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ORGANIC GEOCHEMICAL INVESTIGATION OF SELECTED OIL SHALES OF THE ALBERT FORMATION, NEW BRUNSWICK

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1.0 Abstract

The quantity and quality of organic matter in oil shales have been studied on eighteen (18) samples from two boreholes penetrating the Lower Carboniferous Albert Mines Formation, New Brunswick.

The organic geochemical data indicate good quality source rocks that are well within the hydrocarbon generation zone. Based on the fact that the hydrocarbon concentration of the individual samples is not always in accordance with the quantity and quality of the kerogen, redistribution of hydrocarbons during primary migration is assumed. Pyrolysis-gas chromatography indicates lacustrine or marine algal kerogens and marine kerogens.

2.0 Introduction

Oil shale - by definition - is a compact rock of sedimentary origin with an ash content of more than 33 per cent, containing organic matter that yields oil when destructively distilled but not appreciably when extracted with petroleum solvent (Hunt, 1979). The origin of the organic matter is commonly marine or fresh water algae, but other planktonic organisms and also bacterial biomass may significantly contribute to the kerogen (Tissot and Welte, 1978). According to kerogen classification (Tissot et al., 1974) the amorphous sapropelic organic matter of oil shales belongs to either Type I or Type II.

Oil shales have been deposited in lake basins, shallow seas, bogs and lagoons from late Precambrian to Tertiary times (Tissot and Welte, 1978). A minimum kerogen content of 2.5% was estimated by Burger (1973) to be necessary to guarantee that more energy is obtained than is used to produce shale oil.

Interest in oil shales goes back to the seventeenth century, when in 1694 Martin Eale "found out a way to extract and make great quantities of pitch tar and oil out of a sort of rock" (Cane, 1967). Since then up to the fifties of this century shale oil was produced in many countries. More recently, the low cost of oil, especially from the Middle East, made the production of shale oil uneconomical for most countries except for the USSR and China. The increasing world demand for energy accompanied by the continued exploitation of conventional fossil fuels, will eventually lead to severe depletion of these resources and draw some attention to oil shales as a potential resource again.

According to Yen and Chilingarian (1976) the total world potential of shale oil is estimated at 30×10^{12} bbls; two per cent of which, or 600 x 109 bbls, is available for present-day commercial exploitation.

In Canada, oil shale deposits are known to occur in every province and territory except Prince Edward Island, and range in age from Ordovician to Cretaceous (Macauley, 1981). The best studies of known Canadian oil shale deposits are those on the Albert Formation in the Moncton Subbasin, New Brunswick (Figures 1, 2). Furthermore, the Albert Mines deposit presently appears to be the most economically attractive (Macauley and Ball, 1982).

A detailed study of the lithology and structural attitudes of oil shale penetrated by 11 wells drilled during 1976 has been carried out by Macauley and Ball (1982). Along with the geological information, data are provided for both the inorganic and organic geochemistry of the Albert Formation. This comprehensive study has been used to select the samples for a more detailed geochemical investigation of the organic matter in these oil shales. Furthermore, some of the basic organic geochemical data published in Macauley and Balls' report, have been used here.

The Lower Carboniferous Albert Formation consists of dominantly terrestrial clastics deposited in a series of connected intra-montaine basins within the regionally subsiding Fundy Basin (Figure 1).

From the core data of the Albert Mines area in the Moncton subbasin Macauley and Ball (1982) differentiate three distinct oil shale lithotypes - laminated marlstone, clay marlstone and dolomite marlstone. Based on this oil shale classification, the Frederick Brook Member of the Albert Formation (Figure 3) has been informally divided into an upper unit of clay marlstone, dolomite marlstone and shale, the Albert Mines zone of dominant laminated marlstone, a clay marlstone zone of clay marlstone and shale, and a basal dolomite marlstone section. These units are tentatively correlated eastwards to Boudreau, even though facies changes occur (Figure 3). This classification has been used for the present geochemical study.

Two exploration wells - Canadian Occidental Albert Mines No. 5 and Atlantic Richfield Boudreau No. 1 (Figure 2) have been chosen for a geochemical characterization of the Albert Formation oil shales. These wells seemed well suited, because a detailed geological, lithological and mineralogical report, inorganic and organic geochemical data (Macauley and Ball, 1982), as well as rank parameters (Kalkreuth and Macauley, 1984) of numerous samples from both wells, were available. In addition, the two wells were supposed to cover different oil shale facies and two different maturation levels. The samples selected from both wells represent the four zones (Figure 3) of the oil shale bearing section of the Albert Formation, covering a wide range of organic carbon content. They are distributed over the maximum possible depth range.

3.0 Results and Discussion

3.1 Maturity of Organic Matter

It is well documented that the onset of hydrocarbon generation by thermal alteration of organic matter occurs for different kerogen types at different vitrinite reflectance levels (Powell et al., 1978). Hydrogen rich - Type I-II kerogen, the kerogen type of the investigated samples, with mainly algal and amorphous liptinites, start generating appreciable amounts of liquid hydrocarbons around 0.5% R_0 with maximum generation at about 0.75% R_0. The "death line" or cessation of oil generation in Type I-II kerogens may be around 1.2%, and for wet gas around 1.4% R_0. Vitrinite reflectance measurements have been previously reported by Kalkreuth and Macauley (1984) for three samples from Canadian Occidental Albert Mines No. 5. The mean values indicate a low maturation level (<0.5% R_0). The vitrinite reflectance measured on sample 5 from Atlantic Richfield Boudreau No. 1 is considerably higher (0.86% R_0).

The results of this study, including samples from both wells, strongly suggest that the maturity stage is about the same in both wells. In particular, this can be seen from the high concentration of extractable hydrocarbons, especially in samples from Canadian Occidental Albert Mines No. 5 (>76 mg/g Corg, Table 3) as well as from Atlantic Richfield Boudreau No. 1 (>29 mg/g Corg, Table 4). The concentrations found in samples from Canadian Occidental Albert Mines No. 5 do not relate to their measured vitrinite reflectance. The results of the C_{15+} n-alkane distribution lead to the same conclusion. The relatively high amounts of n-alkanes already generated in comparison to branched and cyclic alkanes can only be explained by assuming a higher maturity stage for the samples from Canadian Occidental Albert Mines No. 5. Similarities in hydrocarbon quantities and distribution patterns suggest a similar maturation for both wells. According to the organic geochemical data, the proposed vitrinite reflectance of <0.5% Rm for Canadian Occidental Albert Mines No. 5 samples is probably too low.

Kalkreuth and Macauley (1984) assume that the presence of alginitic material in the samples from Canadian Occidental Albert Mines No. 5 significantly lowered the vitrinite reflectance, as previously postulated for similar samples by Hutton and Cook (1980). In contrast, the sample from

Atlantic Richfield Boudreau No. 1, with a significantly higher vitrinite reflectance of 0.86% R_o, is characterized by the absence of alginite and the dominance of terrestrial organic matter.

Previous studies have shown that vitrinite reflectance can be lowered by impregnation of the vitrinite particles with water (Harrison, 1965; Harrison and Thomas, 1966) or bitumen-like hydrocarbons (Altebaeumer,A.M., 1982). As stated previously, hydrogen rich Type I kerogens start generating appreciable amounts of liquid hydrocarbons around 0.5% Rm. These newly generated liquid hydrocarbons could have impregnated the vitrinite particles and thus lowered their reflectance. The fact that no fluorescence of the vitrinite particles has been observed (Kalkreuth, pers. comm.) could be explained by the predominantly aliphatic character of bitumens generated by algal-rich kerogens.

Additional information on the maturity of the organic matter is available from RockEval data. The transformation of kerogen into hydrocarbons can be determined by the production index [$S_1/(S_1 + S_2)$] obtained from RockEval pyrolysis results. Normally, there is a continuous increase of this ratio with increasing depth and maturity (Espitalie et al., 1977). Abnormally high or low values (with respect to the maturity level of the samples) are usually considered to be hydrocarbon accumulations or hydrocarbon depleted sections due to migration. The variation of the production index for samples from both wells (Macauley and Ball, 1982) shows no regular trend with increasing depth (Figures 4, 5). From this, it is concluded that redistribution of hydrocarbons within the investigated section has altered the production index. As a rank parameter the production index in this case is useless.

3.2 Quantity of organic matter

Fine grained sediments containing finely disseminated insoluble organic matter (kerogen) are considered to be potential source rocks. With increasing depth and rising temperature hydrocarbons are generated from the kerogen. The content of organic matter in a sediment is commonly calculated from organic carbon determination.

An organic carbon content for clastic source rocks of 0.5% (Ronov, 1958; Baker, 1962; Bray and Evans, 1965; Philippi, 1965 and Schrayer and Zarella, 1966) is considered as the minimum content to generate sufficient hydrocarbons for a commercial accumulation, and a minimum of 0.2-0.3% organic carbon has been established for potential carbonate source rocks (Hunt, 1967). This difference is caused by the fact that shales normally contain large amounts of woody and coaly material, which is not capable of forming large amounts of hydrocarbon. In contrast, the generation of hydrocarbons in carbonates is more efficient, because their organic matter is almost entirely amorphous material derived from plankton (Hunt, 1980).

Organic carbon content of samples analyzed for this study have been published by Macauley and Ball (1982). The organic carbon content ranges from 2.0% to 24.7% in samples from Canadian Occidental Albert Mines No. 5 (Figure 4), and from 0.6% to 13.0% in samples from Atlantic Richfield Boudreau No. 1 (Figure 5). With respect to the different stratigraphic units sampled in both wells, Canadian Albert Mines No. 5 contains 8.0 to 15.8% organic carbon in the upper unit compared to 0.61 to 3.0% in the same stratigraphic unit in Atlantic Richfield Boudreau No. 1 (Figures 4, 5). The Albert Mines zone is characterized by organic carbon values of 9.3 and 25.7% in Canadian Occidental Albert Mines No. 5 and by values between 4.0 to 13.0 in Atlantic Richfield Boudreau No. 1. Samples taken from the clay marlstone zone were only analyzed for Canadian Occidental Albert Mines No. 5, and organic carbon contents are 8.5 and 8.6%. The dolomite marlstone zone produced the lowest organic carbon contents in this well with 2.0 to 8.7% organic carbon. This zone in Atlantic Richfield Boudreau No. 1 produced values of 1.4 to 7.2% organic carbon.

All these samples contain organic carbon in excess of the generally accepted minimum requirements for potential source rocks. Based on their organic carbon content, all samples can be considered as having been taken from excellent potential source rocks.

3.3 Characterization of kerogen

The evaluation of a sediment as a potential source rock, however, cannot be based on quantity alone, even more important is the quality of organic matter. The potential to generate oil and gas by

thermal transformation of the kerogen during burial of the source rocks is very much dependent on kerogen structure and hydrogen content (kerogen type).

The organic matter in sediments has been classified as Type I, II and III kerogens depending on its elemental composition and its evolution path on a van Krevelen diagram, by Tissot et al. (1974). Type I kerogens are rich in aliphatic structures, able to generate oil, have an original high H/C ratio and a relatively low O/C ratio. This group includes algal-rich sediments, in particular those derived from lacustrine Botryococcus and their marine equivalents (like tasmanites). Type II kerogens have been found mainly in marine sediments, in which autochthonous organic material (phytoplankton, zooplankton and other microorganisms) have been deposited under reducing conditions. Hydrogen-lean, but oxygen-rich Type III kerogens are derived from higher land plant material. During burial they generate mainly gas and condensates.

Information on the type of kerogen can be obtained by elemental analysis of the major elements occurring in sedimentary organic matter. The atomic H/C values determined for isolated kerogens in samples from Canadian Occidental Albert Mines No. 5 range between 1.03 and 1.52 (Figure 4, Table 1). Values remain fairly constant between 1.41 to 1.52 in the upper unit, and in the Albert mines and clay-marlstone zones. However, in the dolomite- marlstone zone, lower values between 1.03 and 1.27 were observed. This difference could be due to two different events:

a) A change in depositional environment resulting in a different kerogen-type.

b) A hiatus.

The results of microscopic examinations (Kalkreuth and Macauley, 1984) show, that fluorescence maturation parameters (λmax and red/green quotient) increase regularly with depth, along with a marked increase in fluorescence intensity. From this evidence, it is more likely that a decrease in kerogen quality has to be considered. Additional support for this interpretation is available from maceral analysis (Kalkreuth and Macauley, 1984). Sample 28, containing 10% sporinite, has an H/C value of 1.16; sample 34, with no sporinite, has a considerably higher H/C value of 1.27. If this latter sample is disregarded, a depth-trend of decreasing H/C values, from 1.23 to 1.03, can be recognized in the dolomite-marlstone zone.

H/C values of isolated kerogens from Atlantic Richfield Boudreau No. 1 (Figure 5) range from 1.33 to 1.52. They show no regular trend with depth. Therefore, decreasing or increasing values are considered to reflect facies related variations. Compared to elemental analysis results from Canadian Occidental Albert Mines No. 5, the ratios from Atlantic Richfield Boudreau No. 1 are similar to those observed in the three upper zones of this well. The decrease of H/C values, which has been observed in the dolomite marlstone zone of the Canadian Albert Mines No. 5 well, does not however, become evident from the data relating to the same zone in the Atlantic Richfield Boudreau No. 1 well. For analytical reasons no oxygen values were available, but considering the maturity level, those samples can be postulated as Type I kerogens. However, a definite kerogen classification based on elemental analysis cannot be performed without O/C values. Some additional information can be obtained from the RockEval results published by Macauley and Ball (1982).

Instead of using the atomic ratios of H/C and O/C in a van Krevelen plot, the so-called "hydrogen index" (HI, in mg hydrocarbon pyrolysate per gram of organic carbon) is plotted versus the so-called "oxygen index" (OI, in mg CO_2 per gram of organic carbon) derived from RockEval data. These indices have been shown to broadly correspond to the H/C and O/C atomic ratios of the elemental composition of kerogen (Espitalie et al., 1977) and can be used in very much the same way. In Figure 6, analytical data obtained from RockEval pyrolysis of the oil shale samples are plotted into the hydrogen versus oxygen index diagram established by these authors. In particular, this diagram shows that all samples from Canadian Occidental Albert Mines No. 5 contain a Type I kerogen. The majority of samples from Atlantic Richfield Boudreau No. 1 contain a kerogen classified as Type I as well, except sample 5, which contains a mixed Type II/Type III kerogen. This sample seems to be different in general, featuring a low carbon content of 0.61% and a maceral composition of 50% vitrinite, and 17% inertinitewhich is very different from all other samples. The 33% liptodetrinite portion is considered as mainly terrestrial debris (Kalkreuth and Macauley, 1984).

Nevertheless, because this sample showed a high H/C ratio of 1.39, the elemental analysis data is not in agreement with conclusions derived from RockEval data and microscopic examination. This is most probably caused by the presence of clay minerals, which could not totally be removed during

kerogen isolation. This sample is the only sample that has been characterized by Macauley and Ball (1982) as argillaceous.

Additional information regarding kerogen quality is available from maceral analyses published by Kalkreuth and Macauley (1984). Alginite B, as defined by Hutton et al. (1980), is the main component in all the samples analyzed from Canadian Occidental Albert Mines No. 5, forming up to 99 % Vol. of the organic material. Vitrinite and inertinite contents are generally very low ($\leq 1\%$). Samples 1, 16 and 20 each contain 1%, sample 28 an even 10% of sporinite. Bituminite is present only in sample 1, where it contributes 10 per cent of the maceral composition. Samples 28 and 34 contain four and three per cent liptodetrinite respectively.

The maceral composition in the samples from Canadian Occidental Mines No. 5 indicates the organic material has to be classified as Type I kerogen. In sharp contrast to the samples from Canadian Occidental Albert Mines No. 5, sample 5 (289.0 m) from Atlantic Richfield Boudreau No. 1, consists mainly of vitrinite (17%) and liptodetrinite (33%), while alginite B is absent. From maceral composition this sample has to be classified as Type III kerogen (Leythaeuser et al., 1980). This is much more in accordance with RockEval results which indicate a mixed Type II/Type III kerogen. An H/C value of 1.40 is regarded as too high for this sample.

3.4 Generation and migration of hydrocarbons

In sediments the organic matter that is extractable by organic solvents consists of low volatile C_{15+}-hydrocarbons and NSO-compounds. Quantity and composition of the C_{15+}-soluble organic matter (extract) depends on maturity and kerogen type, because, during catagenesis, C_{15+}-hydrocarbons are generated from the kerogen. The amount of extractable organic matter represents 1-20% of the total organic matter in a source rock depending on its maturity (Tissot and Welte, 1978). Furthermore, because of its solubility it is very susceptible to contamination. As soon as hydrocarbon generation starts the possible effects of migration have to be considered as well. Hydrocarbon generation in the oil shales investigated have been evaluated by determination of yield and composition of the extractable organic matter. Analytical data from these analyses are summarized

in Tables 3 and 4 and presented in Figures 4, 5, 7 and 8. The extractable yields vary from 12,645 to 25,255 ppm in samples from Canadian Occidental Albert Mines No. 5 (Figure 4). In the upper unit, extract yields are highest with values of 20,113 and 25,255 ppm. In the Albert Mines zone, the values are 18,176 and 18,670 ppm; in the clay marlstone zone 19,173 and 19,870 ppm. Within the individual zones, yields are very constant, despite distinct differences in organic carbon contents. The greatest scattering of extract yields can be observed in the dolomite marlstone zone, where values range from 12,645 to 20,465 ppm.

Samples from Atlantic Richfield Boudreau No. 1 show significantly lower extract yields (Figure 5). In the upper unit, values are 2690 and 1582 ppm, which is 12 to 16 times less than the comparable samples determined from the upper unit in Canadian Occidental Albert Mines No. 5. In the Albert Mines zone, the highest values in the No. 1 well were 4495, 9450 and 7985 ppm, which are 2 to 4 times less than the comparable values in the Albert Mines zone in Canadian Occidental Albert Mines No. 5. The dolomite marlstone zone has values of 4760 and 6690 ppm, which are 2 to 4 times less than the Albert Mines No. 5 values. Though there are very marked differences in extract yields between both wells, the determined values of far more than 1000 ppm in both wells indicate good source rocks. The yields of saturate and aromatic hydrocarbons (ppm) are as follows:

The saturate hydrocarbon content of samples from Canadian Occidental Albert Mines No. 5 varies from 4910 to 10,715 ppm, the highest values were determined in the uppermost samples. A distinct depth-trend is not recognizable.

The aromatic hydrocarbon yields remain relatively constant between 2540 and 3785 ppm, with the exception of sample 20, which shows a low value of 790 ppm.

In samples from Atlantic Richfield Boudreau No. 1, saturate hydrocarbon yields range from 393 to 3700 ppm with highest values in the Albert Mines zone. Aromatic hydrocarbon-yields in this well scatter between 147 and 1330 ppm with highest values in the lower part of the Albert Mines zone and the dolomite marlstone zone.

The following differences between results from the two wells are evident:

No depth-trend is visible in the saturate hydrocarbon yields in Canadian Occidental Albert Mines No. 5, whereas hydrocarbon yields increase with increasing depth in Atlantic Richfield Boudreau No. 1.

Aromatic hydrocarbon yields remain fairly constant in Canadian Occidental Albert Mines No. 5. In samples from Atlantic Richfield Boudreau No. 1 there is a trend to higher values within the Albert Mines zone.

In the upper zone, saturate hydrocarbon yields in the oil shales from Canadian Occidental Albert Mines No. 5 are 12 to 27 times higher than those in Atlantic Richfield Boudreau No. 1. In the Albert Mines zone the saturate hydrocarbon yields of oil shales from Canadian Occidental Albert Mines No. 5 are 2 to 8 times higher than in Atlantic Richfield Boudreau No. 1, and in the dolomite marlstone zone the values are 2 to 4.5 times higher in Canadian Occidental Albert Mines No. 5. This comparison indicates a decreasing difference between the two wells with increasing depth. This trend became evident by comparing extract yields from both wells, and in the saturated hydrocarbon fraction it is even more striking.

In the upper zone, aromatic hydrocarbons show extreme concentration differences that decrease with increasing depth.

Figure 9 shows the extract yield (ppm) as a function of organic carbon content for samples from Canadian Occidental Albert Mines No. 5. Samples with a similar organic carbon content have very different extract yields. Furthermore, the sample with the highest organic carbon content (sample 15) yields a relatively low extract. These discrepancies cannot be explained by maturation changes, because there is no trend of increasing extract yields with increasing depth as expected. In addition, maturation changes in the investigated section in general are not very great, since fluorescence properties (λmax and Q) increase regularly with depth (Kalkreuth and Macauley, 1984).

In Figure 10, organic carbon contents of samples from Atlantic Richfield Boudreau No. 1 are plotted versus extract yields. In this diagram, increasing extract yields, as a function of increasing carbon content, are evident from some samples (samples 4, 6, 14). However, there are exceptions. Sample 5 has a relatively high extract yield of 1543 ppm with an organic carbon content of 0.61% and

a significantly lower kerogen quality than all other samples. Sample 13 shows a distinctly higher extract yield compared to samples with higher carbon content. Samples 9 and 10, taken only 3.3 m apart, show nearly the same extract yields, though their organic carbon contents are very different with sample 10 containing 3 times as much organic carbon. This cannot be explained by differences in kerogen quality, as both samples contain the same type of kerogen according to atomic H/C values and hydrogen index data.

To further investigate this observation, the extract yields upon pyrolysis for oil shales from both wells published by Macauley and Ball (1982) have been used. Since the determined oil yields are a product of the kerogen degradation, which is not susceptible to migration effects, this parameter is well suited to investigate the relation between organic carbon content and hydrocarbon yield. Figures 11 and 12 demonstrate a very distinct relationship between the organic carbon content and the Fischer Assay results. The hydrocarbons originally generated show a similar dependence on organic carbon content. The extract data presented, however, show the opposite, and it is assumed that this result is due to redistribution (enrichment or depletion) during primary migration.

Throughout the investigated section the carbon normalized concentrations of extract, total hydrocarbons, and saturated hydrocarbons, show parallel trends (Figures 7, 8). However, especially in the dolomite marlstone zones, these trends are divergent when compared to carbon content and hydrogen-index. Furthermore, the observed trend for the production index (PI) shows a similar variation to the trends observed from the extractable hydrocarbon data (Figure 4).

The depth plot of geochemical parameters for Atlantic Richfield Boudreau No. 1 (Figure 8) shows similar results throughout the whole investigated section. Carbon normalized extract, hydrocarbon and saturate hydrocarbon trends, as well as the production index (Figure 5), are congruent with but diverge from carbon content and hydrogen index trends.

By comparing both wells, it becomes obvious that the carbon normalized extract and hydrocarbon values are higher in the Canadian Albert Mines No. 5 samples, but the difference between the wells is less distinct for the extract and hydrocarbon yields in ppm.

In general, there is a discrepancy between the organic carbon values and the amount of extractable organic matter, which cannot be accounted for as a maturity effect. In order to examine this phenomenon, an organic carbon mass balance has been established (Figures 13, 14). This approach has recently been applied to source-bed type shales bearing different kerogen types by Leythaeuser et al. (1980) and to Type III - kerogens by Altebaeumer, F.J. (1982).

Generally, the organic matter in samples from a source rock can be classified into two broad categories, "reactive" and "inert". The latter remains essentially unaffected by temperatures reached during the main phase of oil generation and is referred to as "dead" carbon. Both types of materials occur in varying proportions in source rocks. For geochemical interpretation of source rock data it is essential to know the amount of dead carbon, because both the reactive and the inert part of the organic matter are included by determining the total organic carbon content of a potential source rock. There is no easy method to measure the amount of "dead" carbon in a sample directly.

Therefore, the amount of "dead" carbon has been determined from mass balance calculations, based on yield measurements of pyrolysis products and of solvent extractable compounds (for details see Leythaeuser et al., 1980). These organic carbon balances are based on several simplifying assumptions and represent only an approximation to the true facts (for example, migration effects and the light hydrocarbons are not included in these calculations). However, this type of mass balance analysis is useful to indicate the relative proportions of four principal carbon-bearing entities in the total organic carbon of a source bed sample:

a) Carboxyl carbon: carboxyl groups of the kerogen will be released as carbon dioxide with maturation progress.

b) Extractable organic matter: the bulk of extractable organic matter is generated during maturation by thermal degradation of kerogen and represents the proportion of organic matter already converted into hydrocarbons.

c) Pyrolysis-degradable carbon: represents that part of the total organic carbon of the kerogen which, upon further burial, will be converted to hydrocarbons.

d) "Dead" Carbon: designates that part of the organic carbon of the kerogen that remains chemically unaffected by subsurface temperatures encountered during the main phase of hydrocarbon generation. "Dead" carbon is thought to have a dual origin. Part of it can be original and inherited from organic precursor material as inertinite particles, e.g. charcoal or oxidized material. Another part of it originates as a by-product of increasing hydrocarbon generation reactions, i.e., it represents the residual kerogen.

Organic carbon mass balances are shown in Figures 13 and 14. Samples are arranged in a sequence of increasing depth. By comparing the mass balances in Figures 13 and 14 no effect of the maturation progress can be seen. The amount of extractable organic matter is clearly independent of the organic carbon content (Figures 9, 10) and the hydrocarbon generation potential. Because, for some samples from Canadian Occidental Albert Mines No. 5 (samples 6, 21, 29, 33) the proportions of organic carbon present in carboxyl-groups, C_{15+} -soluble compounds and the pyrolysis degradable organic matter exceeds 100% of the total organic carbon, it has to be concluded that these samples are impregnated by hydrocarbons due to primary migration. These samples are also characterized by high production indices (up to 0.4). For that reason, no statement can be made about the "dead" carbon content originally present in the samples. Samples from Atlantic Richfield Boudreau No. 1 show less distinct indication of enrichment due to primary migration.

In this study, special attention has been drawn to the investigation of C_{15+} saturated hydrocarbons.

The compositional changes of the C15+-saturated hydrocarbons with depth for both wells are shown in Figures 15 a and b, and 16 a and b. The evaluation of these gas-chromatograms is only qualitative, because the peak-heights and areas depend not only on the absolute quantity but also on different analytical factors, e.g. concentration of the injected sample-solution, injection quantity, split ratio.

The following observations can be made by comparison of the chromatograms for Canadian Occidental Albert Mines No. 5 samples (Figure 15a, b):

- all normal hydrocarbon distribution patterns are unimodal, front-end biased with maximum peaks at n-C_{17}- or n-C_{19}.
- a very distinct dominance of n-C_{17} in samples 19, 20, 28 and 33 together with a very steep decrease toward higher molecular weight hydrocarbons.
- a relative increase of pristane and phytane, compared to n-C_{17} and n-C_{18} respectively, below 280 m.
- an increase of the relative amounts of steranes and triterpanes below 280 m, except for sample 33.
- a general decrease in concentration toward higher carbon numbers and n-C_{17}/n-C_{27} ratios of 2.6 to 3.3, becomes even more distinct in samples 1, 15, 19, 20 and 33, with ratios between 4.4 and 11.2.

There are no obvious depth trends that would indicate an increase in hydrocarbon generation rates over the interval examined. The observed decrease in alkane concentration at carbon numbers below n-C_{17} in all samples can be explained by evaporative losses during the analytical procedures.

The pristane/phytane ratios (Table 5) with values between 0.47 and 0.66 (sample 16 has a higher ratio of 0.94) remain fairly constant throughout the investigated interval (Figure 17). Pristane/phytane ratios below 1 are supposed to indicate a reducing environment in which phytane is predominant (Tissot and Welte, 1978). The pristane/n-C_{17} and phytane/n-C_{18} ratios (Table 5, Figure 17) show a distinct increase below 280 m. Below this depth, pristane/n-C_{17} ratios increase from 0.13 and 0.27 to 0.31 and 0.71, while phytane/n-C_{18} ratios increase from 0.25 to 0.34 and 0.77 to 1.22. The high content of low molecular weight hydrocarbons ($<C_{21}$) together with an odd carbon number preference and the dominance of n-C_{17}, suggest that the organic matter originated as algal material and bacteria (Tissot and Welte, 1978). Sample 21 and, to a lesser extent, sample 29 are different. Besides their maximum at n-C_{19} they have a higher relative amount of n-C_{20}, n-C_{21}, n-C_{22} and n-C_{23} with n-C_{22} being prominent in sample 21. According to Hutton et al. (1980), this can be caused by major contributions of freshwater plants, dinoflagellates and zooplankton. Both samples are characterized by relatively low organic carbon contents (2.07 and 2.09%, respectively), as well as

very high carbon normalized extract and hydrocarbon yields. Furthermore, they have comparatively high pristane/n-C_{17} and phytane/n-C_{18} ratios (Table 5, Figure 17).

The gas chromatograms of the C_{15+}-saturated hydrocarbon fraction of samples from Atlantic Richfield Boudreau No. 1 (Figure 16a, b) show the following features:

- The investigated samples show a great variety of C_{15+}-alkane compositions.
- the majority of the samples have a peak maximum at n-C_{19} with the exception of samples 6 and 10 which have maximum peaks at n-C_{17} and n-C_{18}, respectively.
- Pristane/phytane ratios range from 0.67 to 1.34 without any significant trend (Table 6, Figure 18).
- The pristane/n-C_{17} ratios determined range from 0.20 and 0.80, showing no regular trend (Table 6, Figure 18).
- Phytane/n-C_{18} ratios range from 0.23 to 0.97 without a regular trend (Figure 18). Nevertheless, the pristane/n-C_{17} and phytane/n-C_{18} ratios remain congruent throughout the examined interval (Figure 18).

From these observations the following conclusions have been derived. Besides the input of algal material, there is an important input of freshwater plants, dinoflagellates and zooplankton. This is evident from the dominance of n-C_{19} in most of the n-alkane distributions and the prominance of n-C_{22}. In two of the samples, particularly in sample 5, the influence of higher land plants can be seen, resulting in higher amounts of branched and cyclic alkanes, though quantitatively they are still less important. For sample 5, this is in accordance with maceral analysis, which indicates a high proportion of vitrinite (Kalkreuth and Macauley, 1984). Facies changes can also be seen from pristane/phytane ratios. In general, this ratio tends to be higher in the Boudreau No. 1 well than in Canadian Occidental Albert Mines No.5 with values up to 1.34, compared to 0.53 to 0.67. The higher values in No. 1 are attributed to a less reducing environment.

The investigation of the composition of the C_{15+}-saturated hydrocarbon fraction of oil shales from both wells reveals the following aspects. There are no compositional changes that could be attributed to generation of hydrocarbons due to increasing maturation. However, fluorescence data

by Kalkreuth and Macauley (1984) show a regular increase of maturation with depth. Furthermore, since hydrogen-rich Type I kerogens start generating appreciable amounts of hydrocarbons around 0.7% R_0 (Tissot and Welte, 1978), it is assumed that the oil shales are in a favoured stage of oil generation. The fact that no generation-trend can be observed from the gas-chromatograms is best explained by an assumption of redistribution by migration of hydrocarbons. In contrast to Altebaeumer, A.M. (1982) and Leythaeuser et al. (1984) no preferential depletion or enrichment of low molecular weight hydrocarbons, due to preferential movement of certain compounds and compositional fractionation effects during primary migration, were observed. Since Altebaeumer, A.M. (1982) and Leythaeuser et al. (1984) investigated only Type III kerogens, differences in the observed migration effect could be explained by different kerogen type. The system in which hydrocarbon fractionation presumably occurs is similar to liquid-solid chromatography (Altebaeumer, A.M., 1982; Leythaeuser et al, 1984). The liquid phase consists of part of the pore water, enriched by various amounts of hydrocarbons of different molecular weight and structure. The solid phase consists of clay minerals with certain adsorption and desorption qualities. The relatively low concentration of hydrocarbons generated by Type III kerogens favours fractionation effects due to preferential adsorption and desorption according to differences in polarity and adsorption affinity (Leythaeuser et al., 1984). However, the high amounts of generated hydrocarbons caused by a high kerogen quality leads very quickly to a hydrocarbon concentration in the pore water that exceeds the solubility limits (Type I kerogens generate 10 times more hydrocarbons than Type III kerogens). Oil globules are then formed which would add a third phase to the original two phase system (Leythaeuser et al., 1984). Since water tends to dissolve molecules of a higher polarity we can assume that the third phase will consist of less polar compounds. These, however, will be able to dissolve alkanes without any major fractionation effects. Nevertheless, it is very likely that three effects - facies related changes, maturation increase, and redistribution (depletion and enrichment) by migration-contributed to the alkane composition as it is observed, but cannot be distinguished.

3.5 Pyrolysis of oil shales

Since the kerogen usually represents 80 to 99% of the organic matter in sedimentary rocks (Tissot and Welte, 1978), it is important to examine and characterize this fraction especially during the consideration of oil shales. The proposed structure of the kerogen is a three-dimensional macro-molecule, made of condensed cyclic nuclei linked by heteroatomic bonds or aliphatic chains (Tissot and Welte, 1978). The complex nature of this kerogen bears advantages and disadvantages. One advantage is that the complex structure makes it much less susceptible to contamination and migration, unlike the soluble part (bitumen) of the organic matter (Maters et al., 1977). Kerogen is therefore regarded as an indigenous part of the organic matter in a sediment bearing all the imprints of the orginal organic facies. However, its macro-molecular character makes detailed geochemical analyses far more difficult to carry out.

To eludicate the structure of the kerogen it is necessary to use chemicalor thermal degradation, in order to form lower molecular weight compounds that are easier to analyse (Tissot and Welte, 1978). Products of thermal degradation using pyrolysis methods can be compared to hydrocarbons generated from kerogens in sediments subjected to normal subsidence and temperature increase in a sedimentary basin. As the type of organic matter determines the quantity and composition of the generated hydrocarbons at a given maturation level, the composition of the pyrolysate products allows conclusions to be drawn on the type of organic matter that was originally incorporated in a sediment.

Pyrolysis, as carried out for this study, produces two different types of pyrolysates, which are represented by two well-separated peaks (S_1 and S_2) identified by a flame ionization detector (FID). The compounds represented by these two peaks were analyzed in detail by subsequent capillary gas chromatography. The unaltered, absorbed compounds of already generated hydrocarbons present in the sample evolve at temperatures below 300°C (S_1 peak), while organic compounds generated by degradation of the kerogen structure emerge at temperatures between 300 and 600°C (S_2 peak). The samples investigated by pyrolysis, however, were mainly isolated kerogens from pre-extracted rock samples that contain little or no absorbed hydrocarbons. Nevertheless, some whole rock samples

have also been analyzed, which revealed in S_1 and S_2 peaks and were subsequently analyzed chromatographically (Figure 21a-g).

The pyrograms of isolated kerogens from Canadian Occidental Albert Mines No. 5 (Figure 19a-f) contain mainly straight chain compounds. The characteristic double peaks represent n-alkane plus alk-1-ene of the same carbon number, which are generated from the kerogen by thermal cracking. Peak heights of n-alkanes and alk-1-enes decrease as a function of increasing carbon number, with the maximum peak at C_8 or C_9 and extending to about C_{26}. Relative concentration of alkenes/alkanes are >1 up to carbon number 13 and decreasing toward the higher molecular weight molecules. Sample 20 shows an alkene/alkane ratio <1 from C_{12}, and in samples 21 and 28 the ratio is <1 throughout the pyrogram. For sample 29 the alkene/alkane ratio is above 1 only at carbon number 9. Most of the samples have a smooth unresolved hump toward the end of the pyrogram with a maximum extent at about C_{23}-C_{25}. Pristane and phytane are present in a low relative concentration with pristane/n-C_{17} ratios of 0.07 to 0.22 and phytane/n-C_{18} of 0.10 to 0.30. Pristane/phytane ratios range between 0.50 and 0.90. All pyrograms are very similar to pyrograms of alginite and alginite-rich samples as published by Larter and Douglas (1980) and Douglas et al. (1983). Typical for alginite pyrograms are aliphatic triplets of alkanes, alkenes and alkadiens with a very small contribution of aromatic molecules (Douglas et al., 1983). These triplets can be recognized only vaguely in the first four samples from Canadian Albert Mine No. 5. At increasing depths, increasing contributions of aromatic molecules become apparent. To evaluate the contribution from aromatic compounds, Larter and Douglas (1980) introduced the ratio of m(+p)-xylene to n-octene as an aromatic/alphatic index (Kerogen Type Index). The published data show that alginites have a kerogen type index of less than 0.4, sporinite values range between 0.4 and 1.3, while vitrinites, Carboniferous coals and Tertiary lignites have ratios ranging from 1.3 to more than 20.

For all samples from Canadian Occidental Albert Mines No. 5, kerogen type indices have been calculated (Table 7) to range from 0.25 to 0.59. These values are typical for lacustrine and marine algal kerogens and marine kerogens. The pyrograms obtained by pyrolyzing kerogens from Atlantic Richfield Boudreau No. 1 show the following characteristics (Figure 20a-d):

- The main constituents are doublets of alkenes and alkanes with a maximum at C_9 (C_8 for sample 14) and decreasing amounts with increasing carbon number up to C_{26}.
- The alkene/alkane ratio is >1 up to nC_{11} in sample 5, up to C_{13} in samples 4, 9 and 13, up to C_{14} in sample 10, and up to C_{16} in sample 6. Within the higher moelcular weight range the ratio becomes <1. For sample 14 the ratio is below 1 throughout the pyrogram.
- Kerogen type index values remain in the range of those for algal kerogen, between 0.18 and 0.37.
- Some samples (samples 4, 9, 10) show a very broad distribution pattern with a far less distinct and rapid decrease with increasing carbon number, especially of the n-alkanes. These samples are those with the lowest kerogen type index values (Table 8). The ratio n-C_9/n-C_{17} in sample 4 is 1.17, while in sample 10 it is 1.76 (sample 9 - no values available). This ratio is higher in all other samples (2.2 to 2.44).
- In some of the samples (samples 6, 10 and 11), a smooth but distinct hump can be observed which starts at about C_{14}. In all other samples the hump is less pronounced.

Although it is known from maceral analysis that sample 5 consists of vitrinitic material, the pyrogram does not show much difference. However, there are some differences in sample 5 that ought to be stressed:

- there are relatively more isoprenoids than in all other samples
- the C_{14}-isoprenoid alkene is more prominent than in all other samples
- there is a distinct prist-1-ene peak which does not appear in the other samples and which has been found to be a major pyrolysis product of the Messel oil shale kerogen (Larter et al., 1979).

These rather subtle differences between the pyrolysates of kerogens with a mainly algal source and those of kerogen with a definitely higher vitrinite content, can be explained if it is presumed that liptinites, in general, are more volatile on pyrolysis than vitrinites (Larter et al., 1977). The portion of liptodetrinite that is supposed to be mainly terrestrial debris (Kalkreuth and Macauley, 1984) could be of algal origin and produce higher relative amounts of hydrocarbon compounds, which superimpose and dilute the compounds derived from the vitrinitic proportion of the kerogen.

Pyrograms have also been obtained from the pyrolysate characterized by the S_1-peak, which represents the fraction of the original hydrocarbon potential that has been effectively transformed into hydrocarbons. In comparison to gas chromatograms of the C_{15+}-saturated hydrocarbon fraction the following differences can be observed (Figure 21a-g):

- the distribution is unimodal and includes n-alkanes ranging from about C_{13} to C_{24} with a peak maximum either at C_{15} or C_{17}.
- There is a strong decrease in relative amounts of n-alkanes from C_{19} toward higher molecular weight n-alkanes.
- Pristane and phytane are relatively more abundant in the pyrolysate than in the C_{15+}-saturate fraction of the extract.
- As opposed to the fingerprint of the gas chromatograms from the C_{15+}-saturate fraction, there is a higher percentage of n-alkanes $<C_{17}$ present in the pyrograms, together with a strong decrease toward the heavier molecules as noted above.

These differences are considered to be the result of two different phenomena:

1. The decrease in low molecular weight n-alkanes ($<C_{17}$) in the gas chromatograms of the saturate hydrocarbon fraction of the oil shale extract is due to evaporative losses during the analytical procedure. During pyrolysis these losses are very unlikely to occur, so the front end distribution of the pyrograms are considered to be a more representative fingerprint of the indigenous saturated hydrocarbons in the sample.
2. The strong decrease toward the heavier weight n-alkanes in the pyrogram is probably due to the physical trapping of the larger molecules in the micropores, whereas the exhaustive extraction of the oil shale samples released the larger molecules present in the sample.

Some characteristic features are evident from both the pyrograms and the gas chromatograms of the C_{15+}-saturated hydrocarbons. For example, the predominance of n-C_{17} in sample 20 together with a high phytane/n-C_{18} ratio, is recorded by both methods. The same applies to sample 28 if the n-alkanes below n-C_{17} are disregarded. Additionally, in sample 29, the phytane/n-C_{18} ratio of >1 can be observed in the pyrogram as well as in the gas chromatogram.

The pyrograms of the whole rock samples from Canadian Albert Mines No. 5 show the following features: The alkenes show a maximum at C_9 and a regular decrease toward higher carbon numbers, as observed in the kerogen-pyrograms. However, the relative amount of n-alkanes (<n-C_{15}) is generally lower than the amount of alkenes. Toward the higher molecular weight compounds the relative amount of n-alkanes increases and becomes dominant. This results in a distinct bimodal envelope of the n-alkane distribution in most of the samples, with a first pronounced maximum at n-C_9 and a second maximum at n-C_{19} (samples 1 and 6) or n-C_{21} (samples 16 and 20). In sample 29 the maximum at n-C_{27} is the maximum of the whole n-alkane distribution. In some of the samples (samples 6, 20, 28, 29) there are higher relative amounts of pristane and, especially, phytane in the saturate fraction of the extract compared to the pyrograms from the kerogen.

In addition, the kerogen type index reveals different values in comparing the kerogen pyrograms to the whole rock pyrograms. No clear trend is evident from the comparison of the indices obtained from kerogens and whole rocks, which could eludicate the cause of the differences. The differences are thought to be due to the influence of the mineral matter on the formation of petroleum-like hydrocarbon upon pyrolysis (Horsfield and Douglas, 1980).

The differences observed are seen in the chain-length distribution of the n-alkanes in the pyrolysates as well as differences in the alkene/alkane ratio. Furthermore slight influences in the aromaticity of the pyrolysate were observed. The observation of increasing amounts of n-alkanes above n-C_{15} in pyrolysates from whole rock samples does not agree with the findings of Horsfield and Douglas (1980), who observed an increase of these compounds in the isolated kerogen pyrolysates.

The differences observed between whole sediment and isolated kerogen pyrolysates might be due, in part, to the kerogen being altered chemically by mineral acids during its isolation (Robinson, 1969).

A pyrogram of alginite (Horsfield and Douglas, 1980) shows a similar trend of increasing n-alkanes with increasing carbon number and a maximum of n-C_{19}, as with the pyrograms obtained from some of the whole rock samples. The pyrogram of alginite + Al_2O_3, however, resembles some of the whole rock samples (samples 6, 16, 20, 29) with a less distinct bimodal distribution pattern

(samples 15, 28). These differences cannot be explained so far, but it seems that they are not only due to the presence of mineral matter in general, but also to the type and composition of the mineral matter present. Although x-ray diffraction results are available (Macauley and Ball, 1982) for the investigated samples, the differences in the pyrogram fingerprints could not be related to changes in mineral distribution. These observations suggest that different components require different minerals to act as catalysts. The same type of organic matter could produce a different hydrocarbon composition, dependent on the presence or absence of a certain mineral acting as a catalyst.

Another possible explanation of the increase in n-alkanes $>$n-C_{15} in pyrograms of whole rocks compared to those of kerogens is outlined below.

As mentioned before hydrocarbons which have been already generated from the kerogen are usually released at temperatures below 300°C and represented in the S_1 peak. However, especially high molecular weight n-alkanes ($>$n-C_{15}) could, even at these enchanced temperatures, be physically trapped in the samples (for example in microreservoirs; Barker, 1974). This means, that they would not be released during the initial stage of pyrolysis at temperatures up to 300°C and so would not be included in the S_1 peak. Instead, these components will be released during further temperature increase as soon as the isolated volumes of the microreservoirs rupture. The appearance of these hydrocarbons in the pyrogram therefore occurs at higher temperatures and are added to the hydrocarbons which are generated by pyrolysis of the insoluble kerogen (S_2 peak). Evidence for this hypothesis is seen by comparing the gas chromatograms obtained from the S_1-pyrolysate with the chromatograms from the $C_{15}+$-saturated hydrocarbon fraction obtained by soxhlet extraction. The gas chromatograms of the S_1-pyrolysate show a sudden decrease ion the relative concentration of the higher molecular compounds ($>$nC_{17}) which is not observed in the gas chromatograms of the $C_{15}+$-saturated hydrocarbon fraction from the same sample (e.g., Figure 15a vs Figures 21a-e). The observation of the presence of significantly greater quantities of n-alkanes with increasing carbon number in the S_2-pyrolysate, when compared to the smooth distribution of alkenes in the same molecular range, demonstrates the release of these higher carbon number n-alkanes at temperatures greater than 300°C. Samples 15 and 28, where the effect of increasing n-alkanes is less distinct, are

the samples with exceptionally high n-C_{17}/n-C_{27} ratios calculated from the gas chromatograms of the saturated hydrocarbon fraction. Since there are obviously less higher-molecular-weight n-alkanes present in the sample, the amount of n-alkanes released from microreservoirs is less, and the observed bimodality in the pyrograms is less pronounced.

This effect is also very much dependent on the n-alkane concentration in the sample. Since all changes in gas chromatograms and pyrograms are only qualitative no further statement is possible, but further investigations regarding quantitative aspects are recommended.

4.0 Conclusions

The following conclusions have been drawn:

1. Organic geochemical data, in particular yield and compositional characteristics of the C_{15+}-saturated hydrocarbon fraction, reveal a discrepancy with the vitrinite reflectance measurements published by Kalkreuth and Macauley (1984). In contrast to vitrinite reflectance measurements, no distinct maturation difference was observed between the two wells studied. The low vitrinite reflectance values in oil shales from Canadian Albert Mines No. 5 well are interpreted to be due to impregnation of the vitrinitic particles with hydrocarbons generated from the dominantly algal kerogen.
2. Elemental analysis data, as well as RockEval data (Macauley and Ball, 1982) and maceral analysis (Kalkreuth and Macauley, 1984), suggest that all samples, but one, contain a Type I kerogen. Sample 5 from Atlantic Richfield Boudreau No. 1 well contains a mixed Type II/Type III kerogen with mainly vitrinite particles (Figure 6).
3. Extract yields (mg/gCorg) range from 115 to 979 in oil shales from Canadian Albert Mines No. 5, and between 90 to 337 in Atlantic Richfield Boudreau No. 1, showing that in both wells hydrocarbons have been generated from the kerogen due to increasing maturity.
4. Discrepancies between extract yield and quantity and quality of organic matter are best explained by redistribution (enrichment and depletion) of hydrocarbons.

5. The differences observed in gas chromatograms of the C_{15+}-saturated hydrocarbon fraction are thought to be caused by three different phenomena:

   a. Facies related changes (organic input, depositional environment, bacterial reworking)

   b. Maturation increase

   c. Redistribution (depletion and enrichment) due to migration.

6. Pyrolysis - gas chromatography of isolated kerogens reveal mainly alkenes and alkanes (Figures 19, 20). The distribution is similar to those of alginite or alginite rich kerogens published by Larter and Douglas (1980). Kerogen index type values (Larter and Douglas, 1980) indicate lacustrine and marine algal kerogens and marine kerogens.

5.0 Acknowledgments

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7.0 Appendices

A. Figures

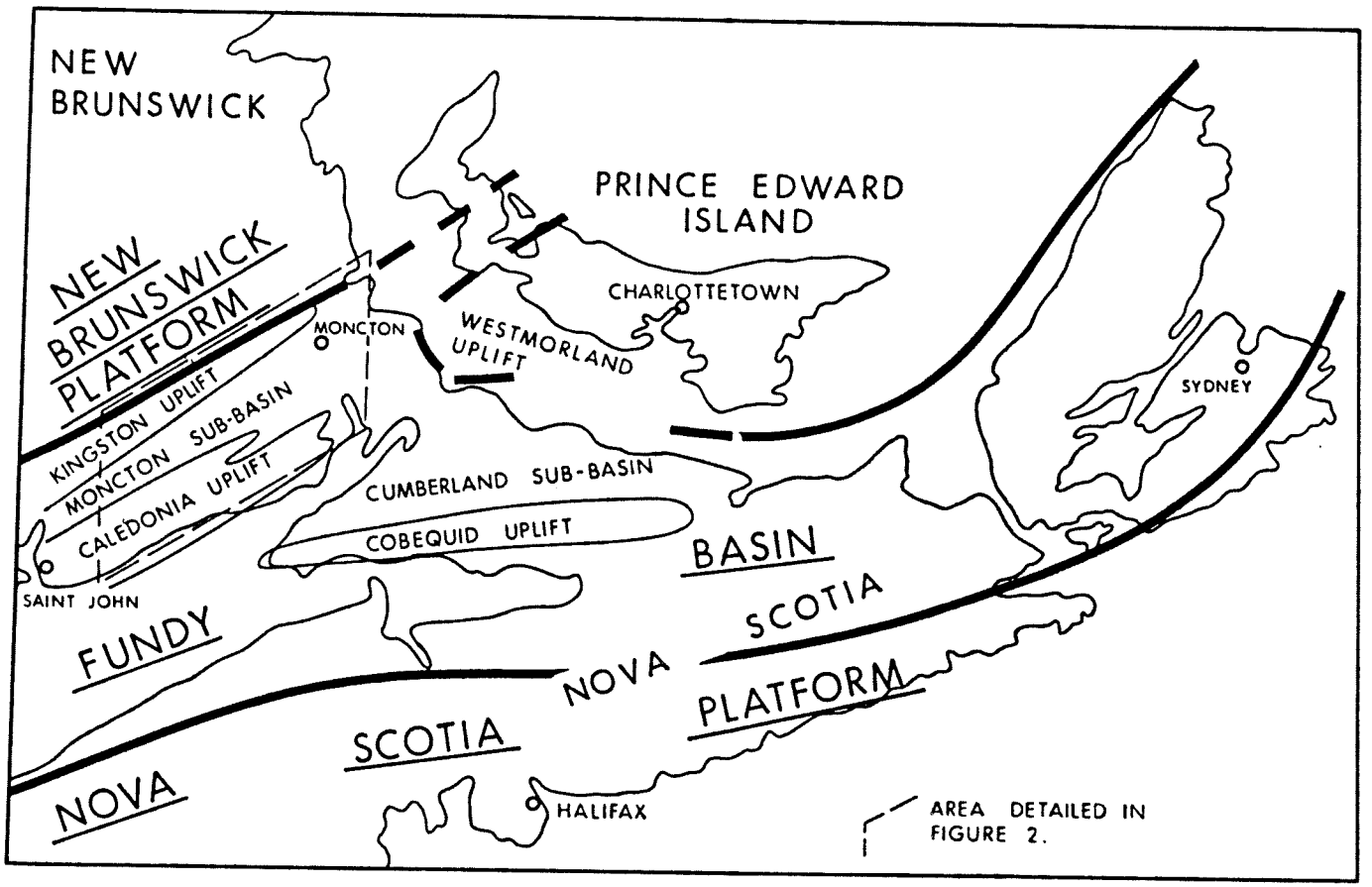


Figure 1: Tectonic elements of the Fundy Basin, New Brunswick - Nova Scotia (from Macauley and Ball; 1982).

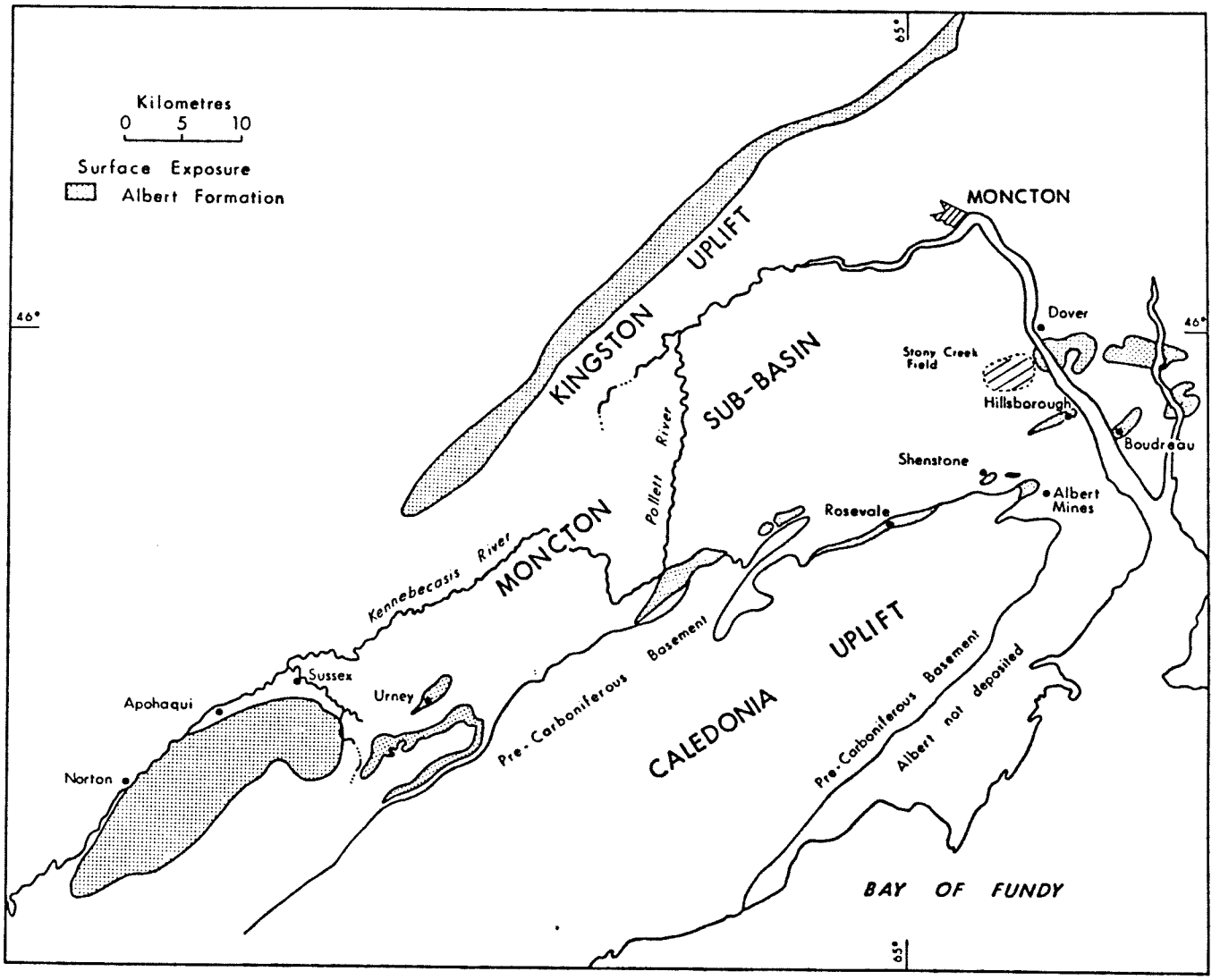


Figure 2: Outcrop distribution of the Albert Formation, Moncton sub-Basin - Kingston Uplift, New Brunswick (from Howie, 1980).

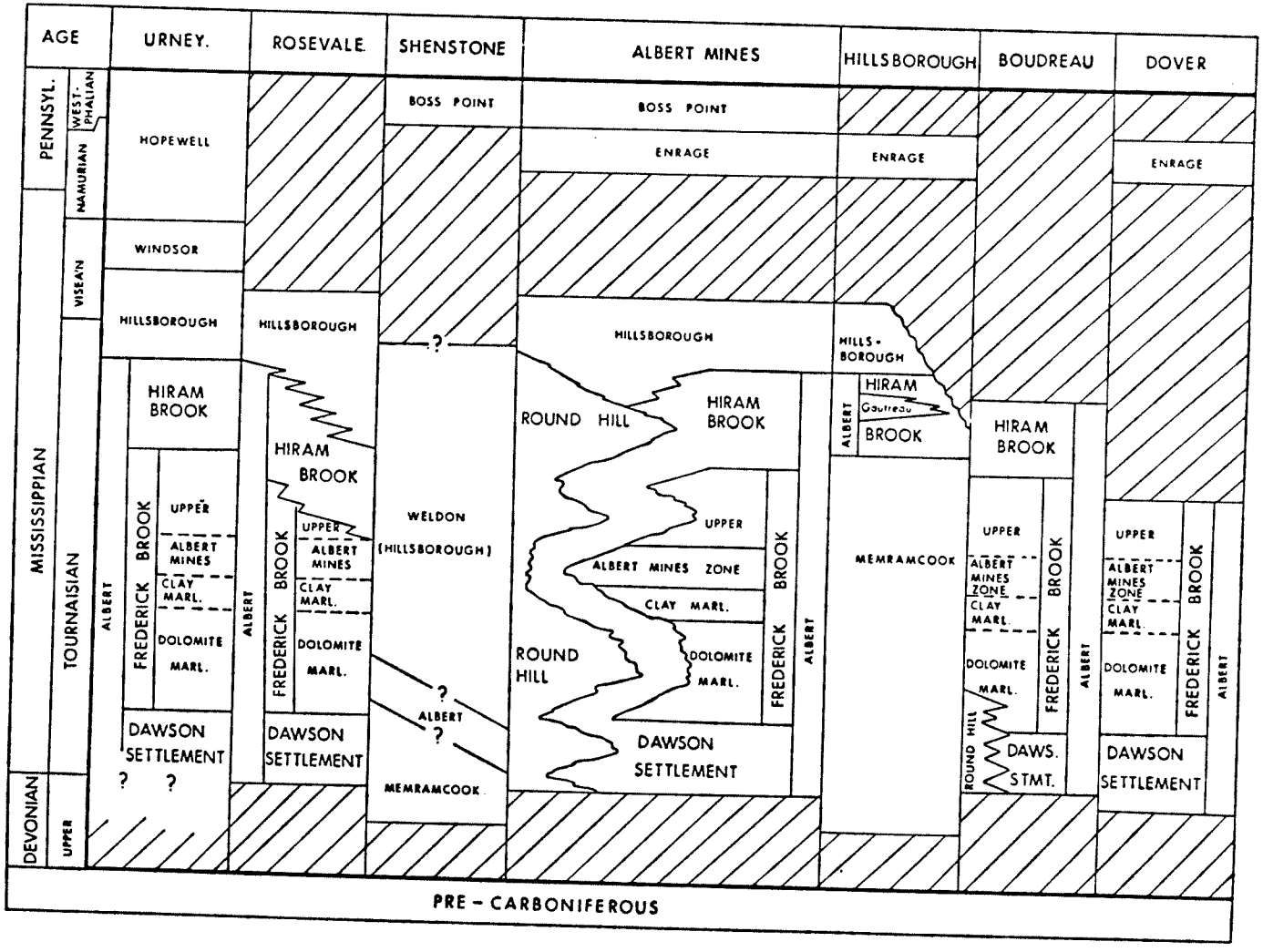


Figure 3: Stratigraphy of the Carboniferous in the Moncton sub-basin, New Brunswick (from Macauley and Ball, 1982).

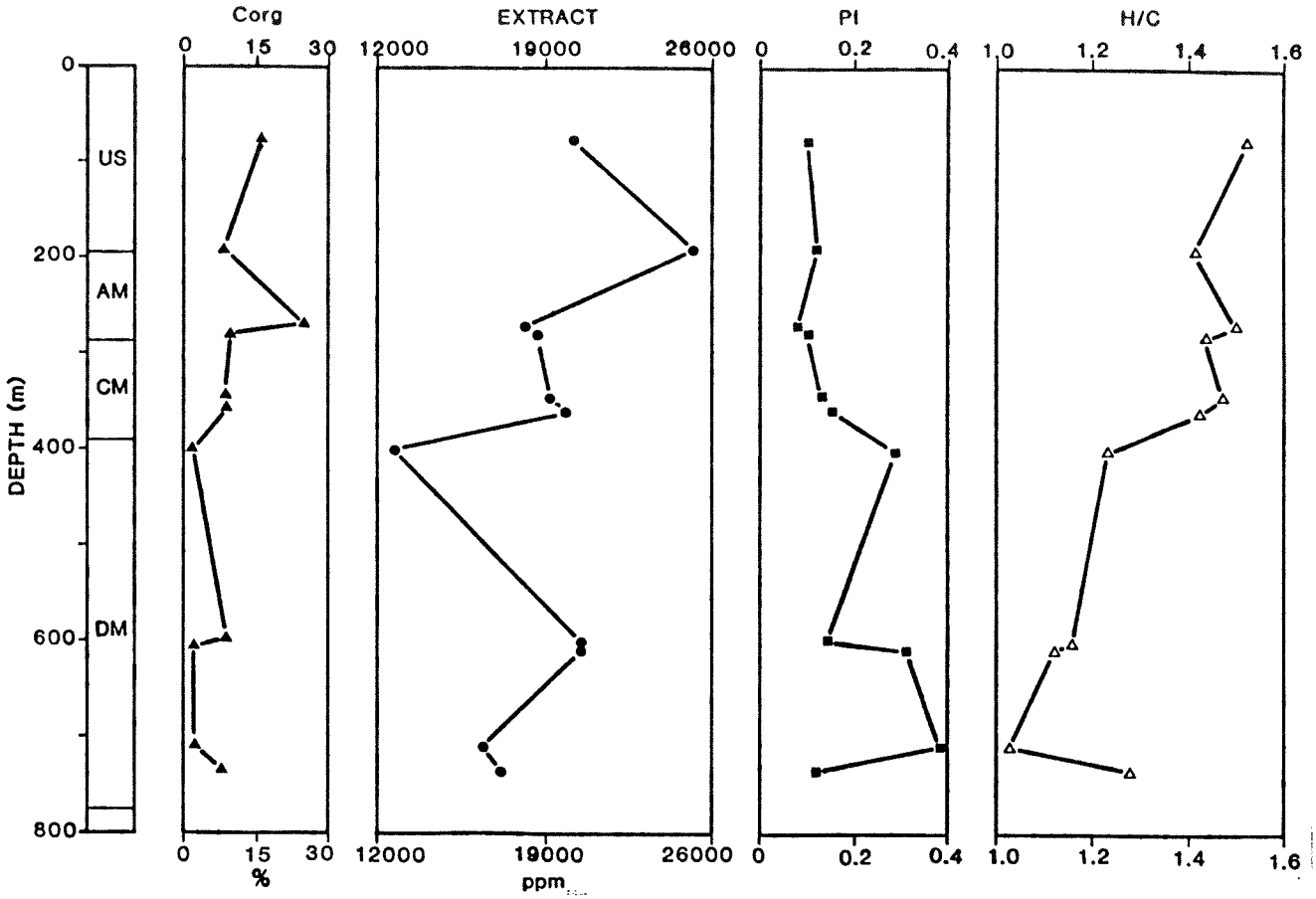


Figure 4: Changes of selected geochemical parameters of oil shales from Canadian Occidental Albert Mines No. 5.

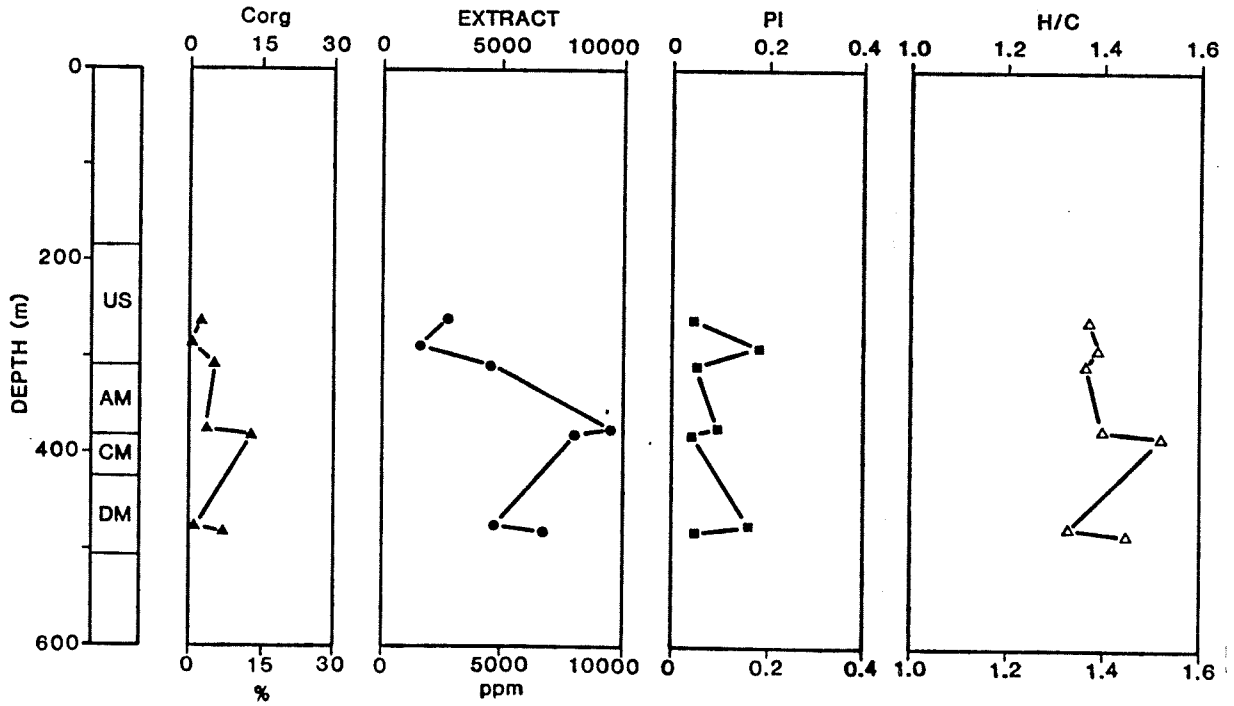


Figure 5: Changes of selected geochemical parameters of oil shales from Atlantic Richfield Boudreau No. 1 with depth.

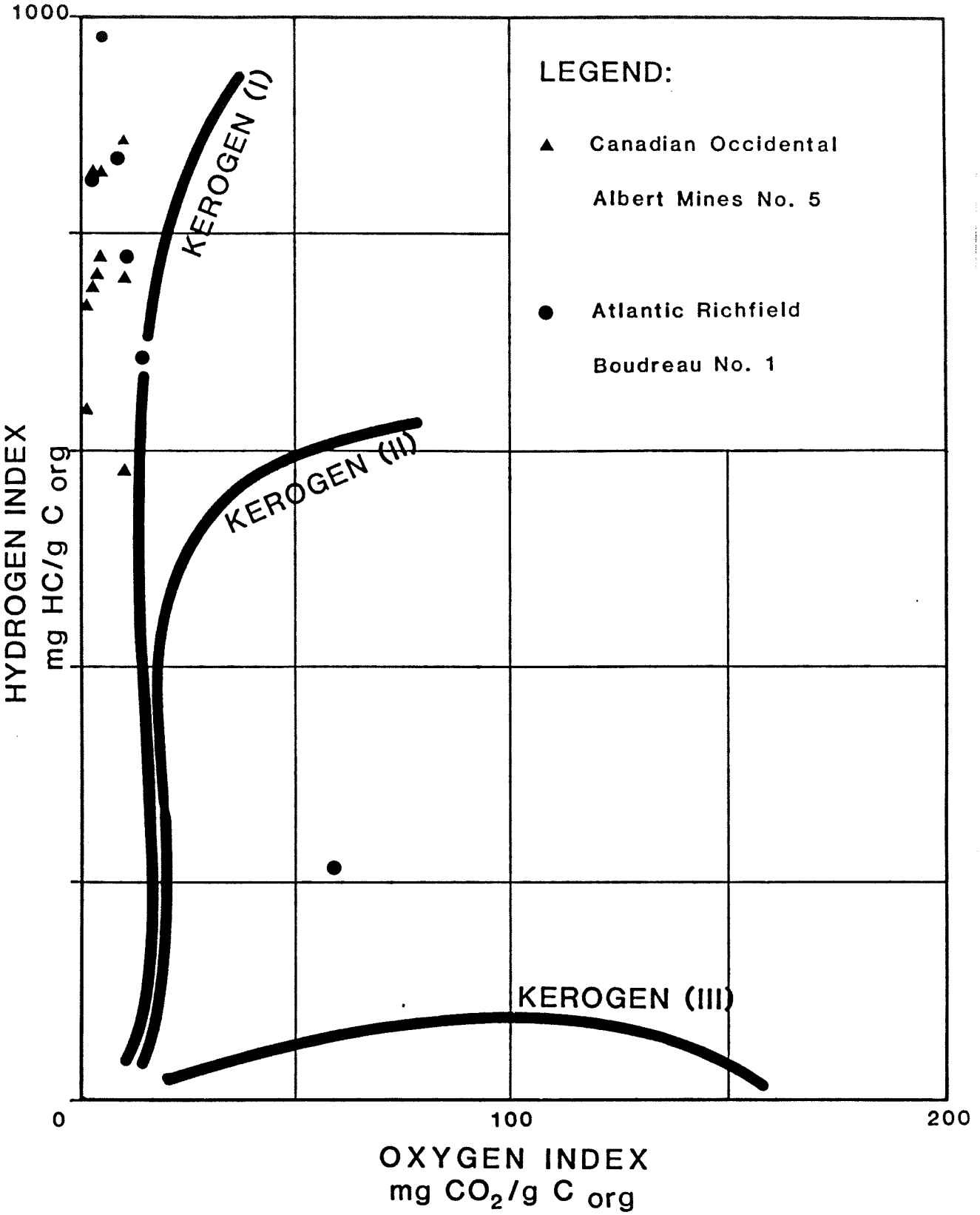


Figure 6: Kerogen classification for oil shale samples from Canadian Occidental Albert Mines No. 5 and from Atlantic Richfield Boudreau No. 1.

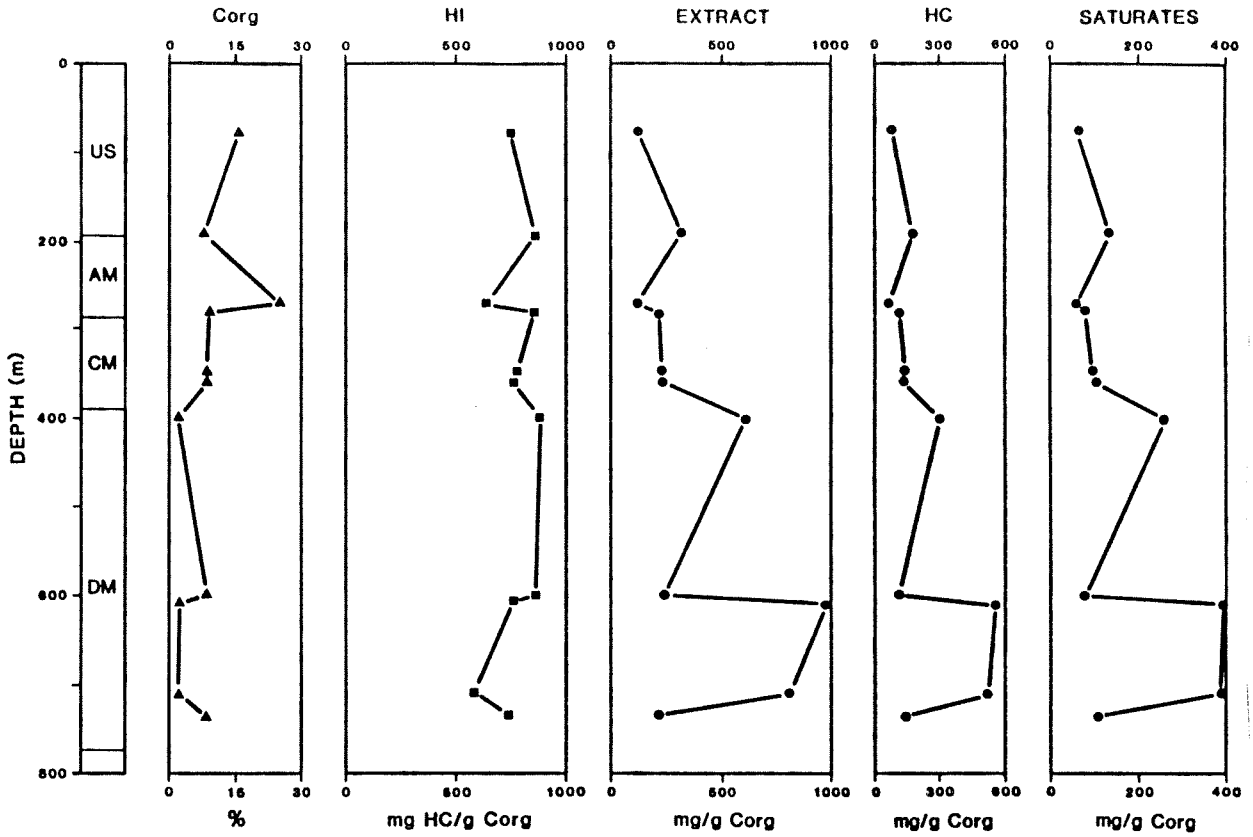


Figure 7: Changes of selected geochemical parameters of oil shales from Canadian Occidental Albert Mines No. 5 with depth.

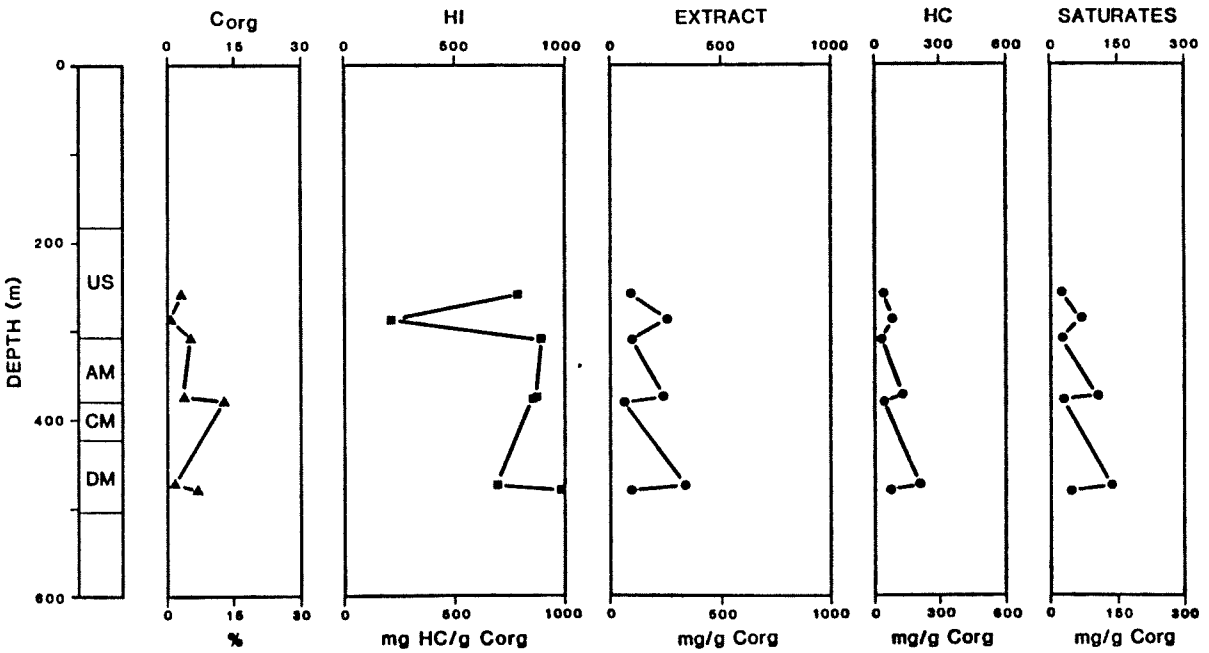


Figure 8: Changes of selected geochemical parameters of oil shales from Atlantic Richfield Boudreau No. 1.

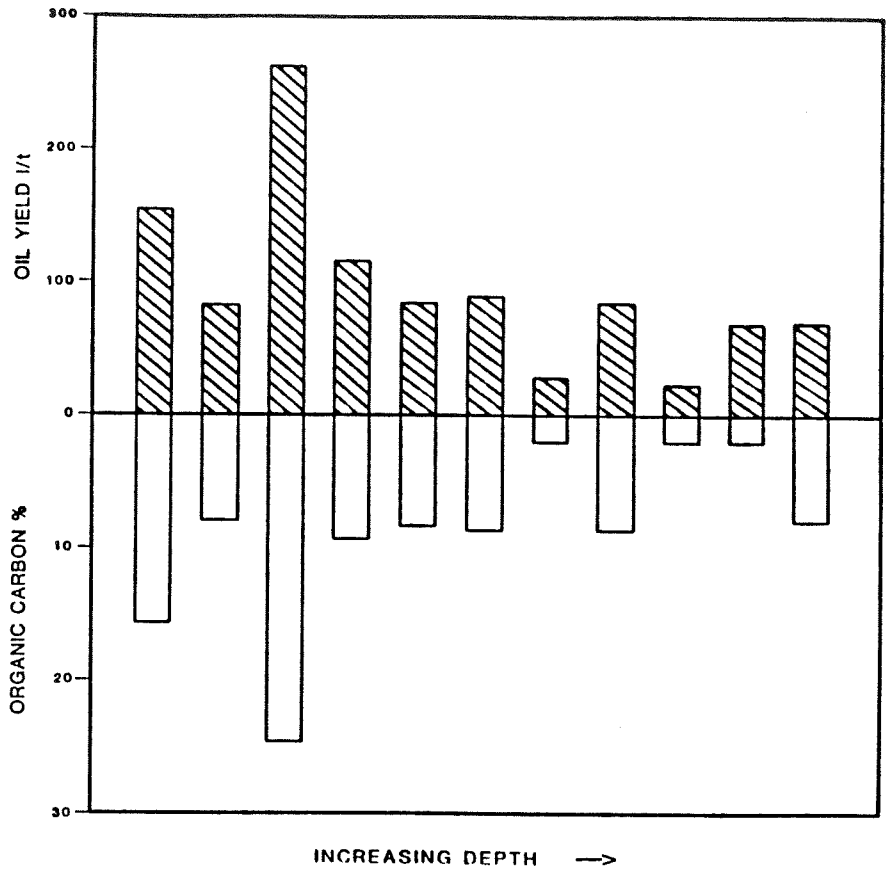


Figure 11: Organic carbon content and yield of shale oil obtained by Fischer Assay for samples from Canadian Occidental Albert Mines No. 5.

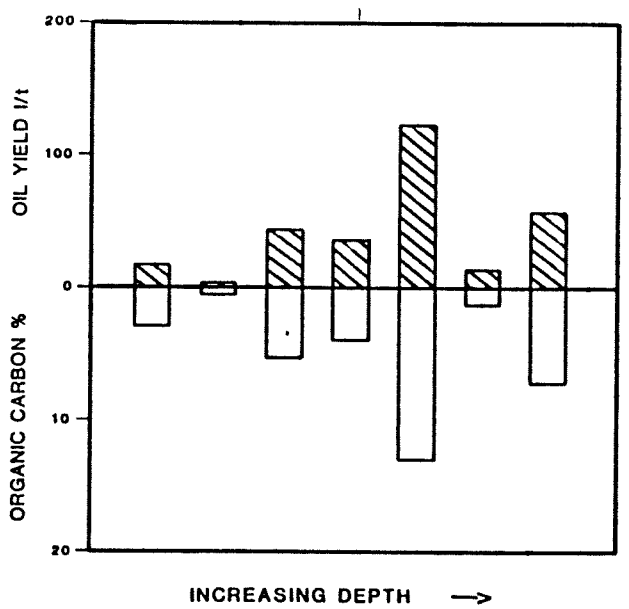


Figure 12: Organic carbon content and yield of shale oil obtained by Fischer Assay for samples from Atlantic Richfield Boudreau No. 1.

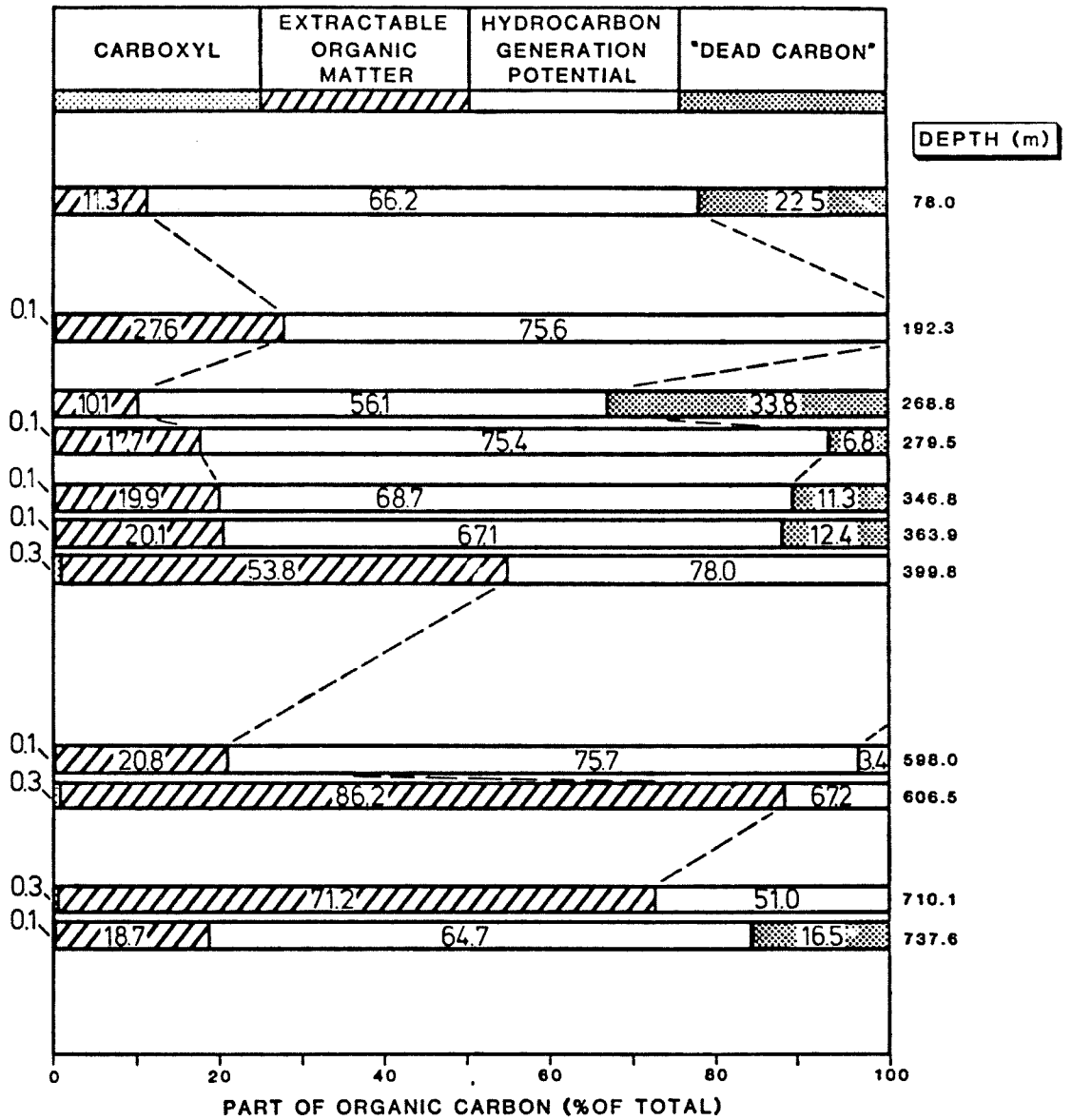


Figure 13; Organic carbon mass balance for oil shales from Canadian Occidental Mines No. 5 as a function of depth.

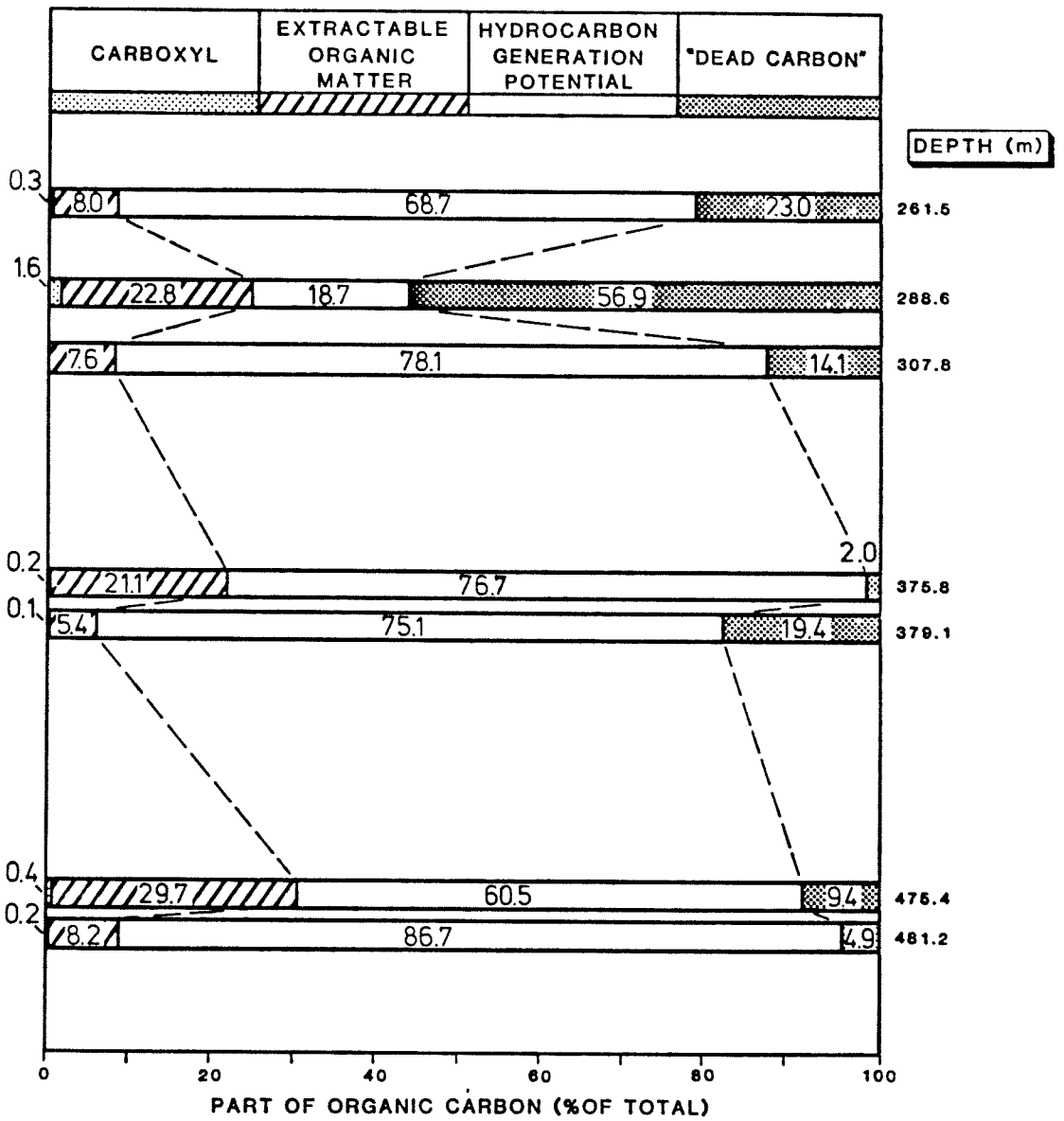


Figure 14: Organic carbon mass balance for oil shales from Atlantic Richfield Boudreau No. 1 as a function of depth.

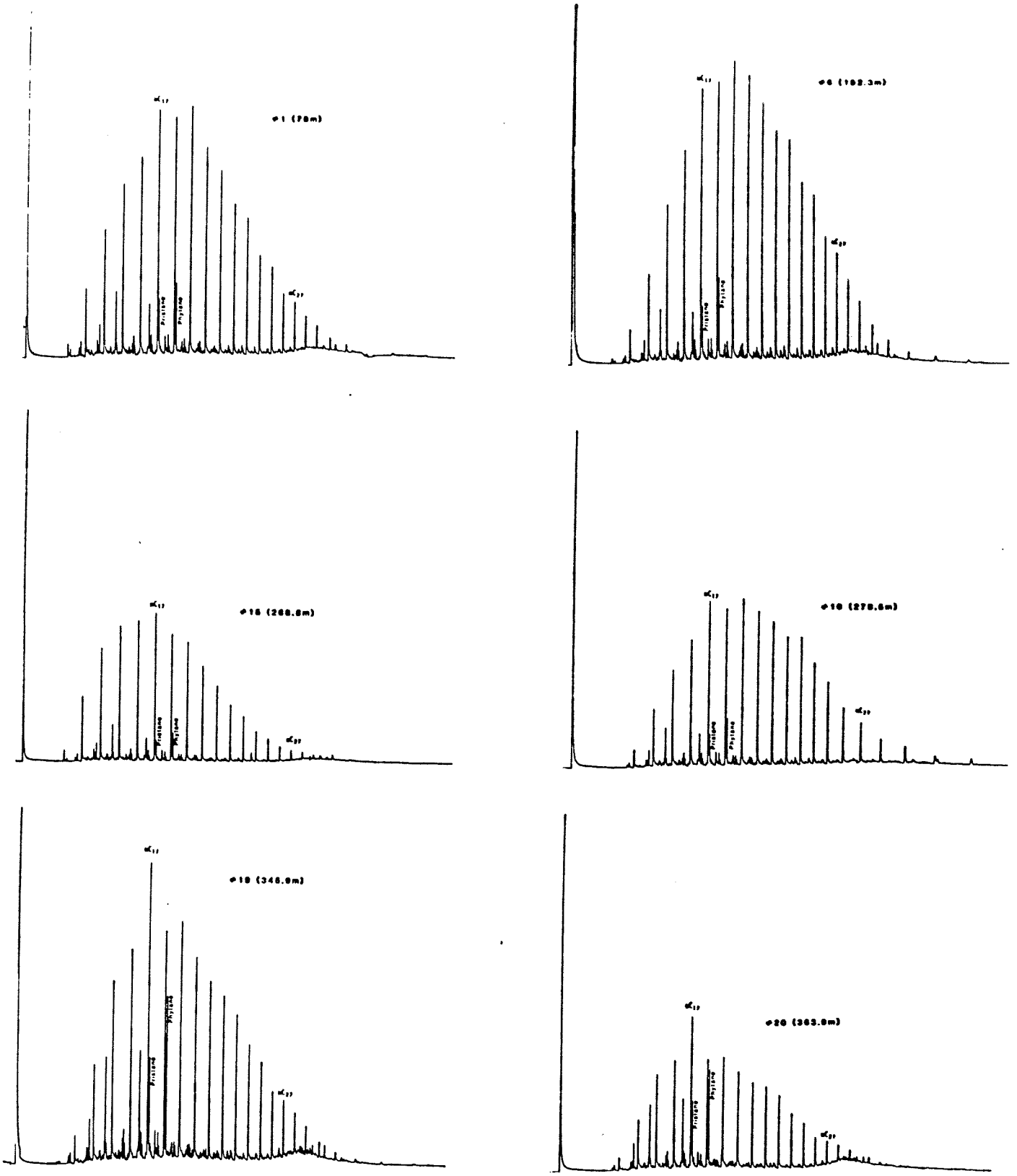
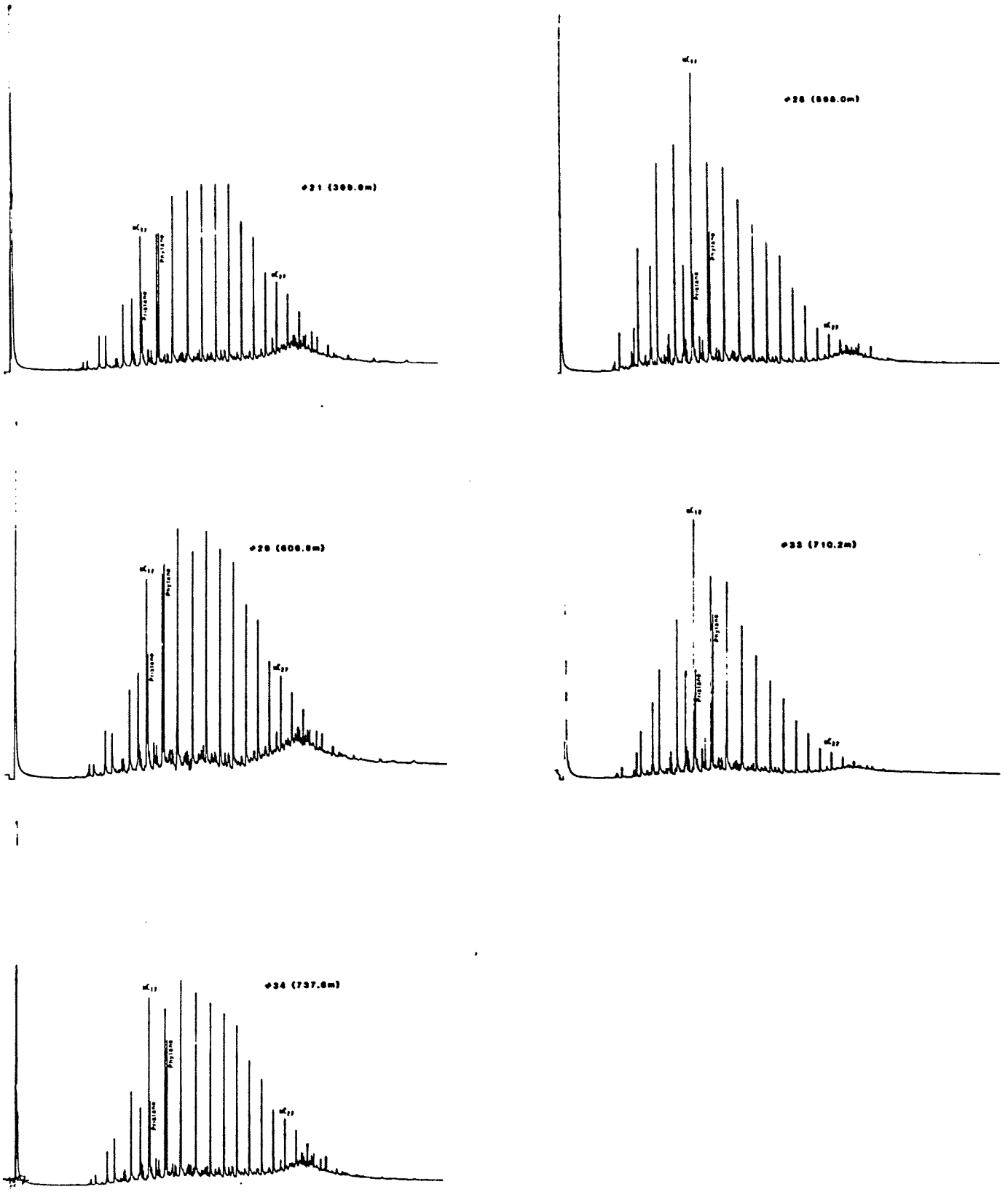


Figure 15a, b: Capillary gas chromatograms showing distributions of C_{15+}-saturated hydrocarbons as a function of depth for the investigated interval (78 m - 737.6 m) from Canadian Occidental Albert Mines No. 5.


Pristane
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Phytane
Pristane
Phytane
Pristane
Phytane
Pristane
Phytane

Figure 15b

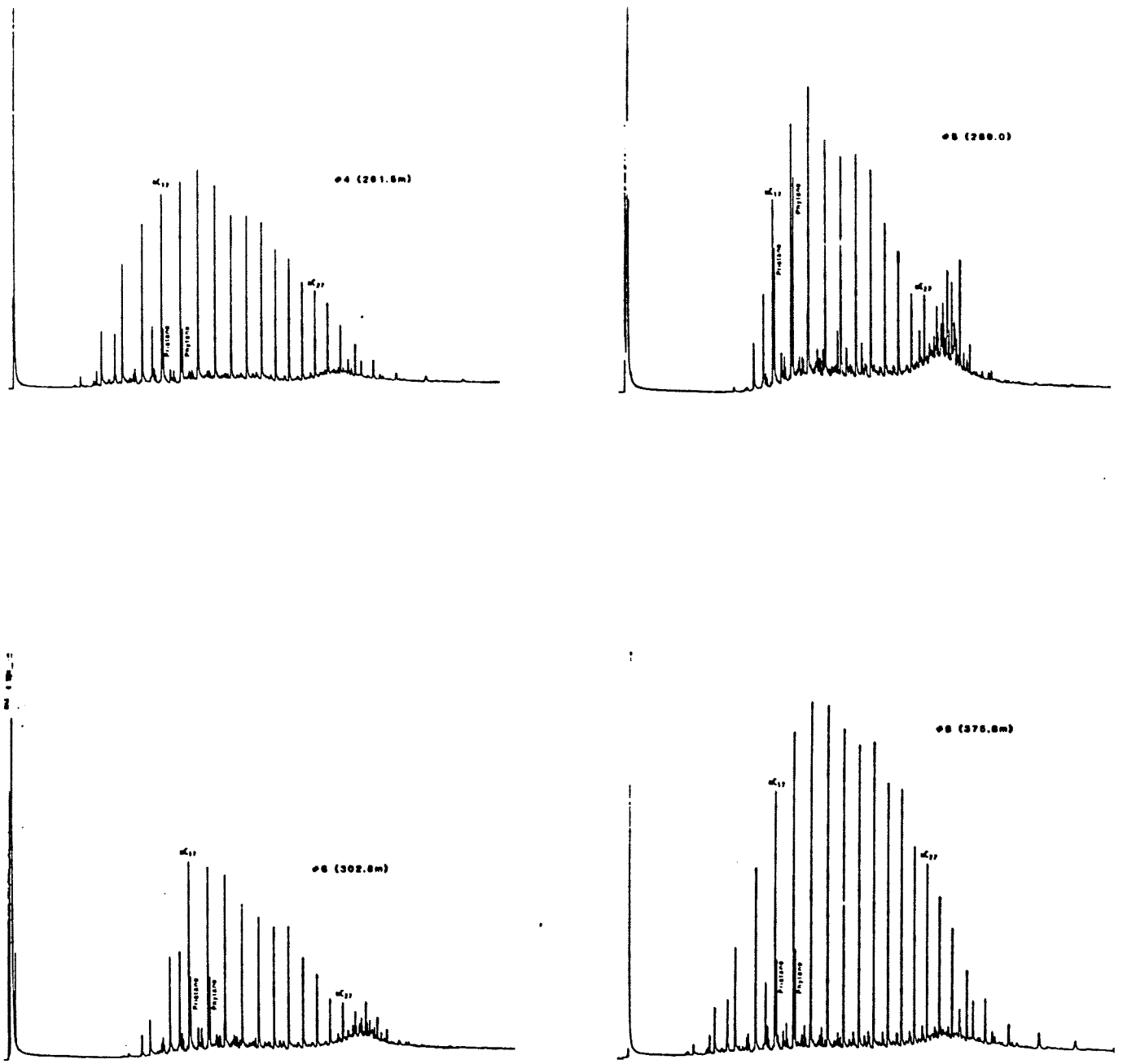
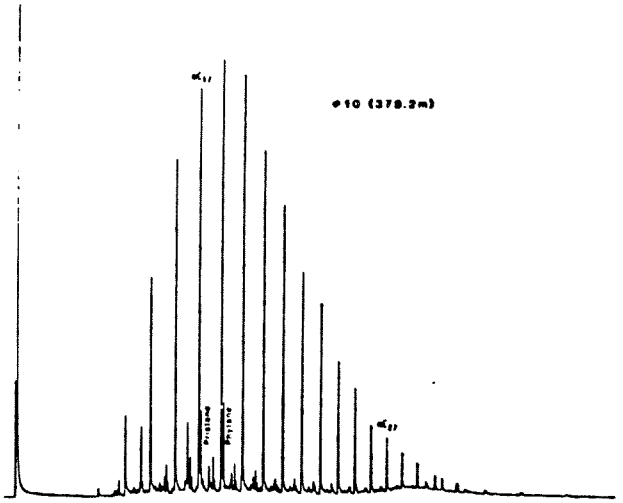
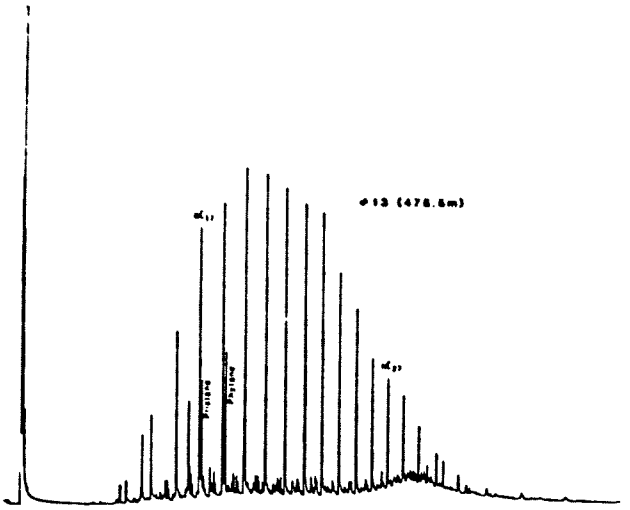


Figure 16a, b: Capillary chromatograms showing distributions of C_{15+}-saturated hydrocarbons for the investigated interval (261 m - 481.3 m) from Atlantic Richfield Boudreau No. 1.





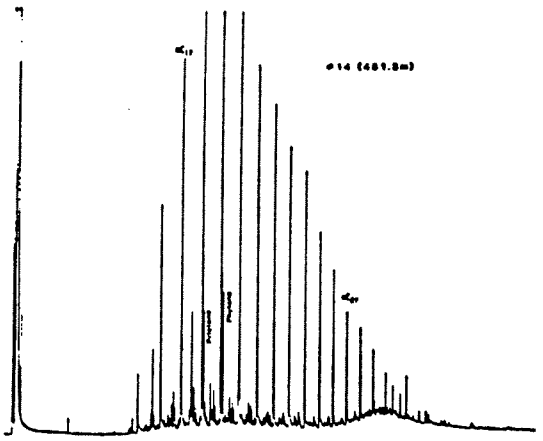


Figure 16b

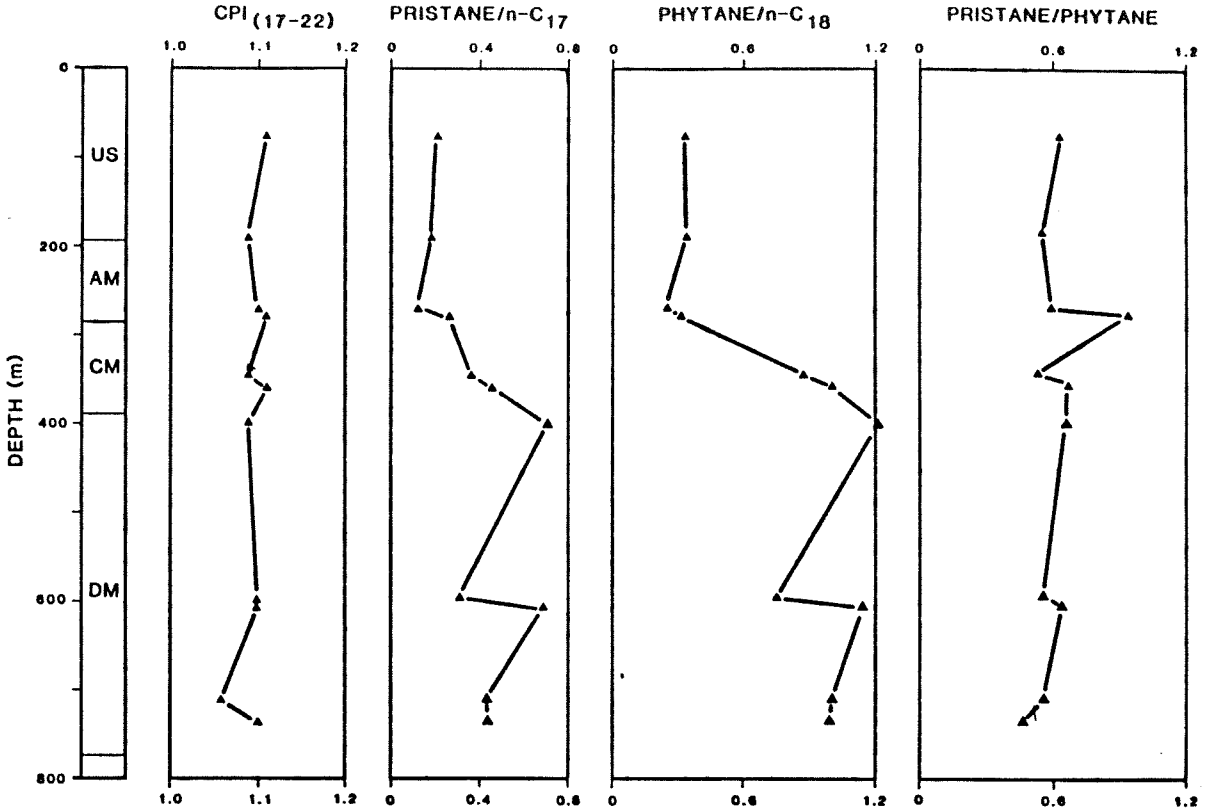


Figure 17: Changes in composition of the C_{15}+-hydrocarbons for oil shales from Canadian Occidental Albert Mines No. 5 with depth.

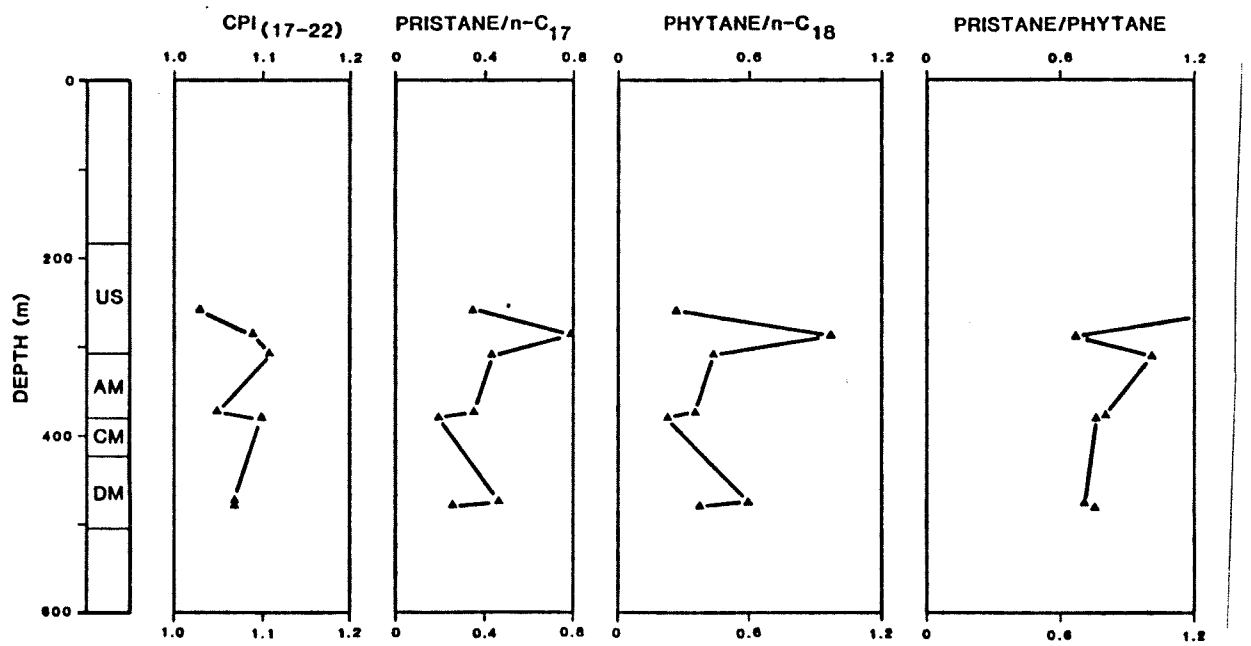
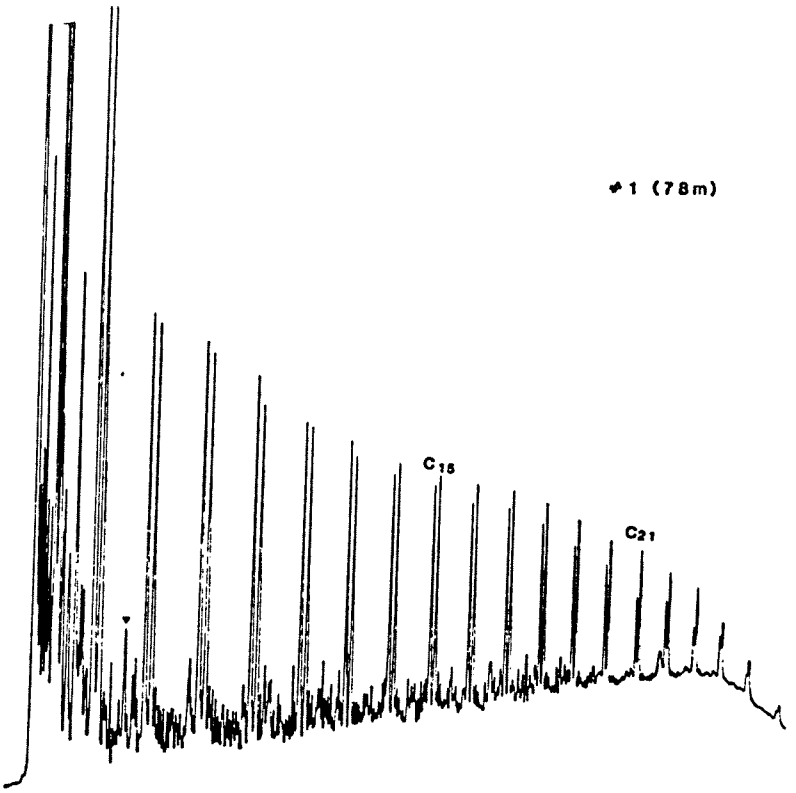
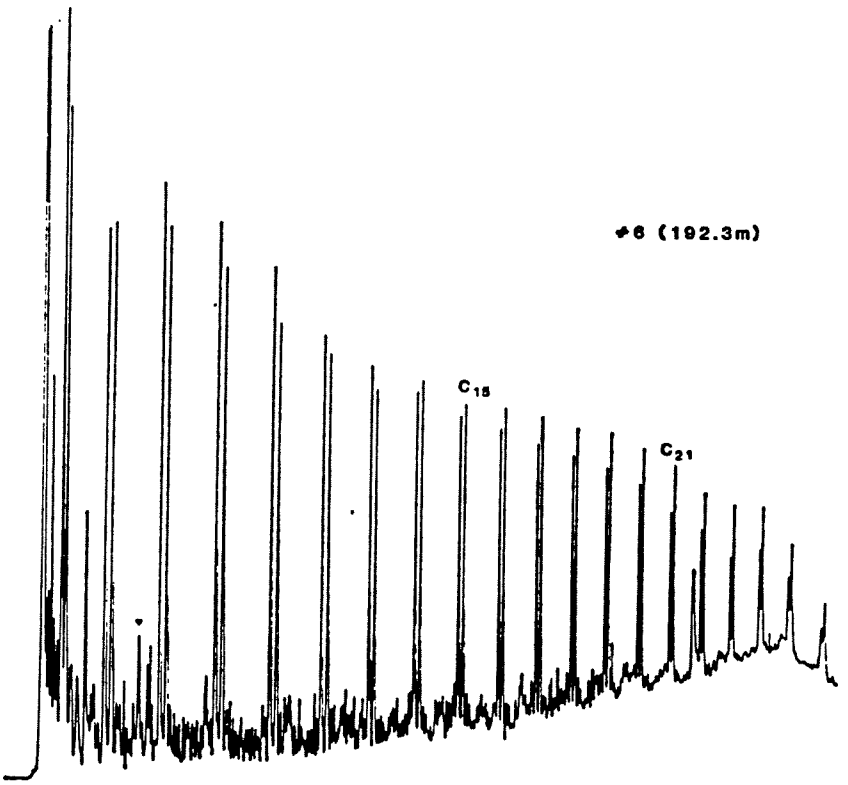
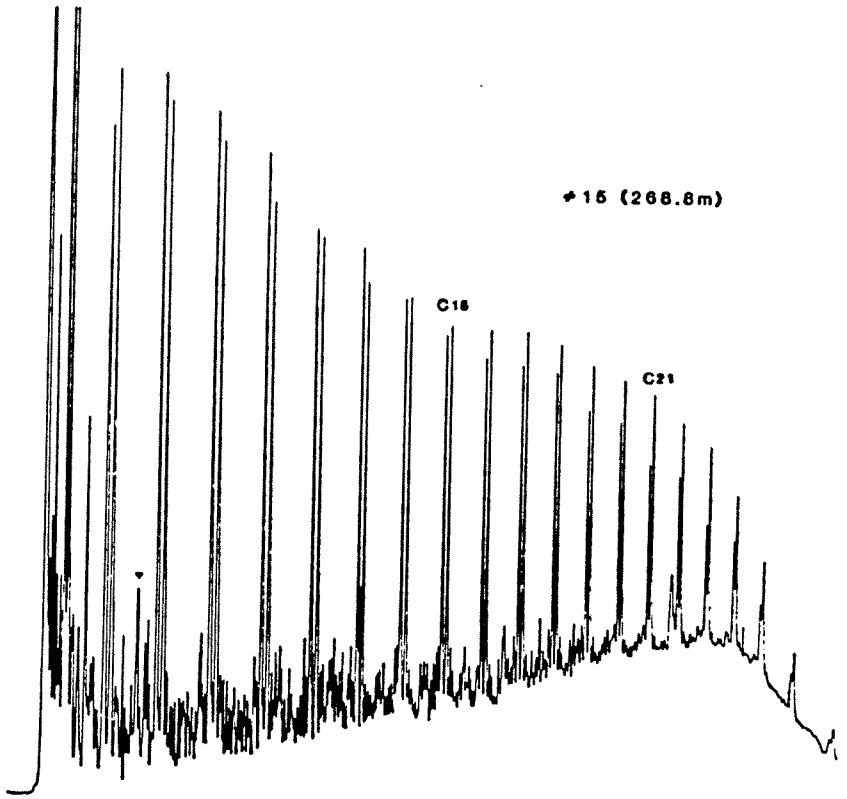


Figure 18: Changes in composition of the C_{15}+-hydrocarbons for oil shales from Atlantic Richfield Boudreau No. 1.





Figures 19a-f: Chromatograms of the S_2-fraction obtained by pyrolysis of isolated kerogens from Canadian Occidental Albert Mines No. 5.



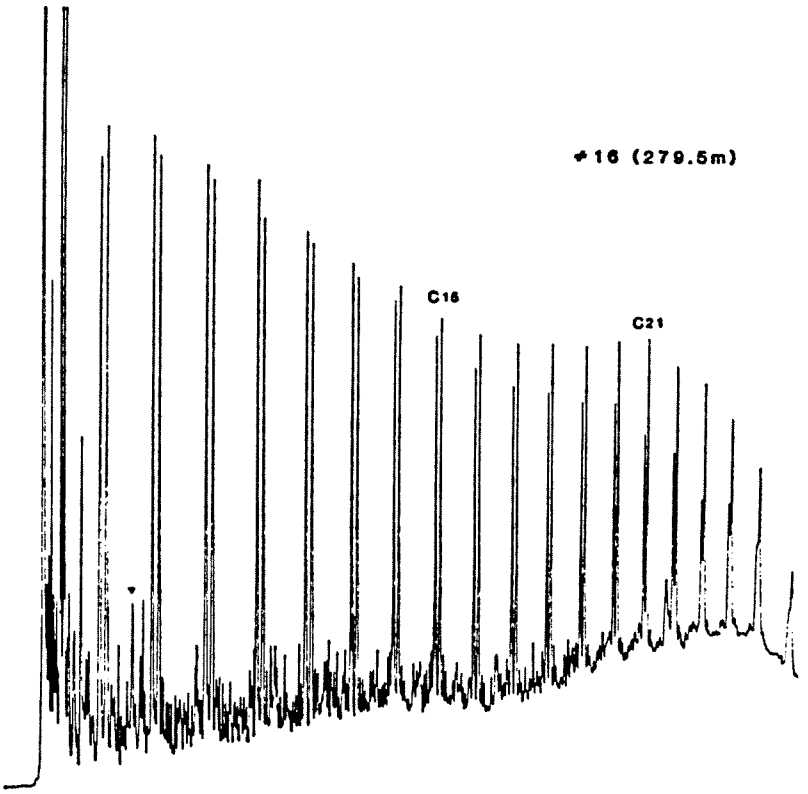
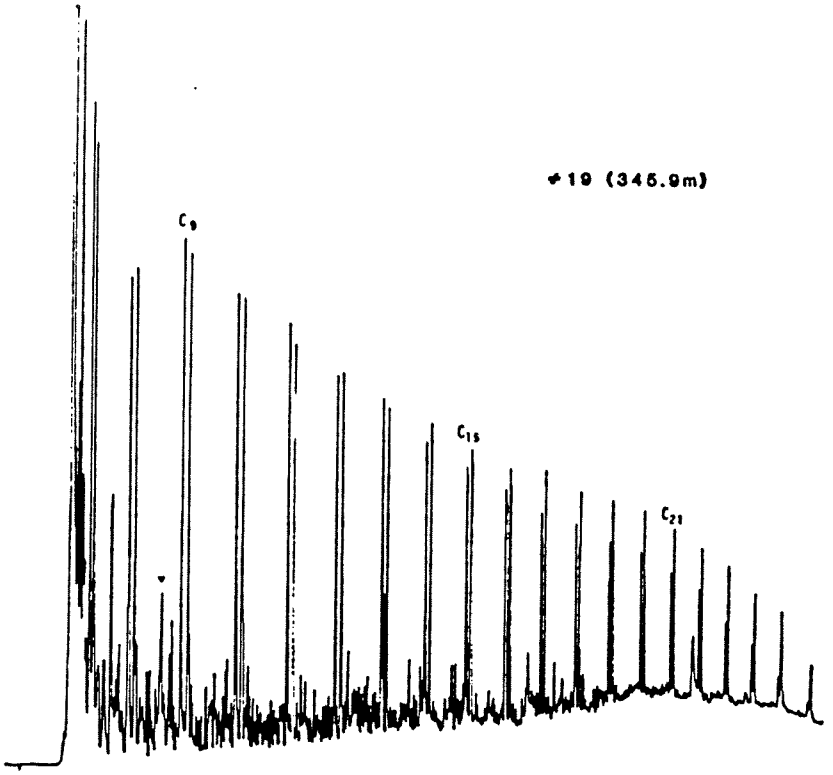


Figure 19b



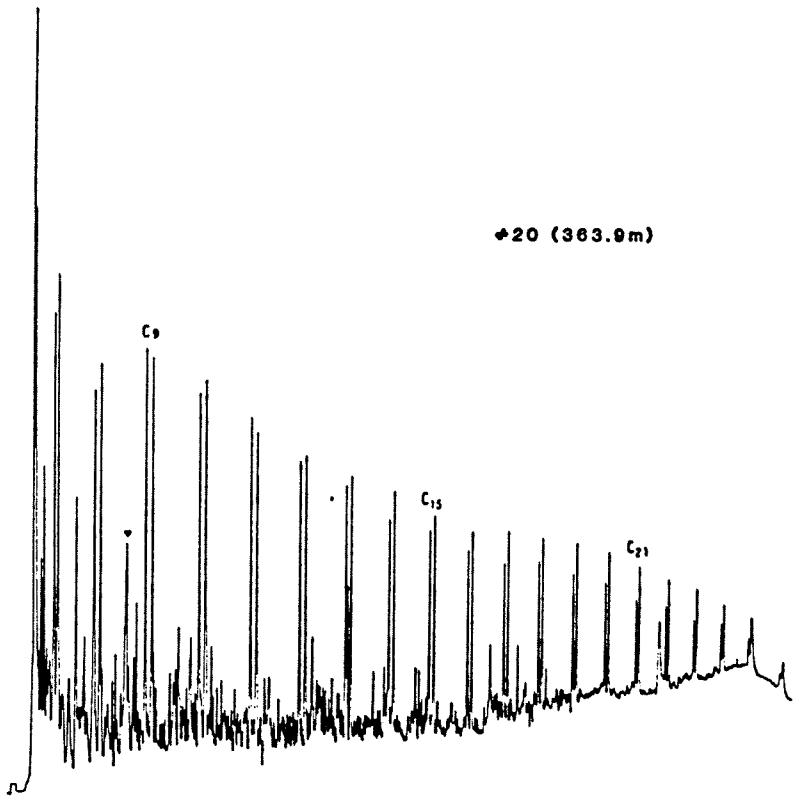


Figure 19c

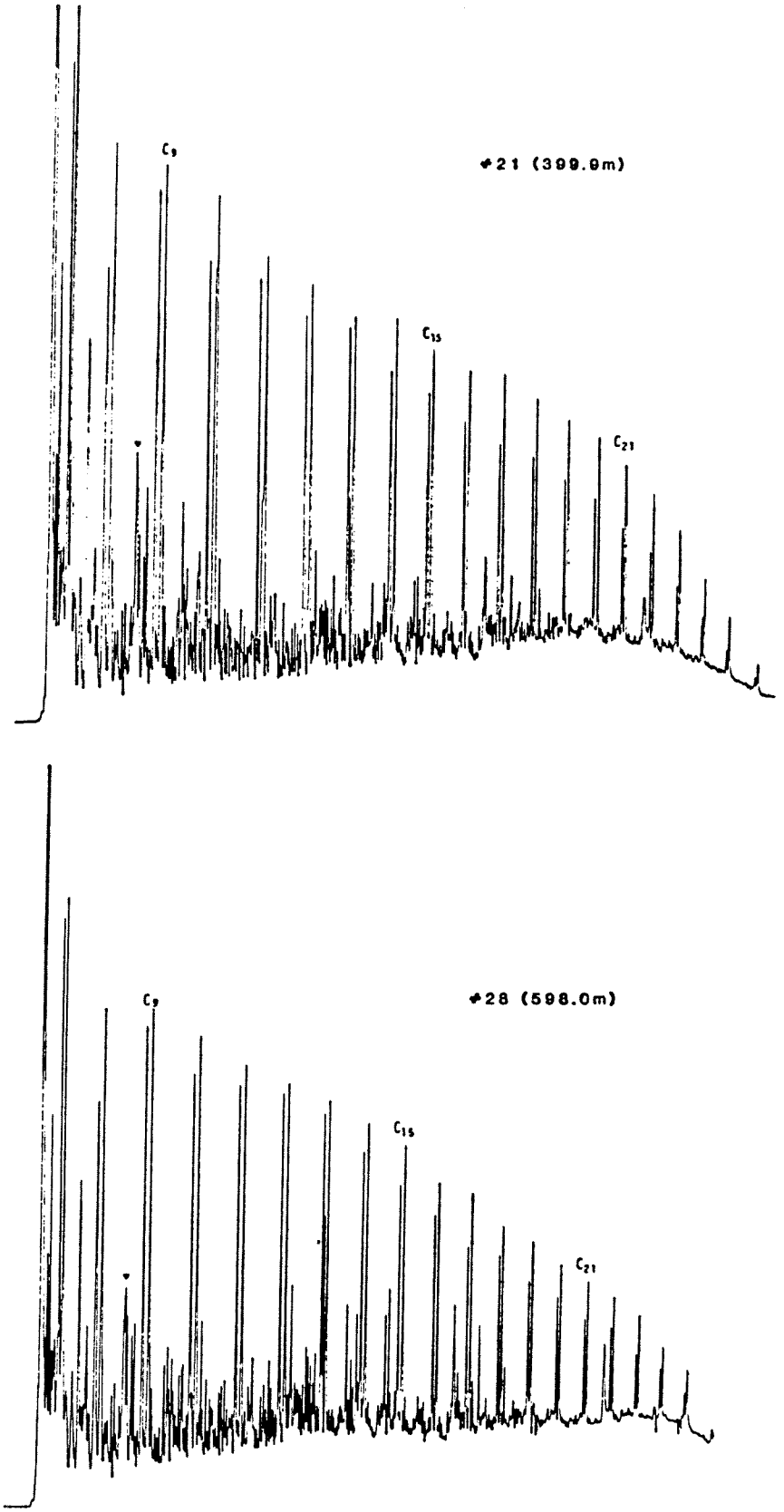


Figure 19d

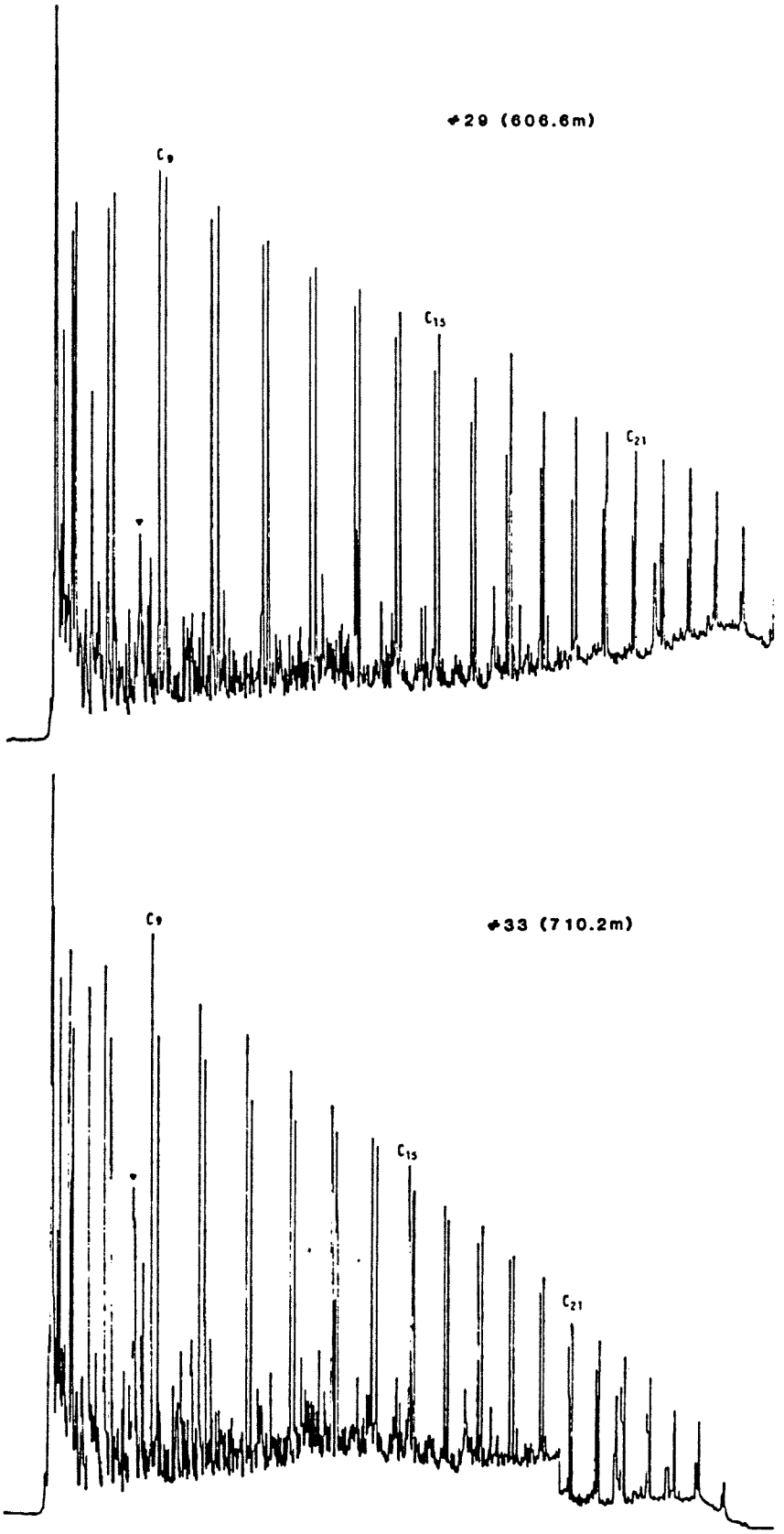


Figure 19e

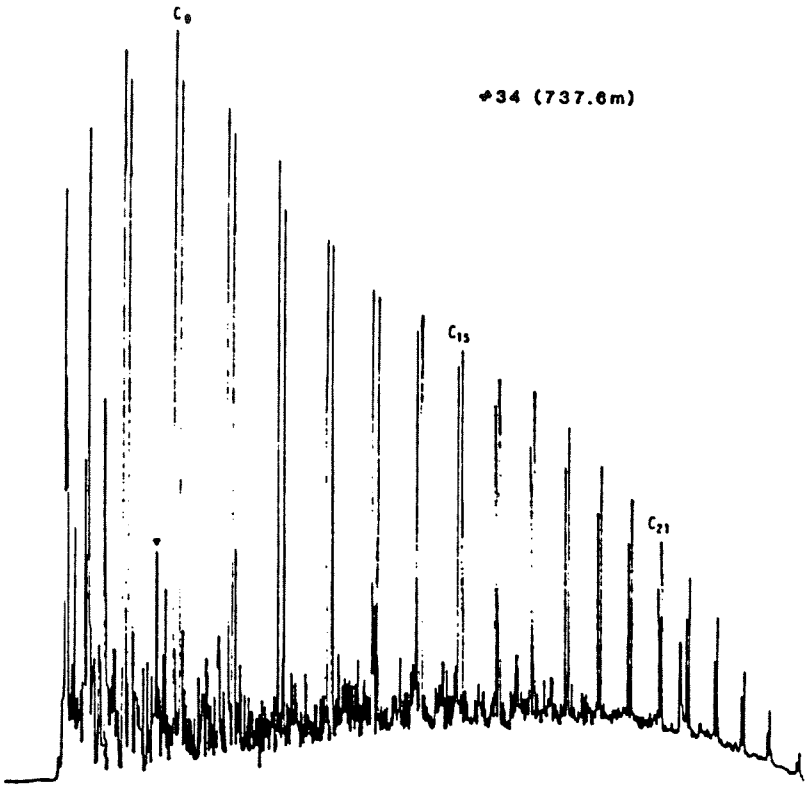
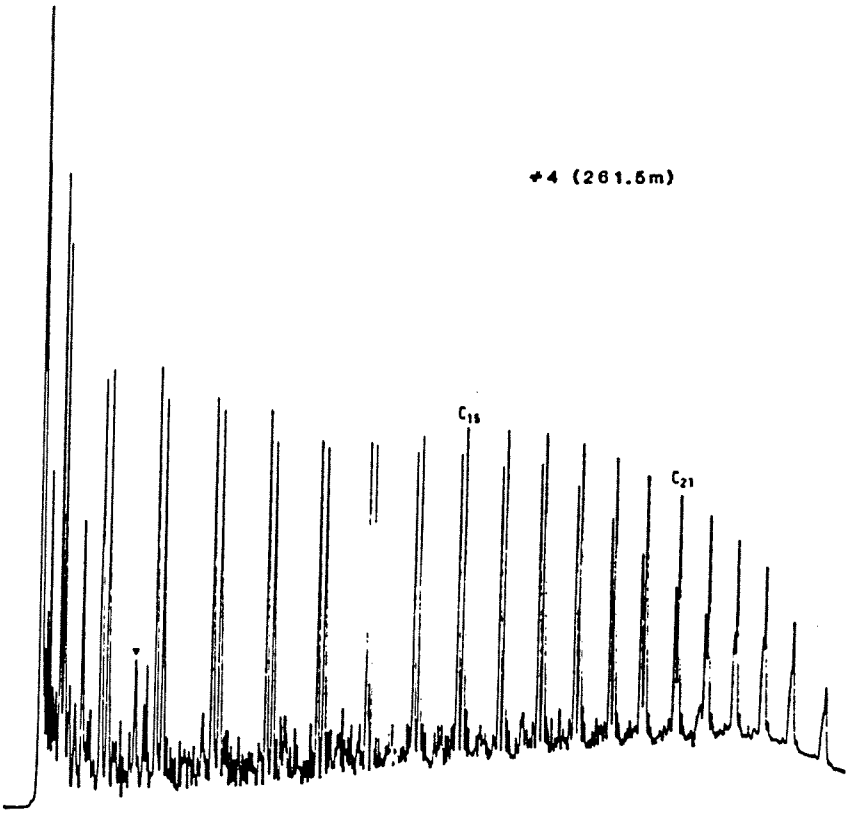
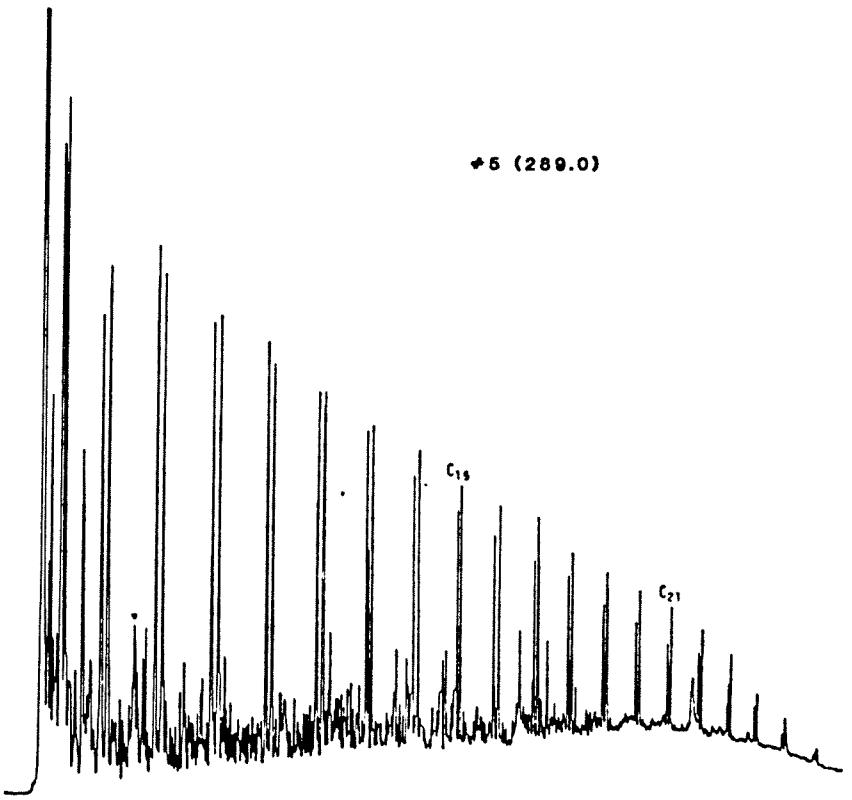
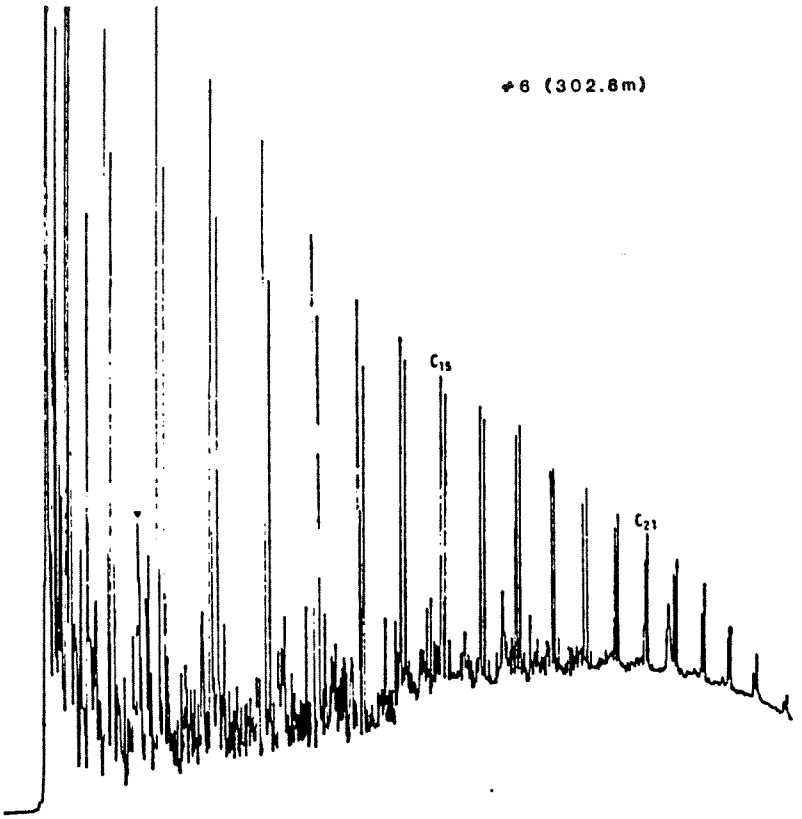


Figure 19f





Figures 20a-d: Gas chromatograms of the S_2-fraction obtained by pyrolysis of isolated kerogens from Atlantic Richfield Boudreau No. 1.



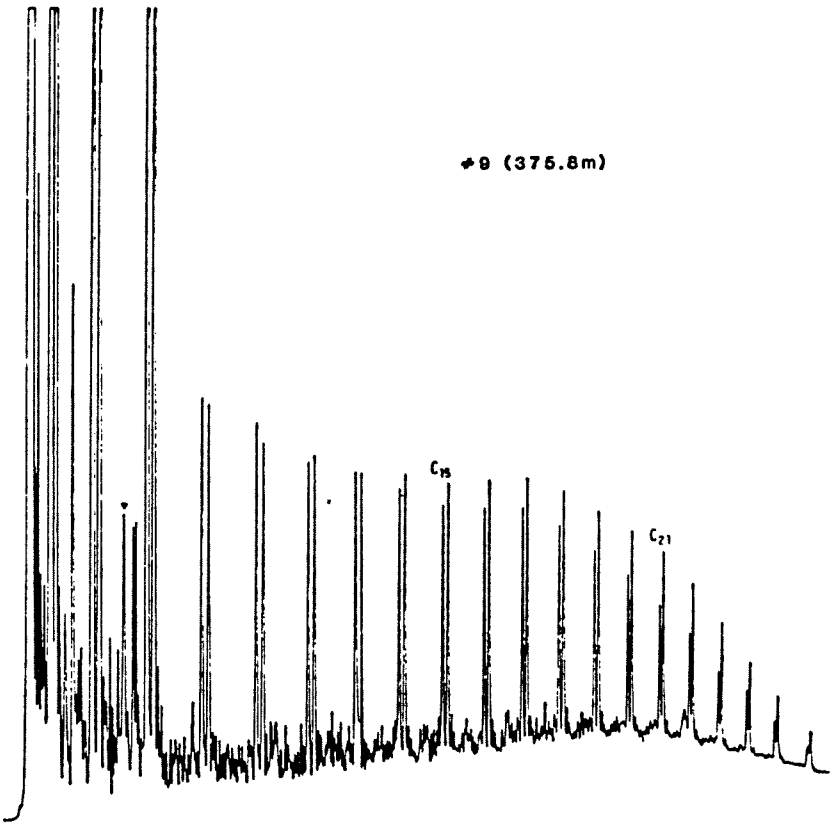


Figure 20b

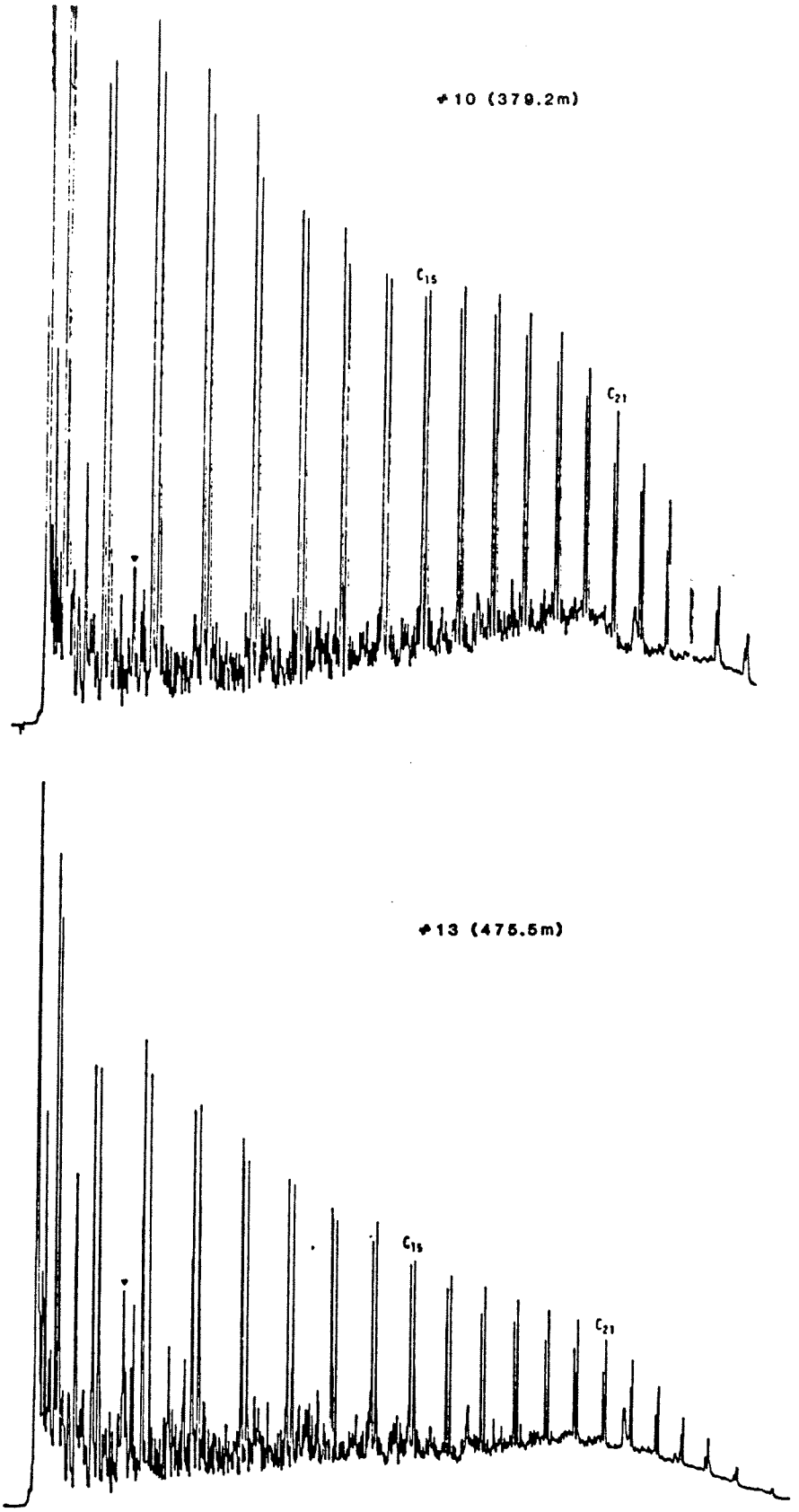


Figure 20c

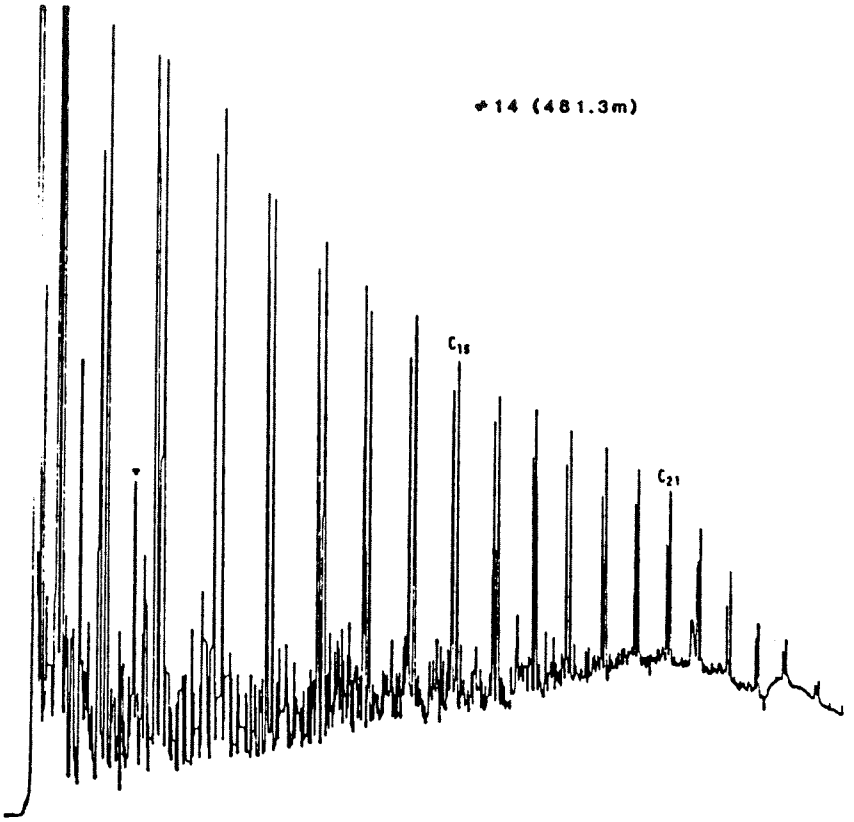
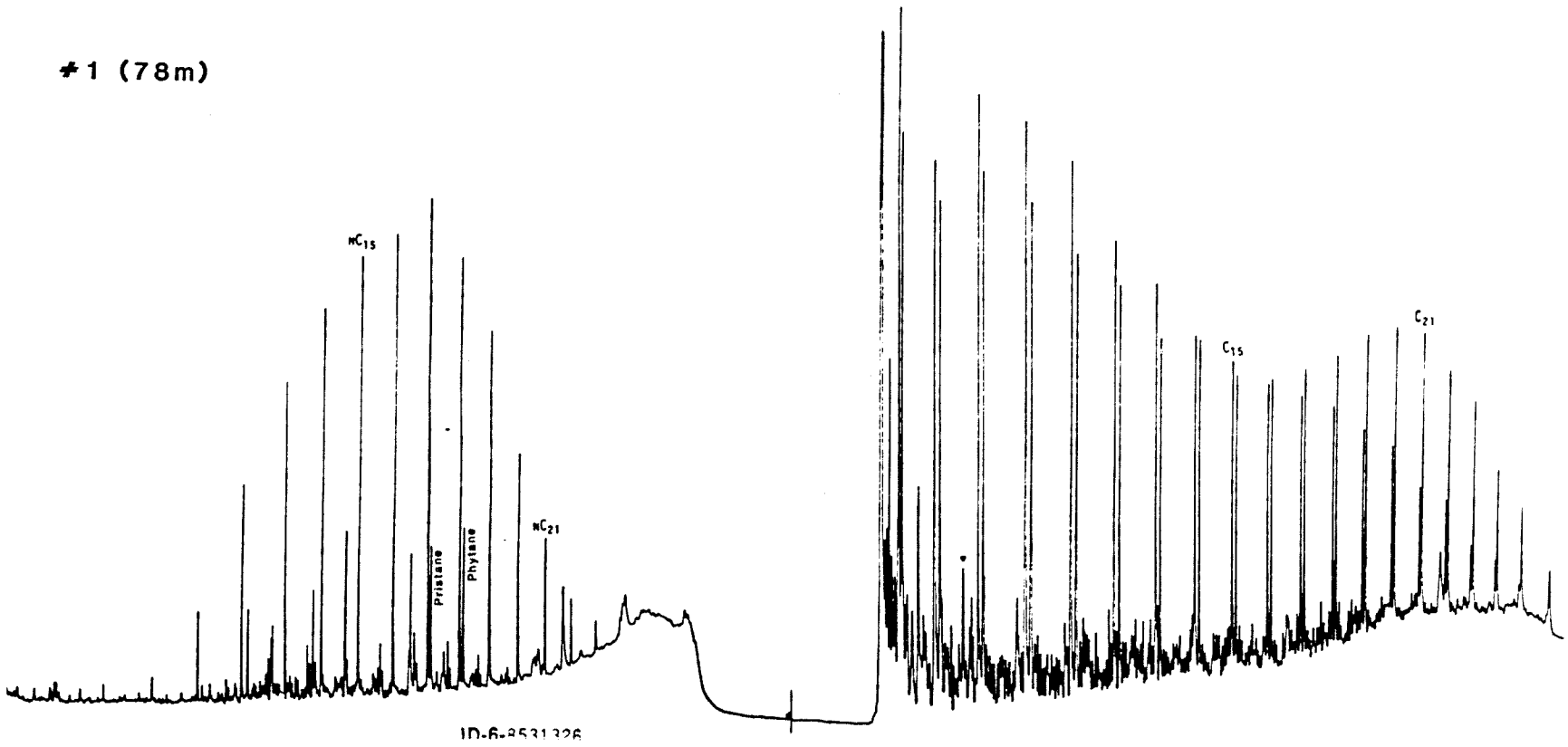


Figure 20d



Figures 21a-g: Gaschromatograms of the S_1 and S_2 fraction obtained by pyrolysis of whole rock samples from Canadian Albert Mines No. 5.

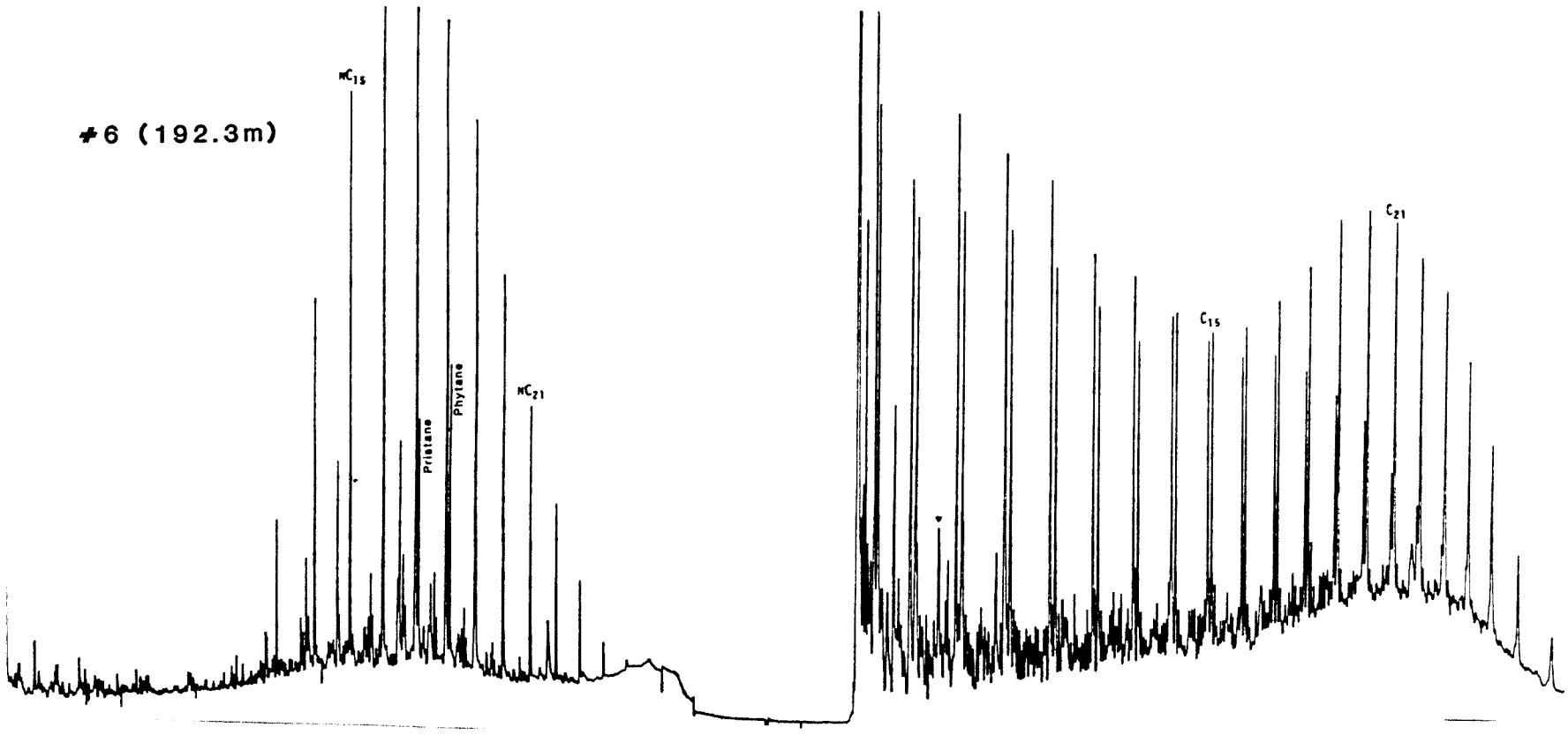


Figure 21b

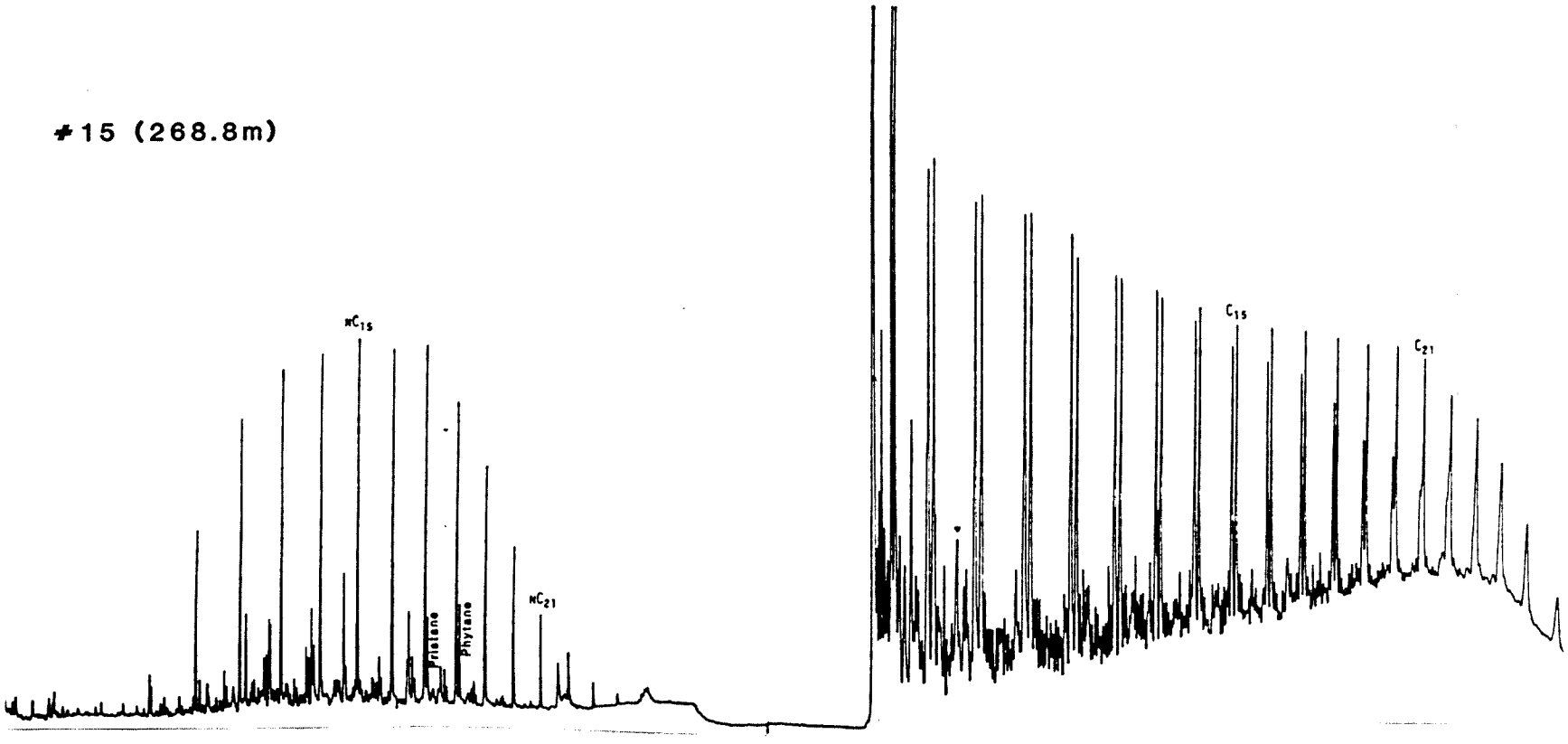


Figure 21c

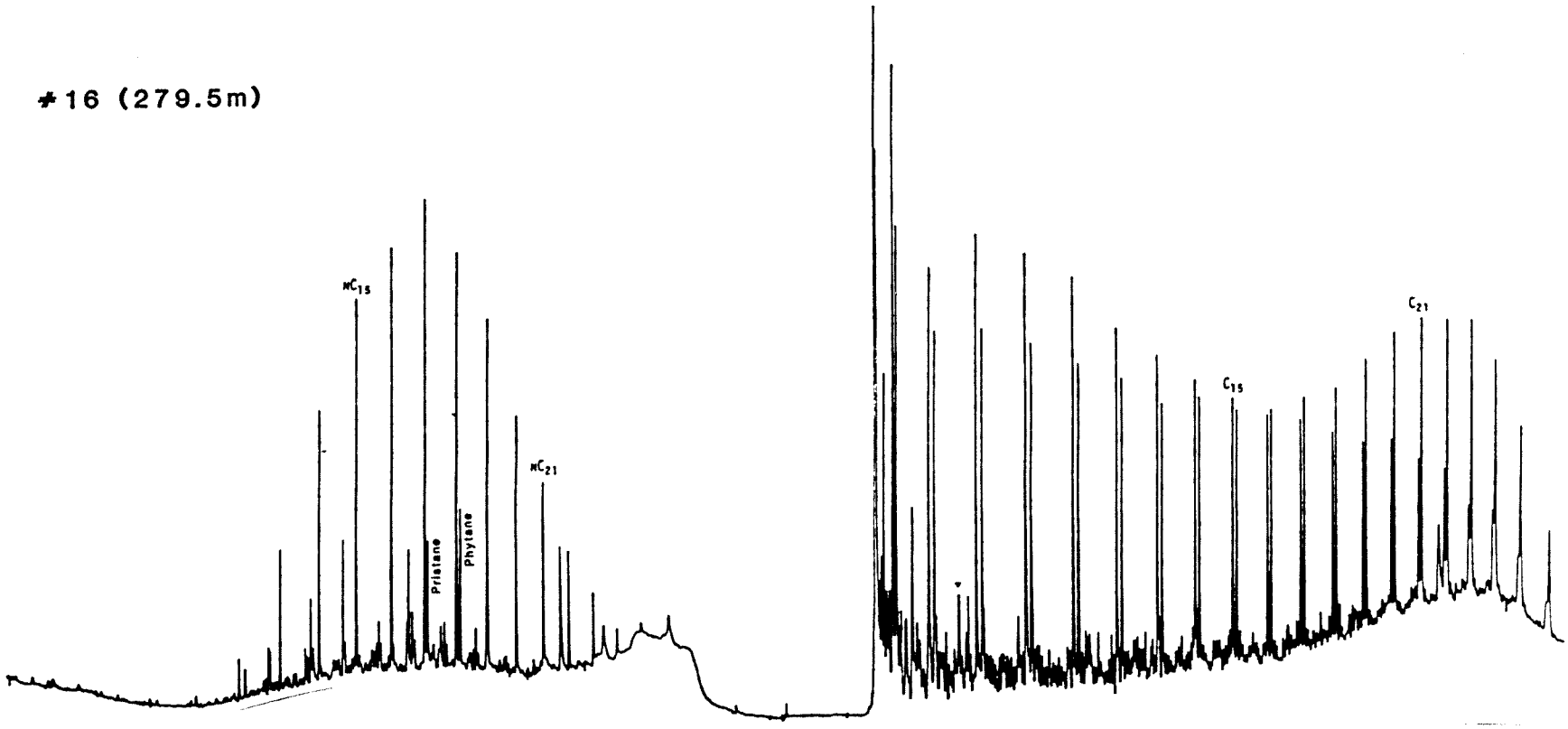


Figure 21d

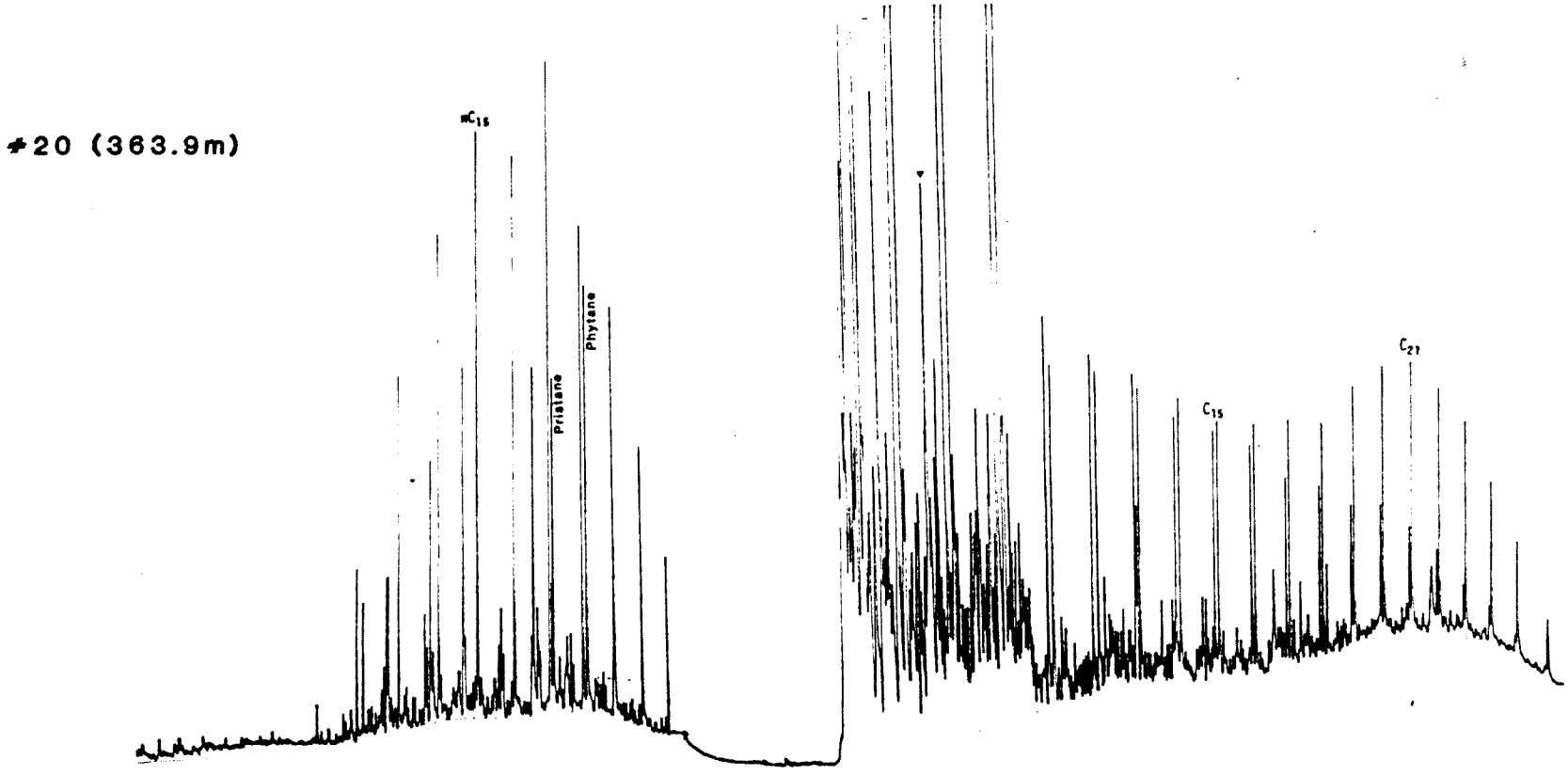


Figure 21e

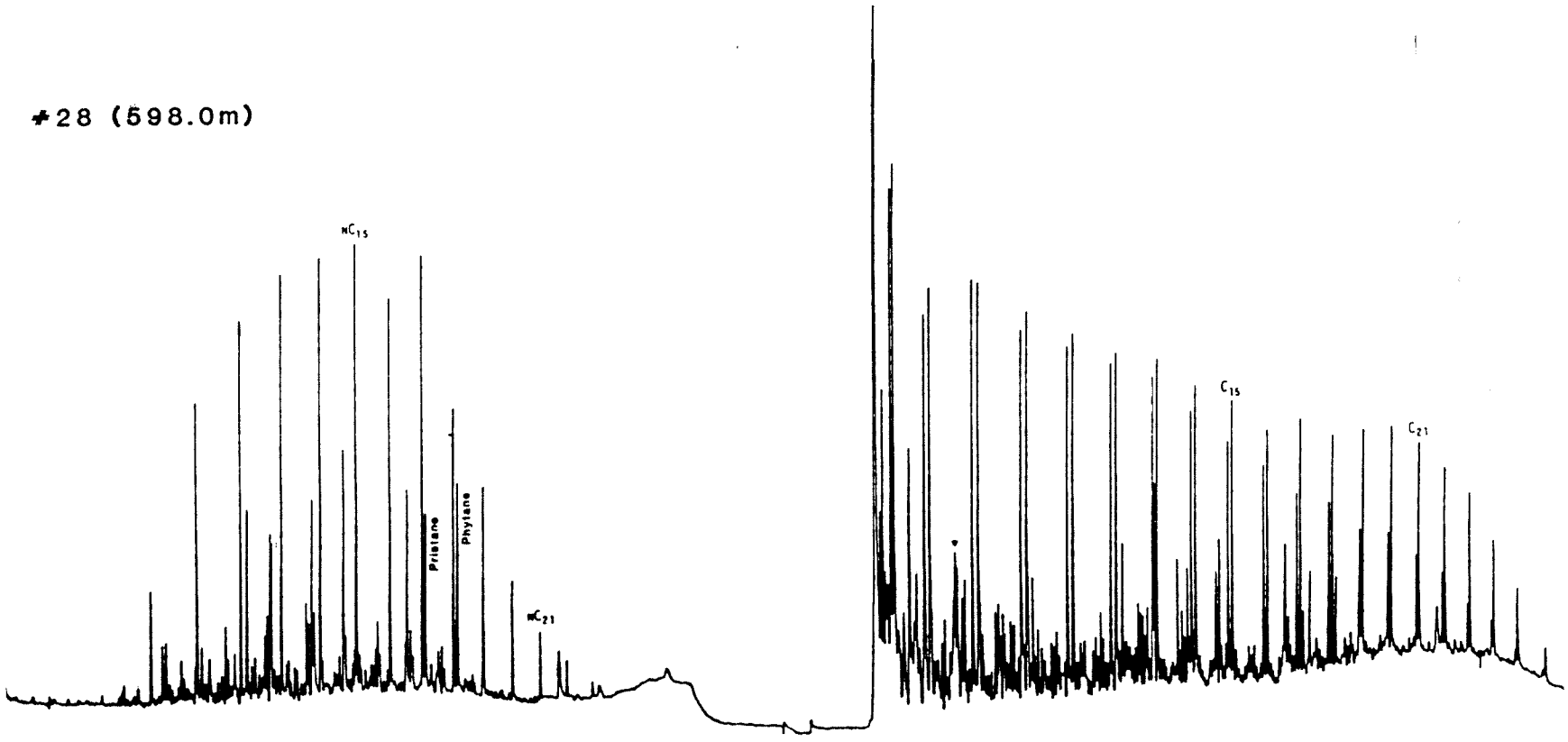


Figure 21f

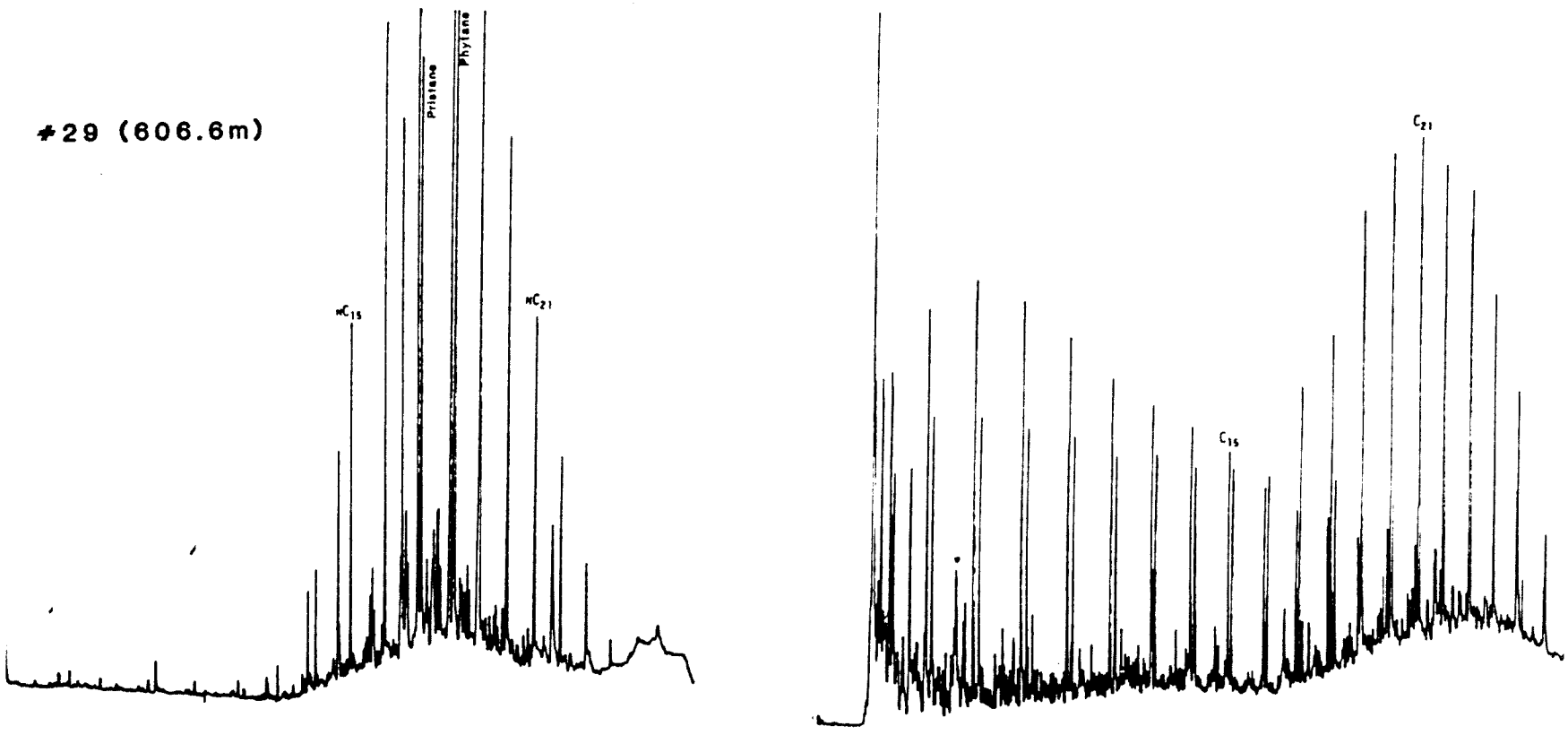


Figure 21g

B. Tables

Table 1

Canadian Occidental Albert Mines No. 5
Elemental Analyses Results

Sample No.	Depth (m)	%N	%C	%H	H/C
1	78.0	1.13	77.17	9.76	1.52
6	192.3	1.30	63.25	7.44	1.41
15	268.8	1.28	70.60	8.81	1.50
16	279.5	1.44	74.72	8.91	1.43
19	345.9	1.48	71.28	8.72	1.47
20	363.9	1.23	56.90	6.73	1.42
21	399.9	1.59	66.09	6.79	1.23
28	598.0	3.68	74.30	7.19	1.16
29	606.6	1.95	56.35	5.35	1.14
33	710.2	1.66	59.72	5.12	1.03
34	737.6	1.62	71.21	7.56	1.27

Table 2

Atlantic Richfield Boudreau No. 1
Elemental Analyses Results

Sample No.	Depth (m)	%N	%C	%H	H/C
4	261.5	0.72	39.17	4.48	1.37
5	289.0	0.88	30.75	3.58	1.40
6	302.8	2.18	68.81	7.87	1.37
9	375.8	1.15	58.32	6.80	1.40
10	379.2	1.16	71.55	9.08	1.52
13	475.5	0.97	42.30	4.69	1.33
14	481.3	1.37	60.83	7.35	1.45

Table 3

Organic geochemical data of oil shales from
Canadian Occidental Albert Mines No. 5

No.	Zone	Depth (m)	Corg (%)	Extract (ppm)	Extract (mg/g Corg)	HC (mg/g Corg)	% of Total Extract				Sat/ Arom.
							Sat.	Arom.	Res.	Asph.	
1	US	78.0	15.76	20113	127.6	79.9	49.6	12.9	19.9	8.4	3.85
6	US	192.3	8.04	25255	314.1	184.5	42.4	15.0	14.7	20.1	2.83
15	AM	268.8	24.69	18176	115.0	76.8	54.0	16.0	12.4	10.6	3.38
16	AM	279.5	9.28	18670	201.2	104.9	37.4	13.6	28.9	16.3	2.75
19	CM	345.9	8.46	19173	226.6	135.2	37.1	18.0	20.7	13.5	2.06
20	CM	363.9	8.59	19870	231.3	130.4	42.4	13.6	20.1	11.9	3.12
21	DM	399.9	2.07	12645	610.9	303.6	38.8	6.2	18.1	21.1	6.26
28	DM	598.0	8.66	20445	236.1	111.2	30.9	13.0	28.4	21.8	2.38
29	DM	606.6	2.09	20465	979.2	544.6	37.8	14.5	18.9	19.5	2.61
33	DM	710.2	2.03	16415	808.6	522.2	43.9	15.7	14.9	19.8	2.80
34	DM	737.6	8.04	17130	213.1	144.3	42.9	15.3	17.4	21.7	2.80

Table 4

Organic geochemical data of oil shales from
Atlantic Richfield Boudreau No. 1

No.	Zone	Depth (m)	Corg (%)	Extract (ppm)	Extract (mg/g Corg)	HC (mg/g Corg)	% to Extract				Sat/ Arom.
							Sat.	Arom.	Res.	Asph.	
4	US	261.5	2.96	2690	90.9	35.9	31.1	9.7	21.7	16.8	3.21
5	US	289.0	0.61	1582	259.3	60.4	24.9	9.3	40.7	14.3	2.68
6	AM	302.8	5.24	4495	85.8	29.6	26.1	8.8	34.2	22.1	2.97
9	AM	375.8	3.95	9450	239.2	134.6	39.2	12.7	22.4	15.3	3.09
10	AM	379.2	13.04	7985	61.2	35.0	35.9	11.9	14.9	16.5	3.02
13	DM	475.5	1.41	4760	337.6	207.9	36.0	17.7	22.4	21.0	2.03
14	DM	481.3	7.23	6690	92.9	65.7	39.6	19.9	20.4	21.2	1.99

Table 5

Data obtained from gas chromatography of the C_{15+}-saturated hydrocarbons in oil shales from Canadian Occidental Albert Mines No. 5

No.	Zone	Depth (m)	CPI 1	CPI 2	CPI 3	CPI 4	LHCPI	ISO 1	ISO 2	ISO 3	ISO 4	n-C_{17}/ n-C_{27}
1	US	78.0	1.11	1.26	1.16	1.25	7.06	0.21	0.33	0.64	0.27	4.40
6	US	192.3	1.09	1.13	1.05	1.11	4.42	0.19	0.34	0.55	0.26	2.63
15	AM	268.8	1.10	1.14	1.01	1.07	14.17	0.13	0.25	0.59	0.19	11.17
16	AM	279.5	1.11	1.26	1.27	1.23	4.51	0.27	0.32	0.94	0.29	3.03
19	CM	345.9	1.09	1.17	1.02	1.10	6.23	0.37	0.88	0.53	0.59	4.86
20	CM	363.9	1.11	1.10	0.95	1.03	7.49	0.46	1.00	0.67	0.68	6.12
21	DM	399.9	1.09	1.13	0.87	0.96	4.04	0.71	1.22	0.66	0.95	2.62
28	DM	598.0	1.10	1.24	1.27	1.31	14.45	0.31	0.77	0.56	0.50	9.83
29	DM	606.6	1.10	1.30	1.30	1.30	5.36	0.69	1.14	0.64	0.91	3.23
33	DM	710.2	1.06	1.31	1.24	1.30	15.84	0.43	1.00	0.56	0.68	11.21
34	DM	737.6	1.10	1.15	1.04	1.06	5.20	0.44	0.99	0.47	0.71	3.29

Table 6

Data obtained from gas chromatography of the C_{15+}-saturated hydrocarbons in oil shales from Atlantic Richfield Boudreau No. 1

No.	Zone	Depth (m)	CPI 1	CPI 2	CPI 3	CPI 4	LHCPI	ISO 1	ISO 2	ISO 3	ISO 4	n-C_{17}/ n-C_{27}
4	US	261.5	1.03	1.06	0.93	1.01	3.34	0.35	0.27	1.34	0.31	2.45
5	US	289.0	1.09	0.99	0.76	0.84	4.30	0.80	0.97	0.67	0.89	2.59
6	AM	302.8	1.11	1.29	0.86	1.18	8./14	0.43	0.44	1.10	0.44	5.09
9	AM	375.8	1.05	1.11	1.05	1.08	2.53	0.36	0.36	0.80	0.36	1.47
10	AM	379.2	1.10	1.15	1.04	1.12	8.17	0.20	0.20	0.76	0.21	4.92
13	DM	475.5	1.07	1.10	0.95	1.02	4.32	0.47	0.47	0.71	0.54	2.41
14	DM	481.3	1.07	1.08	0.90	1.03	6.83	0.26	0.26	0.76	0.32	4.80

Table 7
Kerogen type index [m(+ p)-xylene/n-octene] for isolated kerogens and whole sediment samples from Canadian Occidental Albert Mines No. 5

Sample No.	Zone	Depth (m)	Kerogen Type Index	
			isolated kerogens	whole sediments
1	US	78.0	0.30	0.21
6	US	192.3	0.23	0.33
15	AM	268.8	0.28	0.30
16	AM	279.5	0.25	0.24
19	CM	345.9	0.34	-
20	CM	363.9	0.59	-
21	DM	399.9	0.52	-
28	DM	598.0	0.49	0.39
29	DM	606.0	0.33	0.36
33	DM	710.2	0.53	-
34	DM	737.6	0.30	-

Table 8

Kerogen Type Index [m(+ p)-xylene/n-octene] for isolated kerogens from Atlantic Richfiled Boudreau No. 1

Sample No.	Zone	Depth (m)	Kerogen Type Index for isolated kerogens
4	US	261.5	0.28
5	US	289.0	0.32
6	AM	302.8	0.34
9	AM	375.8	-
10	AM	379.2	0.18
13	DM	475.5	0.37
14	DM	481.3	0.37

C. Analytical Techniques

Kerogen Isolation and Elemental Analysis

Kerogens have been isolated by treating the previously extracted sample sequentially with 6N-HCL at 80°C and HF/6N-HCl (4:1) at room temperature. Any neoformed fluorides or silicates are removed by a final treatment with concentrated HCl at 80°C. The residue consisted of dispersed organic matter and heavy minerals such as apatite, pyrite etc. The isolated kerogen was then washed with distilled water to neutrality, washed with methanol and dried in a vacuum oven at 40°C.

Subsequent elemental analysis for carbon, hydrogen and nitrogen was carried out in a Perkin-Elmer 240A elemental analyzer, automated by Control Equipment Corporation.

Extraction and Liquid Chromatographic Analysis

The pulverized samples (7.5-60g) were Soxhlet extracted for 24 hours using an azeotropic solvent mixture of predistilled chloroform/methanol (87/13). Elemental copper was added to remove sulphur from the sample. The total extract weight after evaporating the solvent in the rotavapor represented the extractable organic matter of the sample. The n- pentane insoluble asphaltenes were then removed by vacuum filtering through glass fibre filter paper. The de-asphaltened extract was subsequently fractionated on an activated alumina-silica (3:1, w/w) column using eluants of increasing polarity, i.e. n-pentane, a mixture of n-pentane and dichloromethane (50:50, w/w), methanol and chloroform, to elute saturated and aromatic hydrocarbons, resins and the residual asphaltenes, respectively. Excess solvent was then removed on a rotary evaporator under reduced pressure at 30-35°C and the fractions were weighed.

C_{15+}-gas Chromatographic Analysis

The saturate hydrocarbon fraction obtained from liquid chromatographic analysis of the total extract was then further characterized by gas chromatography. A sample of the saturate hydrocarbon fraction was introduced through an injection port (which was kept at 250°C) onto a 30 m glass capillary column coated with OV-101 in a Varian 3700 gas chromatograph. This instrument

was equipped with a flame ionization detector held at 300°C. The oven temperature was kept at 60°C and programmed to heat to 250°C at a rate of 24°C/minute, causing the separation of the compounds which were present in the saturated hydrocarbon fraction. The areas under the representative peaks were integrated, allowing the relative quantities of the paraffins to be assessed.

C_{15+}-saturated hydrocarbon analysis permitted the following parameters to be evaluated:

ISO1- Pristane/normal heptadecane (pristane/n-C_{17})

ISO2- Phytane/normal octedecane (phytane/n-C_{18})

ISO3- Isoprenoid ratio pristane/phytane

ISO4- Pristane and phytane/normal heptadecane and normal octadecane (pristane + phytane/n-C_{17} + n-C_{18})

$$CPI\,1 = \frac{1}{2}\cdot\left(\frac{C_{17}+C_{19}+C_{21}}{C_{18}+C_{20}+C_{22}} + \frac{C_{17}+C_{19}+C_{21}}{C_{16}+C_{18}+C_{20}}\right)$$

$$CPI\,2 = \frac{1}{2}\cdot\left(\frac{C_{21}+C_{23}+C_{25}+C_{27}}{C_{22}+C_{24}+C_{26}C_{28}} + \frac{C_{21}+C_{23}+C_{25}+C_{27}}{C_{20}+C_{22}+C_{24}+C_{26}}\right)$$

$$CPI\,3 = \frac{1}{2}\cdot\left(\frac{C_{25}+C_{27}+C_{29}+C_{31}}{C_{26}+C_{28}+C_{30}+C_{32}} + \frac{C_{25}+C_{27}+C_{29}+C_{31}}{C_{24}+C_{26}+C_{28}+C_{30}}\right)$$

$$CPI\,4 = \frac{2\cdot C_{29}}{C_{28}+C_{30}}$$

$$CPI5 = 2\cdot\frac{C_{27}+C_{29}}{C_{26}+2\cdot C_{28}+C_{30}}$$

$$LHCPI = \frac{C_{17}+C_{18}+C_{19}+C_{20}+C_{21}}{C_{27}+C_{28}+C_{29}+C_{30}+C_{31}}$$

Pyrolysis - Gaschromatography

The dried sample was weighed into a quartz tube. The probe and sample were placed into the interface of a Chemical Data Systems CDS 820 Reaction System. After the interface was flushed briefly with helium at room temperature, it was programmed to heat to 300°C, hold for nine minutes, and then programmed to 600°C at 60°/minute. The thermocouple embedded in the sample indicated sample temperatures actually reached about 287° and 585°C respectively. Volatile organic compounds were swept out of the sample in a helium stream. Eighty per cent of the total flow was directed to hydrocarbon traps packed with Tenax via a trap select valve. The remaining 20 per cent of the stream was diverted to a Monitor FID yielding S_1 and S_2-peaks. At room temperature, the Tenax traps absorb C_7 and higher aliphatic hydrocarbons as well as toluene and higher aromatic compounds. Two such traps are used in the system so that peaks S_1 and S_2 may be trapped successively during the analysis.

The detailed composition of S_1 and S_2 was examined by sequential dumping of the traps and subsequent capillary gas-chromatography. The fused silica capillary column was coated with OV-101, the gas chromatograph was programmed to 240°C at 4°/minute. The final temperature was held for thirty minutes.