Org. Geochem. Vol. 6, pp. 817 – 827, 1984
Printed in Great Britain.

0146-6380/84 $03.00+0.00

Quantitative gas chromatography – mass spectrometry analysis of geological samples

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Abstract—The absolute concentration of individual biological markers in the hydrocarbon fractions of crude oils and sediment extracts can be determined by the addition of a known amount of an alkane standard before gas chromatography – mass spectrometry analysis. This method adds a new dimension to biological marker analysis in petroleum exploration. It has shown that the concentrations of steroid and triterpenoid hydrocarbons in sediment extracts decrease considerably between the onset of petroleum generation and its peak. The concentrations of these compounds in more than forty crude oils from the Williston Basin vary by more than a factor of one hundred. This variation, in addition to distribution patterns, in this sedimentary basin helps in the division of oils into families. Furthermore, absolute concentrations of biological markers in crude oils allow to detect mixing of oils of different maturities and uptake of biological markers from the organic matter indigenous to reservoir rocks. This is illustrated with a study of oils from the North Slope of Alaska and from North-west Germany.

Key words: biological markers (quantitation of, maturity assessment by), crude oils (correlation of, maturity assessment of, mixing of), Williston Basin, Alaska North Slope, steranes, triterpanes, aromatic steroid hydrocarbons

INTRODUCTION

Most gas chromatography – mass spectrometry analyses of biological markers in the hydrocarbon fractions of crude oils and sediment extracts ignore the absolute concentrations of the compounds studied. Commonly, distribution patterns are used for oil–oil and oil–source rock correlation (e.g. Seifert *et al.*, 1980; Seifert and Moldowan, 1981; Shi *et al.*, 1982; Welte *et al.*, 1982), and relative concentrations (compound ratios) of related biological marker hydrocarbons are measured to assess the thermal maturation of organic matter (e.g. Mackenzie *et al.*, 1980, 1981, 1983a; Seifert and Moldowan, 1980; Seifert *et al.*, 1983). The latter is a useful concept which has been successfully applied to sediment extracts, and the results are valid when contamination or impregnation with migrated hydrocarbons can be excluded. Crude oils have to be handled with even greater care since they represent mobilized (migrated) hydrocarbon phases. The biological marker concentration and composition in crude oils not only depend on the initial composition and the thermal maturation of the organic matter in the source rock, but also on the maturity range (of the organic matter in the source rock) over which migration into a reservoir is effective and on possible mixing of crude oils from different sources, disregarding secondary effects like biodegradation in the reservoir.

A knowledge of the maturity-dependent concentration changes of steroid and triterpenoid hydrocarbons in sediments and the related effects on the absolute concentrations of these compounds in crude oils adds a new dimension to biological marker analysis in petroleum exploration. The usefulness of quantitative data on biological markers was first recognized by Seifert and Moldowan (1978) in a group type approach. Subsequently, this approach was extended to a GC–MS method (Seifert and Moldowan, 1979) by determining absolute concentrations of steranes in crude oils using 5β-cholane as an internal standard, but this approach has not been extended previously to a range of geological problems.

METHODS

By addition of a known amount of an alkane standard which has m/z = 191.18 ($C_{14}H_{23}^+$) as the base peak in its mass spectrum, the amounts of individual biological markers can be determined for any analysis where the intensity of this mass is monitored. Figure 1 shows a partial m/z = 191 mass fragmentogram with 9-*n*-dodecylperhydroanthracene (Masspec Analytical, Gloucestershire, U.K.) as internal standard containing principally a major and two minor isomers which account for 70 and 30%, respectively, of the total amount of standard (determined from peak heights). The standard does not interfere with the series of 17α(H)-hopanes, but partly coelutes with the two isomeric C_{28} members of the tricyclic terpane series (Moldowan *et al.*, 1983). When the mass spectrometer resolution is set to about 2500 (10% valley), saturated and aromatic steroid and triterpenoid hydrocarbons may be quantitated from a single GC–MS analysis of the unfractioned crude oil

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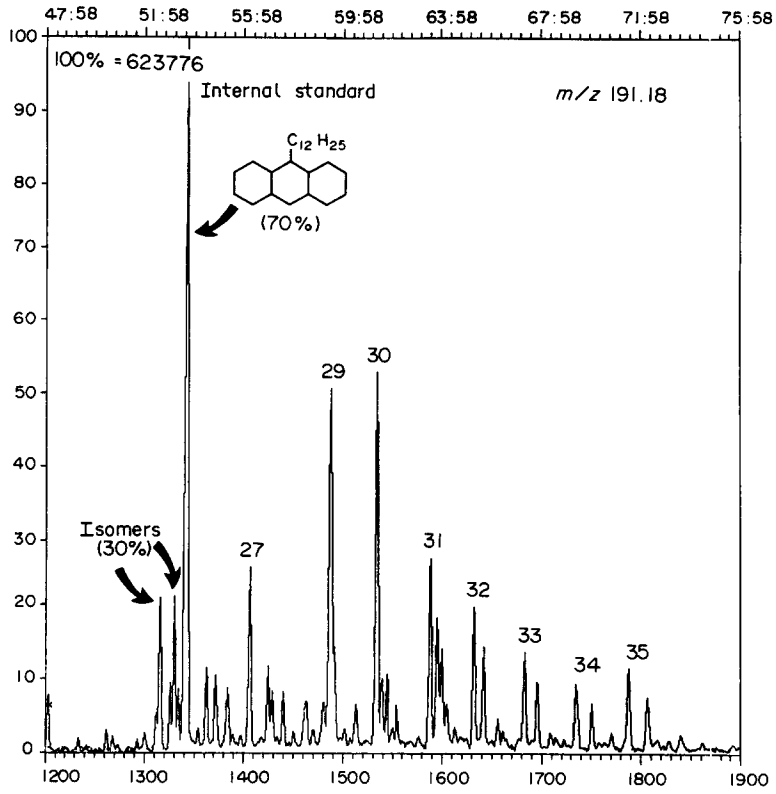


Fig. 1. m/z = 191.18 mass fragmentogram of the total hydrocarbon fraction of a crude oil showing the relative retention time of the 9-*n*-dodecylperhydroanthracene internal standard. Numbers indicate the carbon numbers of the 17α(H)-hopane series. For GC-MS conditions see Mackenzie *et al.* (1983b).

or sediment extract or the total hydrocarbons thereof (Mackenzie *et al.*, 1983b).

Quantitative data of biological marker concentrations given in this study assume that the fraction of total ion current accumulated in the base peak of the mass spectrum is the same for the standard and the biological markers investigated. Although this certainly is not correct, the error introduced does not influence any conclusions drawn from the comparison of quantitative biological marker data of geological samples among each other. True quantitation can only be achieved if the anthracene standard is calibrated against biological marker standards of the different compound classes as shown for the 5β-cholane standard by Seifert and Moldowan (1979). Measurements using the only readily available biological marker standard, i.e. 5α(H)-cholestane(20R), showed that a correction factor of 1.2 has to be applied in order to get the true absolute concentration of this compound. From the mass spectrometric characteristics of the biological markers it can be assumed that the correction factors are similar for other steranes and pentacyclic triterpanes of the 17α(H)-hopane series, whereas they should be higher for the aromatic steroid hydrocarbons which have extremely abundant key fragments in their mass spectra. The correction factors obtained by comparison with biological marker standards relative to 9-*n*-dodecylperhydroanthracene may vary, however, depending on instrument type (Varian MAT 112S mass spectrometer in this study) and performance, as well as on the analytical conditions used. A detailed description of the general GC–MS procedure relevant to this work has been published by Mackenzie *et al.* (1983b).

RESULTS AND DISCUSSION

More than 40 crude oils from the Williston Basin were studied for the variation of absolute biological marker concentrations within a large oil province. For the ease of the following discussion the oils were grouped according to their geographical origin (Fig. 2) from South-west Saskatchewan and North-west Montana (region A), South-east Saskatchewan (region B), and Eastern Montana and North Dakota (region C). It was found that the oils from these regions to a certain extent can also be differentiated with a biological marker source parameter, i.e. the carbon number distribution of the 14β(H),17β(H)-steranes (Huang and Meinschein, 1979; Mackenzie *et al.*, 1982). The triangular diagram representation (Fig. 3) shows, in general, that there is a decrease of the relative C_{28} sterane content in the oils in the order of region A>B>C and an increase of the relative C_{29} sterane content in region C relative to the oils from the other two regions. For a few oil samples from

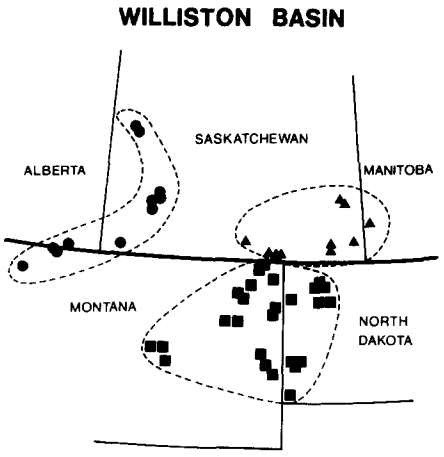


Fig. 2. Map of the Williston Basin area showing the origin of the oil samples from three geographical regions A, B and C.

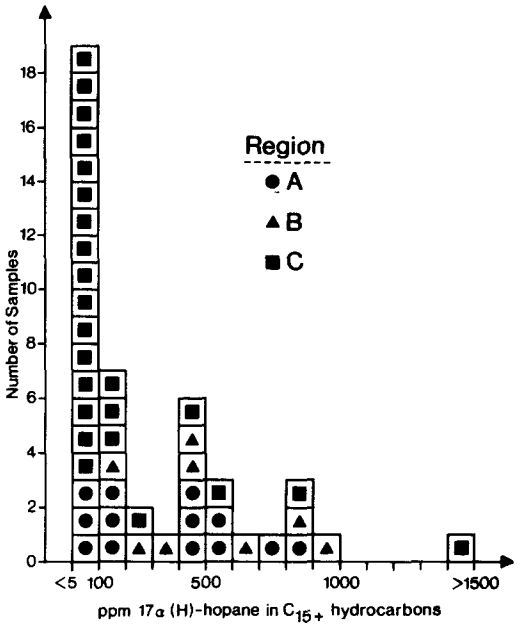


Fig. 4. Frequency distribution of the 17α(H)-hopane content in Williston Basin crude oils

region C the sterane distributions could not be determined with sufficient precision, to warrant their inclusion in Fig. 3, due to their low absolute concentrations of biological marker hydrocarbons.

The range of absolute biological marker concentrations in the oils from the Williston Basin is demonstrated in Fig. 4 using 17α(H)-hopane as an example. The concentrations, measured as ppm of the C_{15+} hydrocarbons of the oils, vary from less than 5 ppm to about 1000 ppm with one oil containing more than 1500 ppm of 17α(H)-hopane (measured value 3790 ppm). The frequency distribution (Fig. 4) also shows that most of the oils from region C have low biological marker concentrations, whereas the oils from region B spread over a wide range with most oils having relatively high concentrations of 17α(H)-hopane. The oils from region A may be split into two groups with 17α(H) hopane concentrations in the range of <5–200 and 400–900 ppm, respectively.

The variation of biological marker concentrations does not correlate with the age of the reservoir rocks (Ordovician to Cretaceous) from which the oils are derived. Since our investigation of the Williston Basin oils still is in a preliminary stage no attempts could be made yet to compare the biological marker quantitation results with crude oil classifications in the Williston Basin established by others primarily on the basis of carbon isotope ratios and hydrocarbon distribution patterns (e.g. Williams, 1974; Zumberge, 1983). An initial attempt to relate the absolute biological marker concentrations to a bulk maturity parameter was, however, successful. In Fig. 5, the absolute concentrations of 17α(H)-hopane in the Williston Basin oils are plotted vs the

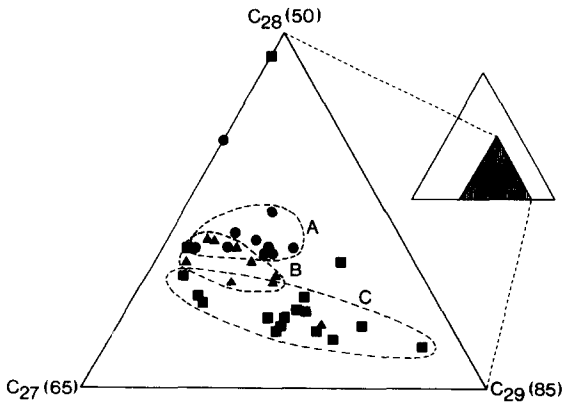


Fig. 3. Triangular diagram section showing the carbon number distribution of 14β(H),17β(H) steranes (20R+20S) of Williston Basin crude oils from regions A (circles), B (triangles) and C (squares).

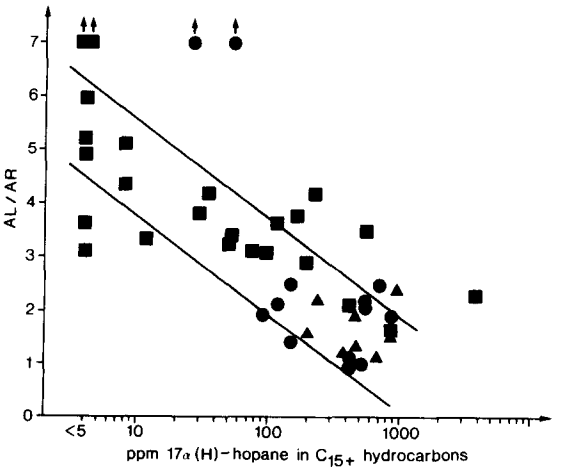


Fig. 5. Relationship between a bulk maturity parameter, i.e. the aliphatic/aromatic hydrocarbon ratio (AL/AR), and the absolute concentration of 17α(H)-hopane for a series of crude oils from the Williston Basin.

aliphatic/aromatic hydrocarbon ratio (AL/AR). Although some influence of different source organic matter types cannot be excluded (cf. Fig. 3), the data in Fig. 5 suggest that an exponential decrease of the 17α(H)-hopane concentration correlates with a linear increase of the AL/AR ratio. Data points below the broad trend marked in Fig. 5 may be explained by the effect of moderate biodegradation which tends to reduce the AL/AR ratio (none of the oils showed biodegradation effects on the biological marker hydrocarbons), and data points above the general trend could indicate admixture of an immature oil rich in biological markers to the bulk of a more mature oil in a reservoir (see also discussion below).

This effect of maturity dependence of biological marker concentrations could be verified by the investigation of a series of rock samples from the North Slope of Alaska, all containing a dominance of terrigenous organic matter (Mackenzie *et al.*, 1985): any organofacies' influence may be assumed to be minimal. The absolute concentrations of 17α(H)-hopane, all C_{29} nonrearranged steranes, the sum of a 20R C_{29} 5β(H) and the corresponding 5α(H) monoaromatic steroid hydrocarbon, and a 20R C_{28} triaromatic steroid hydrocarbon plotted against T_{max} of Rock–Eval pyrolysis (Fig. 6), show striking decreases in the maturity range corresponding to the onset of significant petroleum generation. (The arrows in Fig. 6 mark the generation maximum as derived from total extract yields.) The decrease in concentration extends over about three orders of magnitude for all four different biological marker compound types, but appears to be smoother for the saturated biological marker hydrocarbons than for the aromatic steroid hydrocarbons. The causes of these decreases in concentration are probably two-fold: dilution by material generated from the thermal breakdown of kerogen and by the preferential thermal breakdown of the biological marker molecules themselves. That the latter effect is dominant can be derived from the fact that biological marker concentrations normalized to organic carbon in the rock samples vs T_{max} yield curves with shapes very similar to those shown in Fig. 6. These observations imply, among others, that:

(1) The biological marker distributions of crude oils will exaggerate the relative contribution of less mature sources in the case of multiple sources or of early generation (relatively immature stage) in the case of continuous generation during basin subsidence.

(2) A mature biological marker-poor oil, which originated from well within the oil generation zone, could acquire considerably less mature biological marker distributions by the addition of relatively small amounts of oil from source beds at the early stages of petroleum generation.

This concept has been applied to a series of crude oils from the North Slope of Alaska and provided clues to the interpretation of the composition and bulk characteristics of the oils and their distribution within the basin (cf. Mackenzie *et al.*, 1985). Tables 1 and 2 compare the bulk parameter values and the biological marker maturation data, respectively, for eight oils and a condensate from the North Slope of Alaska. The classification of the oils into two major groups, i.e. Barrow–Prudhoe type and Simpson–Umiat type, was made by Magoon and Claypool (1981) mainly based on carbon isotope data, but this has turned out to be consistent with most other analytical data. Lower API gravities, lower percentage of saturated hydrocarbons (% Al), lower aliphatic/aromatic hydrocarbon ratios, higher asphaltene content, higher sulphur content, more positive $\delta^{34}S$ values and more negative carbon isotope values of the aliphatic hydrocarbons (Table 1) consistently suggest that the Barrow–Prudhoe oils are less mature than the Simpson–Umiat oils and that the condensate probably is the most mature sample in this series. In contrast to this, a number of biological marker compound ratios (Table 2) indicate the opposite maturity sequence for the Barrow–Prudhoe and Simpson–Umiat oils. A higher maturation level of the Barrow–Prudhoe oils would be deduced from the more advanced steroid aromatization (Mackenzie *et al.*, 1981), the larger degree of sterane isomerization (Mackenzie *et al.*, 1980) and from the higher 17α(H)-hopane/moretane ratios (Seifert and Moldowan, 1980). A confirmation of the bulk parameter values is obtained from the calculated vitrinite reflectance equivalents (R_c; Table 2) which are based on the measurement of the methyl-phenanthrene indices (MPI; Radke *et al.*, 1982). This maturity parameter has been shown to be most significant in the main zone of petroleum generation (Radke *et al.*, 1982).

An explanation of the conflicting maturity data derived from bulk parameters and biological marker compound ratios, respectively, appears possible if the absolute concentrations of the biological markers (Table 3) are used as an additional source of information. Most of the concentrations in Table 3 show higher values for the Barrow–Prudhoe type oils. Combined with the conclusions drawn from the maturity trends of biological marker concentrations in rock samples (Fig. 6) this supports evidence for the Simpson–Umiat oils as being more mature than the Barrow–Prudhoe oils. Consequently, the Simpson–Umiat oils most likely received a contribution from an immature source bed, and this affected the biological marker patterns and concentrations in these oils but not their bulk composition (cf. Mackenzie *et al.*, 1985).

The schematic North–South cross-section of the Alaskan North Slope (Fig. 7) shows the location of the oil (open circles) and condensate (black dot) reservoirs and hypothetical migration directions which could explain the results of the oil analyses. The thick curved and straight arrows represent

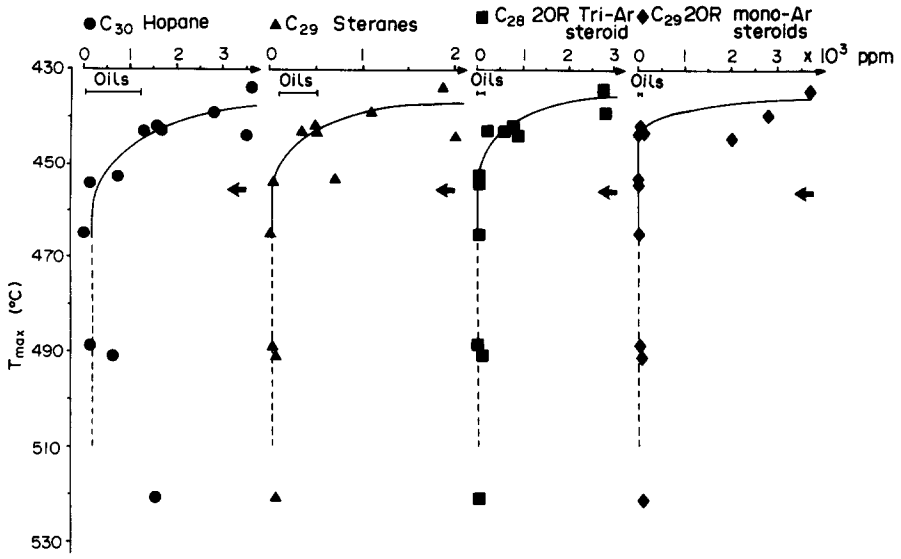


Fig. 6. Biological marker concentrations (in ppm of total hydrocarbons) relative to thermal maturity expressed by T_{max} of Rock-Eval pyrolysis in a series of rock samples from the North Slope of Alaska.

Table 1. Bulk parameter values for a series of crude oils and a condensate from the North Slope of Alaska. API gravity and isotope data are from Magoon and Claypool (1981)

USGS-No.	Well	Depth (m)	°API	% Al	Al/Ar	% Asph.	% S	$\delta^{34}S$	$\delta^{13}C$(Al)
	Barrow-Prudhoe								
R-248-003	S. Barrow No. 19	671–684	21.1	60.3	2.0	1.2	1.7	+0.73	−29.49
-004	Fish Creek No. 1	892–933	15.4	35.7	0.9	3.0	2.0	−3.46	−29.35
-007	Dalton No. 1	2611–2641	6.5	15.6	0.8	23.4	2.6	+5.16	−29.50
-001	Put River D-3	3175–3211	26.3	50.8	1.2	1.5	1.0	ND	−29.23
	Simpson-Umiat								
R-248-008	C. Simpson Seism. L.	c.60	23.7	66.8	2.7	0.8	0.2	−5.80	−28.78
-024	Umiat No. 4	91	31.2	69.3	2.6	<0.1	<0.1	−4.62	−28.76
-005	Simpson Core Test	150–460	22.8	67.0	2.2	0.2	0.2	−7.13	−28.44
-002	S. Barrow No. 20	497–500	30.5	70.6	2.9	0.4	ND	ND	ND
	Condensate								
R-248-006	Seabee No. 1	1636–1644	54.1	89.4	9.3	0	<<0.1	−5.86	−26.56

Table 2. Biological marker maturity data for a series of crude oils and a condensate from the North Slope of Alaska

USGS-No.	Well	Ar steroids (tri/tri + mono)	Steranes (20S/20R+S)	Steranes (ββ/αα + ββ)	Hopanes (αβ/αβ + βα)	R_c (from MPI)
	Barrow-Prudhoe					
R-248-003	S. Barrow No. 19	0.83	0.48	0.72	0.93	0.89
-004	Fish Creek No. 1	0.75	0.47	0.71	0.92	0.89
-007	Dalton No. 1	0.87	0.42	0.70	0.91	0.85
-001	Put River D-3	0.75	0.50	0.67	0.89	0.77
	Simpson-Umiat					
R-248-008	C. Simpson Seism. L.	0.46	0.40	0.64	0.78	ND
-024	Umiat No. 4	0.60	0.37	0.63	0.75	1.02
-005	Simpson Core Test	0.70	0.38	0.70	0.75	0.92
-002	S. Barrow No. 20	0.69	0.40	0.80	0.85	0.95
	Condensate					
R-248-006	Seabee No. 1	0.76	ND	ND	0.96	2.08

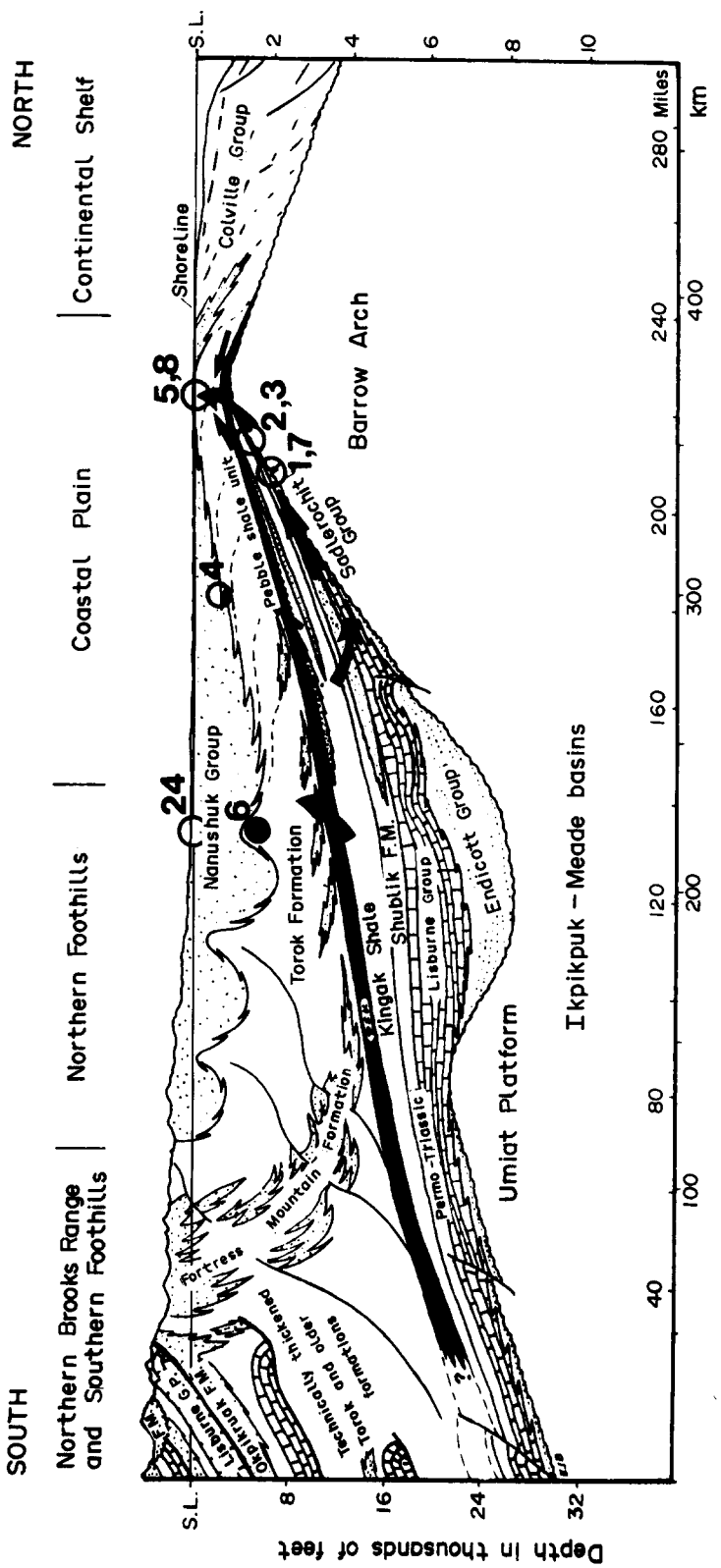
Table 3. Absolute biological marker concentrations (in ppm of total C_{15+} hydrocarbons) for a series of crude oils and a condensate from the North Slope of Alaska

USGS-No.	Well	C_{30}-hopane	C_{29}-steranes	C_{28}-triarom. steroid	C_{29}-monoarom. steroid
	Barrow-Prudhoe				
R-248-003	S. Barrow No. 19	410	155	30	5
-004	Fish Creek No. 1	770	400	205	70
-007	Dalton No. 1	1240	200	135	15
-001	Put River D-3	660	530	210	70
	Simpson-Umiat				
R-248-008	C. Simpson Seism. L.	250	165	35	40
-024	Umiat No. 4	170	80	40	25
-005	Simpson Core Test	175	280	40	15
-002	S. Barrow No. 20	200	120	20	8
	Condensate				
R-248-006	Seabee No. 1	40	—	—	—

proposed major directions of migration, whilst the thinner straight arrows are proposed as less important migration pathways. In a hypothetical model, most of the oil presently accumulated around the Barrow Arch of the North Slope of Alaska is thought to have originated from the organic matter of the Pebble Shale Unit, Kingak Shale and the Permo-Triassic Shublik Shale in the southern part of the Coastal Plain. Most oil generation occurred in the Cretaceous when the three source units were buried by sediments (Torok Formation and Nanushuk Group) derived from the uplifting Brooks Range to the South. The first oil so formed is thought to mainly have migrated laterally and northwards through the highly porous Sadlerochit Sands and Lisburne Limestones, and then upwards to accumulate in traps in the region of the Barrow Arch (oils 1 and 7). More mature oils, generated later, followed the same migration route, but because the deeper traps were now full, they continued upwards to shallower reservoirs (oil 3). At a similar stage some oil escaped upwards through points of weakness in the Pebble Shale seal and into traps in the overlying Cretaceous (oil 4). Up to now, all oils had the characteristics of the Barrow–Prudhoe oils. The later and more mature oils using the major migration route, out of the Kingak, through the Sadlerochit and Lisburne Groups, were forced to continue to still higher reservoirs at (oil 2) or above (oils 5 and 8) the unconformity marked by the Pebble Shale seal, or again escaped through the Pebble Shale seal further south to form the Umiat accumulation (oil 24). These later oils, because of their high maturity, contained very small amounts of biological markers. They were mixed with small amounts of immature oils from the shallower parts of the Pebble Shale Unit and Lower Torok Formation. The latter have only reached the maturity of the early stages of petroleum generation (Mackenzie *et al.*, 1985) and the immature oil derived from them will be rich in biological markers. Therefore, although immature source beds are considered to have contributed little to the main volume of oils 2,5,24 and 8, they have had a major influence on their biological marker patterns (Table 2). These four oils are generally more mature, because they were mainly derived from a later stage of petroleum generation than the other oils considered in this study. The admixture of small amounts of an immature and biological marker-rich oil, means they appear immature when biological marker distributions are considered. The later four oils (2,5,24,8) are all members of the Simpson–Umiat family and the earlier, less mature crudes, belong to the Barrow–Prudhoe family. The condensate (6) is highly mature, probably deriving from the deeply buried source beds of the Northern Foothills (see Mackenzie *et al.*, 1985 for a more detailed discussion of oil generation and accumulation on the North Slope of Alaska).

A different phenomenon of apparently mixed biological marker populations was observed during a study of compositional variations in the course of production of crude oils in North-west Germany. Oils from several fields were sampled at regular time intervals over a period of about 3 years. They all constantly showed a smooth, front-end biased C_{15+} *n*-alkane distribution indicating advanced maturity, and variations mainly occurred in the light hydrocarbon fractions (Riemer *et al.*, 1981). Oils from the Aldorf oil field and related fields close-by in contrast to the mature *n*-alkane distribution, however, had biological marker distributions suggesting low maturity.

The Aldorf oil field is located within a 25 km wide reservoir zone bordering the northern edge of the Lower Saxony Basin in North-west Germany (Boigk,


NORTH
SOUTH
Northern Brooks Range and Southern Foothills
Northern Foothills
Coastal Plain
Continental Shelf
S.L.
Shoreline
Colville Group
Barrow Arch
Pebble shale unit
Sadlerochit Group
Nanushuk Group
Torok Formation
Kingak Shale
Shublik F.M.
Lisburne Group
Permo-Triassic
Endicott Group
Umiat Platform
Ikpikpuk-Meade basins
Fortress Mountain Formation
Tuktu Formation
Okpikruak F.M.
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Depth in thousands of feet
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24
6
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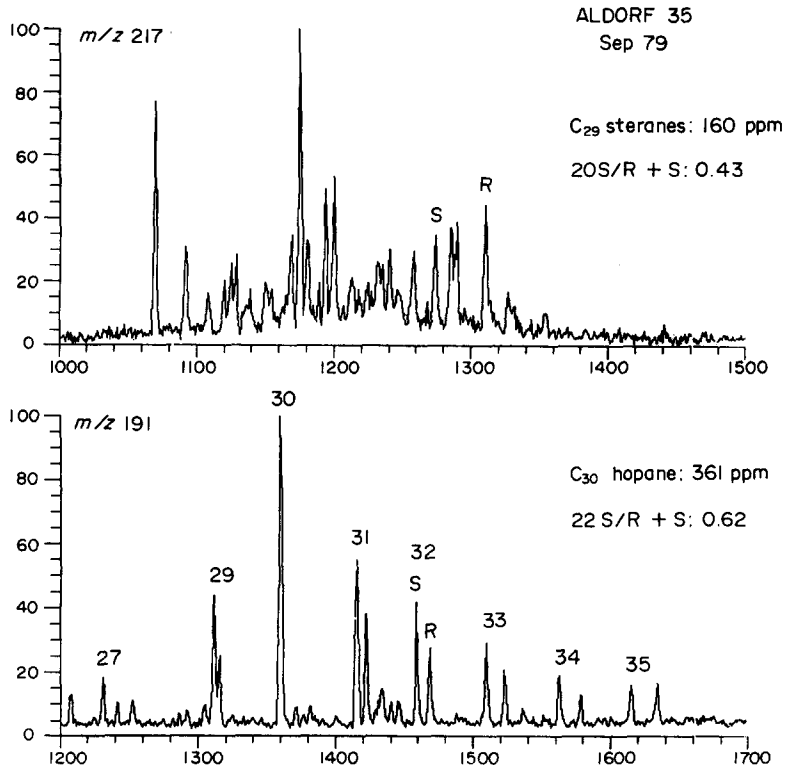

Fig. 8. Sterane (m/z = 217) and terpane (m/z = 191) mass fragmentograms of a crude oil from the Aldorf 35 well sampled in September 1979.

1981). The Aldorf oils are mainly produced from reservoir strata of Dogger and Malm age at about 1000–1200 m depth. The main source rock for these oils is supposed to be the more deeply buried, organic-matter-rich Lias epsilon (Toarcian) shale (Boigk, 1981). The fractured reservoir sandstones contain interbedded thin shales rich in organic matter (up to 2% total organic carbon; W. Riemer, unpublished results).

Figures 8 and 9 show the sterane and triterpane patterns of oils from the producing well Aldorf 35 sampled in September and October 1979, respectively. Although both oils have the same smooth *n*-alkane envelope, they differ considerably in their biological marker distributions, and this is particularly obvious in the sterane fragmentograms (upper traces). The isomerization of the C_{29} steranes at C-20 (Mackenzie *et al.*, 1980) is significantly less advanced in the oil taken in October 1979 (Fig. 9), whereas there appears to be no difference in the isomerization at C-22 of the C_{32} 17α(H)-hopanes (22S/22S + R = 0.62 for both oils, Figs 8 and 9). The differences may be explained by the stronger increase in sterane concentration (160 and 263 ppm in the September and October 1979 samples, respectively) compared to the difference in the C_{30} 17α(H)-hopane concentrations (361 and 462 ppm, respectively). Absolute biological marker concentrations and biological marker compound ratios in oils from the Aldorf 35 well sampled over the 3 years period vary between the values shown in Figs 8 and 9. An extreme example was observed, however, in an oil from the Aldorf South-west oil field located only about 5 km southwest of the Aldorf field. A sample taken in December 1978 shows a 20S/20S + R C_{29} sterane isomerization of only 0.15 and a C_{32} hopane isomerization at C-22 of 0.52 (Fig. 10). Relative to the Aldorf 35 oils the absolute concentrations of the C_{29} regular steranes and of 17α(H)-hopane are higher (391 and 548 ppm, respectively). In view of the low isomerization values measured for this oil these concentrations still appear suspiciously low.

Since the Aldorf and Aldorf South-west oil fields are located very close to each other and since the most likely source rock for the oils in both fields is the same Lias epsilon (Toarcian) shale, we believe that source differences cannot explain the differences in biological marker concentrations and compound ratios, in particular their variation with time during production. We favor rather the assumption of an uptake of immature organic matter rich in biological marker hydrocarbons from the interbedded shales in the reservoir formation. This process may have been enhanced by the application of secondary recovery methods (water injection) for production of the Aldorf and Aldorf South-west oils. In this respect it is

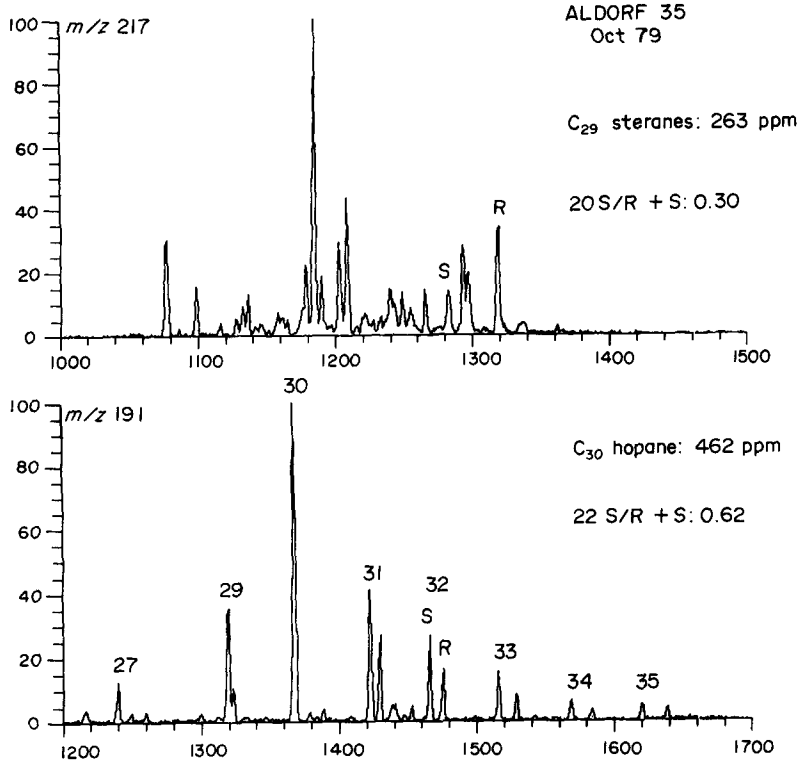

Fig. 9. Sterane (m/z = 217) and terpane (m/z = 191) mass fragmentograms of a crude oil from the Aldorf 35 well sampled in October 1979. This oil shows higher biological marker concentrations and lower biological marker isomerization values (indicating lower maturity) than the oil sampled from the same well about a month earlier (Fig. 8.).

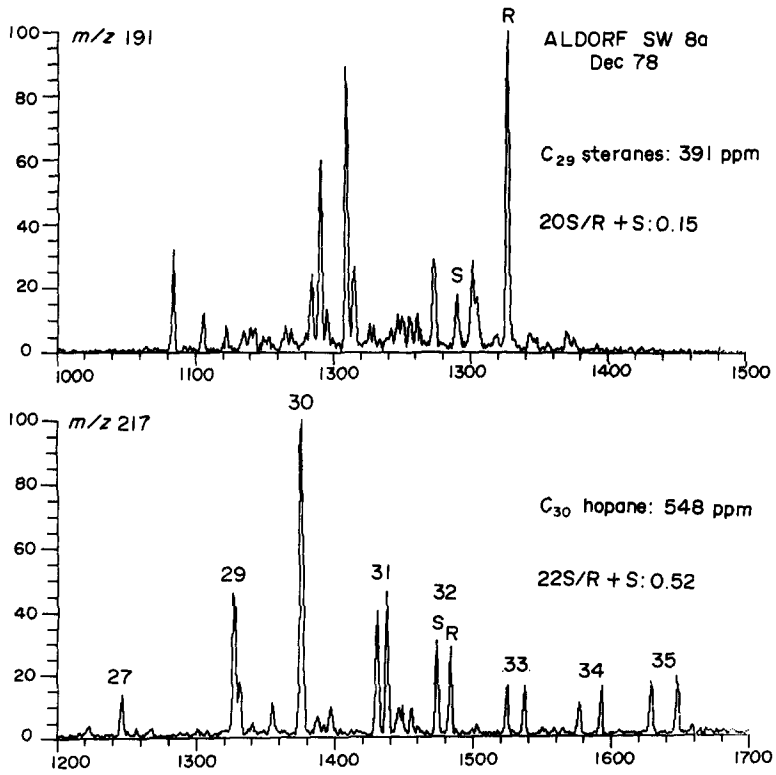

Fig. 10. Sterane (m/z = 217) and terpane (m/z = 191) mass fragmentograms of a crude oil from the Aldorf South-west 8a well. The biological marker distributions suggest extremely low maturity.

noteworthy that oil production in the Aldorf South-west field had been discontinued between 1964 and 1978, and was resumed with secondary recovery techniques only a few months before we started our sampling program. Dissolution of biological markers by crude oils during migration has been noted before for a crude oil from Australia where the unusual biological marker distribution pointed to a contribution from coal located between the source and the reservoir rocks (Philp and Gilbert, 1982).

CONCLUSIONS

The measurement of absolute concentrations of biological markers in sediments and crude oils adds a new dimension to the application of this type of compound to petroleum exploration. This study has revealed the maturity dependent behavior of biological marker concentrations and has shown that absolute concentration measurements may resolve otherwise conflicting bulk parameter and qualitative biological marker data in crude oils:

(1) Biological marker concentrations in sediments from the North Slope of Alaska were shown to decrease exponentially with increasing maturity of the organic matter.
(2) Absolute concentrations of biological markers in crude oils from a single oil province may vary over about three orders of magnitude, as shown for the Williston Basin.
(3) Biological marker concentrations in addition to distribution patterns help in the division of oils into families within a sedimentary basin.
(4) Oil–source rock correlation based solely on the distributions of biological markers will overemphasize the contribution, to the total contents of a given trap, from immature sources. Such effects are seen if expulsion (primary migration) occurs over a wide maturity range and if a number of source beds of similar organic matter composition were deposited in a basin.
(5) Biological markers may reflect a minor contribution of immature oil rich in these compounds to a reservoir and not the origin of most of the mature oil, depleted in biological markers, accumulated in the same reservoir.
(6) Concentrations and distribution patterns of biological markers in crude oils may vary during production if the reservoir rock is rich in interbedded shales bearing immature organic matter.

Acknowledgements—We are grateful to Dr. Leslie Magoon (USGS, Menlo Park) and Dr. George Claypool (USGS, Denver) who provided crude oils and rock samples from the North Slope of Alaska. We thank Wintershall AG, Barnstorf, for oil and rock samples from the Aldorf and Aldorf South-west oil fields and for permission to publish the data obtained on these samples. Technical assistance by U. Disko, Miss A. Fischer, J. Höltkemeier, Mrs. B. Kammer and H. Willsch is gratefully acknowledged. The authors thank Dr. J. M. Moldowan, Chevron Oil Field Research Co., for a careful review of this paper.

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