantial amounts of ash are lost every time. This is probably because of volatilization of some components of the ash during oxidative combustion.

Vitrinite reflectance

The percentage of vertically incident light which is reflected from a polished surface of the coal maceral vitrinite has been found to increase with thermal alteration and increasing rank of the coal (see Krevelen, 1961, for a historical summary). Vitrinite reflectance (Ro) has been used as a thermal alteration index because it is essentially independent of all geological processes except temperature and time (Karweil, 1956). Thus, Ro values (Gunther, 1976a, b and unpublished data) have been used as an independent indicator of the level of thermal alteration of the organic fraction in the sediments of the Mackenzie Delta area.

Data were not available, however, for the Kumak C-58 well, so polished pellets of kerogen were made and Ro values were determined by the author (Table 7). The errors caused by sample contamination of caved material from higher in the borehole and geologically reworked and redeposited material are minimized by plotting a reflectance distribution for 50 observations per sample. By selecting a modal value which is most reasonable in relation to data from other samples from the same borehole, bimodally distributed samples can be interpreted with reasonable certainty (Castaño and Sparks, 1974).

Other data

Drill cuttings gas and organic carbon logs. A substantial amount of chemical and other information pertinent to the study area was available to the author. Cuttings gas and organic carbon logs (Snowdon and McCrossan, 1972; Snowdon and Roy, 1975) were plotted for a number of wells in the Mackenzie Delta. These were used primarily to identify the immature/mature transition zone, thereby defining the level of organic metamorphism. Recent data from this laboratory (as yet unpublished) indicate that organic metamorphic zones recognized by the cuttings gas technique are offset somewhat from the transitions defined by other techniques. Extract and Ro data cross into the 'mature facies' at a somewhat greater depth than the cuttings gas data.

Vitrinite reflectance. Ro values were determined by P.R. Gunther of the Geological Survey of Canada, Calgary for all the wells used in this study except Kumak C-58. These data were used also to determine the level of thermal alteration of the sediments. Table 8 lists Ro extrapolated from downhole curves to the depths which were sampled for this study. The maximum error is probably less than 0.10 Ro units because the sampling density and quality of the available data are quite high. For example, 25 data points were plotted (Gunther, 1976b, Fig. 4) over an 8000-foot (2438.4 m) interval and a 'best-fit' reflectance versus depth curve drawn.

Solvent extraction from other wells. Solvent extractions have been done for sample sets from wells in the Beaufort-Mackenzie Basin by technical support staff in this laboratory. Most of this work is being carried out to obtain a broader regional picture of the basin than is afforded by this study. The data generated from wells in or near this study area corroborate the author's work.

Petroleum occurrences in the Mackenzie Delta. Well history reports containing drill stem test results and recovered sample analyses also were available to the author. These data were useful for indicating zones that may be oil stained (i.e. reservoir) and thus contain a predominance of epigenetic hydrocarbons. Table 9 contains the results of drill stem tests in the wells studied.

RESULTS AND DISCUSSION

Organic carbon

The organic carbon content of the samples (Table 2) covers a very wide range (0.378 - 17.514%) and both maximum and minimum values occur in the fluviodeltaic subenvironment. The wide scatter in carbon content of the fluviodeltaic samples (Fig. 4a) is due in part to variable amounts of coal in the samples. The decreasing mean organic carbon content from fluviodeltaic through delta front to prodelta subenvironments also reflects the coal content in the samples. The delta front and prodelta modal values are essentially identical but the incidence of one or two coal-bearing samples in the former raises the mean organic carbon content significantly. Student T-tests (Perles and Sullivan, 1958, p.240-241) indicate that the mean organic carbon content of the fluviodeltaic samples is significantly higher than that of either of the other subenvironments at the 95 per cent confidence level. The organic carbon distribution is influenced so strongly by the presence of coal that no other trends (such as might result from oxidation/ reduction or variation in organic production levels) can be observed in the data.

Extract yields

The extract yields (mg total extract/g organic carbon) as listed in Table 2 and plotted as histograms in Figure 4b show a very wide range of values for all three subenvironments. Contamination of the sample by refined products, notably diesel fuel, results in a very high yield for the Ellice O-14 . sample from the depth of 796 feet (242.6 m). The gas chromatogram of the saturate fraction (discussed below) clearly confirms the contamination of this sample and other chromatograms indicate that some of the other samples may be contaminated slightly with diesel fuel. The same chromatographic data indicate that in fact all of the core samples from the Ellice O-14 well have been contaminated somewhat by C_{19} and heavier normal alkanes. Thus the yields of seven of the delta front samples are probably slightly high as are three other fluviodeltaic and two prodelta samples. The 411 mg/g yield from the Ellice O-14 sample at 796 feet (242.6 m) was not included in the calculation of the mean extract yields shown in Figure 4b.

Table 5.	Percentag	e distribu	ution of	herbace	ous, coa	ly,
and sapro	opelic mat	erial in k	erogen s	mear sli	ides	

±	SAMPLE feet (met	res)	%HERBACEOUS	%COALY	%SAPROPEL	DEPOSITIONAL ENVIRONMENT
0-13	2340*	(713.2)	73.9	26.1	0.0	delta front
0 10	6380*	(1944.6)	52.3	46.1	1.6	prodelta
0-14	796	(242.6)	80.0	16.1	3.8	fluviodeltaic
	1809	(551.4)	68.7	30.2	1.1	fluviodeltaic
	6306	(1922.1)	77.4	22.7	0.0	prodelta
	6821	(2079.0)	69.7	30.3	0.0	delta front
	7888	(2404.3)	84.8	14.9	0.4	delta front
	7919	(2413.7)	69.3	29.9	0.7	delta front
	8008	(2440.8)	75.4	24.6	0.0	delta front
	8867	(2702.7)	46.5	53.5	0.0	delta front
	9486	(2891.3)	72.5	27.2	0.3	delta front
	(9514	(2899.9)	43.7	56.3	0.0	delta front
	(9514	(2899.9)	51.0	49.9	0.0	
J-06	5250*	(1600.2)	65.0	34.7	0.3	delta front
	6120*	(1865.4)	48.0	52.1	0.0	fluviodeltaic
	7740*	(2359.2)	44.1	55.9	0.0	fluviodeltaic
	8580*	(2615.2)	64.5	35.6	0.0	prodelta
C-58	3230	(984.5)	50.9	47.4	1.7	prodelta
	3410	(1039.4)	61.8	37.6	0.6	fluviodeltaic
	4340	(1322.8)	70.0	28.6	1.4	prodelta
	4430	(1350.3)	72.5	25.2	2.3	delta front
	7010	(2136.6)	48.4	51.6	0.0	fluviodeltaic
	7520	(2292.1)	68.0	31.6	0.4	fluviodeltaic
	7970	(2429.3)	65.4	34.6	0.0	delta front
	8660	(2639.6)	61.5	38.2	0.3	prodelta
	9890	(3014.5)	57.9	41.7	0.4	fluviodeltaic
	9980	(3041.9)	55.0	44.6	0.4	fluviodeltaic
	10190	(3105.9)	69.9	30.2	0.0	delta front
	11150	(3398.5)	72.9	26.7	0.4	prodelta
D-43	3710	(1130.8)	63.9	35.6	0.5	fluviodeltaic
	3950	(1204.0)	43.8	55.8	0.4	delta front
	6820	(2078.7)	53.6	46.4	0.0	prodelta
	(8580	(2615.2)	56.4	43.1	0.5	delta front
	(8580	(2615.2)	59.4	40.0	0.6	
	8890	(2709.7)	75.8	23.6	0.6	prodelta
	9910	(3020.6)	76.3	17.2	6.5	delta front
	10460	(3188.2)	61.2	36.6	2.2	prodelta
	13400	(4084.3)	50.4	49.6	0.0	prodelta
	13910	(4239.8)	58.2	39.5	2.3	fluviodeltaic
	13970	(4258.1)	68.6	31.0	0.4	delta front
B-44	9600	(2926.1)	66.6	30.0	3.3	delta front
	10620	(3237.0)	65.2	34.8	0.0	delta front
	(11460	(3493.0)	64.5	27.8	7.7	prodelta
	(11460	(3493.0)	61.6	37.2	1.2	
B-44	1080+	(329.2)	75.7	19.2	5.2	fluviodeltaic
	2910+	(887.0)	75.4	23.5	1.1	prodelta
	5370+	(1636.8)	61.7	37.8	0.5	prodelta
	9690+	(2953.5)	81.2	15.8	3.0	delta front
	10560+	(3218.7)	71.9	26.9	1.3	delta front
	11400+	(3474.7)	66.9	29.2	3.9	prodelta

*These samples are from intervals adjacent to those of other data types
 due to insufficient sample.
+These samples prepared using a flotation technique after acid digestion.

SAMPLE feet (metres)	ZN	%C	%H	%ash	atomic H/C	atomic C/N
0 10 00/04	1 51	(1. 70	1 05	0.40	007	17 70
(712 2)	1.51	61.78	4.25	9.49	.826	47.73
(713.2)	1 30	59 68	4.30	9.17	.839	47.81
	1.59	59.00	4.00	12.12	.021	50.09
0-13 6380*	0.86	38.48	2.89	35.50	.899	52.20
(1944.6)	1.04	38.72	2.74	36.45	.849	43.44
	0.86	38.97	2.93	33.63	.903	52.87
0-14 796	0.96	55.39	3.78	11.65	.820	67.31
(242.6)	1.04	54.82	3.75	?	.821	61.50
	1.02	55.29	3.78	20.30	.821	63.24
0-1/ 1800	0.80	25 04	1 07	41 61	800	36 52
(551.4)	0.89	25.04	1 83	41.01	.090	32 90
())1.4)	0.74	26.06	1.90	40.40	.909	39.51
0-14 6306	1.57	55.26	3.37	24.27	.731	41.06
(1922.1)	1.54	54.95	3.36	23.96	.735	41.63
	1.62	55.11	3.41	24.28	.742	39.69
0-14 6821	0.58	22.28	1.44	47.48	.778	44.82
(2079.0)	0.64	22.24	1.47	45.34	.791	40.54
	0.57	22.12	1.43	48.46	.773	45.27
0-14 7888	1 62	58 25	3 70	21 97	762	41 95
(2404.3)	1.66	58.13	3.72	21.37	.767	40.85
(210110)	1.77	58.20	3.66	22.21	.754	38.36
0.1/ 7010		54 17				16.10
0-14 /919	1.41	56.17	3.31	?	.708	46.48
(2413.7)	1.40	44.79	3.31	24 66	.712	44.58
	1.50	55.50	5.27	24:00	.700	41.91
0-14 8008	1.68	55.80	3.29	23.45	.708	38.75
(2440.8)	1.71	55.87	3.34	22.88	.718	38.12
	1.71	55.98	3.31	22.37	.709	38.19
0-14 8867	1.46	52.46	3.04	29.81	.696	41.92
(2702.7)	1.37	53.05	3.08	29.63	.696	45.18
	1.37	52.65	3.16	25.78	.720	44.84
0-14 9486	1 55	58 95	3 47	2	706	44 37
(2891.3)	1.60	58.85	3.58	24.55	.730	42.91
(20)210)	1.61	58.20	3.46	24.78	.713	42.17
0-14 9514	1.33	51.39	3.07	31.35	.718	45.08
(2899.9)	1.34	50.97	3.05	?	./18	44.38
	1.20	50.51	2.99	÷	• / 14	40.50
J-06 5250*	1.55	52.64	3.65	18.30	.833	39.62
(1600.2)	1.56	52.54	3.82	17.57	.872	39.29
	1.47	52.30	3.76	17.15	.862	41.51
J-06 6120*	0.87	32.44	2.33	37.66	.864	43.50
(1865.4)	0.92	32.38	2.39	36.06	.886	41.06
	0.89	32.53	2.28	39.10	.843	42.64
1-06 7740*	1 77	62 52	4 60	9 37	833	41.21
(2350 2)	1 76	62.92	4.73	9.15	.902	41.75
(2339.2)	1.77	62.67	4.60	9.73	.881	41.31
J-06 8580*	1.06	35.42	1.95	43.81	.661	38.98
(2015.2)	1.07	35.58	2.10	38.36	./3/	41 51
	T*00	55.50	2.23	50,50		41.51
C-58 3230	0.42	13.66	0.85	65.14	.749	37.94
(984.5)	0.45	14.05	0.88	64.15	.749	36.43
	0.45	14.03	0.89	65.58	.700	36.37

Table 6. Kerogen elemental analysis data: nitrogen, carbon, hydrogen, ash

*These samples are from intervals adjacent to those of other data types due to insufficient samples.

SAMPLES feet (metres)	ZN	%C	% H	%ash	atomic H/C	atomic C/N
C-58 3410	0.46	15.21	0.95	59.80	.746	38.58
(1039.4)	0.45	15.17	0.95	60.79	.752	39.33
	0.48	15.21	0.90	64.02	.708	36.97
C-58 4340	1.59	51.82	3.10	?	.718	38.02
(1322.8)	1.84	52.22	2.85	19.06	.656	33.11
	1.84	51.59	2.97	?	.692	32.71
C-58 4430	0.73	19.30	1.14	54.60	.711	30.84
(1350.3)	0.63	19.41	1.18	51.45	.732	35.94
C-58 7010	1 9/4	67 18	4 51	2 91	806	40.40
(2136.6)	2.01	66.86	4.63	3.70	.831	38.81
(2130.0)	2.14	67.39	4.58	3.00	.816	36.74
C-58 7520	2.01	53.86	3.61	19.36	.805	31.26
(2292.1)	1.87	53.96	3.74	20.65	.832	33.66
,	1.89	54.22	3.81	18.42	.844	33.47
C-58 7970	1.18	36.22	2.49	39.11	.826	35.81
(2429.3)	1.32	36.53	2.34	?	.768	32.29
	1.81?	37.31	2.48	38.88	.821	24.05?
C-58 8660	1.46	50.02	3.40	28.37	.816	39.98
(2639.6)	1.71	50.95	3.43	25.75	.809	34.76
	1.72	51.70	3.56	25.03	.825	35.07
C-58 9890	1.64	55.49	3.90	20.65	.844	39.47
(3014.5)	1.85	55.30	3.95	20.96	.856	34.87
	2.18	55.52	3.90	20.13	.843	29./1
C-58 9980	1.66	55.23	4.13	18.01	.898	38.82
(3041.9)	1.72	55.16	3.99	19.73	.869	37.41
	1.76	54.87	3.93	20.56	.860	36.37
C-58 10190	1.44	55.24	3.81	20.67	.828	44.75
(3103.9)	1 34	54.90	3.75	19 82	.043	43.82
	T*04	04.0T	5.75	19.02	.025	47.55
C-58 11150	0.92	31.96	2.01	49.86	.755	40.53
(3398.5)	0.97	32.35	2.00	48.41	.744	38.91
	0.82	31.69	2.08	45.40	. /88	45.09
D-43 3710	0.79	49.19	3.61	?	.881	72.64
(1130.8)	0.90	49.30	3.59	14.79	.873	63.91
	0.83	48.97	3.56	14.21	.871	68.83
D-43 3950	0.81	40.84	2.59	25.21	.761	58.82
(1204.0)	0.95	40.87	2.65	25.58	.778	50.19
	0.89	41.06	2.53	24.59	.739	53.82
D-43 6820	0.97	53.49	3.82	10.44	.857	64.34
(2078.7)	0.92	52.54	3.74	12.91	.854	66.63
	1.27	53.15	3.81	12.//	.860	48.83
D-43 8580	1.26	45.74	3.11	33.00	.816	42.35
(2615.2)	1.25	46.18	3.10	32.10	.805	43.10
	1.18	46.39	3.18	30.15	.822	45.87
D-43 8890	1.01	28.11	1.87	43.00	.797	32.47
(2/09./)	0.//	28.03	1.89	41.98	.810	42.4/
	1.01	27.91	1.89	12.70	.013	32.24
D-43 9910	1.30	45.36	3.03	33.10	.792	40.71
(3020.6)	1.40	43.30	3.05	32.82	.803	37.97
	1.19:	DT. 20:	3.94:	34.40	. / 99	53.49

Table 6 (cont.)

SAMPLES feet (metres)	7N	%C	%H	%ash	atomic H/C	atomic C/N
D-43 10460 (3188.2)	1.32 1.33 1.53	45.54 45.50 46.17	3.30 2.98 3.30	? 34.12 31.65	.870 .786 .858	40.25 39.91 35.21
D-43 13400 (4084.3)	0.77 0.69 1.00	27.62 27.55 27.15	1.79 1.65 1.72	49.70 50.52 50.44	.779 .720 .760	41.85 46.68 31.68
D-43 13910 (4239.8)	1.94 1.97 2.00	65.30 64.19 65.29	4.47 4.43 4.16	14.53 15.54 15.16	.821 .828 .765	39.27 38.01 38.09
D-43 13970 (4258.1)	1.78 1.68 1.71	57.82 57.44 57.88	4.10 4.09 4.09	22.26 ? 21.49	.851 .855 .849	37.90 39.89 39.49
B-44 9690* (2953.5)	1.76 1.65 1.65	57.97 58.10 57.98	3.68 3.87 3.90	? 20.69 19.98	.762 .799 .807	38.43 41.08 41.00
B-44 10560* (3218.7)	1.11 1.19 1.10	35.64 35.48 35.38	2.14 2.24 2.25	40.61 40.85 ?	.721 .758 .763	37.46 34.78 37.52
B-44 11400* (3474.7)	1.93 1.57 1.74	53.38 58.40 58.57	3.68 3.50 3.75	22.26 22.71 21.91	.756 .719 .768	32.27 43.40 39.27

^{*}These samples are from intervals adjacent to those of

other data types due to insignificant samples.



Figure 4a. Histograms of per cent organic carbon data by subenvironment.



Histograms of total solvent extract yield (mg/g) by subenvironment.

	Depth	Reflectance	(Ro) mode(s)
4340'	(1322.8 m)	0.42	
7010'	(2136.6 m)	0.52,	0.67*
7520'	(2292.1 m)	0.62	
8660'	(2639.6 m)	0.67	
9890'	(3014.5 m)	0.57	
9980'	(3041.9 m)	0.47,	0.57*

Table 7. Vitrinite reflectance data for Shell Kumak C-58 samples

SAMPLE		E	Ro	Membrane colour	
feet (metres)		tres)		monor corecur	
0-13	2340	(713.2)	.58	yellow-dark yellow	
	6380	(1944.6)	.60	yellow-dark yellow	
0-14	796	(242.6)	.44	light yellow	
	1809	(551.4)	.48	light yellow	
	6306	(1922.1)	.65	yellow-dark yellow	
	6821	(2079.0)	.67	yellow-dark yellow	
	7888	(2404.3)	.71	yellow-dark yellow	
	7919	(2413.7)	.71	yellow-dark yellow	
	8008	(2440.8)	.72	yellow-dark yellow	
	8867	(2702.7)	.75	yellow-dark yellow	
	9486	(2891.3)	.78	dark yellow	
	9514	(2899.9)	.78	dark yellow	
J-06	5250	(1600.2)	.48	yellow-dark yellow	
	6120	(1865.4)	.50	yellow-dark yellow	
	7740	(2359.2)	.57	yellow-dark yellow	
	8580	(2615.2)	.60	yellow-dark yellow	
D-43	3710	(1130.8)	.34	light yellow-yellow	
	3950	(1204.0)	.35	light yellow-yellow	
	6820	(2078.7)	.43	yellow-dark yellow	
	8580	(2615.2)	.52	dark yellow	
	8890	(2709.7)	.49	dark yellow	
	9910	(3020.6)	.49	brown	
	10 460	(3188.2)	.50	yellow-dark yellow	
	13 400	(4084.3)	.62	dark yellow-brown	
	13 910	(4239.8)	.72	yellow-dark yellow	
	13 970	(4258.1)	.72	dark yellow-brown	
B-44	1080	(329.2)	.27	light yellow	
	2910	(887.0)	.29	yellow	
	5370	(1636.8)	.40	yellow	
	9690	(2953.5)	.56	dark yellow	
	10 560	(3218.7)	.60	dark yellow	
	11 400	(3474.7)	.62	yellow-dark yellow	
C-58	3230	(984.5)	-	yellow-dark yellow	
	3410	(1039.4)	-	light yellow	
	4340	(1322.8)	-	light yellow-yellow	
	4430	(1350.3)	-	yellow	
	7010	(2136.6)	-	yellow	
	7520	(2292.1)	-	yellow-dark yellow	
	7970	(2429.3)	-	yellow	
	8660	(2639.6)	-	dark yellow	
	9890	(3014.5)	-	dark yellow	
	9980	(3041.9)	-	yellow-dark yellow	
	10 190	(3105.9)	-	dark yellow	
	11 150	(3398.5)	-	dark yellow	

Well	Test Interval feet (metres)			Recovered Fluid	
KUGPIK 0-13	DST #11	6464-6469	(1970.2-1971.8)	slightly gassy mud	
ELLICE O-14	DST #7	4866-4916	(1483.2-1498.4)	mud, water	
KUMAK J-06	DST #1	1942-2400	(591.9-731.5)	gas	
	DST #2	9659-10 365	(2944.1 - 3159.3)	water, mud	
	DST #4	8145-8180	(2482.6-2493.3)	gas, condensate cut mud and filtrate	
	DST #5	8020-8040	(2444.5 - 2450.6)	mud	
	DST #6	7761-7777	(2365.6-2370.4)	gas cut mud, trace condensate	
	DST #7	7566-7590	(2306.1 - 2313.4)	oil, gas	
	DST #8	7048-7068	(2148.2-2154.3)	oil, water, gas	
	DST #9	6214-6243	(1894.0 - 1902.9)	mud, filtrate, water	
	DST #10	4451-4475	(1356.7 - 1364.0)	oil, mud, water	
	WLT #2	4777	(1456.0)	gas, water	
	WLT #3	4470	(1362.5)	water	
	WLT #4	4465	(1360.9)	water	
	WLT #5	3830	(1167.4)	gas, water	
KUMAK C-58	WLT #1	4110	(1252.7)	gas water	
	WLT #2	3364	(1025.3)	water	
	WLT #4	7068	(2154.3)	filtrate	
	WLT #5	6176	(1882.4)	filtrate	
	WLT #6	4565	(1391.4)	gassy filtrate	
TAGLU D-43	DST #1	13 942-13 982	(4249.5-4261.7)	water, mud, filtrate, gas	
	DST #3	12 790-12 840	(3898.4-3913.6)		
		12 856-12 880	(3918.5-3925.8)	water	
	DST #4	9590-9680	(2923.0-2950.5)	gas, condensate	
	DST #5	8380-8400	(2554.2-2560.3)	gas, condensate	
NETSERK B-44	DST #2	10 744-10 845	(3274.8-3305.6)	mud	
	DST #4	10 692-10 723	(3258.9-3268.4)	mud, gas	
	DST #5	10 334-10 364	(3149.8-3158.9)	mud	
	DST #6	9442-9482	(2877.9-2890.1)	water	
	DST #7	9442-9482	(2877.9-2890.1)	mud, gas	

Table 9. Drill stem and wire line test recoveries for the Upper Cretaceous-Tertiary for wells in this study

The increasing extract yield averages (Fig. 4b) indicate an increasing richness in the delta front and prodelta subenvironments. However, a Student T-test indicates that the difference between the means is not significant and may be due to statistical scatter.

similarity of all The extract yield three subenvironments (Fig. 4b) could be a function of the relative levels of maturity of the different samples. That is, if the fluviodeltaic samples were selectively at a lower maturity level than the prodelta samples, one might expect the latter samples to yield more extract than the former, strictly from the different level of alteration. The data in Table 2, however, indicate that the scatter is essentially independent of both maturity and subenvironment of deposition. For example, the fluviodeltaic sample J-06 7740 feet (2359.2 m) has only half the yield of the fluviodeltaic sample immediately above it at 6120 feet (1865.4 m). The three prodelta samples from the same well have yields both greater than and less than those from the fluviodeltaic subenvironment and furthermore show no trend with increasing depth.

A plot of Ro or level of maturity versus the total extract yield for the three subenvironments (Fig. 5) allows the comparison of yields of the various samples that have experienced similar thermal histories. The points are scattered widely and the only apparent trend is the relatively low yield of the delta front samples approaching maturity, that is at Ro values of 0.60 to 0.80.

Four samples have very high total extract yields (>150 mg/g). The two highest values may be somewhat in error. The C-58 7970-foot (2429.3 m) sample may be stained, that is, it may be from a reservoir rock or section that contains epigenetic hydrocarbons (see below). The sample from D-43 8580 feet (2615.2 m) may contain a little diesel fuel contamination (see discussion below of gas chromatograms of saturate fraction).

In general, the wide variation in yields does not seem to be correlative with the various subenvironments of deposition within a delta complex. With the exception of the four high-yield samples, the extract results are consistent with those of Philippi (1956), Tissot et al. (1971), and other unpublished results from this laboratory.



Figure 5. Vitrinite reflectance versus total extract yield.

Hydrocarbon yields

Hydrocarbon yields, that is, the ratio of milligrams of saturates plus aromatics to grams of organic carbon (Table 3), have been used to indicate petroleum source potential (Philippi, ibid.; Tissot et al., ibid.). Using the hydrocarbon fraction yield rather than the total extract yield circumvents the problem caused by using different extraction solvent systems. Chloroform extracts contain substantially less resinous and asphaltic material than do benzene-methanol extracts. Most solvent systems, however, effect the complete removal of hydrocarbons from a rock sample. Powell (in prep.), using literature values (Philippi, ibid.; Tissot et al., ibid.) and data from almost 200 extraction samples in the Canadian Arctic, has established an empirical yield classification system based on the milligram yield of clearly indigenous hydrocarbons (saturates plus aromatics) per gram of organic carbon in the rock. Yields of less than 30 mg/g hydrocarbon are considered to indicate no petroleum source potential while yields of 30 to 50, 50 to 80 and greater than 80 mg/g are considered as marginal, good and excellent potential sources, respectively.

To assess the yields of samples from the various subenvironments, a plot of the hydrocarbon yield versus Ro was made (Fig. 6). Again, the same four samples with a high total extract yield show a high hydrocarbon yield. The C-58 7970-foot (2429.3 m) sample, however, contains an anomalously high proportion of hydrocarbons (74.7%, see Table 3) and thus probably contains epigenetic or migrated petroleum. The three D-43 samples must be classed as having excellent source potential. Another sample, J-06 9720 feet (2962.7 m), is also an excellent potential source rock with a hydrocarbon yield of 117.6 mg/g, but was not plotted in Figure 6 because no Ro data were available from that depth.

According to the classification scheme outlined above, eight of the samples listed in Table 3 are good or excellent potential source rocks. Samples C-58 7520 feet (2292.1 m) and O-14 796 feet (242.6 m) have been excluded because of the probability of epigenetic hydrocarbons. The eight samples all occur at a present depth of 8580 feet (2615.2 m) or more and have Ro values of 0.49 or greater. Only one fluviodeltaic sample is rated as at least a good source rock, while four delta front and three prodelta marine samples fall into this category. This distribution of potential source qualities among the subenvironments of deposition may reflect a difference in the organic matter type contained in the respective sediments but is probably an artifact of the sampling because the fluviodeltaic samples analyzed are fewer than for either of the other two subenvironments.



Figure 6. Vitrinite reflectance versus extractable hydrocarbon yield (mg/g).

The richness of these high-yield samples is essentially independent of the amount of organic carbon present. Although none of the highly coaly samples is classed as a good or excellent potential source rock, the organic carbon content of the samples so classed ranges from 0.830 per cent to 4.792 per cent organic carbon.

The high hydrocarbon extract yields are related to the level of thermal alteration only insofar as a minimum Ro of 0.49 appears necessary before a sample attains a significant yield. Most of the high-yield samples in this study occur between Ro values of 0.49 and 0.60 with only one good potential source at a higher reflectance. Because hydrocarbon evolves principally at Ro values of 0.80 to 0.90 (Vassoevich et al., 1969; Correia and Peniguel, 1975; Gunther, 1976a), it is apparent that thermal maturity is not the principal factor controlling the hydrocarbon yield in this set of samples.

Saturate fraction chrmoatograms

Gas chromatograms were run of the saturate fractions of the extracts (Figs. 7 - 52), to assess the amount of wax in the extracts and to determine the pristane/phytane ratio. The peaks were integrated by an electronic integrator and the quantity of n-alkanes and isoprenoids determined by using internal standards (Table 4). The amount of contamination by diesel fuel also can be estimated from the chromatogram of the saturate fraction. The sample from 796 feet (242.6 m) of Ellice O-14, for example, is contaminated heavily with diesel fuel (Fig. 9). The asphaltene and resin contents of this sample are much lower than those of any other sample at such a low maturity level (see Ro values, Table 3). The narrow boiling range gas chromatographic humps centred at about normal heptadecane (nC_{17}) and the lack of n-alkanes (Fig. 9) are characteristic of the saturate fraction of diesel fuel. The Ellice O-14 1809-foot (551.4 m) sample also is contaminated with diesel fuel (Fig. 10) but the relatively low proportion of saturates and aromatics in the extract (Table 3) indicates that the amount of contamination is probably relatively low. The C-58 3410-foot (1039.4 m) sample on the other hand has an anomalously high hydrocarbon content (Table 3) and a large hump in the diesel fuel range (Fig. 26), indicating substantial contamination. A few other samples have a hump in the chromatogram in the diesel range, but also have substantial amounts of n-alkane and isoprenoid compounds (see for example D-43 3710 feet, 1130.8 m, Fig. 37; D-43 6820 feet, 2078.7 m, Fig. 39). Since the percentage of hydrocarbons in the extract for these samples is not abnormally high the observed hump probably is representative of the sample and contamination by diesel fuel is insignificant.

Another type of contamination also is apparent from the gas chromatograms of the saturates. All of the core samples (Ellice O-14) have the same modal distribution of n-alkanes with eicosane and heneicosane $(nC_{20} \text{ and } nC_{21})$, the largest peaks in every case (Figs. 10 - 18). This contamination with C_{20} and C_{21} (and probably by an entire homologous series of n-alkanes) is common to core samples from not only the Beaufort-Mackenzie Basin, but also the Sverdrup Basin in Arctic Canada and Alberta. It has been observed also in other western Canadian core samples extracted, fractionated and chromatographed in the organic geochemistry laboratory in L'Institut Français du Pétrole in Paris and thus is not an artifact of this laboratory. The source of this contamination has not been identified as yet but a study is presently under way to ascertain whether or not it is due to the shipping and storage containers used for core samples in western Canada.

Although a number of the samples extracted were from the fluviodeltaic subenvironment and contained substantial amounts of coaly, land-derived organic matter (see below). no high-wax samples were found in this study. The results of Hedberg (1968) and Powell and McKirdy (1973b) on crude oils and the results of this project on extracts suggest that either (1) terrestrial input is a necessary but not a sufficient condition for the generation of high-wax crudes, or (2) high-wax crudes are not necessarily generated from sediments with high-wax extracts. Analyses of Mackenzie Delta crudes in this lab (Powell and Snowdon, 1975) indicate that, in fact, high-wax crude petroleums have not been found in the Beaufort-Mackenzie Basin and that large amounts of terrestrial input into the sediment do not necessarily result in the generation of high-wax extracts or crudes.

Ten samples contain more than 5 per cent wax in the saturate fraction (Table 4). Wax is defined as n-alkanes with 22 or more carbon atoms. Six of these samples are from the Ellice O-14 borehole and must be discounted because of the core contamination problem discussed above. The only other samples with more than 5 per cent wax in the saturate fraction represent all three depositional subenvironments: Taglu D-43 3710 feet (1130.8 m) (fluviodeltaic), Netserk B-44 9690 feet (2953.5 m) and 10 560 feet (3218.7 m) (delta front), and Kumak C-58 3230 feet (984.5 m) (prodelta).

Maturation trends can be observed in n-alkane distribution as well as the position of the unresolved hump. The odd to even predominance is defined after Scalan (1970) as follows:



where C_n is the quantity of the n-alkane with n carbon atoms. Table 4 contains the calculated values for OEP (27). The drop from a value of 11.0 to 1.0 for the two samples from the Kugpik O-13 well does not really constitute a trend, but the low value obtained for the 6380-foot (1944.6 m) sample reflects its maturity because the concentration of the nC₂₅ to nC₂₉ alkanes is significant. The results from the O-14 well (Table 4) are unclear, possibly from the contamination by waxy components.

The OEP (27) values drop from greater than 2.4 at depths shallower than 8000 feet (2438.4 m) to less than 1.8 at greater depths in the Kumak J-06 well. The unresolved hump in the triterpane/sterane region (about nC_{26}) decreases in size below 8000 feet (2438.4 m) (Figs. 19 - 24) until there is no triterpane hump visible in the samples from 9720 and 10,620 feet (2962.7 m and 3237.0 m) (Figs. 23, 24).

The OEP (27) values drop off at about 4000 feet (1219.2 m) in the Kumak C-58 well and remain quite low except for the sample from 9890 feet (3014.5 m), for which

the OEP (27) is 1.87. The interpretation of an OEP must be made with considerable caution, however, when the absolute concentrations of the C_{25} to C_{29} components are as low as they are in this latter case.

The Taglu D-43 samples show a continuous decrease in the OEP (27) from 3710 feet (1130.8 m) (3.7) through 10,460 feet (3188.2 m) (1.1). The two deeper D-43 samples, 13,400 and 13,910 feet (4084.3 and 4239.8 m)(Figs. 44, 45) have a slightly higher OEP (1.43 and 1.35, respectively). The factor controlling the OEP apparently is not related to the depositional environment because the former is a prodelta sample and the latter fluviodeltaic. It may be that the nature of the source material is reflected in these higher values, but the organic facies are not coincident with the subenvironments of deposition. The unresolved hump centred at about nC19 for almost all of the samples in the Taglu D-43 well corresponds with the chromatographic retention of diterpenoid derivatives, that is, branched and cyclic alkane isomers with about 20 carbon atoms. Because diesel fuel occurs at about nC_{17} , it is impossible to preclude the possibility of slight contamination of these samples on the basis of the gas chromatograms. The amount of contamination, if any, must be slight because the total height of the hump at nC_{17} retention, which would be a composite of a diesel fuel peak and the C19 distribution flank, is less than the height of nC_{19} peak. Also the diterpane hump in the Taglu D-43 samples is considerably broader than would be expected of a highly contaminated sample.

The maturation trends of decreasing OEP (27) and shifting hump are clearly visible in the chromatograms from the Netserk B-44 well (Figs. 47-52). The OEP (27) drops from 6.5 at 1080 feet (329.2 m) to 1.6 at 11,400 feet (3474.7 m). Over the same depth interval the hump shifts markedly from an nC_{29} primary mode to an nC_{17} primary mode. Again, the trends in the chemical data due to increasing thermal maturation are not modified by simultaneous changes in depositional subenvironment.

The isoprenoid concentrations as weight percent of the saturate fraction are given in Table 4 along with the calculated pristane/phytane ratio. In crude oil samples, ratios of one to three have been associated with low-wax, marine sediments while ratios of three to five have been correlated with high-wax, nearshore to terrestrial deposits (Powell and McKirdy, 1973a). Pristane/phytane ratios in sediments (Powell et al., 1976) range from 1.3 to 4.0 for marine sediments, 2.0 to 5.0 for low-salinity, brackish water sediments, and from 4.0 to 7.4 for coals in northern England for samples with Ro values of about 0.50 to 0.80. Connan (1974) has shown that the pristane/phytane ratio in coals increases with increasing alteration in the reflectance range 0.50 to 0.70. Taking this into account, Powell et al. (1976) still observed an increasing pristane/phytane ratio as the depositional environment became less marine.

The pristane/phytane ratios for this data set are independent of depositional subenvironment but confirm the results of Brooks et al. (1969) and Connan (1974) in that the ratio increases with increasing Ro (Fig. 53). The magnitude of the ratio is somewhat different from the literature values, however, since the maximum ratio for Australian and New Zealand coals reaches about 12 while only one sample from this study is greater than 7.0. This may reflect a slightly lower level of thermal alteration of the samples in this study.

The saturate fraction chromatograms show that a few samples contain anomalous concentrations of pristane relative to the n-alkanes:

Kugpik O-13 6380 feet (1944.6 m), prodelta, Figure 8 Taglu D-43 8890 feet (2709.7 m), prodelta, Figure 41 Taglu D-43 13,910 feet (4239.8 m), fluviodeltaic, Figure 45 Taglu D-43 13,970 feet (4258.1 m), fluviodeltaic, Figure 46 Netserk B-44 9690 feet (2953.5 m), delta front, Figure 50 Netserk B-44 10,560 feet (3218.7 m), delta front, Figure 51



- Figure 7. Gas chromatogram of the saturate fraction of Kugpik O-13 2340 feet (713.2 m).
- Figure 9. Gas chromatogram of the saturate fraction of Ellice O-14 796 feet (242.6 m).
- Figure 8. Gas chromatogram of the saturate fraction of Kugpik O-13 6380 feet (1944.6 m).
- Figure 10. Gas chromatogram of the saturate fraction of Ellice O-14 1809 feet (551.4 m).



Figure 11. Gas chromatogram of the saturate fraction of Ellice O-14 6306 feet (1922.1 m).

- Figure 13. Gas chromatogram of the saturate fraction of Ellice O-14 7888 feet (2404.3 m).
- Figure 12. Gas chromatogram of the saturate fraction of Ellice O-14 6821 feet (2079.0 m).
- Figure 14. Gas chromatogram of the saturate fraction of Ellice O-14 7919 feet (2413.7 m).



Figure 15. Gas chromatogram of the saturate fraction of Ellice O-14 8008 feet (2440.8 m).

- Figure 17. Gas chromatogram of the saturate fraction of Ellice O-14 9486 feet (2891.3 m).
- Figure 16. Gas chromatogram of the saturate fraction of Ellice O-14 8867 feet (2702.7 m).
- Figure 18. Gas chromatogram of the saturate fraction of Ellice O-14 9514 feet (2899.9 m).



Figure 19. Gas chromatogram of the saturate fraction of Kumak J-06 5250 feet (1600.2 m).

Figure 20.

- Gas chromatogram of the saturate fraction of Kumak J-06 6120 feet (1865.4 m).
- Figure 21. Gas chromatogram of the saturate fraction of Kumak J-06 7740 feet (2359.2 m).
- Figure 22. Gas chromatogram of the saturate fraction of Kumak J-06 8580 feet (2615.2 m).



- Figure 23. Gas chromatogram of the saturate fraction of Kumak J-06 9720 feet (2962.7 m).
- Figure 25. Gas chromatogram of the saturate fraction of Kumak C-58 3230 feet (984.5 m).
- Figure 24. Gas chromatogram of the saturate fraction of Kumak J-06 10,620 feet (3237.0 m).
- Figure 26. Gas chromatogram of the saturate fraction of Kumak C-58 3410 feet (1039.4 m).



- Figure 27. Gas chromatogram of the saturate fraction of Kumak C-58 4340 feet (1322.8 m).
- Figure 28. Gas chromatogram of the saturate fraction of Kumak C-58 4430 feet (1350.3 m).
- Figure 29. Gas chromatogram of the saturate fraction of Kumak C-58 7010 feet (2136.6 m).
- Figure 30. Gas chromatogram of the saturate fraction of Kumak C-58 7520 feet (2292.1 m).



Figure 31. Gas chromatogram of the saturate fraction of Kumak C-58 7970 feet (2429.3 m).

Figure 32.

- Gas chromatogram of the saturate fraction of Kumak C-58 8660 feet (2639.6 m).
- Figure 33. Gas chromatogram of the saturate fraction of Figure 34. Kumak C-58 9890 feet (3014.5 m).
- Gas chromatogram of the saturate fraction of Kumak C-58 9980 feet (3041.9 m).



Figure 35. Gas chromatogram of the saturate fraction of Kumak C-58 10,190 feet (3105.9 m).

Figure 36.

- Gas chromatogram of the saturate fraction of Kumak C-58 11,150 feet (3398.5 m).
- Figure 37. Gas chromatogram of the saturate fraction of Taglu D-43 3710 feet (1130.8 m).
- Figure 38. Gas chromatogram of the saturate fraction of Taglu D-43 3950 feet (1204.0 m).



- Figure 39. Gas chromatogram of the saturate fraction of Taglu D-43 6820 feet (2078.7 m).
- Figure 41. Gas chromatogram of the saturate fraction of Taglu D-43 8890 feet (2709.7 m).
- Figure 40. Gas chromatogram of the saturate fraction of Taglu D-43 8580 feet (2615.2 m).
- Figure 42. Gas chromatogram of the saturate fraction of Taglu D-43 9910 feet (3020.6 m).



- Figure 43. Gas chromatogram of the saturate fraction of Taglu D-43 10,460 feet (3188.2 m).
- Figure 45. Gas chromatogram of the saturate fraction of Taglu D-43 13,910 feet (4239.8 m).
- Figure 44. Gas chromatogram of the saturate fraction of Taglu D-43 13,400 feet (4084.3 m).
- Figure 46. Gas chromatogram of the saturate fraction of Taglu D-43 13,970 feet (4258.1 m).



- Figure 47. Gas chromatogram of the saturate fraction of Netserk B-44 1080 feet (329.2 m).
- Figure 49. Gas chromatogram of the saturate fraction of Netserk B-44 5370 feet (1636.8 m).
- Figure 48. Gas chromatogram of the saturate fraction of Netserk B-44 2910 feet (887.0 m).
- Figure 50. Gas chromatogram of the saturate fraction of Netserk B-44 9690 feet (2953.5 m).



Figure 51. Gas chromatogram of the saturate fraction of Netserk B-44 10,560 feet (3218.7 m).

This phenomenon was observed by Deroo et al. (1974, Fig. 5) in Albertan heavy oils and was attributed to the selective removal of n-alkanes via biodegradation. The substantial n-alkanes in the anomalous pristane samples in this study, however, suggest from the level of alteration that significant pristane has been generated in the sediment but that the n-alkane generation has not yet reached its optimum rate. It is suggested, therefore, that the anomalous pristane phenomenon is a transient feature observed in samples with sufficient quantities of the necessary precursors and at a particular, relatively low level of thermal diagenesis.

A number of samples contained large amounts of one or two compounds that did not have a chromatographic retention time corresponding to any of the n-alkanes or isoprenoid compounds (Figs. 7, 19, 20, 21, 29, 30, 52). Mass spectra were run for the two largest of these peaks in sample J-06 7740 feet (2359.2 m) (Fig. 21) on a Finnigan GCMS guadrupole system by Eric Peake at the University of Calgary. The fragmentation masses and relative ion intensities are given in Table 10. The parent ion of the largest gas chromatograph peak (m/e=276) suggested a saturated tricyclic C20 compound, that is a diterpane, related to abietic acid or abietane (Douglas and Grantham, 1974). Themain fragmentation peaks for authentic fichtelite as given by Douglas and Grantham (see Table 10) are similar to those of the unknown compounds in the J-06 7740 feet (2359.2 m) sample except that the M-43 peak of the fichtelite, which corresponds to the loss of an isopropyl side chain, is not present in the spectrum of the unknown compound. The very strong M-29 peak (m/e=247) of the unknown sample suggests an ethyl side chain on a neocarbon atom (quadruply bonded to other carbon atoms). This suggests that the structure is that of sandaracopimarane (Fig. 54), which was isolated from Agathis australis resin by Thomas (1969).



Figure 52. Gas chromatogram of the saturate fraction of Netserk B-44 11,400 feet (3474.7 m).



Figure 53. Vitrinite reflectance versus pristane/phytane ratio.

Although no parent ion peak was observed for the second major unknown component, the gas chromatographic retention and the mass spectral fragmentation pattern are both consistent with a saturated C_{19} diterpane, which could be derived via the decarboxylation of sandaracopimaric acid, also found in *A. australis* resin by Thomas (ibid.). Because authentic standards of these compounds were not available for mass spectral analysis on the quadrupole instrument used, positive identification could not be made.

m/e	Largest Peak relative intensity	Second largest peak relative intensity	<u>Fichtelite (from</u> Douglas & Grantham, 1974)
96	15	?	64
97	23	42	30
98	3	5	22
105	10	8	3
107	23	-	13
108	13	16	7
109	53	86	100
110	8	13	35
111	10	13	8
121	28	13	12
123	88	100	30
124	18	14	12
125	13	5	7
135	23	13	11
136	10	-	3
137	45	39	12
138	10	5	2
139	5	8	2
149	13	-	6
150	13	-	4
151	30	20	4
163	98	13	26
164	23	2	4
165	18	2	3
177	15	8	4
179	8	-	3
191	63	5	43
192	15	2	7
205	8	-	-
219	_	· _	22
231	3	-	-
233	3	25	-
247	100	2	9
248	20	-	2
261	28	-	-
262	10	?	40
276	23	_	-
277	5	-	-

Table 10. Fragmentation mass and relative abundance data from mass spectra of "extra" peaks in the saturate fraction gas chromatogram of sample J-06 7740 feet (2359.2 m)



Figure 54. Chemical structure of sandaracopimarane

Anders and Robinson (1971) observed both C19 and C20 tricyclic alkanes (among others) in the Green River Formation but interpreted these as alteration products of pentacyclic triterpanes. They noted also the absence of the M-43 peak or loss of an isopropyl group, but used these data to suggest that the m/e = 191 peak was derived from the ABC rings of a pentacyclic triterpane. Reed (1977), however, reported an entire homologous series of tricyclic diterpane compounds in oil seep saturated samples from the same geographic area. This homologous series may indicate that these compounds were related to diterpenoids rather than derived from triterpanes. The low level of thermal degradation of both the Green River Shale and the Beaufort-Mackenzie samples supports this interpretation. Furthermore, the saturated tricyclic compounds in this study in substantial concentrations indicate that they were in fact derived from diterpenoids and that there was a high resin input into the sediment. One may further speculate that the resin-generating plants were not of the Juniperus or Pinus genera because of the apparent lack of abietic acid derived compounds such as fichtelite, which are common to these plants (Douglas and Grantham, 1974).

The northward deepening of the high concentrations of sandaracopimarane(?) and related compounds (2340 feet, 713.2 m, in Kugpik O-13; 7740 feet, 2359.2 m, in Kumak J-06; and 11,400 feet, 3474.7 m, in Netserk B-44) follows both the trend in maturation and also stratigraphic time planes. Thus these compounds may be a maturation phenomenon and represent a particular stage of thermal alteration of the organic matter or, conversely, their occurrence may be a time marker caused by the deposition in all three subenvironments of the delta complex of resins derived from a particular species or genus of plants that grew within the drainage basin over a restricted time interval.

Kerogen-type distribution

The results of the visual kerogen distribution analysis are contained in Table 5. The coaly content ranged from about 15 to 56 per cent of the organic matter. Based on a Student T-test of the various averages, the distribution of coaly material was found to be independent of the subenvironment of deposition (Fig. 55) with the possible exception that very coaly samples (>50%) do not occur in the prodelta subenvironment. The herbaceous organic matter content was predominant in almost all the samples and sapropelic material comprised less than 3 per cent of the total in all but four samples (O-14 796 feet, 242.6 m, fluviodeltaic; D-43 9910 feet, 3020.6 m, delta front; B-44 9600 feet, 2926.1 m, delta front; and B-44 11 460 feet, 3493.0 m, prodelta).

The sapropel content also was found to be independent of the depositional subenvironment. Of the four samples with more than 3 per cent sapropel, only the B-44 11,460-foot (3493.0 m) sample represented prodelta deposition.

The organic matter type distributions as determined by Gunther (1976a) for the Taglu D-43 and Kugpik O-13 wells are generally similar to those determined in this study, except that much less sapropel was observed in the latter. This may be a function of the slide preparation technique or the objectivity of the point count quantification method used in this study. To test the preparation technique used by Gunther, six kerogen samples from Netserk B-44 were floated on a solution of zinc bromide in hydrochloric acid, which had a specific gravity of 2.0, to remove the heavy minerals such as pyrite, anatase, rutile and synthetic fluorides. The fraction which sank was noted to be black. Point counts of the organic matter types were made for smear slides of float fraction and results have been included in Table 5. The herbaceous content of the density-separated set is consistently higher than in the comparable samples that were not density-separated. This suggests that either mineral matter in the undifferentiated slides was identified mistakenly as coaly material, or coaly fragments in the density-differentiated sample had a specific gravity greater than 2.0. Opaque minerals such as pyrite and rutile, however, have a relatively distinct morphology and were identified as inorganic by using reflected light. Thus the second explanation for the fractionation would seem to be more probable than the former. Fragments associated with mineral matter would have the external morphology of coaly material and be identified as such in transmitted light, but could have high densities due to the mineral content of the fragment.

A third set of organic matter type data for the Taglu area (Hawkings and Hatlelid, 1975) suggests that the Neogene sediments contain about 40 per cent sapropel and that the Paleogene sediments contain about 15 per cent sapropel. The basis of the classification scheme of the various organic types was not specified, but the absence of a 'coaly' fraction and the occurrence of 40 to 70 per cent woody material suggest that the data from this study are not relatable in any way to the Hawkings and Hatlelid data. This third data set demonstrates that visual kerogen analyses are subjective at best and almost meaningless for comparison with the results of other workers unless the methods used are specified.



Figure 55. Histograms of per cent coaly material in kerogen smear slides.

Membrane and spore colorations were noted for the smear slides during the point counting, and the results are listed in Table 8. There is a correlative trend of increasing Ro and darkening membrane with increasing depth within wells such as Ellice O-14 and Taglu D-43. However, given Ro values do not correlate with given colorations from one borehole to another. For example, light yellow membranous material in the O-14 well corresponds with Ro values of 0.44 to 0.48, whereas essentially similar Ro values in the D-43 well occur in samples in which the membranous material is yellow to dark yellow. The acid preparation of all the samples was the same and furthermore the samples were not prepared in well or depth sequences. Thus the variation of colour for a given Ro must be due to inherent organic differences between the wells or errors in colour assignment or Ro values.

It is apparent that both organic matter type distribution and coloration determinations are somewhat subjective. The subjectivity of the former is related to preparation techniques and the identification and classification system. Similarly, evaluations of membrane and spore coloration are subjective in that it must be decided whether particles are geologically recycled clasts or caved from higher in the borehole during drilling, or if they contain natural pigments that enhance the observed colour. Thus comparing results of different workers or interpreting any results in terms of hydrocarbon potential must be attempted with caution.

Staplin (1969), Tissot et al. (1974) and Gunther (1976a) have suggested that herbaceous and coaly organic matter will tend to yield natural gas rather than oil in response to thermal degradation. The petroleum discoveries in the Richards Island area, especially the Taglu gas field (Bowerman and Coffman, 1975), along with the predominantly herbaceous and coaly organic content of all of the subenvironments of deposition of the Upper Cretaceous-Tertiary (Table 5), tend to support the above conclusions. Tissot et al. (1974) also suggested that the yields of hydrocarbons from herbaceous and coaly organic matter should be substantially lower than for sapropelic material. Typical extract yields from Douala Basin herbaceous samples range up to about 60 ma/a (Vandenbroucke et al., 1976). Results from this study, however, indicate that much higher yields of hydrocarbon (over 100 mg/g) are possible, even from samples containing substantial amounts of coaly material (Fig. 56). It is also significant to note that yields are high at Ro values of 0.45 to 0.65 (Fig. 6). This level of maturity is lower than stated as necessary by Bowerman and Coffman (1975), who interpreted the Taglu gas source as being from the more deeply buried flanks of the reservoir structure, and Gunther



Figure 56. Per cent coaly organic matter versus hydrocarbon yield.

(1976a), who suggested that hydrocarbon generation from herbaceous material would be initiated at Ro values of 0.50 to 0.80 and not reach a maximum until Ro values were 0.80 to 0.90.

A possible explanation for these apparently anomalously high hydrocarbon yields from herbaceous organic matter at low levels of thermal alteration is that the evolved petroleum (natural gas and condensate) is derived from resinite, a coal maceral derived from tree resins, or from dispersed resinous material. The large diterpane hump and large concentration of individual diterpane compounds in the saturate fraction gas chromatograms discussed above indicate an anomalous resin input into the sediment. The presence of resinite and/or resinous material was confirmed using ultraviolet fluorescence microphotometry (Gijzel, 1971). Spores, pollen, cuticlar material, dinoflagellates, bitumen and resins as well as some mineral entities were observed to fluoresce under UV excitation. Both transmitted and reflected tungsten light were used to identify the fluorescing species. The orange to dark brown low-level fluorescence of the resinous material was observed frequently in juxtaposition with a yellow to greenish yellow fluorescent phase called exudatinite by Teichmüller (1974). This material frequently diffused into the slide mounting medium, an epoxy casting resin. The halo effect was observed only rarely in kerogen samples that were prepared from previously extracted rock, and thus it is probable that this yellow halo is due to extractable organic matter in the kerogen and mobilized by the mounting medium solvents.

The relatively large proportion of coaly material in the high extract yield samples is consistent also with the resin source hypothesis. Some of the coaly fragments contained pods of resinite, which fluoresced under UV excitation. Also, it is possible that substantial dispersed resinous material was lost through solubilization or volatilization during the acidization of the rock samples. A small amount of greasy material floated on the hydrofluoric acid phase of a few of the samples even after centrifuging and was decanted with the acid and not recovered. This could have been resinous material. Because of this loss during the kerogen preparation, the atomic hydrogen/carbon ratios of the high-yield samples may be too low.

In general, herbaceous organic matter at low to moderate levels of thermal alteration tends to yield relatively low amounts of extractable hydrocarbon. However, the data from this study imply that specific examples of high-yield, herbaceous-rich sediments do occur at low



Figure 57. Vitrinite reflectance versus atomic hydrogen/ carbon ratio.

levels of thermal alteration, and that a substantial amount of recoverable hydrocarbon is associated with them. This observation is valid whether or not the resin source hypothesis is correct.

Elemental distribution

Triplicate elemental analyses of the kerogens were made to determine whether the organic matter tended to change from the Type III (low atomic hydrogen/carbon ratio) to Type I (high atomic hydrogen/carbon ratio) of Tissot et al. (1974) as the subenvironment changed from fluviodeltaic to prodelta. The data from this study (Table 6) all fall in the range of Type III organic matter, that is, cellulose-, humicand lignin-rich higher land plant debris. The atomic hydrogen/carbon ratios do not show an increasing trend as the subenvironment becomes more marine (Fig. 57), as was observed by McIver (1967) for the Lower Cretaceous Mannville Shale of Alberta. In fact, only a single analysis (Taglu D-43 13,910 feet, 4239.8 m) of fluviodeltaic kerogen has a hydrogen/carbon ratio of less than 0.80, while about half of the delta front and prodelta samples fall below this level. No trend towards lower H/C ratio with increasing reflectance is apparent at the levels of maturity represented in this sample set.

The nitrogen content of the kerogen is expected to decrease with both increasing maturity and increasing terrestrial character (ibid.). The atomic C/N ratios (Table 6, Fig. 58) are clustered in a rather small group. No trends with depositional environment are apparent, but the lowmaturity samples (Ro less than 0.45) tend to have higher atomic C/N ratios than samples of higher maturity. This is the reverse of the trend observed by McIver (ibid.) for the Mannville Shale of Alberta. The atomic C/N ratios of the Mannville Shale range between 43.7 and 151.0, suggesting that the level of maturity of the samples in this study, where the range is from about 30 to 70, may not be sufficient to result in a decreasing nitrogen content in the kerogen. The high C/N ratios of the most immature samples could be the result of very low nitrogen input into the sediment. Another possible but equally speculative explanation is that, during the isolation of the very immature kerogens, nitrogen-containing organic molecules such as amino acids were lost because of volatilization or dissolution. Increased levels of diagenesis would lead to further polymerization and stronger binding of these entities to the kerogen macromolecule and thus preclude this volatilization/dissolution loss, resulting in lower atomic C/N ratios.



Figure 58. Vitrinite reflectance versus atomic carbon/ nitrogen ratio.

The range of atomic hydrogen/carbon ratios of this study is consistent with the observed distribution of organic matter types. The H/C ratio of vitrinite at a low level of thermal alteration is about 0.60 to 0.70 (Tissot et al., 1974) and thus a predominantly vitrinitic coal with some of the exinitic maceral would be expected to have an atomic H/C ratio of about 0.70 to 0.90. This is also the range observed for Type III or herbaceous organic matter (McIver, 1967; Tissot et al., 1974).

The apparent lack of correlation of a specific organic matter type with hydrocarbon yield noted above is confirmed also by the elemental analysis data (Table 6). The high hydrocarbon yield samples, C-58 7970 feet (2429.3 m) (140.8 mg/g), D-43 8580 feet (2615.2 m) (112.4 mg/g), D-43 9910 feet (3020.6 m) (92.6 mg/g), and D-43 10,460 feet (3188.2 m) (88.0 mg/g) have respective atomic H/C ratios of about 0.821, 0.816, 0.792 and 0.858. All of these points fall in the middle of the observed H/C ratio range for the data set (Fig. 59). Thus the hydrogen content of the kerogen of the high-yield samples confirms the coaly/herbaceous nature of the organic matter observed microscopically. As noted above, a hydrogen-rich resin fraction may have been partly removed during kerogen preparation, resulting in a lowering of the atomic H/C ratio.

Other results

Other physical and chemical data available from various sources and pertinent to the organic geochemical study of the Beaufort-Mackenzie Basin are essentially supportive of the analytical results described above. Cuttings gas and organic carbon logs (Snowdon and McCrossan, 1972; Snowdon and Roy, 1975) were generated in this laboratory for four of the wells sampled in this study (Figs. 60 - 63). Total gas includes methane, ethane, propane, isobutane and n-butane, whereas 'wet gas' consists only of the homologs heavier than methane. The organic or acid-insoluble carbon is weight per cent as determined using a Leco combustion analysis described above. Carbon determinations were not made for the Kumak J-06 samples.

A predominance of wet gas indicates that hydrocarbons have been generated via thermal degradation (Snowdon and McCrossan, 1972). Unpublished data from the Sverdrup Basin suggest that heavier hydrocarbons (>C₁₅) are not present in significant quantities in the sediment until a few thousand metres below the crossover to a predominance of wet gas. Thus the mature hydrocarbon zone or 'oil window'



Figure 59. Extractable hydrocarbon yield versus atomic hydrogen/carbon ratio.

(Pusey, 1973) occurs at depths of greater than about 3000 feet (914.4 m) in Kugpik O-13, 6500 feet (1981.2 m) in Kumak J-06, 5000 feet (1524.0 m) in Kumak C-58, and 9000 feet (2743.2 m) in Netserk B-44. The overmature zone or bottom of the oil window is not clearly apparent in any of the four gas logs.

It is interesting to note that the total gas yield peaks essentially always correspond with organic carbon peaks, indicating that all the gas observed is syngenetic. Frequently the high gas yields also correspond with a decrease in the percentage of wet gas, indicating that the gas is associated with coaly material that produces predominantly methane. This is consistent with the substantial amounts of coaly material observed in the kerogen smear slides.

Solvent extract data from other geographical locations in the Mackenzie Delta have been generated in this laboratory. The results are essentially similar to those of this study. Hydrocarbon yield calculations and alkane distribution have been made but elemental analyses and microscopic examination of the kerogen have not been done as yet. Some of the core samples from other Taglu wells show the C_{19} to C_{23} anomaly and high pristane/phytane ratios observed in cores from the Ellice O-14 well. The proportion of contamination in the Taglu core samples with high yield, however, is much lower and the C_{19} to C_{23} contaminants are not as obvious as in the low-yield samples.

Table 9 contains a brief summary of drill stem and wire line test recoveries from the six boreholes sampled in this study. Reservoired condensate and natural gas occur in the Upper Cretaceous-Tertiary section of the Beaufort-Mackenzie Basin in juxtaposition with the potential petroleum source rocks delineated in this study. Rigorous correlation of petroleum source rocks with petroleum occurrences remains to be done.

Geological implications

The homogeneity of the organic matter preserved in the Richards Island Basin suggests that the character of the terrestrial organic input into the system was more or less constant throughout much of Late Cretaceous-Tertiary time. Furthermore, the organic homogeneity indicates that the various geological processes that resulted in recognizably different lithotopes were ineffective in sorting or fractionating the organic debris. Because the chemical parameters determined in this study were almost all essentially invariable with respect to geological parameters, they



- Figure 60. Cuttings gas and organic carbon log for Kugpik O-13 borehole.
- Figure 62. Cuttings gas and organic carbon log for Kumak C-58 borehole.

Figure 61. Cuttings gas log for Kumak J-06 borehole.

Figure 63. Cuttings gas and organic carbon log for Netserk B-44 borehole.

cannot be used generally to elucidate the geological processes which were operative in this sequence of delta complexes.

Because the organic chemical parameters apparently are controlled by the input supply and not by the geological processes operative in the different sedimentary environments, there is no particular relationship between the sedimentological parameters as observed by Young (1975) and Young et al. (1976) and the organic chemistry of the sediments. In other words, there is a range of clastic particle sizes put into the system and the geological processes sort and alter the input mixture to some extent, so that, for example, the prodelta facies is predominantly but not totally shale, and delta front facies is predominantly but not wholly sandstone. The organic debris, on the other hand, ranges from predominantly herbaceous to predominantly coaly regardless of the depositional environment, and the controlling factor is the nature of the source.

Two notable exceptions to this trend, however, were the extractable hydrocarbon yield and the anomalous concentrations of tricyclic diterpanes, which may be attributable to high concentrations of tree resins in the sediment. However, high hydrocarbon yields were obtained for samples from two of the three depositional subenvironments categorized in this study and the high diterpane concentrations were observed in samples from all three environments. Thus the controlling factor was probably not a geological process alone, but more likely a combination of biological, temporal and geological circumstances. Insufficient data on the chemical structure and probable precursors of the tricyclic diterpanes preclude more than speculative interpretation of the results. An adequate hypothesis to explain the spatial and temporal distributions of the anomalous hydrocarbon yields and diterpane occurrences has not yet been developed.

CONCLUSIONS

The results of this study clearly indicate that there is no correlation of the organic matter type and the widely varying subenvironments of deposition within the Upper Cretaceous-Tertiary delta complexes of the Beaufort-Mackenzie Basin. The only environment-specific chemical parameter observed was the total organic carbon content, which was found to be significantly higher on average in the fluviodeltaic samples than in both the delta front and prodelta samples. This reflects the higher proportion of in situ coal in the delta plain environment. The extractable hydrocarbon content, normal alkane content, pristane/ phytane ratio, atomic hydrogen/carbon ratio, atomic carbon/nitrogen ratio and distribution of coaly and herbaceous material were found to be independent of the subenvironment of deposition. Tricyclic diterpanes probably related to sandaracopimaric acid were found in terrestrial as well as delta front and marine sediments. Waxy components were not restricted to nonmarine subenvironments. In summary, the predominantly land derived herbaceous and coaly debris dominated the organic input throughout the geological history of the deposition of the delta complex system even during transgressive phases and the deposition of marine or prodelta sediments. Marine organisms preserved in the sediment were diluted by terrestrially derived material to the extent that the organic parameters measured were essentially uninfluenced by the changing depositional setting. The large input of terrestrial organic debris and extensive sediment reworking due to local tectonic events have resulted in an essentially organically homogenous sequence of sediments throughout three major cycles of deltaic sedimentation during much of Tertiary time.

A few anomalous samples were observed, however. The solvent-extractable hydrocarbon yield of a few samples was much higher than the median for the entire data set. These indicated the presence of good or excellent potential petroleum source rocks even though they were at very low levels of thermal alteration. Because the organic matter in these samples was largely herbaceous and coaly and because this type of organic matter does not normally yield large amounts of hydrocarbon and does not achieve maximum yields at reflectance values below about 0.80, the high-yield potential source rocks probably are related to resins or resinite. This conclusion was supported further by the observation of diterpanes in some of the gas chromatographic traces of the saturate fraction and fluorescent material in the kerogen smear slides.

The chemical structure of at least one of the highconcentration tricyclic diterpanes suggests that the input organic matter has not always been derived from the genera indigenous to the area today. The high resin input into the sediment may have been due to the specific nature of the early to mid-Tertiary biomass. It was not possible on the basis of the data available to differentiate between changes in the character of organic input and thermal diagenesis as possible explanations for the deepening northward pattern of occurrence of the anomalous tricyclic diterpanes.

The interrelationships of the various organic parameters were not well elucidated in this study because rather narrow ranges of organic matter types and levels of thermal alteration were represented in the three delta complexes sampled. The elemental analysis data were found to be consistent with the optical kerogen data, as was the distribution of saturated hydrocarbons. Again, however, the anomalously high hydrocarbon yields did not correspond to any other parameter. The only chemical parameter which was found to be functionally dependent on the level of thermal alteration was the pristane/phytane ratio, which increased with increasing reflectance. The proportion of coaly material in the kerogen smear slides varied considerably, but the elemental distributions, extract yields and saturate hydrocarbon character were found to be essentially independent of the changing amount of coaly material in the kerogens.

There were no classical sapropel-rich petroleum source rocks identified in the Upper Cretaceous-Tertiary of the Beaufort-Mackenzie Basin. The levels of thermal alteration were generally too low to have resulted in the generation of significant quantities of liquid petroleum from the herbaceous/coaly organic debris in the samples studied. Good or excellent potential source rocks were identified, however, and were interpreted as related to resinous organic material. The n-alkane distribution of the extracts and occurrence of substantial condensate and gas reserves suggest that large amounts of hydrocarbon have been evolved from the relatively immature, predominantly herbaceous and coaly organic debris. The good to excellent potential petroleum sources in rocks of low thermal maturity suggest that the classical petroleum generation sequence of heavy oil, oil, gas condensate and finally methane-rich gas should include the possibility of an early phase of condensate production. This early condensate phase would be dependent on specific biological precursors, namely resins. The organic matter was essentially homogeneous throughout all three depositional subenvironments and the good source potential was not related to any particular geological process. Because the potential source rocks are not subenvironmentally specific, it was felt unlikely that any particular reservoir facies would be favoured to contain hydrocarbons. For example, it is just as likely for point bar or stream bed sands to be juxtaposed to a potential source as for a delta front sand.

Extrapolation of the results of this study to other geographical regions must be done with extreme caution. The conclusions of this study were essentially dependent on the homogeneity of the organic matter even in the prodelta (marine) subenvironment and also may be specific to the plant genera contributing to the organic debris. The characteristics of a sedimentary basin in which there was a more significant marine influence probably would be quite different from those observed in this case. Similarly, extrapolation of many aspects of geochemical models established in other sedimentary basins have not been totally applicable to the Beaufort-Mackenzie Basin.

Future work

It is hoped that gas chromatographic - mass spectrometric analysis of extracted hydrocarbon fractions from the Beaufort-Mackenzie Basin and similar data for the condensates and oils will support the conclusions concerning the source of the Upper Cretaceous - Tertiary petroleum reserves discovered thus far. If the extracts and condensates contain substantial amounts of tricyclic compounds, this would tend to support the resin source hypothesis.

Carbon isotope analyses on fractions of crudes and extract are currently being carried out on contract by a commercial laboratory and these results also may assist in clarifying the oil/source correlation.

Analyses of samples from far offshore of the Mackenzie Delta may demonstrate that marine influence does increase in the more distal prodelta environment. A current offshore drilling program should provide samples to test for this possible change in organic character.

Another follow-up study that would be of interest is the comparison of this data set for the Beaufort-Mackenzie Basin with similar data for other Tertiary deltas. Differences and similarities in the results of such studies would yield considerable insight into the influence of geological processes on the chemical character of organic debris preserved in the sediment, and may permit the establishment of a general model usable for both quantitative and qualitative petroleum potential evaluation.

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